

7<sup>th</sup> European Symposium  
on Organic Reactivity

7<sup>th</sup>  
ESOR

August 22<sup>nd</sup> - 27<sup>th</sup> 1999  
Ulm / Germany

Book of Abstracts

University of Ulm

Gesellschaft Deutscher  
Chemiker



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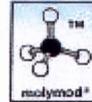

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Special gratitude should be given to the University of Ulm, the host for this conference, for generous support.

# **General Information**

## WELCOME ADDRESSES

**Prof. Dr. Hans-Ullrich Siehl**

**Chairman of the local organising committee**



Dear Colleagues,

On behalf of the organisers, I have the great honour and pleasure to welcome you to the 7<sup>th</sup> European Symposium on Organic Reactivity (ESOR-7) in Ulm.

At the turn of the millennium, ESOR-7 will provide the opportunity to demonstrate some of the high standards to which Physical Organic Chemistry and related areas have risen and to highlight some of the recent methods and techniques which help to solve problems in the areas of Organic Reactivity, Bioorganic Chemistry, and Material Science.

Ulm is best known for its majestic cathedral, which features the highest church spire in the world, and as the birthplace of Albert Einstein as well. Already in the 13th and 14th centuries, Ulm was a wealthy imperial city at the intersection of important long-distance trade roads. Today, the architectural heritage of those days is present in historical buildings, city walls and fortifications, churches and abbeys. Moreover, there are a lot of other things to see and to do in and around Ulm. Upper Swabia and its famous Baroque Route, the Lake of Constance and the mountain ranges of the Alps are all within easy reach of the city.

The Organising Committee, in co-operation with the German Chemical Society, will organise a conference of high scientific standard and a memorable one to all participants.

*Hans-Ullrich Siehl*

Hans-Ullrich Siehl

Chairman of ESOR-7

**Prof. Dr. Hans Wolff**

**Rector, University of Ulm**



Dear participants and dear guests,

I have the great honour and pleasure to welcome you to the 7<sup>th</sup> European Symposium on Organic Reactivity (ESOR-7). We are very proud of the fact that we have been able to attain this scientifically renowned Symposium and to organize it here in Ulm at the turn of the millennium – even more, as it is the very first time for ESOR to take place in Germany.

With the participation of high-ranking scientists - among them two Nobel prize winners – the Symposium represents the actual highlights of Physical Organic Chemistry. It will introduce new methods and techniques in the field of reactivity of organic molecules, of bio-organic chemistry and of material sciences; it will, however, also provide the opportunity to establish new or to intensify already existing scientific contacts even with colleagues from Eastern and Central Europe. Furthermore, it is our special concern to demonstrate by our own contributions the high scientific standard of Chemistry at the University of Ulm.

Only 32 years old, the university of Ulm is the youngest among the universities of the State of Baden-Wuerttemberg. According to its constitutional concept as „university under one roof,, it supports systematically the continuous dialogue between experts of different research areas – mainly of the represented study programs as there are Medicine / Medical Dentistry, Biology, Physics, Chemistry, Mathematics as well as Mathematics and Management Studies, Engineering Science (Electrical Engineering) and Computer Science. Being a crystal nucleus as well as an essential part of the "Science City of Ulm", our University – which is located in the

immediate neighbourhood to the Science Park (with the Daimler-Chrysler-Research Center among others) cooperates with institutes of pre-competitive and of industrial research as well as with the "Fachhochschule Ulm" which is a 4-years technical college. Several "First Class Research Centers" supported by the DFG (German Research Foundation) and research projects which are supported by public funds as well as partnerships with international top-ranking research institutes bear testimony to its efficiency and its motivation.

I wish and do hope that the interdisciplinary atmosphere of the Science City will also have a fruitful impact upon your discussions and that you experience the days to come at our university as a professional and personal enrichment.

A handwritten signature in black ink, appearing to read 'H. Wolff', written in a cursive style.

Prof. Dr. Hans Wolff

**Klaus von Trotha**

**Minister for Science, Research and Arts  
State of Baden-Württemberg**



Ladies and Gentlemen,

It is with great pleasure that I welcome you to the 7<sup>th</sup> European Symposium on Organic Reactivity in Ulm, the city of science.

Science and research are of great importance to the State of Baden-Wuerttemberg. No other German state offers a greater range of research activities; no other region in Europe has a greater share of high-tech employment than does Baden-Wuerttemberg. Expenditures for research and development total 3.7 percent of the state's GNP with industry's contribution covering nearly two-thirds of this amount.

This favourable research environment has its roots in Baden-Wuerttemberg's governmental policies, which are based on the following guiding principles:

Our support for research has one main goal--the creation of optimum conditions for creative and internationally competitive scientific work to take place. The careful selection of research scientists is viewed as a crucial element in meeting this goal.

Furthering research also requires that young scientists are well educated and have opportunities to hone their skills in carrying out their own research projects.

For research to be competitive, it must be interdisciplinary and international. Research institutes must transcend institutional boundaries.

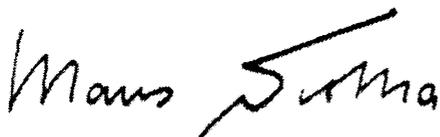
It is essential that scientists develop ongoing partnerships to ensure the transfer of scientific and technical knowledge to settings where such knowledge is applied. However, this flow of

information must be reciprocal, in other words, scientific hypotheses should be no less informed by knowledge rooted in applied settings as by knowledge rooted in ideas.

For research to succeed certain structural conditions must be met. Reliable statutory regulations as well as adequate financial and institutional support form the core of this structure. Without them, research will be unable to meet the interdisciplinary and international challenges of modern science.

The field of Physical Organic Chemistry is an excellent example of an interdisciplinary research network. It connects pure and applied research from the fields of Supramolecular Chemistry, Computational Chemistry and the New Organic Materials sciences. Fields such as Physical Organic Chemistry, which links together Chemistry, Physics, Biology, and the Material Sciences, will occupy a central place in the future advancement of science and technology.

Allow me to interpret the fact that the scientific community has chosen to hold its 7th European Symposium on Organic Chemistry in Germany and at Ulm, as evidence of the high standing University of Ulm researchers enjoy among their colleagues. To all participants of the ESOR-7, I extend my best wishes for a fruitful conference as well as for the continued success of your scientific endeavours in this cutting-edge field.

A handwritten signature in black ink, appearing to read 'Klaus von Trotha'. The signature is fluid and cursive, with a prominent horizontal stroke across the middle.

Klaus von Trotha

Minister for Science, Research and Arts

State of Baden-Wuerttemberg

## Message of Greeting by Ms Edelgard Bulmahn

### Federal Minister of Education and Research



We need new technologies, new processes and new products which are key to Germany's future economic and scientific performance. In particular we need technologies for sustainable growth - a sustainable chemical sector.

In other words, what we need is people-oriented technology. This applies particularly to the chemical sector, including high-performing chemical industry and successful chemical research.

The topic of the symposium - organic reactivity and physical organic chemistry - is part of the vast field of organic chemistry. About 98% of known chemical compounds are organic compounds. More than 300,000 compounds are added each year.

The central task of organic chemistry are the identification of structures and properties and the synthesis of natural products and active agents for applications in many fields, above all in the pharmaceutical sector, where organic synthesis makes indispensable contributions to saving lives every day.

The branches of organic chemistry, whether target structures, synthetic methods or analytical chemistry, are shaped by concepts such as molecular decoding, supramolecular interaction, self-organisation, self-synthesis and self-reproduction. Work with complex systems whose structures and properties are determined by non-covalent molecular interactions is already quite normal today in organic chemistry. Research no longer focuses on molecules for their own sake but on the functions and properties produced. The molecular design of the superstructure takes centre-stage in research efforts. Mere synthesis has become secondary.

Physical organic chemistry, with which this symposium is dealing, must get ready for the 21st century. It must absorb and develop with priority new aspects such as supramolecular chemistry, organometallic chemistry, scientific computing and others. The BMBF is funding

innovative R&D projects in these fields. Organic electrochemistry could also provide new opportunities for future-oriented work.

Another development has also become visible in recent years: Chemistry has entered other disciplines. True progress made in many fields of biochemistry and medicine is largely based on a better understanding of the processes of life at the molecular and supramolecular level and is thus actually an achievement of the chemical sector.

Organic chemistry exemplifies in a particular clear manner that, to make progress, an interdisciplinary approach including biology, medicine, physics and mathematics is necessary not only in application but also in research. This requires co-operation among researchers both at the European and at the global level. ESOR-7 will make a substantial contribution towards that goal.

At this symposium here in Ulm you will discuss possibilities and prospects and establish important standards. I wish you every success in doing so.

A handwritten signature in black ink, appearing to read 'E. Bulmahn'. The signature is written in a cursive, flowing style with a large initial 'E'.

Ms Edelgard Bulmahn

### *Local Organising Committee*

The conference will be organised by the University of Ulm, Division of Organic Chemistry I, in co-operation with the Gesellschaft Deutscher Chemiker (GDCh, Frankfurt).

Prof. Dr. Hans-Ullrich Siehl, University of Ulm

Prof. Dr. Gerhard Maas, University of Ulm

Dr. Jürgen Schatz, University of Ulm

Dr. Leonhard Kiessling, GDCh, Frankfurt am Main

### *International Advisory Board*

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### *Conference Office*

The conference office is located in the lobby of the lecture halls during the symposium.

Conference office opening hours:

Monday	August 23, 1999	08:00 - 16:30
Tuesday	August 24, 1999	08:00 - 16:30
Wednesday	August 25, 1999	08:00 - 12:00
Thursday	August 26, 1999	08:00 - 16:30
Friday	August 27, 1999	08:00 - 12:00

On Sunday, August 22, registration is possible at the site of the welcome mixer (Grüner Hof 5c) from 18:00 to 21:00 h.

During the conference you can be contacted by telephone or fax. Personal computers for e-mail access are available (please follow the signs "e-mail access" from the lobby to the computer center).

Phone	+49 731 50-23910
Fax:	+49 731 50-23911

### *Banking*

A bank (phone: +49 731 51043 fax: +49 731 51043) is located near the conference site on campus (see map on backside cover).

Banking hours are:

Monday	08.30-13.30 and 14.45-18.00
Tuesday	08.30-13.30 and 14.45-17.00
Wednesday	08.30-12.30
Thursday	08.30-13.30 and 14.45-18.00
Friday	08.30-13.30 and 14.45-17.00

## SOCIAL AND OPTIONAL PROGRAM

### Sunday, August 22

18:00 - 21:00 Welcome mixer with registration, Ludwig-Heilmeyer Saal  
Grüner Hof 5c (downtown)

### Monday, August 23

14:00 - 17:00 Guided walking tour: Historical city and cathedral of Ulm

19:00 - 20:00 Reception by the Mayor of Ulm

20:30 - 21:00 Organ Recital, cathedral of Ulm

### Tuesday, August 24

14:00 - 16:00 Guided Tour: Baroque monastery at Wiblingen (baroque  
library)

### Wednesday, August 25

13:00 - 18:00 Congress excursion to Steinhausen, Zwiefalten, and Bad  
Schussenried

18:30 - Congress dinner, Bad Schussenried

### Thursday, August 26

09:00 - 17:00 Excursion to Aalen. Visit of the disused iron mine "Tiefer  
Stollen" and castle "Schloß Fachsenfeld"

18:00 - 22:00 Get-together at University Campus and Evening Lecture:  
*Chemistry on Stamps and Related Things* (Z. Rappoport,  
Jerusalem)

For details concerning the social and optional program please refer to the brochure: *Social and  
Optional Program*.

Time	Monday	Tuesday	Wednesday	Thursday	Friday
08:30-09:00	Opening Ceremony				
09:00-10:00	PL1 G. Olah	PL3 A. Zewail	PL5 J. M. Lehn	PL7 K. R. Seddon	PL9 J. Gladysz
10:00-11:00	PL2 H. Schwarz	PL4 W. Sander	PL6 R. J. M. Nolte	SL8 M. Olivucci	PL10 F.-G. Klärner
11:00-11:30	Coffee	Coffee	Coffee	Coffee	Coffee
11:30-11:50	SL1 SL2	SL5 SL6	SL9	A13 B13 C1 R. Herges M.-F. Ruasse J. J. Michels	PL11 Y. Apeolig
11:50-12:10	S. Fornarini J. Gauss	A. Bagno P. Majoral	Th. Carell	A14 C2 Z. B. Maksic P. Schreiner A. Dölle	
12:10-12:30	A1 B1 Y. Tsuno Th. Müller	A9 B9 E. Humeres M. Hirota	Excursion	A15 C3 J. F. King L. Garcia-Rio M. R. de Jong	
12:30-12:50	A2 B2 P. Müller H. Yamataka	A10 B10 More O'Ferrall Th. Schrader		A16 C4 H. F. Koch J. C. Mejuto W. N. Nau	Closing Remarks
12:50-14:30	Lunch	Lunch		Lunch	
14:30-14:50	SL3 SL4	SL7 SL8		A17 B17 C5 A. Thibblin S. Kobayashi M. Nüchter	
14:50-15:10	I. Williams K. Lammertsma	B. Rieger E. Anders		A18 C6 C. I. F. Watt M. Bonifacic C. Erk	
15:10-15:30	A3 B3 C. Taeschler V. D. Shteingarts	A11 B11 H. Mayr C. F. Bernasconi	A19 C7 J. Bakke M. Canle Ch. Reichardt		
15:30-15:50	A4 B4 O. Kronja E. I. Finkelstein	A12 B12 I. Akhrem H. Zipse	A20 C8 Dae Dong Sung P. Rademacher		
15:50-18:40	Coffee	Coffee	Coffee		
16:40-17:00	A5 B5 T. Okuyama A. J. Kirby	Poster- Session	A21 C9 H. Maskill A. Stanger		
17:00-17:20	A6 B6 T. J. J. Müller Th. Laube		A22 C10 M. R. Crampton D. Kuck		
17:20-17:40	A7 B7 Z. Rappoport J. P. Guthrie				
17:40-18:00	A8 B8 A. F. Hegarty R. S. Brown				
18:00-19:00					
19:00-20:00			EL Z. Rappoport		

## SCIENTIFIC PROGRAMME – ORAL PRESENTATIONS

*Monday, August 23, 1999*

### *Plenary Lectures (Lecture Hall H4/5)*

**Chair:** Michael Hanack (Tübingen, D)

- 09:00     **PL1:** George A. Olah (Los Angeles, California, USA)  
*Protolytic Activation of Electrophiles in Organic Reactions*
- 10:00     **PL2:** Helmut Schwarz (Berlin, D)  
*Holy Grails in Gas-Phase Chemistry: In Search of Elusive Molecules*
- 11:00     Coffee

### *Session A (Lecture Hall A)*

**Chair:** Zvi Rappoport (Jerusalem, ISR)

- 11:30     **SL1:** Simonetta Fornarini (Roma, IT)  
*Gas Phase Reactions of Arenium Ions*
- 12:10     **A1:** Yuho Tsuno (Fukuoka, JPN)  
*Conformation Dependence of Substituent Effects in the Solvolysis of 1,1-Diaryl-2,2,2-trifluoroethyl System*
- 12:30     **A2:** Paul Müller (Genève, CH)  
*The Stability of Bridgehead Carbocations*
- 12:50     Lunch
- Chair:** Shinjiro Kobayashi (Fukuoka, JPN)
- 14:30     **SL3:** Ian Williams (Bath, GB)  
*Computational Exploration of Mechanistic Borderlines for Reactions in Solution*
- 15:10     **A3:** Christoph Taeschler (Calgary, Alberta, CAN)  
*Rearrangement of Bicyclo[3.3.3]undecyl dication*
- 15:30     **A4:** Olga Kronja (Zagreb, HR)  
*The Ring Enlargement Process in the 2-Cyclopentyl-2-propyl Cation*
- 15:50     Coffee

**Chair:** Eduardo Humeres (Florianópolis, BR)

- 16:40 **A5:** Tadashi Okuyama (Himeji, JPN)  
*Reactivity of Vinyl Iodonium Salts. New Aspects of Vinyl Cation Chemistry and Vinylic Substitution Reactions*
- 17:00 **A6:** Thomas J.J. Müller (München, D)  
*First Diastereoselective Electrophilic Propargylations with Planar Chiral (Arene)Cr(CO)<sub>3</sub>-Substituted  $\alpha$ -Propargyl Cations*
- 17:20 **A7:** Zvi Rappoport (Jerusalem, ISR)  
*Long-Lived Enols of Carboxylic Acids Derivatives with  $\beta$ -Electron-Withdrawing Substituents*
- 17:40 **A8:** Frank Hegarty (Dublin, IRL)  
*Direct Observation of Simple Enols of Amides: The Ketonisation of 1-N-Methylanilino-2-methylpropen-1-ol*

**Session B (Lecture Hall B)**

**Chair:** Massimo Olivucci (Siena, IT)

- 11:30 **SL2:** Jürgen Gauss (Mainz, D)  
*Determination of Molecular Geometries: Interplay of Theory and Experiment*
- 12:10 **B1:** Thomas Müller (Frankfurt a. M., D)  
*Novel Intramolecularly Stabilized Silylium Ions*
- 12:30 **B2:** Hiroshi Yamataka (Osaka, JPN)  
*Dynamics in  $S_N2$ /ET Processes: Ab Initio MD Simulations*
- 12:50 Lunch
- Chair:** Wolfram Sander (Bochum, D)
- 14:30 **SL4:** Koop Lammertsma (Amsterdam, NL)  
*The Rich Chemistry of Phosphinidenes, the Phosphorous Analogues of Carbenes*
- 15:10 **B3:** Vitalij Shteingarts (Novosibirsk, RUS)  
*Isomerism of Radical Anions and Regiochemistry of Partial Reduction of Polynitroarenes*
- 15:30 **B4:** Eugene I. Finkelshtein (Moscow, RUS)  
*Radical Stabilization Energy as a Measure of Properties Trends in Homologous Groups*
- 15:50 Coffee

**Chair:** Jürgen Sauer (Regensburg, D)

- 16:40     **B5:** Anthony J. Kirby (Cambridge, GB)  
*A New Twist to the Amide Group*
- 17:00     **B6:** Thomas Laube (Schaffhausen, CH)  
*Relationship Between Carbonyl Pyramidalization and Conformation of Ketones*
- 17:20     **B7:** J. Peter Guthrie (London, Ontario, CAN)  
*Predicting the Rates of Organic Reactions: Nucleophiles Plus Carbonyls, Iminium Salts, and Carbocations*
- 17:40     **B8:** Robert S. Brown (Kingston, Ontario, CAN)  
*Divalent  $M^{2+}$ -Catalyzed Methanolysis of Acetylimidazole, Acetylpyrazole and a Distorted Anilide*

**Tuesday, August 24, 1999**

**Plenary Lectures (Lecture Hall H4/5)**

**Chair:** Helmut Schwarz (Berlin, D)

- 09:00     **PL3:** Ahmed Zewail (Pasadena, California, USA)  
*Femtochemistry - Organic Chemistry in the Femto Age*
- 10:00     **PL4:** Wolfram Sander (Bochum, D)  
*Reactions of Super-Electrophilic Carbenes*
- 11:00     Coffee

**Session A (Lecture Hall A)**

**Chair:** François Terrier (Versailles, FR)

- 11:30     **SL5:** Alessandro Bagno (Padova, IT)  
*Acyl vs. Nitrogen Protonation in Carboxylic and Non-Carboxylic Amides in the Gas Phase and in Solution. Patterns of NMR Properties and Hydration Energies*
- 12:10     **A9:** Eduardo Humeres (Florianópolis, SC, BR)  
*Acid Decomposition of Aryldithiocarbamates. The Torsional Effect*
- 12:30     **A10:** Rory A. More O'Ferrall (Dublin, IRL)  
*Diffusion Controlled Trapping of an  $\alpha$ -Hydroxycarbocation by Hydroxylamine*
- 12:50     Lunch

**Chair:** Paul Müller (Genève, CH)

- 14:30     **SL7:** Bernhard Rieger (Ulm, D)  
*The Design of Transition Metal Catalysts for New Polyolefin Materials*
- 15:10     **A11:** Herbert Mayr (München, D)  
*Carbocationic Polymerization of Olefins: Determination of Initiation, Propagation and Transfer Rate Constants*
- 15:30     **A12:** Irena Akhrem (Moscow, RUS)  
*Polyhalomethanes Combined with Aluminum Halides in Alkane Chemistry*
- 15:50     Coffee
- 16:15     Poster Session

***Session B (Lecture Hall B)***

**Chair:** Frank-Gerrit Klärner (Essen, D)

- 11:30     **SL6:** Jean-Pierre Majoral (Toulouse, FR)  
*Phosphorous-Containing Dendrimers*
- 12:10     **B9:** Minoru Hirota (Yokohama, JPN)  
*Intramolecular CH/ $\pi$  Interaction. Substituent Effect as a Probe for Hydrogen-bond-like Character*
- 12:30     **B10:** Thomas Schrader (Düsseldorf, D)  
 *$\beta$ -Sheet Stabilization of Peptides with Aminopyrazoles*
- 12:50     Lunch

**Chair:** Koop Lammertsma (Amsterdam, NL)

- 14:30     **SL8:** Ernst Anders (Jena, D)  
*Experimental and Theoretical Investigations of Novel Group Transfer Reagents*
- 15:10     **B11:** Claude F. Bernasconi (Santa Cruz, California, USA)  
*Kinetic and Thermodynamic Acidities of Fischer Carbene Complexes*
- 15:30     **B12:** Hendrik Zipse (München, D)  
*C-H Bond Activation In Ribonucleotide Reductase - Do Short Strong Hydrogen Bonds Play a Role?*
- 15:50     Coffee
- 16:15     Poster Session

*Wednesday, August 25, 1999*

*Plenary Lectures (Lecture Hall H4/5)*

**Chair:** Per Ahlberg (Göteborg, S)

- 09:00     **PL5:** Jean-Marie Lehn (Strasbourg, FR)  
*Towards Programmed Supramolecular Materials*
- 10:00     **PL6:** Roeland J. M. Nolte (Nijmegen, NL)  
*Design and Synthesis of Novel Molecular Materials*
- 11:00     Coffee

*Section Lecture (Lecture Hall H4/5)*

**Chair:** Jacques Fastrez (Louvain-La-Neuve, B)

- 11:30     **SL9:** Thomas Carell (Zürich, CH)  
*From Mechanistic Investigations to Artificial Repair Enzymes*

*Thursday, August 26, 1999*

*Plenary Lectures (Lecture Hall H4/5)*

**Chair:** Yitzhak Apeloig (Haifa, ISR)

- 09:00     **PL7:** Ken R. Seddon (Belfast, GB)  
*Ionic Liquids: Neoteric Solvents for Organic Synthesis*
- 10:00     **PL8:** Massimo Olivucci (Siena, IT)  
*Computational Organic Photochemistry*

**Session A (Lecture Hall A)**

**Chair:** Anthony J. Kirby (Cambridge, GB)

- 11:30     **A13:** Rainer Herges (Braunschweig, D)  
*AICD a New Method for the Visualization of Delocalization*
- 11:50     **A14:** Zvonimir B. Maksic (Zagreb, HR)  
*Computer Aided Design of Organic Superbases*
- 12:10     **A15:** James F. King (London, Ontario, CAN)  
*Variation of the Rate of  $\alpha$ -Sulfonyl Carbanion Formation with the H-C-C-X Torsion Angle in  $\beta$ -Substituted Sulfoxones: Geometry Dependence of the Taft  $\sigma^*$  Values*
- 12:30     **A16:** Heinz Koch (Ithaca, NY, USA)  
*Comparison of Methanolic Sodium Methoxide-Promoted Dehydrohalogenation and Exchange Reactions that are Initiated at the Benzylic vs. 9-Fluorenyl Positions*
- 12:50     Lunch

**Chair:** Rory More O'Ferrall (Dublin, IRL)

- 14:30     **A17:** Alf Thibblin (Uppsala, S)  
*Mechanisms of Solvolytic Elimination Reactions of Tertiary Substrates: Stereospecific 1,2-Elimination Reactions*
- 14:50     **A18:** Ian Watt (Manchester, GB)  
*The Kinetics of Disproportionation of Secondary Alcohols*
- 15:10     **A19:** Jan M. Bakke (Trondheim, N)  
*Nitration of Pyridine, Impregnating the Impregnable*
- 15:30     **A20:** Dae Dong Sung (Pusan, ROK)  
*Substituent and Solvent Effect on Nucleophilic Substitution Reactions of Aromatic Sulfonyl Halides*
- 15:50     Coffee

**Chair:** Marie-Francoise Ruasse (Paris, FR)

- 16:40     **A21:** Howard Maskill (Newcastle upon Tyne, GB)  
*Heterolytic and Homolytic Mechanism in Solvolyses of Arenediazonium Salts*
- 17:00     **A22:** Michael R. Crampton (Durham, GB)  
*The Ambident Reactivity of Aniline and Some Derivatives Towards 4,6-Dinitrobenzofuroxan*

*Session B (Lecture Hall B)*

**Chair:** Ramon Leis (Santiago, E)

- 11:30     **B13:** Marie-Francoise Ruasse (Paris, F)  
*Optimization of Micellar Catalysis of Nucleophilic Substitutions in Buffered Solutions of Cetyltrimethylammonium Salts*
- 11:50     **B14:** Peter Schreiner (Göttingen, D)  
*No Heavy Metals, No Enzymes, No Fuss: Aliphatic Hydrocarbon Halogenation in Multi-Phase Systems*
- 12:10     **B15:** Luis Garcia-Rio (Santiago de Compostela, E)  
*Microemulsion Promoted Mechanistic Changes. Solvolysis of Substituted Benzoyl Chlorides*
- 12:30     **B16:** Juan C. Mejuto (Vigo, E)  
*Reactivity in Mixed Micelles of CTACl/Octylamine*
- 12:50     Lunch

**Chair:** Alessandro Bagno (Padova, IT)

- 14:30     **B17:** Shinjiro Kobayashi (Fukuoka, JPN)  
*Steric Effect of Diffusion Limited Reactions Studied by Laser Flash Photolysis*
- 14:50     **B18:** Marija Bonifacic (Zagreb, HR)  
*Reactions of N-Centered Radicals Derived from  $\alpha$ -Amino Acids; A Time Resolved Study*
- 15:10     **B19:** Moises Canle Lopez (A Coruña, E)  
*Photochemically-Induced Thiazolidine Ring-Opening Reactions*
- 15:50     Coffee

*Session C (Lecture Hall C)*

**Chair:** Jean-Pierre Majoral (Toulouse, FR)

- 11:30     **C1:** J. Michels (Enschede, NL)  
*Building Supramolecular Assemblies of Calix[4]arene-Based Surfactants and Cyclodextrins*
- 11:50     **C2:** Andreas Dölle (Aachen, D)  
*Structure, Molecular Dynamics and Host-Guest Interactions of a Water-Soluble Calix[4]arene*
- 12:10     **C3:** Menno R. de Jong (Enschede, NL)  
*Fluorescent Water-Soluble  $\beta$ -Cyclodextrin-Dimers as Sensor Molecules for the Detection of Neutral Analytes*
- 12:30     **C4:** Werner M. Nau (Basel, CH)  
*A Novel Structural and Dynamic Probe for the Investigation of Supramolecular Assemblies: An Exploratory Study of Cyclodextrins by NMR, Fluorescence, UV-Absorption, and Induced Circular Dichroism*
- 12:50     Lunch

**Chair:** Herbert Mayr (München, D)

- 14:30     **C5:** Matthias Nüchter (Jena, D)  
*Organic Processes Initiated by Nonclassical Energy Sources*
- 14:50     **C6:** Cakil Erk (Istanbul, TUR)  
*The Novel Chromophore Crown Ethers and Cationic Recognition with Optical Spectroscopy and MM+ Calculations*
- 15:10     **C7:** Christian Reichardt (Marburg, D)  
*Chiral Polymethine Dyes - Remarkable but Forgotten Conjugated  $\pi$ -Systems*
- 15:30     **C8:** Paul Rademacher (Essen, D)  
*Synthesis, Electronic Structures and Cycloadditions of Polycyclic Hetarenes*
- 15:50     Coffee

**Chair:** Ernst Anders (Jena, D)

- 16:40     **C9:** Amnon Stanger (Haifa, ISR)  
*SIBL in Strained Aromatic Molecules with Extended  $\pi$ -Systems*
- 17:00     **C10:** Dietmar Kuck (Bielefeld, D)  
*Strained Benzoannulated cis, cis, cis, trans-[5.5.5.6]Fenestranes: Synthesis and Properties*

***Evening Lecture (Lecture Hall H4/5)***

**Chair:** Hans-Ullrich Siehl (Ulm, D)

19:00     **EL:** Zvi Rappoport (Jerusalem, ISR)  
*Chemistry on Stamps and Related Things*

***Friday, August 27, 1999***

***Plenary Lectures (Lecture Hall H4/5)***

**Chair:** Gianfranco Scorrano (Padova, IT)

09:00     **PL9:** John Gladysz (Erlangen, D)  
*Chemistry with Teflon Pony Tails: The Fluorous Solvent Approach to Synthesis and Catalysis, and Separations*

10:00     **PL10:** Frank-Gerrit Klärner (Essen, D)  
*Molecular Tweezers as Synthetic Receptors: Molecular Recognition of Electron-Deficient Aromatic and Aliphatic Substrates*

11:00     Coffee

**Chair:** Mirjana Eckert-Maksic (Zagreb, HR)

11:30     **PL11:** Yitzhak Apeloig (Haifa, ISR)  
*Organosilicon Chemistry: A Field of Fruitful Interplay Between Experiment and Theory*

12:30     Closing Remarks

## SCIENTIFIC PROGRAMME – POSTER PRESENTATIONS

- P1 Matthias Nüchter, Bernd Ondruschka, Ute Sundermeier  
*Microwave-assisted Degradation of Persistent Organic Pollutants in Water*
- P2 Andreas Schenk, Carlheinz Röcker, Don C. Lamb and G. Ulrich Nienhaus  
*Determining Chemical Rate Coefficients Using Time-gated Fluorescence Correlation Spectroscopy*
- P3 Don C. Lamb, Jan Kriegl, Klaus Kastens, G. Ulrich Nienhaus  
*Quantum-Mechanical Tunneling of Water in Heme Proteins*
- P4 N. Strashnikova, V. Papper, P. Parkhomyuk, G. Lihtenshtein  
*Quartz Surface Modification by Stilbene: Key to Novel Sensor for Study of Surface Properties*
- P5 Brian A. Murray and Edwin Carey  
*Tautomeric Equilibrium in Nimesulide, a Sulphonamide Pharmaceutical*
- P6 Pablo Herves, Isabel Fernandez, Jorge Perez-Juste, D. Lyn, H. Williams  
*Kinetic Study of some Proton Transfer Controlled Reactions*
- P7 Francois Terrier, Gilles Moutiers, Sandrie Pelet  
*Rapid Marcus Curvature Due to Extremely strong Solvational Imbalances in the Deprotonation of Polynitrobenzylic Carbon Acid by Oximate Bases*
- P8 Mirjana Eckert-Maksic, Zoran Glasovac, Ivava Antol  
*Acidity of Cyclopropanes: Ab Initio and Experimental Studies*
- P9 Mirjana Eckert-Maksic and Zoran Glasovac  
*Acidity of Benzocyclobutene: Ab Initio and Gas Phase Results*
- P10 Juan M. Antelo, Florencio Arce, Juan Crugeiras, Cristina Pastoriza  
*Kinetics and Mechanism of Oxidation of Benzylamine by Aqueous Chlorine and N-Chlorosuccinimide*
- P11 Juan M. Antelo, Florencio Arce, Paula Calvo, Juan Crugeiras  
*Acid-base Catalysis in the Disproportionation reaction of N-Chlorotaurine*
- P12 Viesturs Lūsis, Dzintra Muceniece, Ivars Turovskis  
*Basicity of Partially Hydrogenated Pyridines and Acid Catalyzed Recyclization of 1,4-Dihydroisomers*
- P13 Ishwara Bhat, Howard Maskill, Peter Miatt  
*The Preparation and Kinetic Study of N-Nitrosohydroxylamines*

- P14 Kallol K. Ghosh and Pankaj Tamrakar  
*Structure - Reactivity Effects on The Protonation Equilibria of Benzohydroxamic Acid*
- P15 Gerardo R. Echevarria, Andrea Basagoitia, Jose G. Santos, Francisco Garcia-Blanco  
*Determination of the Rates of Formation and Hydrolysis of the Schiff Bases Formed by Pyridoxal 5'-Phosphate with L-Tryptophan and its Methyl Ester.*
- P16 G. R. Echevarria, M. P. Martin, M. P. del Pozo, A. Basagoita, F. G. Santos  
*Kinetic Study of the Schiff-base Formation between Pyridoxal 5'-Phosphate and GABA. Influence of Temperature*
- P17 Satu Mikkola, Kirsi Nirmi, Eeva Stenman  
*Metal Ion promoted Hydrolysis of RNA: General Acid Catalysis By Zn(II) Aquo Ion on the Departure of Leaving Group*
- P18 Kathryn H. Brown, Michael R. Crampton, John H. Atherton  
*Condensation Reactions of Formaldehyde and Amines with and without the Presence of Sulfite*
- P19 Enrique A. Castro, Leonardo Leandro, José G. Santos  
*Kinetics and Mechanism of the Aminolysis of O-Phenyl 4-Nitrophenyl Dithiocarbonate in Aqueous Ethanol*
- P20 Daniel Arellano, Enrique A. Castro, Paulina Pavez, José G. Santos  
*Kinetics and Mechanism of the Phenolysis and Thiolytic of O-Ethyl S-(2,4-Dinitrophenyl) Thiol and Dithiocarbonates*
- P21 Fatima Norberto, Susanna Santos, Pablo Herves, Javier Pazos  
*Reactivity of Thiobenzoyl Carbamates*
- P22 Gabriel Chuchani, Rosa M. Dominguez, Alexandra Rotinov  
*The Homogeneous, Unimolecular Gas Phase Elimination Kinetics of 2-Substituted Ethyl Dimethylcarbamates. A Taft Correlation With Three Slopes*
- P23 Gennady I. Borodkin, Rodion V. Andreev, Innokenty R. Elanov, Vyacheslav G. Shubin  
*Complexes of N-Heterocyclic Compounds with Nitrosonium Cation: Structure and Dynamic Behaviour*
- P24 J. A. Moreira, I. Garcia-Rio, J. R. Leis, F. Norberto  
*Nitroso Group Transfer From Substituted N-Methyl-N-Nitrosobenzenesulfonamides To Amines. Intrinsic And Apparent Reactivity*

- P25 Stefan Salzbrunn, Jürgen Simon, G. K. Surya Prakash, Nicos A. Petasis, George A. Olah  
*Electrophilic Substitution of Arylboronic Acids*
- P26 V. A. Bacherikov, V. V. Kuznetsov, A. I. Gren'  
*A Simple Procedure of Obtaining of Alkyl(aryl)boric Esters*
- P27 V. M. Vlasov, I. A. Khalifina, A. A. Tabatskaya  
*Reactivity and Selectivity Control in the Nucleophilic Aromatic Substitution Reactions*
- P28 Michael R. Crampton, Lynsey C. Rabbitt  
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- P29 Einar Uggerud  
*Mechanism of Nucleophilic Substitution and Elimination*
- P30 Yu. G. Skrypnik, N. V. Vasiljeva, S. N. Lyashchuk  
*Heteroarylation of CH-Acids by Azines*
- P31 Gennadii D. Titskii, Tatyana Gaidash  
*Nucleophilic Catalysis in Oxidative Activated Nucleophilic Substitution*
- P32 Maria K. Turovskaya, Gennadii D. Titskii  
*Reaction of Photocleavage of N-O Bond in Acyloxypyridinium Salts*
- P33 Elena S. Mitchenko, Gennadii D. Titskii  
*Isoparametric Correlation of Charge-Charge Type in ANRORC Substitution*
- P34 T. Vaganova, E. Panteleeva, I. Bilkis, V. Shteingarts  
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- P35 Benito Agulla, Juan M. Antelo, Mercedes Parajo  
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- P36 P. Morris, T. W. Bentley  
*Alkoxide and Carbonate-catalysed Hydrolyses of a Chloro-triazine in Alcohol-water Mixtures*
- P37 Michael L. Kostrikin, Anatolii A. Afonkin, Alexander E. Shumeiko, Anatolii F. Popov.  
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- P38 M. Lurdes S. Cristiano, Amadeu F. Brigas, Robert A. W. Johnstone  
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- P39 Nouria A. Al-Awadi, Rana N. Malhas, Osman M. E. El-Dusouqui  
*Gas-Phase Thermolysis of Ketoanilides, Hydrazones, and Related Systems*
- P40 Nouria A. Al-Awadi, Osman M. E. El-Dusouqui  
*Concerted Six-Membered T. S. in Thermal Elimination Reactions: Structure - Reactivity Correlations*
- P41 Jorge Martin-Ortiz, Saturnino Calvo-Losada, Jose Joaquin Quirante  
*The Thermal Decomposition of Vinyloxetanes: A Theoretical Study*
- P42 Yu.G.Skrypnik, S.N.Lyashchuk, S.Wysocki  
*Quantum Chemical Study of Thioformaldehyde-S,S-Dioxide Structure and Possibility of it Izomerization into Ylide*
- P43 Thies Thiemann, Daisuke Ohira, Kazuya Arima, Tsuyoshi Sawada, Shuntaro Mataka, Frank Marken  
*Synthesis and Reactivity of Thiophene-S-Oxides*
- P44 Anthony F. Hegarty, Stephen J. Eustace and Suzanne Fergus  
*Formation of Nitrile Ylides via 2-Azaallenium Ions*
- P45 Xiangyang Zhang and Werner M. Nau  
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- P46 Martin Halupka, Christoph Kolano, Olaf Schade, Wolfram Sander, Götz Bucher  
*Photochemistry of Ethyl-9-fluorenylidenaminoxalate*
- P47 Michael Exner, Andreas Balster, Wolfram Sander  
*5-Fluoro- and 5-Methyl-1,3-didehydrobenzene - a Matrix Isolation Study*
- P48 Hans Henning Wenk, Wolfram Sander  
*Photochemistry of 9,10-Dicarbonyl-9,10-dihydroanthracene: A Source of 9,10-Dehydroanthracene ?*
- P49 Kerstin Schroeder, Klaus Block, Wolfram Sander  
*Investigations in Carbonyl Oxide and Dioxirane Chemistry*
- P50 Carsten Kötting, Wolfram Sander  
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- P51 Holger Bornemann, Wolfram Sander  
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- P52 Götz Bucher  
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- P53 Joseph Keogh, Anthony F. Hegarty  
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- P54 Stephen Connon, Anthony F. Hegarty  
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- P55 Dietmar Kuck, Jean-Yves Salpin, Michael Mormann  
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- P56 Christa S. Krämer, Herbert Mayr, Thomas J. J. Müller  
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- P57 Cinzia Chiappe, Antonia De Rubertis, Peter Lemmen, Dieter Lenoir  
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- P58 Mizue Fujio, Tohru Nakashima, Ryoji Fujiyama, Yuho Tsuno  
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- P59 Alexander Christian Backes, Hans-Ullrich Siehl  
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- P62 Christoph Freudenberger, Hans-Ullrich Siehl  
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- P65 Ruben Elvas-Leitao, Lidia Albuquerque, Paulo Santos, Filomena Martins  
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- P73 Mykola A. Turovskyj, Iosip O. Opeida, Anatolij A. Turovskyj, Alim M. Nikolaevskyj  
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- P103 Ralph Puchta, Verena Seitz, Nico van Eikema Hommes, Rolf Saalfrank  
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- P104 Oskar Middel, Willem Verboom, Victor Snieckus, and David N. Reinhoudt  
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- P105 Yan Zhang, Hushan Yuan, Chuanfeng Chen, Zhitang Huang, Jinwei Zhou, Yuji Kawanishi  
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- P107 Jürgen Schatz, Frank Schildbach, Marion Baur  
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- P111 Luis Garcia-Rio, Pablo Hervés, Juan C. Mejuto, Jorge Pérez-Juste  
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- P115 Sabrina Pucci, Chantal Dax, Colette Denier, Casimir Blonski  
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- P119 Zdenek Slanina, Xiang Zhao, Eiji Osawa  
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# **Oral Presentations**

# CHEMISTRY ON STAMPS AND RELATED THINGS

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In addition to their application in postal services, stamps and postal cancellations are used by governments for commemorating events and personalities, for displaying a country's achievements and its pride in successful citizens, for propaganda purposes and for raising money. The stamps and other philatelic material dealing with chemistry and affiliated topics enable us to see how our profession is seen and its topics of interest displayed by the outside world. Chemistry, chemists and chemical reactions, minerals and petroleum, Nobel laureates, medicines, drugs and ecologically dangerous chemicals are among the topics displayed. By looking at Nobel laureates' stamps with a chemist's and a layman's eye, one can study the history of chemistry, recognize topics of past and current interest, learn about centers of scientific excellence, teacher-student relationships or the fashion of the time. The liberty that stamp designers sometime take may fascinate us with elusive structures, new types of chemical bonds, unusual symmetries and bond angles and strange chemical reactions. Small countries may achieve great Philatelochemical originality in this respect. Chemical genealogy, scientific family connections (brothers in law, husband-wife, parents-children), chemists in other professions (heads of states and governments, musicians, authors and even unfortunately, tax collectors) can be seen on stamps, a philatelo periodic table can be constructed, and chemical names of villages and cities on postal cancellations can be recognized and sometimes raise penetrating questions (e.g., is the atmosphere around Ne, Kentucky, rich in Ne?)

Interconnections involving chemists, chemicals, reactions coupled with personal associations make it easy to dedicate stamps to friends and conference lecturers. Looking at chemistry in an easy-going way, by using stamps as a vehicle, also has minor fringe benefits to the lecturer. If the slides are accidentally mixed just before the lecture, the lecture can continue without interference, and the lecturer can ask the organizers to add at the bottom of this abstract any stamps of *their* liking.

Some of the topics mentioned above will be presented in the lecture.

## PROTOLYTIC ACTIVATION OF ELECTROPHILES IN ORGANIC REACTIONS

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Electrophiles that are capable of further interaction (coordination, solvation) with strong acids are activated in this way. This results from the formation of superelectrophiles, i.e., electrophiles with doubly electron-deficient (dipositive) nature whose reactivity substantially exceeds that of their parent electrophiles.<sup>[1]</sup> As representatives of the protolytic activation the following electrophiles and their reactions in superacidic media are discussed: onium ions, oxonium, carboxonium, sulfonium, selenonium, and telluronium ions; acyl cations; protonated CO, CO<sub>2</sub>, COS, and carbonic and thiocarbonic acids; carbocations and heteroatom-substituted carbocations (and some of their boron analogs); halonium ions; azonium (including nitronium ion) and carbazonium ions. Emphasis is placed on structural and experimental chemical investigations, as well as theoretical calculation of the involved systems.

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HOLY-GRAILS IN GAS-PHASE CHEMISTRY: IN SEARCH OF ELUSIVE  
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Over the last decade, neutralisation-reionisation mass spectrometry (NRMS)<sup>[1]</sup> has emerged as a powerful method for the generation and structural characterisation of small, neutral molecules that are not accessible in the condensed phases and which are believed to play a central role in many fields of chemistry.<sup>[1]</sup>

Systems that will be discussed in detail include the celebrated

- Water, methanol and ammonia oxides<sup>[2]</sup>
- Ethylendione (C<sub>2</sub>O<sub>2</sub>)<sup>[3]</sup>
- HC≡SiX (X = F, Cl), the first molecules with formal carbon-silicon triple bonds.<sup>[4]</sup>

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FEMTOCHEMISTRY - ORGANIC CHEMISTRY IN THE FEMTO AGE

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In this lecture, we will give an overview of recent advances in femtochemistry, and highlight some new directions of the field.

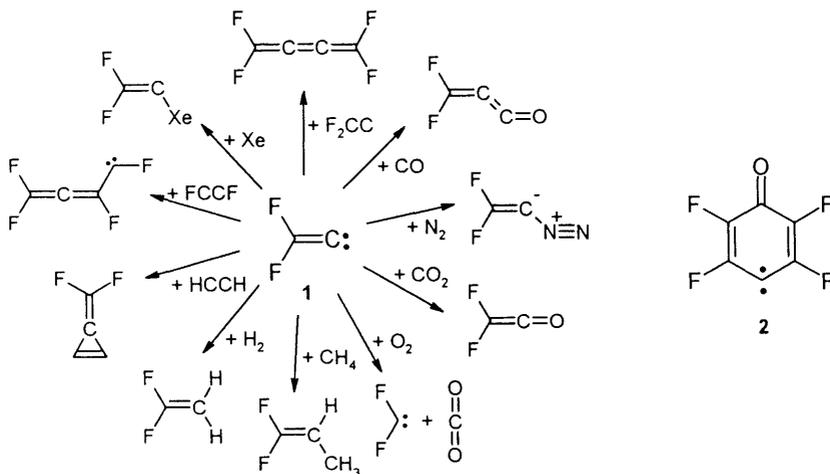
## REACTIONS OF SUPER-ELECTROPHILIC CARBENES

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The concept of philicity has proven to be a useful tool to rationalize carbene reactivity.<sup>[1]</sup> During the last years the nucleophilic carbenes of Arduengo- and Wanzlick-type, which are stable at room temperature and even can be crystallized, attracted much attention.<sup>[2]</sup> In contrast, highly electrophilic carbenes are much less well studied.



In the lecture the chemistry of difluorovinylidene 1 and 4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene 2 as prototypes of electrophilic singlet and triplet carbenes, respectively, is discussed.<sup>[3]</sup> The reactivity of these carbenes is governed by their extreme electrophilicity and electron affinity. Insertion reactions into CH bonds and even into  $\text{H}_2$  proceed at temperatures below 30 K without activation barriers. The reactions of 1 and 2 with acetylenes clearly proceed stepwise with formation of diradicals or carbenes as isolable reactive intermediates. The most striking example for the electrophilicity of 1 is the thermal reaction with Xe to give a charge transfer complex with a characteristic IR spectrum.

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## TOWARDS PROGRAMMED SUPRAMOLECULAR MATERIALS

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Supramolecular chemistry has relied on more or less preorganized molecular receptors for effecting molecular recognition, catalysis and transport processes. A step beyond consists in the design of systems undergoing *molecular self-organization*, i.e. systems capable of spontaneously generating a well-defined supramolecular architecture by *self-assembling* from their components in a given set of conditions.

These *programmed supramolecular systems* operate via the *molecular information* stored in the components and acting through selective molecular interactions.

Several areas of investigation concerning supramolecular entities of either organic or inorganic nature have been developed:

- 1) *supramolecular polymer chemistry*, in particular the generation of *mesophases* and *liquid crystalline polymers* of supramolecular nature from complementary components;
- 2) the induction of molecular recognition directed processes in *supramolecular assemblies* and in solid state *crystal engineering*;
- 3) the *self-assembly of inorganic species* based on ligand design and on the use of suitable coordination algorithms as expressed in - the formation of helical metal complexes, the *double-stranded and triple-stranded helicates*, - the spontaneous generation of *closed cage structures*, - the self-assembling of *inorganic grids* of metal ions based on suitably designed ligands.

A selection of results obtained in these areas will be described.

The design of molecular information controlled, “*programmed*” systems represents new horizons in supramolecular chemistry towards “*smart materials*”, network engineering and polymolecular patterning.

A rich variety of architectures and functional properties may be expected to result from the blending of supramolecular chemistry with materials science.

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A supramolecular approach to the design and synthesis of molecular materials from low molecular weight and polymeric building blocks will be described in this lecture. The following topics will be discussed in some detail:

- (i) Molecular clips from glycoluril which have been provided with long aliphatic tails and dendritic functions. These molecules can be clipped to polymers, e.g. polystyrene derivatives, providing these macromolecules with liquid crystalline properties. Related compounds with water solubilizing groups self-assemble in aqueous solution to give nanomolecular objects of well-defined shape and structure.<sup>[1]</sup>
- (ii) Mesogenic compounds composed of a central benzene ring to which porphyrin rings have been attached. These compounds generate nanometer to micrometer-sized 'wheels' by self-assembly and aided assembly processes. These objects are of interest as analogues of the naturally occurring light-harvesting systems and are being studied by different physical methods, including scanning probe techniques (AFM and SNOM).<sup>[2]</sup>
- (iii) Isocyanopeptides which can be polymerized using nickel(II) ions to give polymers that combine different structural motives in one polymer chain, viz. a helix structure and a  $\beta$ -sheet like structure. They may be considered as new synthetic analogues of naturally occurring polypeptides and proteins. Block copolymers of isocyanopeptides and styrene which display amphiphilic properties have also been prepared. On dispersal in water these 'super amphiphiles' generate different types of supramolecular structures, e.g. vesicles, multilayer sheets and super helices.<sup>[3]</sup>

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## IONIC LIQUIDS: NEOTERIC SOLVENTS FOR ORGANIC SYNTHESIS

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Clean technology concerns the reduction of waste from an industrial chemical process to a minimum: it requires the rethinking and redesign of many current chemical processes. The *E*-

factor of a process is the ratio (by weight) of the by-products to the desired product(s).<sup>[1]</sup> The Table illustrates that the 'dirty' end of the chemical industry, oil refining and bulk chemicals, is remarkably waste conscious: it is the fine chemicals and pharmaceutical companies who are using inefficient, dirty, processes, albeit on a much smaller scale. Volatile organic solvents are the normal media for the industrial synthesis of organics (petrochemical and pharmaceutical), with a world-wide usage of *ca.* 4,000,000,000 p.a. However, the Montreal Protocol has resulted

Industry	Production / tons p. a.	<i>E</i> -factor
Oil Refining	10 <sup>6</sup> - 10 <sup>8</sup>	0.1
Bulk Chemicals	10 <sup>4</sup> - 10 <sup>6</sup>	1-5
Fine Chemicals	10 <sup>2</sup> - 10 <sup>4</sup>	5-50
Pharmaceuticals	10 <sup>1</sup> - 10 <sup>3</sup>	25-100

in a compelling need to re-evaluate many chemical processes that have proved otherwise satisfactory for much of this century.

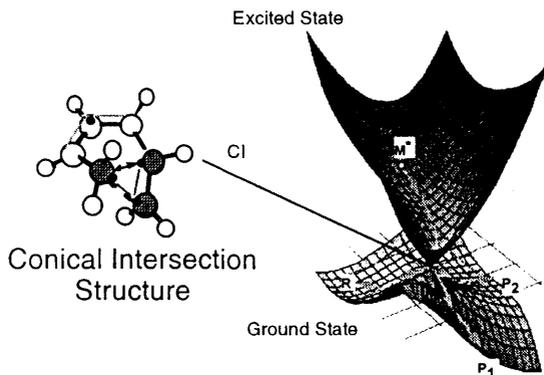
The principal aim of our programme is to explore, develop and understand the role of ionic liquids as media for industrially-relevant organic chemistry. Ionic liquids possess, *inter alia*, the following desirable properties: (1) they have a liquid range of 300 °C, allowing tremendous kinetic control, (2) they are outstandingly good solvents for a wide range of inorganic, organic and polymeric materials: high solubility implies small reactor volumes, (3) they exhibit Brønsted, Lewis, and Franklin acidity, as well as superacidity, (4) they have no effective vapour pressure, (5) their water sensitivity does not restrict their industrial applications, (6) they are thermally stable up to 200 °C, and (7) they are relatively cheap, and easy to prepare. Unlike water and other hydroxylic solvents, they will dissolve a wide range of organic molecules: exploratory work in our own laboratories (carried out in collaboration with BP and Unilever) has demonstrated that a wide range of catalysed organic reactions (including oligomerizations, polymerizations, alkylations, and acylations) occurs in room-temperature ionic liquids, and that these are serious candidates for commercial processes.

Examples of industrial relevance which will be discussed include: Syntheses of poly(isobutene) and linear alkyl benzenes, Friedel-Crafts chemistry, *N*- and *O*- alkylations, Diels-Alder chemistry and arene hydrogenation reactions.

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As a result of computational work in the last few years, novel aspects of the behaviour of electronically excited intermediates have emerged. The most general of these is that their lifetime, reactivity and photoproduct selectivity seems to depend on the evolution towards a critical molecular structure which corresponds to a real crossings (conical intersections and singlet/triplet crossings) between potential energy surfaces of the chemically relevant electronic states (usually the first excited and ground states).<sup>[1]</sup> Since real crossings provide fully efficient channels for the radiationless deactivation of the intermediate  $M^*$ , the investigation of the "pathways" which describe the evolution towards the crossing point (e.g. a conical intersection structure) is becoming of central importance in mechanistic photochemistry.



In this lecture, we briefly revise the computational strategies used by our group to construct interstate photochemical reaction pathways. The mechanistic information obtained by using these techniques will be illustrated through the discussion of few case-studies including: the photolysis and quenching of azo-alkanes,<sup>[2]</sup> the ring-opening of cyclohexadienes<sup>[3]</sup> and the ultrafast photoisomerization of retinal chromophore in rhodopsin proteins.<sup>[4]</sup>

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CHEMISTRY WITH TEFLON PONY TAILS: THE FLUOROUS SOLVENT  
APPROACH TO SYNTHESIS AND CATALYSIS, AND SEPARATIONS

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The design of new or improved chemical transformations invariably turns to catalysis. Two especially active frontiers are (1) non-traditional reaction media, and (2) new catalyst immobilization or recovery strategies to facilitate re-use. Towards these ends, a conceptually new protocol, "fluorous biphasic catalysis", has been developed. The term "fluorous" is used as an analog to "aqueous" for highly fluorinated alkane, ether, and tertiary amine solvents. A variety of such solvents are commercially available, and commonly give bilayers with organic solvents. As such, fluorous media represent a greatly underutilized "orthogonal phase" for synthesis and separation. Furthermore, many solvent combinations become miscible at elevated temperatures. This allows chemistry to be effected under homogenous one phase *or* heterogeneous two phase conditions.

How can catalysts be engineered to have high affinities for fluorous media? Our approach has been to append fluoroalkyl groups or "pony tails" such as  $(\text{CH}_2)_y(\text{CF}_2)_x\text{CF}_3$ . These serve, when of sufficient length and quantity, a "like dissolve like" function. Similar strategies are used to design dyes capable of sticking to Teflon. The  $(\text{CH}_2)_y$  spacers provide tuning elements that can be adjusted to insulate the active site from electron withdrawing fluorines, or enhance Lewis acidity. This presentation will first describe the preparation of various phosphine, amine, and transition metal containing fluorous reagents or catalysts. Key physical properties (absolute and relative solubilities, crystal structures, etc.), will be highlighted. Applications in metal-catalyzed additions to alkenes and other organic transformations will then be detailed.

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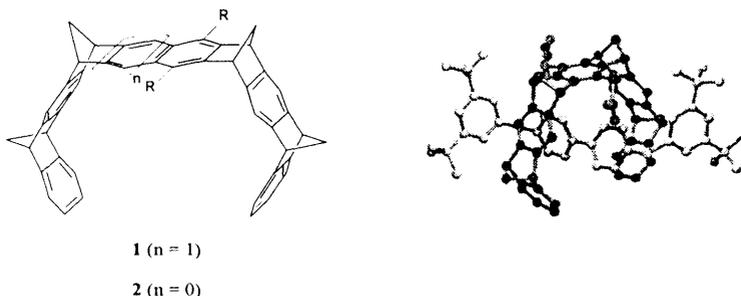
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MOLECULAR TWEEZERS AS SYNTHETIC RECEPTORS: MOLECULAR  
RECOGNITION OF ELECTRON-DEFICIENT AROMATIC AND ALIPHATIC SUBSTRATES

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Syntheses and supramolecular properties of the molecular tweezers **1** and **2** containing naphthalene and benzene spacer units, respectively, are described. They selectively bind electron deficient aromatic and aliphatic substrates<sup>[1]</sup>. They also form stable complexes with cationic substrates<sup>[2]</sup>. The crystal structure of a clipped pseudorotaxane consisting of the benzene spaced tweezer as a "broken wheel" and a viologene derivative as the "axle" is depicted in the scheme. Quantitative investigations by the use of the NMR titration method shows that the naphthalene-spaced tweezer **1** forms stronger complexes with aromatic and quinoid substrates than the benzene-spaced tweezer **2** ( $\Delta\Delta G = 1.5 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$ ), whereas the aliphatic substrates are only complexed by **2** as receptor. HPLC studies with chemically bonded stationary phases (CBSP<sub>s</sub>) containing the benzene- or the naphthalene-spaced-tweezer give similar results.<sup>[3]</sup> Force-field calculations (AMBER\*) and single crystal structure analyses reveal that **1** has an almost ideal geometrical topology for the complexation of aromatic substrates while complexation of these substrates by the smaller receptor **2** requires a significant expansion of the tweezer's tips (by about 2 Å) which causes an extra strain energy in **2** by about 1-2 kcal·mol<sup>-1</sup>. According to semiempirical AM1 calculations the electrostatic potential surfaces (EPSs) of **1** and **2** are surprisingly negative on the concave sides of the molecules and, hence, complementary to those of the electron deficient substrates.<sup>[4]</sup>



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ORGANOSILICON CHEMISTRY: A FIELD OF FRUITFUL INTERPLAY BETWEEN  
EXPERIMENT AND THEORY

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Many fundamental aspects of silicon chemistry have begun to be unravelled only in the last two decades, examples being the synthesis and characterization of the first stable compounds with multiple-bonds to silicon and of the first stable silylenes. These exciting developments were occurring at the time when theory (in particular *ab initio* molecular orbital theory and density functional methods) was reaching the stage where these methods could be used to calculate reliably the properties of molecules of moderate size. Indeed, computational quantum chemistry made numerous crucial contributions to silicon chemistry by providing interpretations to experimental findings, and more importantly, **by making predictions and directing experiments**. This crucial role of theory continues.

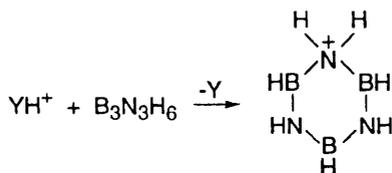
In this lecture I will demonstrate the synergism of theory and experiment in silicon chemistry by discussing several examples from recent work of my research group (both theoretical and experimental). Some topics that will be discussed are: (a) The mechanisms of addition reactions to C=Si and Si=Si multiple bonds. (b) Multiply-bonded silicon compounds and their isomers, in particular, triply-bonded silicon compounds, such as silynes  $RC\equiv SiR'$  and disilynes  $RSi\equiv SiR'$ . Our theoretical predictions have lead recently to the preparation in the gas-phase of the first known silyne. A theoretical prescription for the first **stable** triply-bonded silicon compounds will be presented. (c) How to prepare the first ground-state triplet silylenes. (d) Polysilyl radicals and anions.

## GAS PHASE REACTIONS OF ARENIUM IONS

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Mechanistic studies of gaseous arenium ions were aimed to characterize the intrinsic features of these intermediates and at the same time to use them as models for the investigation of elementary processes such as proton migrations. The prototypical arenium ion,  $C_6H_7^+$  from the protonation of benzene, shows a reactivity behavior conforming to a  $\sigma$ -complex species, when its bimolecular ion chemistry is studied in gaseous environments at pressures ranging from a few Torr to 1 atm. Among the proposed alternative structures, an edge protonated species is found to play a role as the transition state for relatively fast 1,2-hydrogen shift processes, leading ultimately to complete scrambling of the seven H's ( $k \approx 10^9 \text{ s}^{-1}$  at  $40^\circ\text{C}$ ).<sup>[1]</sup> Intermolecular processes of  $H^+/D^+$  transfer are responsible for the isotope exchange taking place when deuterated arenium ions,  $XC_6D_6^+$ , react with an exchange reagent, AH. These processes have been exploited to evaluate the sites involved in the protonation of substituted benzenes. The gas phase chemistry of organic arenium ions has been recently related to that of potential inorganic analogues, such as the ions obtained from addition of charged electrophiles to borazine,  $(\text{HBNH})_3$ , also termed "inorganic benzene". The experimental gas phase basicity of borazine, equal to 185 kcal/mol, involves protonation at nitrogen, leading to  $\text{H}_3\text{B}_3\text{N}_3\text{H}_4^+$  ions, similar in structure to benzenium ions, as shown by ab initio calculations.



These ions are unreactive with  $\text{D}_2\text{O}$  but undergo H/D exchange of up to four hydrogens with  $\text{CD}_3\text{OD}$ . At variance with benzenium ions, no isomerization processes by stepwise 1,2-hydrogen shifts do occur. According to calculations, protonation at boron is unfavored by 28 kcal mol<sup>-1</sup> with respect to protonation at nitrogen and  $\text{H}_4\text{B}_3\text{N}_3\text{H}_3^+$  ions are prone to undergo cleavage of  $\text{H}_2$ , their structure resembling a  $[\text{B}_3\text{N}_3\text{H}_5 \dots \text{H}_2]^+$  complex. The thermodynamic parameters for the association of  $\text{Me}_3\text{Si}^+$  to borazine place borazine in a correlation line pertaining to model aromatic compounds.

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# DETERMINATION OF MOLECULAR GEOMETRIES: INTERPLAY OF THEORY AND EXPERIMENT

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Molecular structures are key quantities for the understanding of chemical concepts concerning bonding, molecular properties, or chemical reactivity. The accurate and reliable determination of molecular geometries, however, is a non-trivial task, as experimental difficulties, surrounding effects, and rovibrational averaging often limit the accuracy which can be achieved.

In this lecture, it will be demonstrated how high-level quantum chemical calculations can be used to facilitate and improve the analysis of experimental data and thus enhance accuracy and reliability of experimentally determined structures. This interplay of theory and experiment will be demonstrated by the following examples:

- Analysis of experimental rotational constants using quantum chemically calculated anharmonic force fields: quantum chemical calculations enable here the determination of well-defined  $r_e$  geometries with an overall accuracy for bond distances of  $\pm 0.001$  Å instead of the less well-defined  $r_o$ ,  $r_s$ , ... structures. Examples will include cyclopropane (for which a controversy exists in the literature about its  $r_e$  geometry), dioxirane, ketene, LiCCH, as well as molecules of astrophysical interest such as  $\text{H}_2\text{C}=\text{C}=\text{C}$ ,  $\text{H}_2\text{C}=\text{C}=\text{C}=\text{C}$ , and  $\text{SiC}_3$ .
- Analysis of electronic excitation spectra to determine excited state geometries: In case of *s*-tetrazine, reliable results for the geometry of the corresponding  $S_1$  state are obtained from a Franck-Condon analysis of a vibrational progression only if the analysis is assisted by quantum chemical calculations.

The importance of methodological developments in quantum chemistry to enhance this interplay of theory and experiment will be emphasized.

COMPUTATIONAL EXPLORATION OF MECHANISTIC BORDERLINES FOR  
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Computational simulation of simple identity reactions  $\text{H}_2\text{O} + \text{R-OH}_2^+ \rightarrow {}^*\text{H}_2\text{O-R} + \text{OH}_2$ , using a semiempirical MO method with a continuum treatment of aqueous solvation, illustrates the changing energy surface topography accompanying  $\text{S}_{\text{N}}2/\text{S}_{\text{N}}1$  mechanistic changeover along the series  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  ${}^i\text{Pr}$  and  ${}^t\text{Bu}$ , and permits determination of kinetic isotope effects for *both* pathways with *each* alkyl group. However, molecular insight into solvation structures and specific interactions with reacting solutes cannot be obtained from a continuum model, but requires instead a description involving discrete solvent molecules. Our GRACE software is now being employed to investigate and characterize intermediates, transition structures (TSs), intrinsic reaction coordinates and vibrational frequencies for very large flexible systems using hybrid quantum/classical methods.<sup>[1]</sup>

We present some results of semiempirical and *ab initio* QM/MM simulations (including) obtained recently for hydrolysis of simple substrates  $\text{R-Cl}$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  ${}^i\text{Pr}$  and  ${}^t\text{Bu}$  and  $\text{MeOCH}_2$ ) with QM substrate + nucleophile and several hundred MM water molecules. The  $\text{S}_{\text{N}}2$  TSs determined for  $\text{H}_2\text{O} + \text{R-Cl} \rightarrow {}^*\text{H}_2\text{O-R} + \text{Cl}^-$  with AM1 + 496 TIP3P waters and MP2/6-31G\* + 200 TIP3P waters are structurally early and late, respectively, and yield secondary  $\alpha\text{-}^2\text{H}$  kinetic isotope effects  $k_{\text{H}}/k_{\alpha\text{-D}_3}$  of 0.86 and 0.92 at 90°C, as compared with the experimental value of 0.92.

For  $\text{R} = \text{MeOCH}_2$  we have found two TSs with different energies. The intrinsic reaction coordinate from each TS leads forwards directly to the product complex and backwards directly to the reactant complex, but inspection of the transition vectors suggests one is  $\text{S}_{\text{N}}2$ -like and the other  $\text{S}_{\text{N}}1$ -like.

Our calculations to date involve full relaxation of all degrees of freedom, subject to boundary constraints on the solvent sphere, and lead to well characterized individual structures for each solvated system. These structures are not unique, and for each reaction path there very probably exists a multitude of nearly degenerate structures with slightly different arrangements of solvent molecules, just as we have found families of similar transition structures for an enzyme-catalyzed reaction.<sup>[1]</sup> Accurate evaluation of Gibbs free energy changes would require averaging over very many configurations.

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THE RICH CHEMISTRY OF PHOSPHINIDENES, THE PHOSPHOROUS  
ANALOGUES OF CARBENES

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Since their discovery in the early 80s rapid progress has been made to develop the chemistry of Fischer and Schrock-type phosphinidenes. These transition metal complexed phosphinidenes behave in many respects like their carbene analogues. This will be highlighted for the reactivity of several electrophilic phosphinidenes, all of which are generated in situ. The more stable, isolable nucleophilic species will also be addressed, particularly with respect to their transition metal dependent properties. The focus of the presentation, however, is on the application and the comparison of the electrophilic  $\text{PhPW}(\text{CO})_5$  and  ${}^1\text{Pr}_2\text{NPF}e(\text{CO})_4$  species.

Novel applications of the popular  $\text{PhPW}(\text{CO})_5$  include the synthesis of a variety of new, highly strained, stable polycyclic and (poly)spiro compounds. Also a variety of new heterocyclic systems can be formed with this phosphinidene. It will be demonstrated that this popular system adds in a 1,2- and a 1,4-manner to conjugated olefins and even aromatics. Emphasis is placed on  $\text{W}(\text{CO})_5$ -decomplexation, but also on several new rearrangements involving the vinylphosphirane unit for which kinetic parameters will be presented. The analogy with the well-studied vinylcyclopropanes is astounding. However, the chemistry of the phosphorus analogues displays more controlled behavior. Controlling the properties of the  $\text{W}(\text{CO})_5$ -complexed products also let us to the first uncomplexed 7-phosphanorbornadiene.

The at  $-30\text{ }^\circ\text{C}$  in situ generated  ${}^1\text{Pr}_2\text{NPF}e(\text{CO})_4$  provided us recently with another entry into the versatile chemistry of electrophilic phosphinidenes. Depending on the reaction conditions this species either generates a broad spectrum of Fe/P-clusters or gives well controlled phosphinidene additions to unsaturated systems. The similarities and differences of this system with  $\text{PhPW}(\text{CO})_5$  will be addressed.

ACYL VS. NITROGEN PROTONATION IN CARBOXYLIC AND NON-CARBOXYLIC  
AMIDES IN THE GAS PHASE AND IN SOLUTION. PATTERNS OF NMR PROPERTIES  
AND HYDRATION ENERGIES

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Amides with the general formula  $Acyl-NR_2$ , where *Acyl* is a group derived from an organic or inorganic acid (e.g.  $RC(O)O$ ,  $RS(O)$ ,  $RSO_2$ ,  $NO$ ,  $NO_2$ ,  $CN$ , etc.), are species of widespread occurrence. All such compounds behave as bases of widely varying strength, and possess more than one site for protonation, i.e. the nitrogen atom and a basic atom in the acyl moiety, most often N, S, or O. Therefore, under moderately acidic conditions (i.e. only capable of mono-protonation) an ambiguity exists with regard to the preferred site of protonation.

We present the results of a combined experimental and theoretical effort to determine the protonation site of representative amides derived from various acids: carboxamides, thiocarboxamides, sulfenamides, sulfenamides, sulfonamides, nitrosamides, nitramides, cyanamides, phosphorous and phosphoric triamides. All these compounds may undergo protonation at either the amide nitrogen or at one of the atoms contained in the acyl group (O, N, P, S). Thus, we have monitored the changes in the NMR chemical shifts and longitudinal relaxation rates of  $^{14}N$ ,  $^{17}O$  and  $^{31}P$  in solutions containing either the neutral or the protonated form. These are compared with the theoretically calculated nuclear shieldings and quadrupolar coupling constants. It will be shown that NMR properties and calculated energies (both in the gas phase and in water, modeled by the IPCM continuum method) allow one to pinpoint the most stable protonated form.

## PHOSPHOROUS-CONTAINING DENDRIMERS

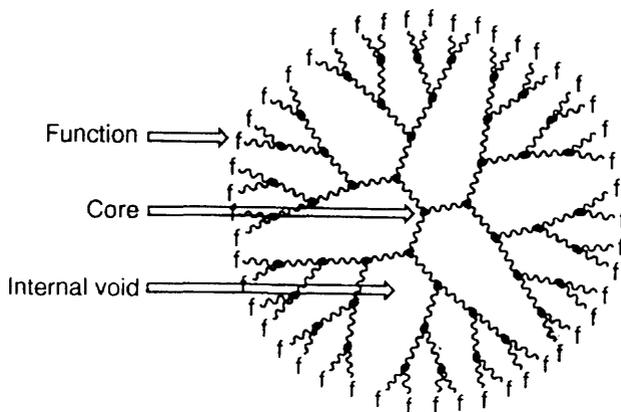
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Dendrimers are three-dimensional, highly ordered polymers formed by reiterative reaction sequences starting from smaller molecules. Several new methods of synthesis of dendrimers incorporating P-N or P=N bonds will be reported.<sup>[1]</sup> Some examples of the reactivity of these macromolecules will be presented with emphasis on reactions done within the cascade structure. Such reactions allow to incorporate a variety of functional groups into the internal voids and to develop an organic or organometallic chemistry into the cavities. Functionalization of the core of dendrimers allow the preparation of a large number of multidendritic systems through core-core or core-surface couplings. The key role played by phosphorus in all these reactions will be emphasized.

Lastly several applications of phosphorus containing dendrimers will be presented and discussed.



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THE DESIGN OF TRANSITION METAL CATALYSTS FOR NEW POLYOLEFIN  
MATERIALS

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The first high molecular weight alternating propene-CO copolymers (up to  $5 \times 10^5$  g/mol) [1] and propene-ethene-CO terpolymers (up to  $1.2 \times 10^6$  g/mol) were prepared by the use of palladium(II) complexes, like  $[(dppp)Pd(NCCH_3)_2][BF_4]_2$ . This precursor was activated by an optimized amount of methanol or water. Excess activator acts as chain-transfer reagent as indicated by the decrease of molecular weight of the products.

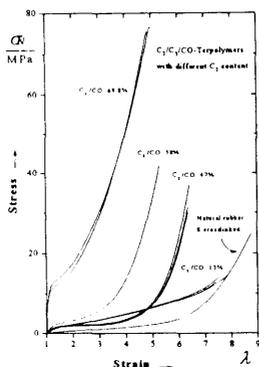


Figure 1: Stress-Strain Measurements

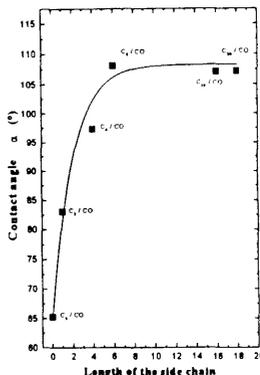


Figure 2: Contact Angles

Propene-CO copolymers with molecular weights exceeding  $M_w = 1.0 \times 10^5$  g/mol are thermoplastic elastomers [2]. The polymers are soluble in organic solvents. Enhancement of the elasticity of P-CO copolymers was achieved by incorporating ethene-CO units randomly along the polymer main chain [3]. When the ratio of E-CO to P-CO is adjusted below 50%, the products are thermoplastic elastomers with properties comparable to flexible PVC. Above this ratio the materials are crystalline thermoplastics (Fig. 1).

The high polarity of the ethene- or propene based polyketones can be easily controlled by incorporation of higher  $\alpha$ -olefins ranging from 1-butene to 1-eicosene [4]. The alternating octadecene-CO and eicosene-CO copolymers are comb-like structures with properties dominated by the unpolar nature of the side chains. The possibility to switch between polar and apolar behavior is demonstrated by contact angle measurements (Fig. 2) which are performed on a drop of water located on the surfaces of a copolymer film. The increase of the contact angle ( $\alpha$ ) from  $65^\circ$  to  $110^\circ$  with the length of the branches ( $C_0$  to  $C_{18}$ ) indicates the broad range of surface polarity that can be covered.

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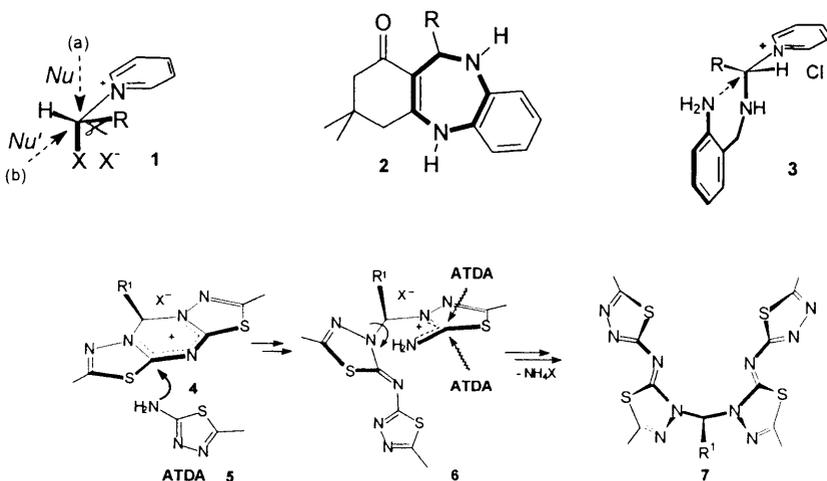
EXPERIMENTAL AND THEORETICAL INVESTIGATIONS ON  
SPECIAL GROUP TRANSFER REAGENTS

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The properties of a variety of novel reactive intermediates **1** - **7** have been investigated experimentally and with high level DFT and *ab initio* calculations. We focus in this lecture on N-(haloalkyl)pyridinium halides **1** which have been reacted, in many cases *in situ*, with a variety of nucleophiles. Systematic investigations have yielded many useful products (five-, six- and seven-membered ring systems, e.g. **2**) and intermediates such as **3** or the novel 5/6/5 heterocycles **4**. The latter compounds are generated in the course of several successive reaction steps in which specific proton migrations, as well as bond breaking and forming processes occur. Compounds **4** have been reacted with a variety of ambident nucleophiles. A mixture of compounds **4** and **5** leads to an unexpected multi-step reaction cascade in the course of which the multi-aza/thia heterocycles **7** are formed.<sup>[1,2]</sup> These compounds **7** deserve interest as potential ligands for synthetic models of the active center of carbonic anhydrase (CA).



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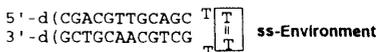
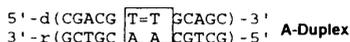
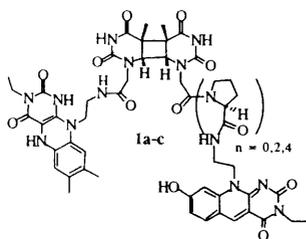
## FROM MECHANISTIC INVESTIGATIONS TO ARTIFICIAL REPAIR ENZYMES

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UV-irradiation causes severe genome damage as a result of the formation of cis-syn cyclobutane pyrimidine dimer DNA-lesions. The efficient repair of these main DNA-lesions is essential for every cell in order to avoid cell death and carcinogenic cell growth. DNA-photolyases are repair enzymes which catalyze the [2p+2p] cycloreversion of these lesions in many species. The elemental process during the repair process is the recognition of the mutagenic DNA-lesions within a structurally heterogeneous genome, which possibly requires flipping of the lesioned base out of the double helix. The cycloreversion is driven by a light induced electron transfer from a flavin to the dimer lesion. This process is fueled by energy that is donated by a deazaflavin cofactor.

A) In order to investigate why photolyases separate the required cofactors by an unusually large distance of  $> 18 \text{ \AA}$ , a series of model compounds **1a-c** were prepared, which contain the essential flavin and deazaflavin cofactors at systematically increased distances. Compounds which possess the worst energy transfer and the largest cofactor separation exhibit paradoxically the best repair. This finding suggests that the catalytic repair process is compromised by a competitive intercofactor electron transfer that needs to be suppressed by increasing the distance between the cofactors.

B) In order to gain insight into why specific genome areas are repaired with significantly lower efficiency (mutation hotspots), we investigated the parameters, which influence the recognition of DNA-lesions within DNA. To this end, DNA-lesion phosphoramidites were synthesized and incorporated into double stranded oligonucleotides possessing different conformations. It was found that DNA-lesions induce a moderate local melting of the double helix. The degree of local melting determines the repair efficiency possibly by influencing the ease of lesion flipping.



CONFORMATION DEPENDENCE OF SUBSTITUENT EFFECTS IN THE SOLVOLYSIS  
OF 1,1-DIARYL-2,2,2-TRIFLUOROETHYL SYSTEM

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The solvolysis rates of 1,1-(X,Y-diaryl)-2,2,2-trifluoroethyl tosylates were determined for a wide range of substituents (X, Y) at 25.0 °C in 80% aqueous ethanol. The substituent effects (X) on the solvolysis rates were analyzed by the Yukawa-Tsuno (Y-T) equation (1) for typical fixed Y-sets, Y = *p*-MeO, *p*-Me, H and *m*-Cl, as well as the symmetrically disubstituted set X = Y;

$$\log(k/k_0) = \rho(\sigma^0 + r\Delta\sigma_R^+)$$
 (1)

The symmetrical X = Y set gave an excellent linear Y-T correlation for the whole substituent range with a  $\rho = -4.14$  and  $r = 1.20$ . The fixed Y = *p*-MeO set showed a bilinear correlation; the correlation for the strong  $\pi$ -donor class substituents is involved in the correlation for the X = Y set, and a discrete correlation with significantly reduced  $\rho$  was given for substituents less electron donating than *p*-Me. The substituent effect in any fixed Y sets comprises three separate correlations; the range of substituents where X's are the same resonance class with Y conform the correlation for X = Y set, and for stronger electron donating class substituents than Y a correlation with  $\rho = -6.0$  and for the substituent range more electron withdrawing than Y a separate correlation with a reduced  $\rho$  of ca -2 are obtained.

In  $\alpha,\alpha$ -diarylcarbocations where X = Y, the molecule adopts a propeller-shaped twisted conformation to avoid steric repulsion reserving the charge delocalization into the ring, while in unsymmetrical X \_ Y carbocations, the propeller shape is destroyed; the geometries of twisted conformers are determined by the *ab initio* MO optimization. The nonlinear correlations of substituent effects in the solvolysis should be related to the substituent-induced change in conformation of the transition state, reflecting geometries of the intermediate carbocations. Thus we attempted to interpret the non-linear correlations for substituent effects on these Y-sets in terms of geometries of transition states simulated by corresponding cations.

The correlation found for the symmetrical set must be essential of the *E*-conformation where both aryls are equivalently twisted ( $\theta_X = \theta_Y \cong 30^\circ$ ). The three comprising correlations in any Y set also can be assigned as essential of three conformers, as *E*-conformer correlation for substituents in the same resonance class with Y, as *P*<sub>X</sub>-conformer correlation (X-phenyl coplanar, Y-phenyl twisted) for the electron donating class substituents, and as *T*<sub>X</sub>-conformer one (X-phenyl twisted, Y coplanar) for another class, respectively.

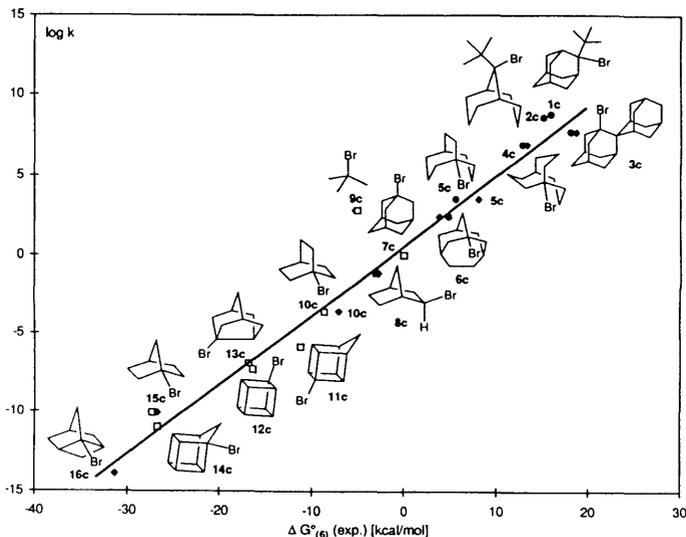
## The Stability of Bridgehead Carbocations

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The stability of bridgehead carbenium ions has been measured in the gas phase from dissociative proton attachment (DPA) of bridgehead bromides, chlorides and alcohols using Fourier Transform Cyclotron Resonance Spectroscopy (FT ICR). The stability of the ions, relative to that of their precursors, correlates with the rates of solvolysis of the corresponding bridgehead derivatives over a rate range of 23 log. units. The Gibbs energies for hydride transfer from R-H of these compounds, relative to adamantane, calculated at the MP2/6-311G\*\* level, are in full agreement with the experimental results.<sup>[1]</sup>

In contrast, acyclic tertiary derivatives such as *t*-butyl halides solvolyze faster than predicted on the grounds of carbenium ion stabilities. The significance of nucleophilic solvent participation in the solvolysis of tertiary non-bridgehead derivatives will be discussed.



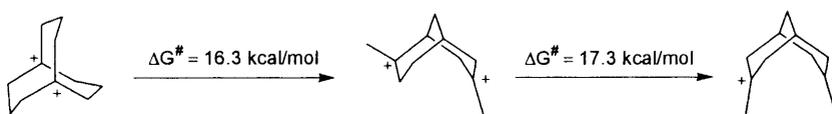
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## REARRANGEMENT OF BICYCLO[3.3.3]UNDECYL DICATION

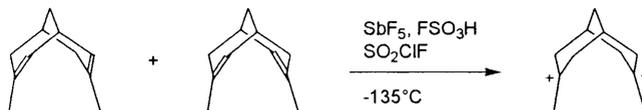
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The cation centers in the bicyclo[3.3.3]undeca-1,5-dication are in an exceptional close proximity, which provides a large driving force for its rearrangement reaction. In superacidic media, the bicyclo[3.3.3]undeca-1,5-diyl dication was found to rearrange into the 2,7-dimethylbicyclo[3.3.1]nona-2,7-diyl dication and subsequently into the 3,7-dimethylbicyclo[3.3.1]nona-3,7-diyl dication. Energy barriers of  $16.3 \pm 0.4$  kcal/mol or  $17.3 \pm 0.4$  kcal/mol, respectively, were measured.



The final rearrangement product was also obtained by protonating a mixture of the 3,7-dimethylbicyclo[3.3.1]nona-2,7-diene and 3,7-dimethylbicyclo[3.3.1]nona-2,6-diene.



The two rearrangement products were also investigated by ab initio NMR calculations at the Becke3LYP / 6-31G\* and the MP2 / 6-31G\* level of theory, and these results were in good agreement with the experimentally measured data. The chemical NMR shifts of the a and b carbons of the bicyclo[3.3.3]undeca-1,5-diyl dication and the 3,7-dimethylbicyclo[3.3.1]nona-3,7-diyl dication provided valuable information about the hyperconjugation interactions in these systems, which could also be reproduced with ab initio calculations at the same levels of theory.

A plausible mechanism for the overall rearrangement was proposed and ab initio calculations at the Becke3LYP / 6-31G\* level were used to estimate the relative energy of all intermediates involved.

THE RING ENLARGEMENT PROCESS IN THE 2-CYCLOPENTYL-2-PROPYL  
CATION

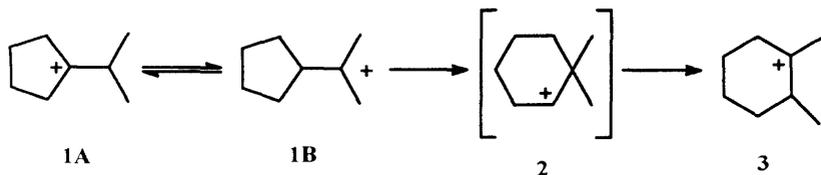
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In order to investigate the five membered ring enlargement in dammarenyl carbocation, which is the key step in the phytosterol biosynthesis, rearrangement processes in the simplest model carbocation, the 2-cyclopentyl-2-propyl cation **1**, were followed by means of <sup>13</sup>C NMR spectroscopy. The cation **1** was prepared in SbF<sub>5</sub>-SO<sub>2</sub>Cl<sub>2</sub>/SO<sub>2</sub>ClF from the corresponding alcohol precursors, using the molecular beam method. <sup>13</sup>C NMR spectrum of the starting cation **1** at -130 °C indicates that the ring expansion has not occurred during the cation preparation. At this temperature the cation **1** undergoes rapid nondegenerate hydride shift between the two structures **1A** and **1B**. At about -100 °C the ring enlargement process takes place. The product obtained is 1,2-dimethylcyclohexyl cation **3** in which the degenerate rapid hydride shift occurs over a low barrier. The formation of product **3** can be rationalized if presumed that the rearrangement proceeds by mechanism presented in Scheme 1. The first step is the expansion of the five membered ring of the less stable isomer **1B** involved in a fast preequilibrium **1A**?**1B**. The outcome is the formation of the relatively unstable secondary cation **2**. The next step, the 1,2-methyl shift in **2** leads to the formation of the cation **3**. The computational simulation of the reaction **1A**?**3** was carried out, and the relative energies between the species involved in the rearrangement process were obtained on HF/6-31G(d) and on B3LYP/6-31G(d) levels of theory.



REACTIVITY OF VINYL IODONIUM SALTS. NEW ASPECTS OF VINYL CATION  
 CHEMISTRY AND VINYLIC SUBSTITUTION REACTIONS

*Tadashi Okuyama*

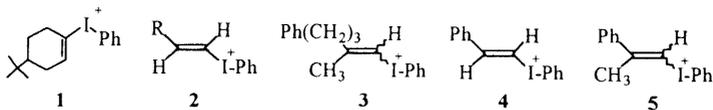
Himeji Institute of Technology, Kamigori, Hyogo 678-1297, Japan

Vinyl ionic salts are good precursors of the vinyl cations and undergo nucleophilic substitution reactions due to the high nucleofugality of the iodonio group. Solvolysis of 4-*tert*-butyl-1-cyclohexenyl(phenyl)iodonium (**1**) tetrafluoroborate is about 106 times as fast as that of the corresponding triflate. 1-Cycloheptenyliodonium salt is too unstable to be isolated above 0 °C while 1-cyclopentenyliodonium tetrafluoroborate is quite stable at 50 °C reflecting the stability of cyclic alkenyl cations.

Simple primary vinyl cations seemed hard to be generated from the 1-alkenyliodonium (**2**) salts under usual solvolytic conditions. However, a  $\beta,\beta$ -dialkylvinyliodonium salt, 2-methyl-5-phenyl-1-pentenyl(phenyl)iodonium (**3**) tetrafluoroborate, undergoes extensive rearrangement during solvolysis suggesting formation of vinyl cations. The *E* and *Z* isomeric substrates result in more but not exclusive migration of the alkyl group *trans* to the leaving iodonio group. These results can be explained in most cases by the  $\beta$ -alkyl participation leading directly to the rearranged secondary vinyl cation with *trans*-alkyl migration followed by rapid hydride shift to give the other secondary cation corresponding to the *cis*-alkyl migration, but non-stereoselective formation of a small amount of the unrearranged substitution product suggests generation of the primary vinyl cation in some poorly nucleophilic solvents.

(*E*)-Styryl(phenyl)iodonium (**4**) tetrafluoroborate undergoes solvolysis through formation of 1,1-vinylenebenzenium ion intermediate to give solely the *E* product with complete scrambling of the phenyl group in 2,2,2-trifluoroethanol. The  $S_N2$  products of inversion of configuration are also found in more nucleophilic solvents like acetic acid and methanol. Solvolysis of the *E* isomer of 2-phenyl-1-propenyliodonium (**5**) salt was found about 5000 time faster than the *Z* isomer in TFE.

Reactions of (*E*)-1-decenyl(phenyl)iodonium (**2**) salt with chloride, bromide and iodide ions in aprotic solvents resulted mainly in formation of substitution products of exclusive inversion of configuration. These results are discussed in terms of the in-plane vinyl cation  $S_N2$  mechanism.



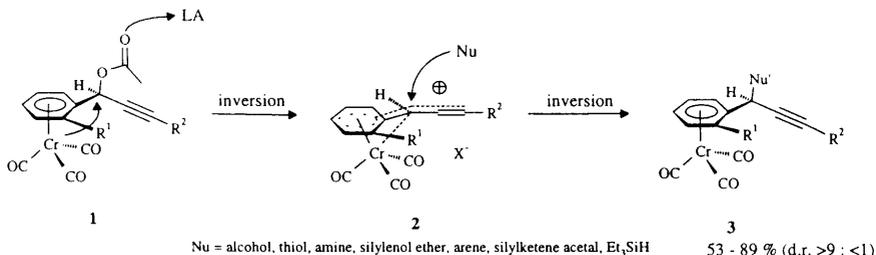
## First Diastereoselective Electrophilic Propargylations with Planar Chiral (Arene)Cr(CO)<sub>3</sub>-Substituted $\alpha$ -Propargyl Cations

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Nucleophilic substitutions classically proceeding through the trigonal planar carbenium ion inherently lose the stereochemical integrity at that center and only a few cases of neighbor group assistance led to stereocontrolled substitution products.<sup>[1]</sup> However, the advent of transition metal stabilization of  $\alpha$ -carbenium ions<sup>[2]</sup> enables nucleophilic substitutions with carbenium ions with retention of configuration as a result of a double inversion mechanism. Therefore, Cr(CO)<sub>3</sub>-complexed benzylic cations have found applications in stereoselective syntheses.<sup>[3]</sup> We are particularly interested in the reactivity and synthetic potential of ambident cationic sidechains<sup>[4]</sup> like propargyl cations giving rise to propargyl or allenyl derivatives.

Recently, we have found that the irreversible Lewis-acid mediated ionization of the acetates **1** leads to areneCr(CO)<sub>3</sub>-substituted propargyl cations **2**.<sup>[4a]</sup> The NMR-spectroscopic studies indicate that the propargyl cation sidechain is conformationally fixed and configurationally stable. Thus, the nucleophilic trapping reaction gives rise to propargylated products **3** in good yields and high diastereoselectivities. The areneCr(CO)<sub>3</sub>-substituted  $\alpha$ -propargyl cations **2** are complementary to related Nicholas' cations,<sup>[5]</sup> and for the first time, the problem of diastereoselective cationic propargylations can be solved without complexation of the triple bond.



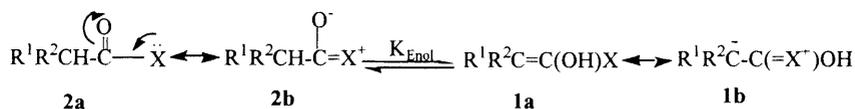
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LONG-LIVED ENOLS OF CARBOXYLIC ACIDS DERIVATIVES WITH  $\beta$ -ELECTRON-  
WITHDRAWING SUBSTITUENTS

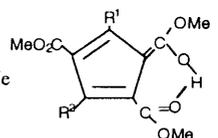
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Chemistry, The Hebrew University, Jerusalem 91904, Israel

Enols of carboxylic esters and amides (**1**, X = OR, NHR), are usually much less stable (lower  $K_{\text{Enol}}$ ) compared with their isomeric acid derivatives (**2**) than enols of aldehydes and ketones (**1**, X = H, R) due to resonative stabilization of **2a**. However, stabilization of the enol when  $R^1$  and  $R^2$  are negative charge delocalizing groups (cf. **1b**) should increase the life time of the enols.



We found that several long-lived enols of carboxylic amides and esters can exist in the solid state and in solution when substituted by proper  $\beta$ -electron withdrawing groups. With anilides **3** when  $R^1R^2\text{CH} =$  Meldrum acid (MA) both the crystal structure and the NMR spectra in  $\text{CDCl}_3$  show the enol structure **4**. For the cyano ester  $R^1 = \text{CN}$ ,  $R^2 = \text{CO}_2\text{Me}$  the solid has the enol structure **4** and in  $\text{CDCl}_3$  solution both **3** and **4** are present.



- 6:  $R^1 = R^2 = \text{CO}_2\text{Me}$   
 7:  $R^1 = \text{CO}_2\text{Me}$ ,  $R^2 = \text{H}$   
 8:  $R^1 = R^2 = \text{H}$

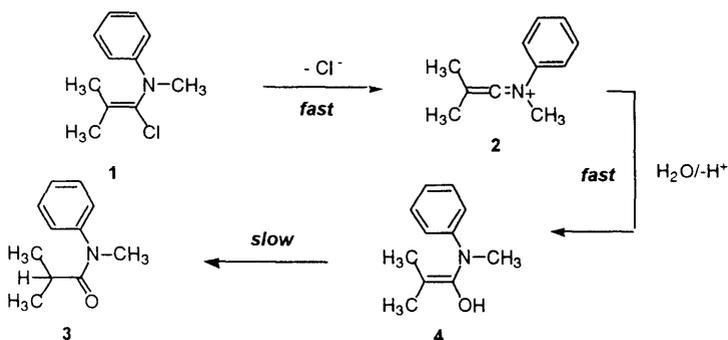
When  $R^1 = R^2 = \text{CO}_2\text{Me}$  the solid has the amide structure **3** which also predominates in  $\text{CDCl}_3$ . The C-H proton rapidly exchanges with  $\text{D}_2\text{O}$  and small amounts of an enol which is either **4** or **5** or both are present in solution. BLYP calculations show high and slight preference for the enol forms  $R^1R^2\text{C}=\text{C}(\text{OH})\text{NH}_2$  when  $R^1R^2 = \text{MA}$ ,  $R^1 = R^2 = \text{CN}$ , respectively, over their acid isomers. Penta-, tetra- and 1,2,4-tricarbomethoxy derivatives **6-8** are intramolecularly H-bonded enols of an ester group in the crystal and in  $\text{CDCl}_3$  solution.

DIRECT OBSERVATION OF ENOLS OF SIMPLE AMIDES: THE KETONISATION OF  
1-N-METHYLANILINO-2-METHYLPROPEN-1-OL

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Substituted vinyl alcohols (enols) are found in equilibrium with their carbonyl tautomers, which are generally the more stable form. However esters, amides and carboxylic acids have greatly reduced enol contents when compared to either aldehydes or ketones, due to the stabilisation by the  $\alpha$ -hydroxy, amino or alkoxy substituent of the carbonyl group. Although many reactions of amides and peptides are known to occur in the  $\alpha$ -position (including deprotonation leading to racemisation), the corresponding simple enols are in most cases not known.



We now wish to report that the enol, 1-*N*-methylanilino-2-methylpropen-1-ol (**4**) can be formed via the  $\alpha$ -chloroenamine (**1**), which undergoes reaction to the corresponding 1-azaallenium ion (**2**). Subsequent nucleophilic trapping by water at very low buffer concentrations gave the enol (**4**), which underwent tautomerisation to (**3**) at measurable rates. This reaction showed the characteristics of an enol ketonisation: hydronium and hydroxide ion catalysis, strong buffer catalysis and the observation of significant solvent isotope effects. A full rate-pH profile for formation of the amide **3** will be reported and commented on.

## ACID DECOMPOSITION OF ARYLDITHIOCARBAMATES. THE TORSIONAL EFFECT

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The pH-rate profiles of the acid decomposition of p-substituted aryldithiocarbamates, arylDTC, show a dumbbell shape with a plateau where the observed first order rate constant is equal to the rate constant of the spontaneous decomposition  $k_0$ . From the pH-rate profiles were calculated  $pK_a^o$  and  $pK_a^+$ , the acid dissociation constants of the dithiocarbamic acid and its conjugate acid respectively. Comparatively,  $k_0$  is about  $10^4$  fold faster than that of alkyldithiocarbamates (alkDTC). From the plots of  $pK_a^o$  (or  $pK_a^+$ ) vs  $pK_N$  (the acid dissociation constant of the conjugate acid of the parent amine), it was observed that the values for arylDTC were higher than those of the corresponding alkDTC, indicating that the aryl nitrogen is 4.5 and 8.3 pK units, respectively, more basic. An increase of the basicity of the nitrogen in about 8 pK units places the arylDTC in the range of  $pK_N$  values where the mechanism of cleavage has been proposed to occur through an intramolecular S to N proton transfer concerted with the C-N bond cleavage.<sup>[1]</sup> The driving force to reach the transition state is the needed torsion of the C-N bond that inhibits the resonance with the thiocarbonyl group increasing the basicity of the nitrogen and making the proton transfer thermodynamically favorable. Theoretical *ab initio* calculations at 3-21G\* level gave values of the torsional angle  $\theta$  measured between the vertical to the S-C-S plane and N--H bond being formed. For methyl and phenyldithiocarbamic acids  $\theta$  was 42.4 and 76.5° respectively. For phenylDTC the increase of basicity of the nitrogen must be assisted by the lack of coplanarity of the benzene ring and the dithiocarbamic group. The calculations also supported the hypothesis that the reaction is catalyzed by one water molecule with only one imaginary frequency. Furthermore, proton inventory of the acid decomposition of phenylDTC showed two protons on flight at the transition state.

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### Reference

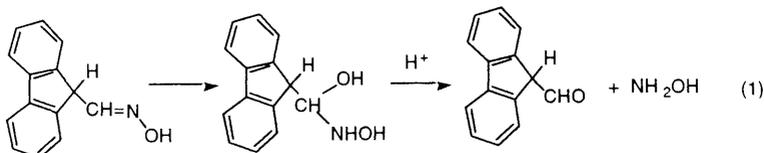
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DIFFUSION CONTROLLED TRAPPING OF AN  $\alpha$ -HYDROXYCARBOCATION BY  
HYDROXYLAMINE

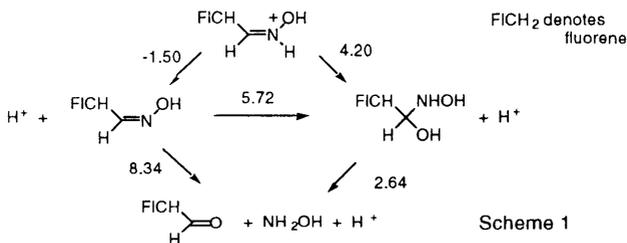
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Measurements of rate and equilibrium constants for formation and hydrolysis of the oxime of 9-formylfluorene (eq 1) yield the network of  $pK_a$ ,  $(-\log K)$  for the reaction steps shown in Scheme 1.



Of interest here are  $pK_a = -1.5$  and  $pK_R = 4.5$  for the protonated oxime. Values of  $pK_a$  and  $pK_R$  can also be derived for the O-protonated 9-formylfluorene, based on the following assumptions: (a) that hydrolysis in strongly acidic media (3M-12M  $HClO_4$ ) corresponds to conversion of the protonated oxime to protonated aldehyde, with rate determining reaction of an N-protonated carbinolamine, and (b) that the reverse reaction, attack of hydroxylamine upon the protonated aldehyde, is diffusion controlled. Then, combining  $k_1 = 5 \times 10^9$  for the diffusion reaction with  $k_1 = 7.5 \times 10^{-3}$  for hydrolysis gives  $K = 1.5 \times 10^{-12}$  ( $pK = 11.8$ ).



Combining this equilibrium constant with the  $pK_a$  for the protonated oxime and  $pK = -8.34$  for conversion of the aldehyde (and hydroxylamine) to oxime, we obtain  $pK_a = -4.76$  for the protonated 9-formylfluorene. Again, combining this value with the known equilibrium constant for hydration of 9-formylfluorene, we find  $pK_R = -5.5$ .

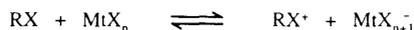
As an extension of these results the possibility of using measurements of  $pK_R$  to furnish equilibrium constants for reactions of electrophiles not only with water but with a wide range of nucleophiles will be discussed.

## Carbocationic Polymerizations of Olefins: Determination of Initiation, Propagation and Transfer Rate Constants

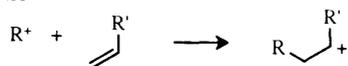
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 hmy@cup.uni-muenchen.de

Alkyl halide/Lewis acid induced polymerizations of alkenes are usually considered to proceed according to the following mechanism.

Ion generation



Cationation



Propagation



Termination



It has been shown that our methods to determine rate constants for the reactions of carbocations with alkenes and hydride donors<sup>[1,2]</sup> can be employed to determine initiation and transfer rate constants. A diffusion clock method has been developed to determine propagation rate constants<sup>[3]</sup> which are several orders of magnitude greater than those previously reported. The reason for the discrepancy will be discussed.

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POLYHALOMETHANES COMBINED WITH ALUMINUM HALIDES IN ALKANE  
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Alkanes and cycloalkanes still offer huge unrealized resources for organic syntheses. Therefore, the creation of active systems for their efficient transformations into valuable products is one of the most desirable goal in alkane chemistry.

The elaboration of new superelectrophilic systems based on polyhalomethanes and aluminum halides ( $CX_3 \cdot nAlX_3$ ,  $CHX_3 \cdot nAlX_3$ , etc.,  $X = Br, Cl$ ,  $n = 1, 2$  or  $3$ ) has considerably enriched alkane chemistry. Stoichiometric and catalytic transformations of alkanes and cycloalkanes by the polyhalomethanes -  $AlX_3$  superelectrophiles will be considered. They include such reactions as cracking, isomerization, oxidative coupling and selective one-step functionalizations (carbonylation of  $C_2$ - $C_5$  alkanes and  $C_5$ - $C_8$  cycloalkanes, formylation of adamantane, ionic dibromination of ethane and monobromination of higher alkanes and cycloalkanes, sulfurization of propane and cycloalkanes with elemental sulfur, alkylation of deactivated aromatics with alkanes and cycloalkanes etc.). Most of these reactions occur selectively in good yields. Some of them were performed for the first time.

## AICD A NEW METHOD FOR THE VISUALIZATION OF DELOCALIZATION

Rainer Herges,\* D. Geuenich

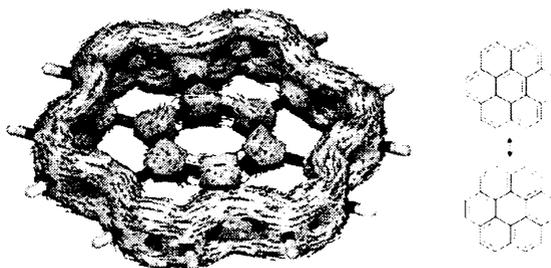
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Delocalization and conjugation are among the most important concepts in chemistry. MO-theory is well suited to treat such effects, however, in many cases orbital diagrams are difficult to set up even for a theorist or do not provide unambiguous explanations. Most chemists prefer a pictorial approach to models and concepts in chemistry. We are using magnetic properties of molecules to visualize delocalization. Plots of the density current vectors have been used for this purpose, but they are only applicable to planar  $\pi$  systems.

We defined the anisotropy of the induced current density (AICD) which is generally applicable to any chemical system e.g. to

- Planar and 3-dimensional  $\pi$  systems - Spiroconjugation
- Through bond conjugation - Classical and non classical cations
- Through space conjugation - Conjugation in transition states
- Hyperconjugation etc.

In a simplified view AICD values directly visualize delocalized electrons in a 3-dimensional plot as an isosurface. The method can be used to predict and interpret the reactivity, regiochemistry, stereochemistry and a number of other chemical properties of molecular systems. Even subtle effects such as the anomeric effect in glucose are directly visible (conjugation of the ring oxygen lone pair with the neighboring axial OH is more pronounced than with an equatorial OH). The AICD plot below illustrates that the lower mesomeric structure is a more adequate representation of coronene.



## COMPUTER AIDED DESIGN OF ORGANIC SUPERBASES

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The problem of tailoring powerful organic superbases is addressed by utilizing modern ab initio quantum chemistry models and it is illustrated by some characteristic examples. It appears that the imino group is the key structural and electronic motif, which leads to highly pronounced basicity of organic compounds particularly if it is attached to a quinoid six-membered ring.<sup>[1]</sup> The latter is aromatized upon protonation yielding to a considerable amplification of the proton affinity (PA). It will be shown that strong organic superbases involving bis-imino (poly)quinoid backbone exhibit the PA up to 300 kcal/mole. The latter can be further enhanced by additional bonding patterns like e.g. the hydrogen bonding triggered by the protonation. Some other highly basic systems exhibiting a similar aromatic spin-off domino effect will be discussed in detail.

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**Variation of the Rate of  $\alpha$ -Sulfonyl Carbanion Formation  
with the H-C-C-X Torsion Angle in  $\beta$ -Substituted Sulfones:**

**Geometry Dependence of the Taft  $\sigma^*$  Values**

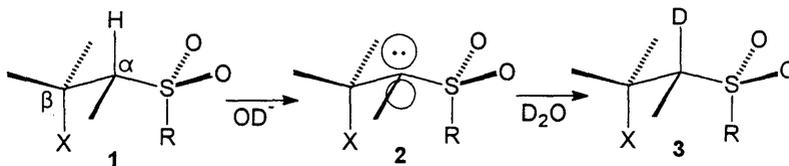
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The rate of H-D exchange in 1 (i.e., 1  $\rightarrow$  3 via 2) when X = OR has been studied in a series of eighteen  $\beta$ -alkoxy sulfones with varied, fixed, known torsion angles. We may define  $k_N = (k_{ex})_X / (k_{ex})_{model}$  where the model has X = H or an alkyl group, and have found<sup>[1]</sup> that  $k_N$  varies with the H-C-C-OR torsion angle according to the general relationship  $\log k_N = a + b \cos 2\theta$ . This relationship is interpreted in terms of a model of the substituent effect involving three components: (i) the inductive effect (angle independent), (ii) field effect (only slight angle dependence in the present case), and negative hyperconjugation (generalized anomeric effect) with an approximately  $\cos 2\theta$  variation with the torsion angle; the last is the most important component when maximal. This study has been extended with a limited set to other substituents: X = SR, SO<sub>2</sub>R, NR<sub>2</sub>, and N<sup>+</sup>R<sub>3</sub>, and analogous torsion angle dependence observed. A torsion angle dependent set of Taft  $\sigma^*$  values may be obtained from the expression  $\sigma^*_\theta = (a + b \cos 2\theta) / \rho^*$ . Since the hyperconjugative effect may be expected to be zero when  $\theta = 90^\circ$ ,  $\sigma^*_{90}$  provides the magnitude of the polar effect without hyperconjugation, and  $\sigma^*_0$  the total substituent effect with full hyperconjugation. This study provides an experimental method for obtaining insights into the nature of substituent effects and intramolecular interactions in general.



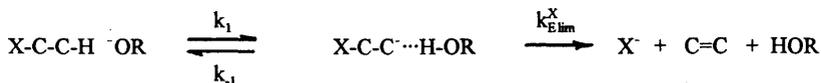
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## COMPARISON OF METHANOLIC SODIUM METHOXIDE-PROMOTED DEHYDROHALOGENATION AND EXCHANGE REACTIONS THAT ARE INITIATED AT THE BENZYLIC vs. 9-FLUORENYL POSITIONS.

**Heinz F. Koch<sup>\*</sup>**, Jason Nichols, Erik L. Ruggles, Martijn van Laren, Anne-Marie van Roon, Masaaki Mishima and Han Zuilhof.

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We favor a two-step process that features internal-return to describe the mechanism associated with alkoxide-promoted dehydrohalogenation reactions:



The Arrhenius behavior of hydrogen isotope effects associated with the methoxide-promoted dehydrohalogenations of  $\text{YC}_6\text{H}_4\text{C}^{\text{H}}\text{ClCH}_2\text{X}$  ( $\text{X} = \text{Br}, \text{Cl}$  or  $\text{F}$ ) are used to calculate the amount of internal return,  $k_{-1}/k_{\text{E lim}}^{\text{X}}$  [*J. Am. Chem. Soc.* 1997, 119, 9965-74]. When corrected for internal return, the experimental isotope effects [ $k^{\text{H}}/k^{\text{D}}$ , varies from 2.2 for dehydrofluorination to 5.0 for dehydrobromination] give similar values for the hydron-transfer step,  $k_1$ , for all three hydrogen-halides,  $k^{\text{H}}/k^{\text{D}} = 4.8$  to 5.0. The measured isotope effects are therefore due to differences in the amount of internal return and not due to the symmetry of the transition state structures. We have extended our studies to the 9- $\text{CH}_2\text{X}$ -fluorenes and find that the experimental hydrogen isotope effects at 25°C are the same for dehydrofluorination,  $k^{\text{H}}/k^{\text{D}} = 6.4$ , and dehydrochlorination,  $k^{\text{H}}/k^{\text{D}} = 6.3$ , and larger for dehydrobromination,  $k^{\text{H}}/k^{\text{D}} = 9.8$ . The element effect associated with these reactions are smaller than usual:  $k^{\text{HBr}}/k^{\text{HCl}} = 14$  and  $k^{\text{HCl}}/k^{\text{HF}} = 4$  at 25°C. Results will be discussed in terms of the two-step mechanism and *ab initio* molecular orbital calculations.

MECHANISMS OF SOLVOLYTIC ELIMINATION REACTIONS OF TERTIARY  
SUBSTRATES: STEREOSPECIFIC 1,2-ELIMINATION REACTIONS<sup>1</sup>

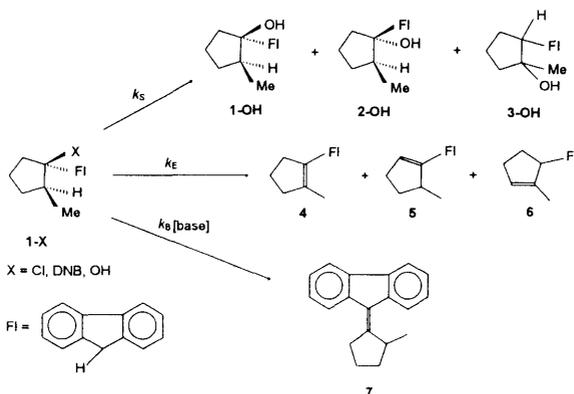
*Alf Thibblin and Qingshui Meng*

Institute of Chemistry, University of Uppsala, P.O. Box 531, S-751 21 Uppsala, Sweden  
email: Alf.Thibblin@kemi.uu.se

We report here a study of the kinetics, product distributions, and stereochemistry of solvolytic elimination reactions of the chloride **1-Cl** and the corresponding 3,5-dinitrobenzoate **1-DNB** (Scheme). The alkenes **4** and **5** are the main products, e.g. the chloride **1-Cl** gives a product ratio **4/5** of 35:65 in 25 vol% acetonitrile in water at 25 °C. The former product is formed by an *anti* elimination route, which shows that the elimination reaction *does not* have a concerted unimolecular mechanism.

The reaction to give **4** is suggested to occur via a carbocation ion pair in which the leaving chloride ion abstracts the β-hydron. Alternatively, the reaction may have an enforced uncoupled concerted mechanism in which water acts as the hydron-abstracting base. The putative ion-pair intermediates of these reactions are concluded to have similar or shorter lifetimes than that formed from *tert*-butyl chloride.

Also, solvolysis of 2-methyl-1-phenylcyclopentyl *p*-nitrobenzoate yields the more stable alkene by *anti* stereochemistry. The paper also addresses the question of why chloride ion shows such a high reactivity as a Brønsted base in many solvolytic elimination reactions.



*References:*

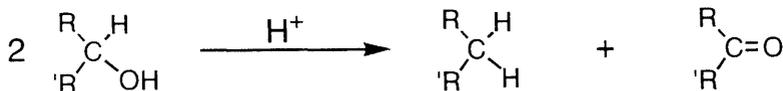
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THE KINETICS OF DISPROPORTIONATION OF  
SECONDARY ALCOHOLS

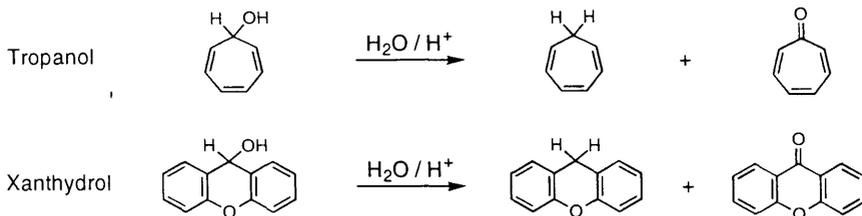
*Farhana Qusar, Felicity Turner, and C. Ian F. Watt.*

Department of Chemistry, University of Manchester, Manchester, M13 9PL, England

Under acid catalysis, secondary alcohols are known to react yielding corresponding hydrocarbons and ketones.



The suggested mechanism involves transfer of the alcohol methine hydrogen to the carbocation formed from the alcohol and this has been tested in this work by examination of the behaviour of two alcohols, tropanol and xanthyrol, which form carbocations observable in dilute aqueous acid.



Detailed product studies have confirmed clean conversion of these alcohols to corresponding hydrocarbons and ketones, and experiments with deuteriated alcohols and solvents have established the source of hydrogens in the hydrocarbons.

The course of reactions are easily followed by UV spectrophotometry, monitoring appearance of tropane in the case of the tropanol, or disappearance of cation in the case of the xanthyrol. The results of the kinetic experiments will be presented and shown to be consistent with the original suggestion, with the rate limiting step over a wide range of acidities being transfer of the alcohol methine hydrogen, as hydride, from alcohol to cation.

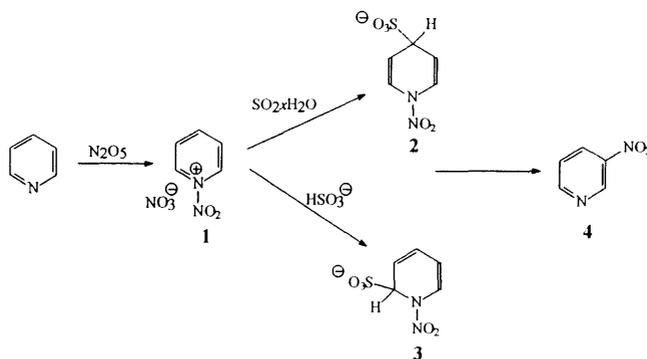
Rate constants for the hydride transfer step have been extracted. The results of a search for buffer catalysis indicating coupling between proton and hydride transfer will also be presented.

## NITRATION OF PYRIDINE, IMPREGNATING THE IMPREGNABLE.

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Due to the electron deficiency of the pyridine ring, electrophilic substitutions take place only under strained conditions.<sup>[1]</sup> In spite of this, we found it possible to nitrate pyridine and substituted pyridines with good yields by the use of dinitrogen pentoxide ( $N_2O_5$ ) in liquid  $SO_2$ .<sup>[2]</sup> Later we found that the nitration could be performed by the reaction of pyridine and  $N_2O_5$  in an organic solvent and subsequent reaction of the formed *N*-nitropyridinium nitrate (**1**) in an aqueous solution of  $SO_2$  or  $NaHSO_3$ . In this way a large number of  $\beta$ -nitropyridines have become readily available.<sup>[3]</sup> By NMR spectroscopy two intermediates in the reaction were detected, one 1,4-dihydro- (**2**) and one 1,2-dihydropyridine derivative (**3**). From these two, 3-nitropyridine (**4**) was formed by first order reactions.<sup>[4]</sup> We will discuss the reactions of these two intermediates, particularly the mode of migration of the nitro group from the 1- to the 3-position of the pyridine ring.



## References:

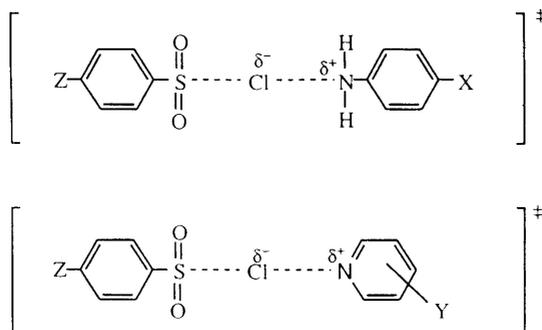
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## Substituent and Solvent Effect on Nucleophilic Substitution Reactions of Aromatic Sulfonyl Halides

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Enormous amounts of works have been accumulated in the chemistry of most stable tetracoordinate aromatic sulfonyl halides. However, the correlation between reactivity and the bonding nature of double-bond character is, still a matter of controversy in aromatic sulfonyl halides. In view of this point, we investigated that the nucleophilic substitution reactions of aromatic sulfonyl halides with various nucleophiles in various solvents and discussed with substituent effect and solvent effect. A correlation of intrinsic nucleophilicity between gas phase and solution phase is verified. The gas phase basicity and the proton affinity are increased with increasing in the nucleophilicity in the reaction of methyl tosylate with substituted pyridines. Hammett  $\rho_N$  values are affected by the protic solvent systems or the dipolar aprotic solvent systems in the reactions of *p*-substituted benzene sulfonyl chlorides with substituted anilines. The self ionization ability of the aromatic sulfonyl halides deactivates in the dipolar aprotic solvents.



Heterolytic and homolytic mechanisms in solvolyses of arenediazonium salts.

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Newcastle upon Tyne, NE1 7RU, UK.

Rates of solvolysis of arenediazonium salts in a range of solvents have been investigated and products have been analysed.<sup>[1,2]</sup> In aqueous and other polar solvents, reactions usually have high enthalpies of activation and appreciably positive entropies of activation, see Table 1 for the 3-fluoro compound, whereas kinetic parameters for reactions in ethanol are very different.

Table 1: Kinetics results for solvolysis of 3-fluorobenzenediazonium tetrafluoroborate

Solvent	$10^6 k_{25}/s^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$
TFE	1.18	124	59
95:5 TFE:H <sub>2</sub> O	0.36	126	64
50:50 TFE:H <sub>2</sub> O	1.31	126	67
H <sub>2</sub> O	1.31	134	81
EtOH	941	64	-87

Product analysis confirmed that reactions in ethanol are qualitatively different from those in more polar media with hydrodediazoniatio (reduction) rather than nucleophilic substitution now being the major reaction, see Table 2 for 3-fluorobenzenediazonium tetrafluoroborate.

Table 2: Product analyses for solvolysis of 3-fluorobenzenediazonium tetrafluoroborate

Solvent	Fluorobenzene	1,3-Difluorobenzene	3-Fluorophenyl alkyl ether
TFE	<0.1%	35%	65%
EtOH	79%	<1%	21%

To investigate these reactions further, we have analysed the products of reactions of 3-fluorobenzenediazonium tetrafluoroborate, and also the parent and methyl-substituted analogues, in FCH<sub>2</sub>CH<sub>2</sub>OH and F<sub>2</sub>CHCH<sub>2</sub>OH to explore the factors which determine mechanism. Results will be presented and discussed in terms of substituent and solvent effects upon parallel competing heterolytic and homolytic reaction pathways.

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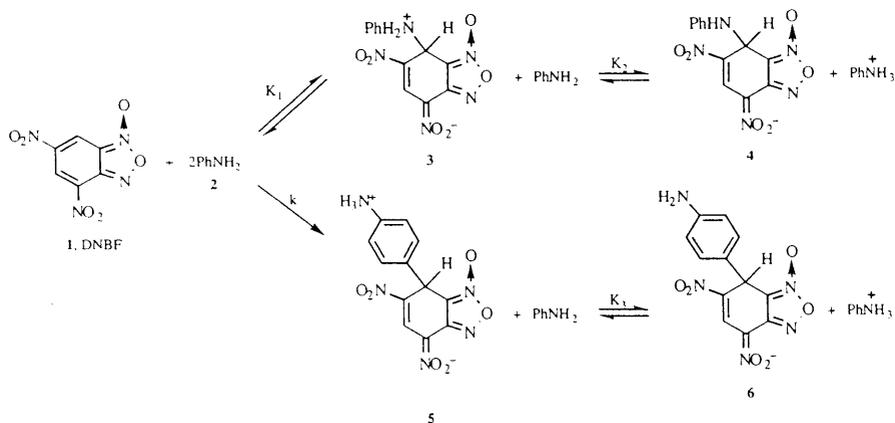
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## The Ambident Reactivity of Aniline and Some Derivatives, Towards 4,6-Dinitrobenzofuroxan

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Kinetic and equilibrium results will be reported for the reactions, as shown in the Scheme, of aniline and six of its derivatives with 4,6-dinitrobenzofuroxan (DNBF) in dimethylsulfoxide (DMSO) and in water-DMSO mixtures.



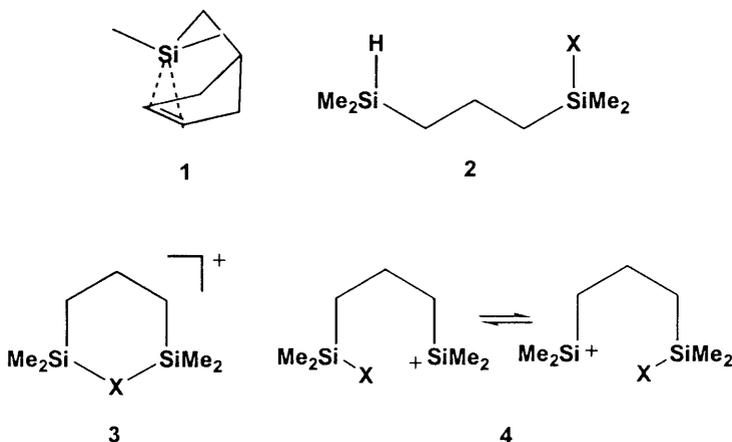
Reaction via the nitrogen centre of aniline is rapid and yields the  $\sigma$ -adducts, 4. Equilibrium constants for this process correlate with the  $pK_a$  values of the corresponding anilinium ions. Slower reactions are observed yielding 5, the products of electrophilic substitution by DNBF at ring-carbon atoms of the anilines. A value of 2.0 for  $k_H/k_D$ , the kinetic isotope effect indicates that bond formation is largely rate-determining here. The results allow estimates to be made for the  $pK_a$  values relating to carbon protonation of the anilines.

## NOVEL INTRAMOLECULARLY STABILIZED SILYLIUM IONS

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Intramolecular stabilization by electron donating groups is one of the successful strategies for the synthesis of stable silylium ions in the condensed phase. This was recently demonstrated in our group by the synthesis of 2-silanorbornylcations **1** in which the remote double bond stabilizes the electron deficient silicon center.<sup>[1]</sup> 2,6-Dimethyl-2,6-disilaheptanes **2**, which are in the 6-position substituted with an electron donating group X are suitable precursors for the generation of another class of intramolecular stabilized silylium ions. We will present in this lecture evidence for the formation of free silylium ions in arene solutions which were characterized by NMR spectroscopy and ab initio and density functional calculations. For X = aryl static structures **3** of the resulting ions were found, while for X = H a fast degenerate equilibrium between identical trivalent silylium ions was deduced from the IR spectrum.



## References:

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DYNAMICS IN S<sub>N</sub>2/ET PROCESSES: AB INITIO MD SIMULATIONS

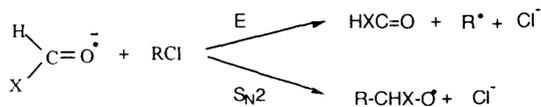
*Hiroshi Yamataka*<sup>†1</sup>, *Misako Aida*<sup>†2</sup>, and *Michel Dupuis*<sup>†3</sup>

Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, 567-0047 Japan, <sup>†1</sup> Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima, 739-8526 Japan, <sup>†2</sup> and Pacific Northwest National Laboratory,

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Ab initio molecular dynamics (MD) simulations in which the energy and the forces of the system are computed from an ab initio molecular orbital (MO) treatment of the reactive system<sup>[1]</sup> are carried out for reactions of substituted formaldehyde radical anion and alkyl chloride (reactions 1-3).<sup>[2]</sup> Reactions 2 and 3 were previously shown by ab initio MO calculations to proceed through a single transition state (TS) connected to an S<sub>N</sub>2 or electron-transfer (ET) product, whereas reaction 1 was shown to proceed through a well-characterized single TS connected to an ET product on the steepest descent path, with a C-substitution S<sub>N</sub>2 product separated from the ET product by a flat ridge.<sup>[1]</sup> The present ab initio MD simulations, simulating a finite temperature reaction, indicate that trajectories starting from respective TSs reach either the ET product or the S<sub>N</sub>2 product for reactions 2 and 3. On the other hand, trajectories from the TS of reaction 1 give both ET and S<sub>N</sub>2 products, reflecting borderline characteristics of the reaction. The two kinds of trajectories have different characteristics. Trajectories which lead to the S<sub>N</sub>2 product state are simple, with C-C bond formation and C-Cl bond breaking essentially completed within 50 fs. By contrast, trajectories leading to the ET product are more complex with a sudden electron reorganization taking place around 15 - 30 fs and the major bonding changes and electron and spin reorganization completed after 250 fs.



Reaction 1: X = H, R = CH<sub>3</sub>

2: X = CN, R = CH<sub>3</sub>

3: X = CN, R = (CH<sub>3</sub>)<sub>2</sub>CH

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RADICAL STABILIZATION ENERGY AS A MEASURE OF PROPERTIES TRENDS IN  
HOMOLOGOUS GROUPS

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The free radical reactivities and spectral properties of molecules are shown to depend on the stabilization energy ( $E_s(R^{\bullet})$ ) of radicals. For different types of radicals the correlation relations for addition to double bonds and H-atom abstraction were found and discussed. It was also shown that the  $\nu$  values of different stretch vibrations are dependent on the radical stabilization energy of the radical adjacent to the bond in consideration or formed by its rupture. The  $E_s(R^{\bullet})$  values (in kJ/mole) were found from the expression:<sup>[1]</sup>  $E_s(R^{\bullet}) = D(\text{CH}_3\text{-H}) - D(\text{R-H})$ . For the  $\nu_{\text{as}}(\text{CH}_3)$  stretch vibration<sup>[2]</sup> the following relation was found:  $\nu_{\text{as}}(\text{CH}_3) = (3010 \pm 9) - (0.83 \pm 0.12)E_s(R^{\bullet}) \text{ cm}^{-1}$  ( $r = 0.959$ ). For  $\nu(\text{O-H})$ ,  $\nu(\text{C-O})$ , and  $\nu(\text{N-H})$ <sup>[3]</sup> similar relations were obtained:  $\nu(\text{O-H}) = (3645 \pm 3) - (0.72 \pm 0.10)E_s(R^{\bullet})$  ( $r = 0.936$ ) for  $E_s(R^{\bullet})$  from 0 to 40 kJ/mole,  $\nu(\text{C-O}) = (1120 \pm 8) - (0.739 \pm 0.2)E_s(R^{\bullet})$  ( $r = 0.909$ ),  $\nu(\text{N-H}) = (3475 \pm 3.7) - (0.765 \pm 0.17)E_s(R^{\bullet})$  ( $r = 0.912$ )  $\text{cm}^{-1}$ . The IR spectra of several peroxy radicals ( $\text{CH}_3\text{O}_2^{\bullet}$ ,  $\text{C}_2\text{H}_5\text{O}_2^{\bullet}$ ,  $i\text{-C}_3\text{H}_7\text{O}_2^{\bullet}$ ,  $t\text{-C}_4\text{H}_9\text{O}_2^{\bullet}$ <sup>[4]</sup> and allyl- $\text{O}_2^{\bullet}$  ( $\text{C}_3\text{H}_5\text{O}_2^{\bullet}$ )<sup>[5]</sup>) were published. For the first four radicals the straight-line dependence of  $\nu(\text{C-OO}^{\bullet})$  on  $E_s(R^{\bullet})$  also holds, but the data for  $\text{C}_3\text{H}_5\text{O}_2^{\bullet}$  do not fit it. The IR spectrum of allyl peroxy<sup>[5]</sup> was reinterpreted, and on the basis of comparison of all the peroxy radical spectra the line at  $492 \text{ cm}^{-1}$  was assigned to the  $\nu(\text{C-OO}^{\bullet})$  vibration of  $\text{C}_3\text{H}_5\text{O}_2^{\bullet}$ . The following relation for the peroxy radicals was found:  $\nu(\text{C-OO}^{\bullet}) = (916.4 \pm 7.9) - (5.82 \pm 0.17)E_s(R^{\bullet})$  ( $r = 0.998$ ). The linear decreasing of  $\nu(\text{C-OO}^{\bullet})$  with raising  $E_s(R^{\bullet})$  may be regarded as a confirmation of decreasing of the  $\text{C-O}_2^{\bullet}$  bond strength by moving from  $\text{CH}_3\text{O}_2^{\bullet}$  to  $\text{C}_3\text{H}_5\text{O}_2^{\bullet}$ <sup>[1]</sup>. The derived expressions were used to calculate the unknown  $E_s(R^{\bullet})$  and bond energy values for some radicals and molecules.

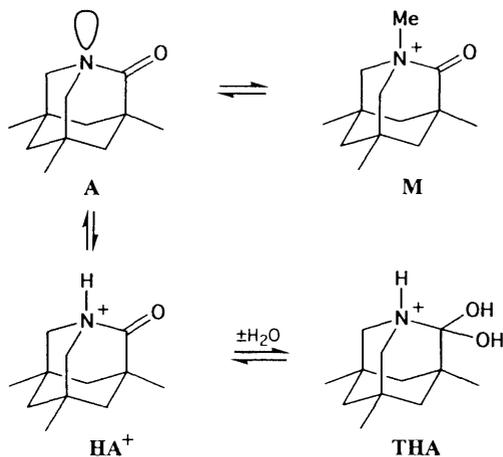
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## A NEW TWIST TO THE AMIDE GROUP

*Anthony J. Kirby, Igor V. Komarov, Klaus Kowski and Paul Rademacher*

We will report new results for the "most twisted amide" **A**<sup>[1]</sup> including its He(I) photoelectron spectrum.



The first ionisation potential of **A** is higher by 0.36 eV than expected for a 1-azaadamantane, and the N-methyl derivative **M** is an active alkylating (as well as acylating) agent. These properties are evidence for the sharply reduced basicity of the nitrogen lone pair of **A**. In contrast, the second ionisation potential IP[n(O)], is shifted by only 0.1 eV compared with a typical tertiary  $\delta$ -lactam, an indication of the surprising insensitivity of the structure of the C=O group to the nature of the group attached. Main topics for discussion will be the electronic structure of the amide group and the equilibria shown in the Scheme.

## References:

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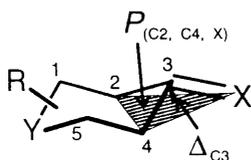
## Relationship Between Carbonyl Pyramidalization and Conformation of Ketones

Thomas Laube\*

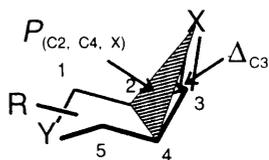
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e-mail: laube-th@dial.eunet.ch

A statistical investigation of precise crystal structures from the Cambridge Structural Database shows that cyclohexanones have a predictable pyramidalization of the carbonyl group ( $\Delta_{C3}$  = distance of the carbonyl C atom C3 from the plane  $P_{(C2, C4, X)}$ ; R = any substituent, X = O, Y =  $C_{sp^3}$ ) in the chair conformation which depends on the puckering of the ring.



"axial" pyramidalization



"equatorial" pyramidalization

This information may help to predict the stereochemical course of nucleophilic additions to cyclohexanones and it shows that the potential energy surfaces for cyclohexanones around the chair conformation are possibly more complicated due to the carbonyl nonplanarity than usually assumed. It is conceivable that a cooperation between electronic effects (hyperconjugation) and steric effects (relief from torsional strain) leads to this unique correlation. No such conformation/pyramidalization correlations are observed for other ketones ( $Y = -, -(C_{sp^3})_n-$  with  $n \geq 2$ , no bond or chain).

\* The work presented here has not been made for Cilag AG.

PREDICTING THE RATES OF ORGANIC REACTIONS: NUCLEOPHILES PLUS  
CARBONYLS, IMINIUM IONS, AND CARBOCATIONS.

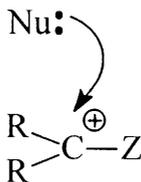
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No Barrier Theory asserts that when only one thing happens there is no barrier but only a quadratic potential function, and that the kinetic barriers associated with almost all chemical reactions result from the need for more than one simple thing to happen simultaneously for the reaction to occur. This theory permits calculation of the free energies of activation for chemical reactions given only the equilibrium constants in solution and the distortion energies corresponding to the hypothetical "one thing at a time" transformations. This approach will be illustrated for the addition of various nucleophiles (water, hydroxide, amines, etc) to carbonyl groups (aldehydes to amides), iminium ions (N-methylimines, N-phenylimines, oximes, and semicarbazones) and carbocations. The calculations are much less demanding than direct calculation of the structure and energy of the solvated transition state, and generally come within 2 kcal/mol of the observed value.

$\Delta G^\ddagger$  for



DIVALENT  $M^{2+}$ -CATALYZED METHANOLYSIS OF ACETYLMIDAZOLE,  
ACETILPYRAZOLE AND A DISTORTED ANILIDE.

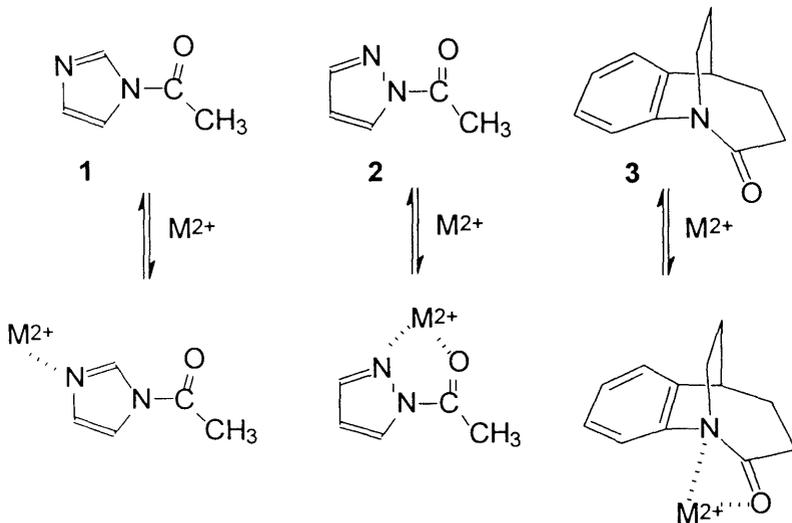
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The methanolysis of acetylimidazole (1), acetylpyrazole (2), and a distorted anilide (3) was studied in the presence of  $Zn^{2+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ , and  $Ni^{2+}$  perchlorates in anhydrous methanol at 25 °C. In aqueous solution, none of these metal ions shows substantial acceleration of the hydrolysis process, but in methanol there is both saturation binding of the metal to the amide and strong catalysis of the methanolysis. In the cases of acetylimidazole and acetylpyrazole, the metal ions are generally much better catalysts of methanolysis than is proton, while the reverse is true in water. Solvent kinetic isotope studies on the methanolysis in MeOH and MeOD indicate rather large  $d_{k_{obs}}$ 's and that the  $Zn^{2+}$ -catalyzed process involves a transition state where there are two or more protons in flight. The data for the metal catalyzed methanolysis and possible mechanisms for the observed catalysis will be presented.



## Intramolecular CH/ $\pi$ Interaction. Substituent Effect as a Probe for Hydrogen-bond-like Character

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In recent years, it has become gradually accepted that the CH/ $\pi$  interaction is important in considering a variety of chemical and biochemical phenomena. We can regard the CH/ $\pi$  interaction as a weakest extreme of the hydrogen bond: hydrogen bond occurring between a soft acid (CH) and a soft base ( $\pi$ -electrons). Since XH/ $\pi$  interaction is assumed to be originated from the charge-transfer from  $\pi$ -system to XH, an electronegative substituent on the X atom and an electron-donating substituent on the  $\pi$ -system will favor the interaction. This should actually be reflected in the substituent effect. In addition, geometrical arrangement of the interacting XH and  $\pi$  components is important in the cases of intramolecular interaction. From this point of view, both *ab initio* calculations (B3LYP/6-31+G\*) on model CH/ $\pi$  interacted systems and NOE experiments to verify the substituent effect are carried out.

In the intramolecular cases, the interaction energy cannot be evaluated straightforwardly by the calculations because it is obscured by other interactions terms comprising the conformational energy. Thus, we used the non-bonded overlap populations to demonstrate the presence of delocalization interaction. Non-zero and positive bond populations were observed between proximate H and  $sp^2$ -C in 1-pentene and 1,5-hexadiene derivatives.

NOE is a powerful method to detect the "through-space" proximity of two atoms which may be separated by a several bonds. In the CH/ $\pi$ -interacted conformation, the CH proton is located close enough to one or several aromatic C atoms to show a considerable NOE enhancement of attached H. As NOE is a short range effect, no enhancement is expected in the stretched conformers free from CH/ $\pi$  interaction. Many CH/ $\pi$  interacted compounds showed NOE enhancements of the aromatic H signal(s) when the donor H atom was irradiated. Comparison of the magnitudes of NOE through a series of similar compounds allows us to estimate the relative strengths of the CH/ $\pi$  interaction. The  $\rho$ -values of Hammett plots can be a relative scale for the strengths of charge-transfer contribution, because it reflects the free energy variation due to the electronic effect by the substituents.

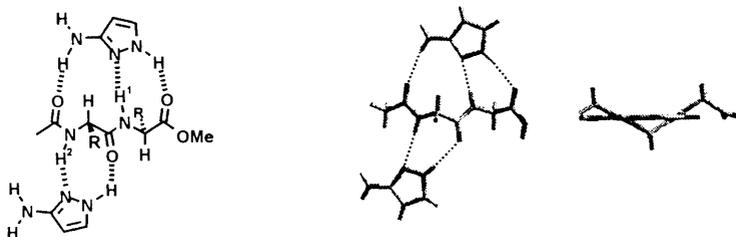
In conclusion, CH/ $\pi$  interaction can be assumed to be a weakest interaction similar to hydrogen bonding, in which delocalization contributes to some extent, and should be distinguished from mere coulombic and hydrophobic interactions.

$\beta$ -SHEET STABILIZATION OF PEPTIDES WITH AMINOPYRAZOLES*Thomas Schrader, Christian Kirsten*

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Unravelling the factors controlling the formation of  $\beta$ -sheets is of prime importance since abnormal folding of proteins is suspected to induce diseases such as the common memory disorder Alzheimer's, the infectious BSE/Creutzfeld-Jakob disease and other prion diseases.<sup>[1]</sup> New discoveries in the protein domain may thus lead to improved drug design. The synthesis of low molecular weight, soluble model compounds is therefore of high interest and has represented an area of intense research over the past years.

We recently introduced 3-aminopyrazole derivatives as the first artificial templates that stabilise the  $\beta$ -sheet conformation in *N/C*-protected dipeptides by purely intermolecular interactions.<sup>[2]</sup> Force-field calculations show that five hydrogen bonds can be formed by interaction of two molecules of the rigid template with one molecule of an *N*-acylated dipeptide ester (Figure 1). Various detailed NMR-spectroscopic experiments will be presented which unanimously confirm that the suggested complex structure also exists in solution.



**Figure 1.** 2:1-complex between 3-aminopyrazole and Ac-Gly-Gly-OMe. Left: Side view; Middle: Top view.

Polymerizable aminopyrazoles have been used as new binding sites for molecular imprinting; thus the racemic resolution of dipeptides leads to separation factors  $\alpha$  of up to 2.7.<sup>[3]</sup> Finally, preliminary results about the interaction of oligomeric aminopyrazoles with naturally occurring peptides and proteins will be presented, with an emphasis on the effect on the aggregation kinetics of the Alzheimer and the Prion protein.<sup>[4]</sup>

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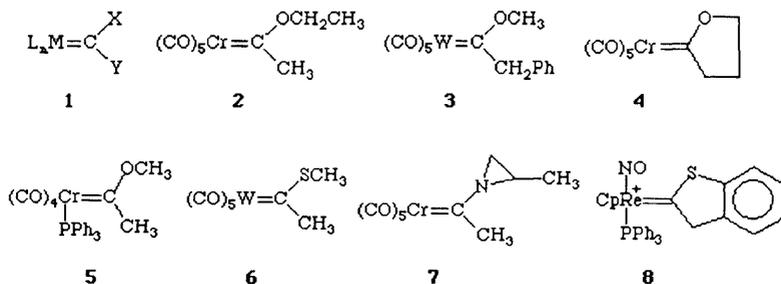
THERMODYNAMIC AND KINETIC ACIDITIES OF FISCHER CARBENE  
COMPLEXES

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Fischer carbene complexes are compounds of the general structure 1. M is a transition metal, L are ligands while X and Y represent a variety of groups including alkyl, aryl, vinyl, alkynyl, amino, alkoxy, alkylthio, halo, and others; typically X or Y is a  $\pi$ -donor such as alkoxy, amino, or alkylthio which provides stabilization of the electron deficient carbene carbon. Carbene complexes with a hydrogen in the  $\alpha$ -position represent an interesting class of carbon acids with  $pK_a$  values ranging from about 1 to >16 in aqueous acetonitrile; some examples are shown as 2-8.



We have studied the thermodynamic and kinetic acidities of these and other carbene complexes in 50% MeCN-50% water and in pure acetonitrile. Our objective is to understand the complex interplay of the various factors that determine these acidities. Some of the major factors include delocalization of the negative charge of the conjugate base into the  $L_nM$  moiety,  $\pi$ -donor effects of RO, RS and  $R_2N$  groups, the effect of substituents at the  $\alpha$ -carbon and the identity of the metal. We found both similarities and differences between Fischer carbene complexes and purely organic carbon acids in how structural features affect their kinetic acidities. For example, resonance effects in the conjugate base of the carbene complexes manifest themselves, as expected, in enhanced intrinsic barriers to proton transfer. On the other hand, the evidence for transition state imbalances which are characteristic of proton transfers from organic carbon acids activated by  $\pi$ -acceptors is ambiguous.

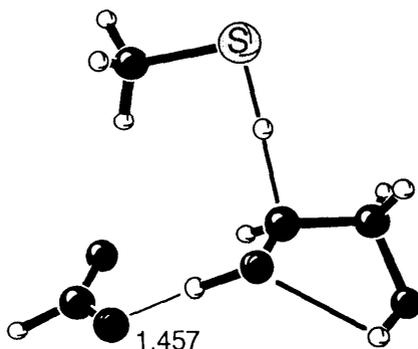
## C-H BOND ACTIVATION IN RIBONUCLEOTIDE REDUCTASES - DO SHORT STRONG HYDROGEN BONDS PLAY A ROLE?

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The C-H bond activation step in the ribonucleotide reductase catalyzed reduction of ribonucleotides has been studied using small model systems composed of methyl thiyl radical and methanol, ethylene glycol, or 3,4-dihydroxytetrahydrofuran. In order to mimic the influence of specific protein residues on the C-H functionalization step, the reaction between methyl thiyl radical and ethylene glycol has also been studied in the presence of hydroxide, formate, hydronium, and neutral formic acid.



In the presence of these residues, the activation barrier as well as the reaction thermochemistry are influenced, in part, dramatically. The most efficient catalysis of the C-H bond activation step as measured by the ratio between reduction of the activation barrier and reduction of the reaction thermochemistry is achieved by formate. Acidic functional groups are, in contrast, very inefficient catalysts for this reaction.

OPTIMIZATION OF MICELLAR CATALYSIS OF NUCLEOPHILIC SUBSTITUTIONS  
IN BUFFERED SOLUTIONS OF CETYLTRIMETHYLAMMONIUM SALTS

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Optimization of micellar catalysis of nucleophilic substitutions requires to enforce the micellar binding of the hydrophilic anionic nucleophile by exchange with the surfactant counter-ion, in the view of increasing its concentration at the water-micelle interface where it can react with the hydrophobic substrate. These reactions involve generally buffers to control the overall anionic nucleophile concentration. Now, the basic components of the buffers are in most cases organic anions which can also bind the micelles, in competition with the reactive nucleophile. It has, therefore, been suggested that very weakly bound buffers must be used to obtain significant micellar effects.

We present kinetic results on a model reaction, the p-nitrophenyldiphenylphosphate-butanedione monooximate reaction, in aqueous solutions of cetyltrimethylammonium salts, CTAX, with  $X^- = \text{Br}^-, \text{Cl}^-$  and  $\text{AcO}^-$ , in the presence of various buffers, carbonate, borate, glycine, ethanolamine and AMP (2-amino-2-methyl-1,3-propanediol) working in the 9-10 pH range.

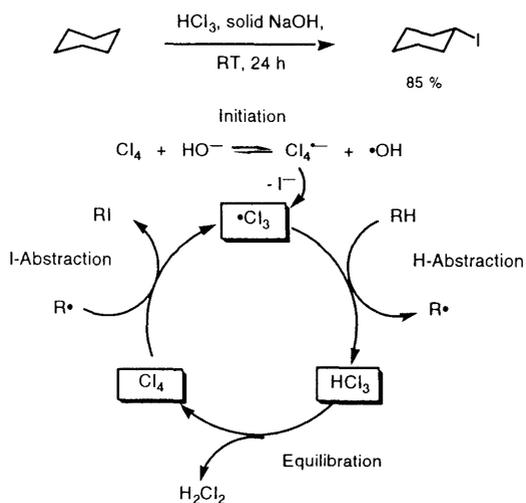
The PIE (pseudophase ion-exchange) model fails for analysing the corresponding rate-[surfactant] profiles in terms of  $k_m$ , the micellar rate constant, and  $K_X^{\text{Ox}}$ , the counter-ion/oximate exchange constants. Nevertheless, the data can be fairly well interpreted when competitive binding of the three anions involved in the reactive system (surfactant counter-ion, the nucleophile and the buffer base) is considered. The results will be discussed in terms of efficiency of micellar catalysis and its critical dependence on the buffers and the counter-ions.

NO HEAVY METALS, NO ENZYMES, NO FUSS: ALIPHATIC HYDROCARBON  
HALOGENATIONS IN MULTI-PHASE SYSTEMS

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Recently, we reported a phase-transfer catalyzed method to transform even the simplest aliphatic hydrocarbons into their corresponding bromides.<sup>[1]</sup> We meanwhile also succeeded in developing the first efficient iodination of unactivated alkanes.<sup>[2]</sup> As these reactions offer new and general avenues for solving the long-standing problem of C-H-activation of paraffins, the scope and limitation as well as the mechanistic implications of these approaches are presented. Variants of this method may be applied to biomedically relevant compounds, for instance, in radio-iodinations, but are also valuable for the production of otherwise not as easily accessible alkyl iodides which may be useful for the pharmaceutical industry.



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## Microemulsion Promoted Mechanistic Changes. Solvolysis of Substituted Benzoyl Chlorides

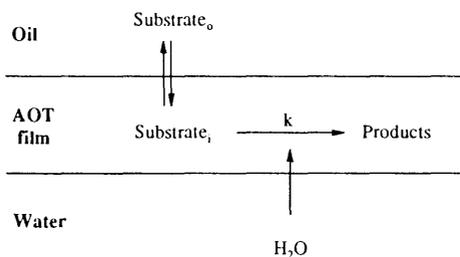
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Microemulsions are stable and transparent mixtures of water, oil, and surfactant, with or without a cosurfactant. Water properties are a function of the molar ratio of water to surfactant, defined as  $W=[\text{H}_2\text{O}]/[\text{AOT}]$  that is also related with the volume of the water droplet. An extension of the pseudophase model to microemulsions easily explain the kinetics of solvolysis of substituted benzoyl chlorides. Bearing in mind the poor solubility of substituted benzoyl chlorides in water it is safe to assume that the amount of these substrates in the water pseudophase is negligible and that the reaction should occur at the interface, where the water and benzoyl chlorides are both present as shown in the following scheme.



The change from a dissociative to an associative reaction path with increasingly electron-withdrawing substituents occurs much later in water than in AOT/isooctane/water microemulsions of  $W=50$ . This is due to the fact that the rate of associative reaction is independent of the leaving group, while the dissociative reaction is strongly dependent on the nature of the leaving group and on its solvation. When  $W$  decreases the associative pathway is favoured and benzoyl chlorides with electron donating substituents follow this mechanism.

## REACTIVITY IN MIXED MICELLES OF CTACI/OCTYLAMINE

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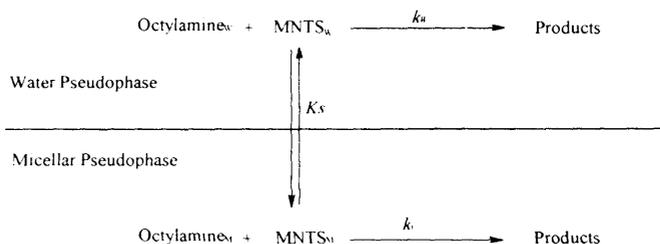
Transnitrosation between N-methyl-N-Nitroso-p-toluenesulfonamide (MNTS) and Octylamine in CTACI/Octylamine mixed micelles has been studied.

The Octylamine is a primary alkylamine, which by its structural characteristics drives to micellar aggregates. The mixtures of Octylamine (OA) and a cationic surfactant as CTACI (cetyl trimethyl ammonium chloride) are mixed micellar systems stable in the whole range of molar fractions.

Preliminary studies of transnitrosation between MNTS and OA under its critic micellar concentration, thus obtaining the reactivity constant in water ( $k_w$ ) were carried out.

A kinetic study for the several mixtures of CTACI/Octylamine ( $X_{OA}=0-1$ ). The simultaneous role of OA as reactant and surfactant must be underlined. In all the range of mixed system compositions a catalytic effect was observed. This behaviour is due to the concentration of both reactants in the small volume of the micelle.

The kinetic behaviour has been explained on the basis of the micellar pseudophase model. The binding constants of MNTS ( $K_S$ ) and the reactivity constants in the micellar pseudophase ( $k_i$ ) have been obtained.

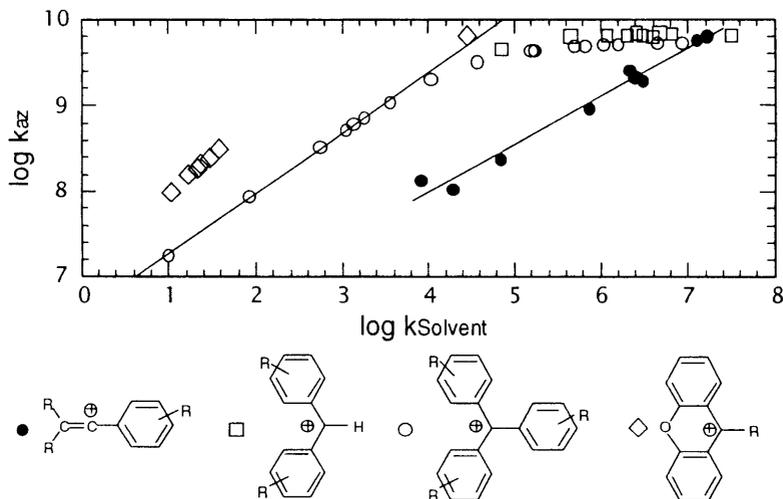


STERIC EFFECT OF DIFFUSION LIMITED REACTIONS STUDIED BY LASER  
FLASH PHOTOLYSIS

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Laser flash photolysis is a new tool to investigate reactive intermediates under reaction conditions. It provides the rate constants of nucleophiles to unstable carbocations. McClelland et al studied on nucleophilic attack of azide ion and solvent to various di- and tri-aryl substituted carbocations in the 1:2 mixture (v/v) of acetonitrile and water as shown in the below figure.<sup>[1]</sup> The reactivity difference comes from the electronic effect of the substituents. We found a steric effect of the  $\beta$ -substituents of vinyl cations to a nucleophile.<sup>[2]</sup> Our recent work on vinyl cations provides another group in the figure as shown by closed circles. The vinyl cations have a fixed *p*-methoxyphenyl group on the  $\alpha$ -position and various substituents on the  $\beta$ -positions. There is no large difference in the stability among the vinyl cations, but a large steric effect on the nucleophilic attack to them. There seems to be a large difference of nucleophilic attack between an anion, azide ion, and neutral molecule like solvent.



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REACTIONS OF N-CENTERED RADICALS DERIVED FROM  $\alpha$ -AMINO ACIDS; A  
TIME RESOLVED STUDY*Marija Bonifacic*Department of Physical Chemistry, Ruder Boskovic Institute, Bijenicka c. 54,  
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Time resolved methods (pulse radiolysis and laser flash photolysis) were used to investigate reactions of aliphatic  $\alpha$ -amino acids in anionic form with hydroxyl radicals ( $^{\bullet}\text{OH}$ ) and 4-carboxybenzophenone triplet ( $\text{CB}^*$ ) in aqueous solutions.

Besides H-atom abstraction from  $\alpha$ -C and/or side-chain C-H bonds,  $^{\bullet}\text{OH}$  radicals also readily undergo a one-electron transfer reaction from the free electron pair on nitrogen. The resulting aminium radicals,  $\text{H}_2\text{N}^{\bullet+}\text{-CR}_2\text{-CO}_2^-$  (R = H, alkyl), decarboxylate and transfer a proton to  $\text{OH}^-$ , which is still located within the solvent cage, at a ratio of ca 1:2. As products, strongly reducing  $\alpha$ -aminoalkyl and oxidizing aminyl radicals are respectively formed. The aminyl radicals further degrade via  $\beta$ -scission, yielding  $\text{CO}_2^{\bullet-}$  as another reducing species. In the presence of proton donors, they can also be re-protonated into the fast decarboxylating aminium radical, or may abstract H-atoms from, e.g.,  $\text{C}_{\alpha}\text{-H}$  bonds in the amino acid anions.

The quenching of  $\text{CB}^*$  by amino acid anions proceeds via the one-electron transfer mechanism, resulting in the formation of aminium radicals as the main initial product. Within the solvent cage, with  $\text{CB}^{\bullet-}$  as the counter ion, this radical either decarboxylates or deprotonates at a ratio of ca 9:1. Deprotonation into aminyl radicals by the  $\text{OH}^-$  ions in the bulk starts to be competitive at  $[\text{OH}^-] \geq 1 \text{ M}$ . This reaction enabled the determination of a rate constant of  $(1.0 \pm 0.3) \times 10^{11} \text{ s}^{-1}$  for the actual aminium radical decarboxylation process.

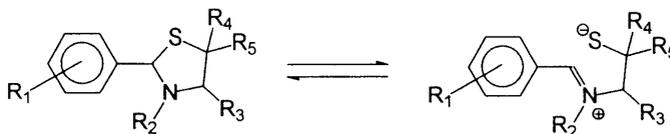
Specific scavenger methods were used to experimentally determine yields and rate constants of individual radical products from glycine, alanine and 2-aminoisobutyric acid.

## PHOTOCHEMICALLY-INDUCED THIAZOLIDINE RING-OPENING REACTIONS

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One of the possible processes that penicillins can undergo in basic solution is the ring opening of their thiazolidine ring to yield an imine-thiolate anion, with the subsequent rearrangement of the so-formed imine to the corresponding enamine.<sup>[1]</sup> An appropriate and desirable model to study such process is the ring-opening of thiazolidines to an iminium-thiolate zwitterion:



Some work has been already carried out on these systems using standard UV/Vis spectroscopy, and showing how the ring-opening / ring-closure processes depend on the state of protonation of the different acid positions in the molecule, through a complex pattern of equilibria.<sup>[2]</sup> However, it has been also observed that, depending on the substituents present in the molecule, it can be extremely difficult to ring-open the thiazolidine ring to a reasonable extent that may allow mechanistic investigation.

We have now shown that the ring opening of thiazolidines (and also oxazolidines) can be easily achieved by photochemical means.

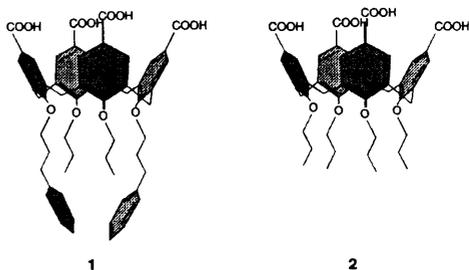
The use of 248 or 266 nm laser flash-photolysis allows to produce in good yields the iminium ion ( $\lambda=400$  nm) with a variety of compounds ( $R_1 = -OH, -OMe, -MMe_2$ ;  $R_2 = -H, -nBu$ ;  $R_3 = -H, -CO_2H$ ;  $R_4 = R_5 = -H, -Me$ ). Results will be presented for the photochemically-induced ring-opening process, as well as for the mechanism of ring-closure under different conditions.

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BUILDING SUPRAMOLECULAR ASSEMBLIES OF CALIX[4]ARENE-BASED  
SURFACTANTS AND CYCLODEXTRINS*Jasper J. Michels, Jurriaan Huskens, and David N. Reinhoudt*Laboratory of Supramolecular Chemistry and Technology, MESA<sup>+</sup> Research Institute,  
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Calix[4]arenes are known for their capabilities to act as host molecules in supramolecular chemistry. Especially calix[4]arenes occupying the cone conformation, which actually encompass a cavity, are able to accommodate guest molecules. In contrast, we envisaged that interesting



supramolecular systems would arise from using calix[4]arenes as *guest* molecules for binding into cyclodextrins. Moreover, the synthetic versatility of calix[4]arenes allows them to act as platforms on which several functionalities or guests for CDs can be combined. In order to quantitatively study the non-covalent interactions between calix[4]arenes and  $\gamma$ -cyclodextrin, water soluble calix[4]arene **1** was synthesized. The calix[4]arene lower rim is functionalized with two pendant phenyl groups, which act as a binding site for  $\gamma$ -cyclodextrin; this particular cyclodextrin is known for the ability to complex *two* aromatic rings strongly. Water soluble calix[4]arene **2**, which lacks a distinct binding site for  $\gamma$ -cyclodextrin, was synthesized as a reference compound for investigation of the influence of the aromatic groups.

The aggregation behavior of the calix[4]arene-based surfactants **1** and **2** in water was studied by UV spectroscopy and titration microcalorimetry. Critical micelle concentrations (CMCs) were determined. The experiments reveal that the increase in hydrophobicity caused by the pendant phenyl groups in the case of **1**, lowers the CMC of the surfactant significantly. The binding of **1** in  $\gamma$ -cyclodextrin was studied by NMR and titration microcalorimetry. A high complex stability was observed. Furthermore, the binding stoichiometry was determined to be 1:1 using a Job's plot analysis. The binding of **1** in  $\gamma$ -cyclodextrin is enthalpy-driven which, together with the confirmed 1:1 binding stoichiometry, suggests that indeed both phenyl rings are included in the  $\gamma$ -cyclodextrin cavity.

STRUCTURE, MOLECULAR DYNAMICS AND HOST–GUEST INTERACTIONS OF A  
WATER–SOLUBLE CALIX[4]ARENE

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By measurement of  $^2\text{H}$ ,  $^{13}\text{C}$  and  $^{14}\text{N}$  relaxation data the reorientational molecular dynamics for the following water–soluble calixarenes and host–guest systems were evaluated:

- calix[4]arene-p-sulfonic acid (**1**) and its pentasodium salt (**2**),<sup>[1]</sup>
- calixarenes **1** and **2** as hosts, tetramethyl-, trimethylphenyl- and trimethyladamantanyl-ammonium cations as guests in the corresponding host–guest systems.<sup>[2]</sup>

For the pure host systems the  $^{13}\text{C}$  spin–lattice relaxation times and nuclear Overhauser enhancements were measured in acidic and neutral aqueous (**1** and **2**) as well as methanolic (**1**) solutions. Furthermore, the  $^2\text{H}$  spin–lattice relaxation times of bulk  $^2\text{H}_2\text{O}$  were measured. From the temperature dependence the activation parameters for the reorientational motion were evaluated. The same data were obtained for the host–guest systems. Additionally,  $^{14}\text{N}$  relaxation data were determined for the guest molecules.

The reorientational molecular dynamics were compared for the different systems, and the influence of host–guest interactions on the molecular dynamics and thus the relaxation data was studied. While the effect of the host–guest interactions on the host dynamics was not very large, it was considerable for the guests. A proposal for the structure of the host–guest complexes in solution was made on the basis of the relaxation data.

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FLUORESCENT WATER-SOLUBLE  $\beta$ -CYCLODEXTRIN-DIMERS AS SENSOR  
MOLECULES FOR THE DETECTION OF NEUTRAL ANALYTES

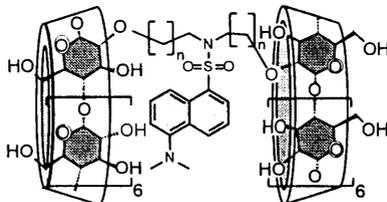
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The complexation ability of cyclodextrins for organic species in aqueous solutions can be used for the development of fast responding, on-line sensing techniques for organic analytes in water. In the past, fluorescent cyclodextrins were prepared by appending a fluorophore to give fluorescent sensing molecules. Competition for the hydrophobic cavity between an analyte and the covalently linked fluorophore results in a change in the optical properties of the latter which is dependent on the concentration of the species to be detected. However, little attention has been paid to the alteration of the naturally given selectivity of cyclodextrins for complex formation with organic species.

The aim of this work is to improve the selectivity of cyclodextrin based sensing systems by changing the complexation properties. Earlier studies have shown that extending the cyclodextrin cavity leads to dramatically improved binding capabilities for large guests.<sup>[1]</sup>



In order to obtain a sensing molecule, we connected two cyclodextrin units via fluorophore containing spacers of varying lengths ( $n=1,2$ ). In aqueous solution, these molecules respond to the presence of steroids with an increase or decrease of the fluorescence intensity, depending upon the substitution pattern of the steroid. More remarkably, stabilities of the steroid complexes differ greatly for strongly resembling steroids. These differences in stabilities and the opposite fluorescence responses are studied by fluorescence lifetime measurements and isothermal titration calorimetry. In the presence of smaller organic analytes the fluorescence response was found to be less pronounced. As such, the selectivities of these novel fluorescent cyclodextrin dimers differ markedly from that of native  $\beta$ -cyclodextrin.

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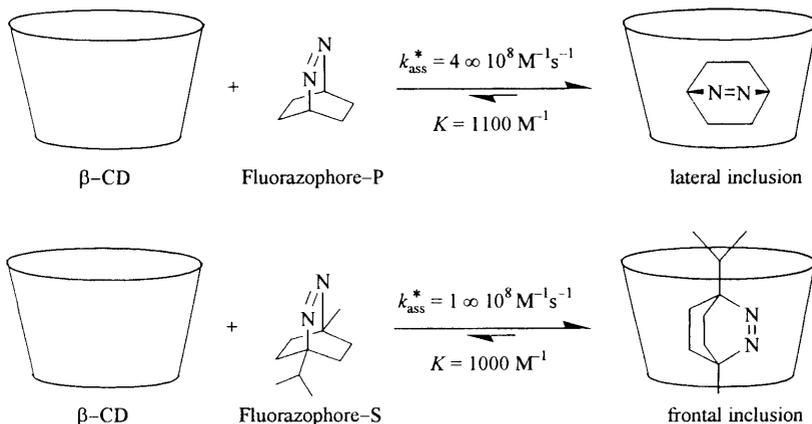
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A NOVEL STRUCTURAL AND DYNAMIC PROBE FOR THE INVESTIGATION OF  
 SUPRAMOLECULAR ASSEMBLIES: AN EXPLORATORY STUDY OF CYCLODEXTRINS  
 BY NMR, FLUORESCENCE, UV-ABSORPTION, AND INDUCED CIRCULAR  
 DICHROISM

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The azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene and its derivatives have been introduced as the first fluorescent probes for monitoring antioxidant activity<sup>[1]</sup> and supramolecular kinetics.<sup>[2]</sup> When used as fluorescent probes, we refer to these compounds as fluorazophores.<sup>[3]</sup> In the present study, we have employed the parent compound, Fluorazophore-P, and compared the structural and kinetic data of its host-guest cyclodextrin complexes with those for the sterically elaborated, more selective derivative Fluorazophore-S.



NMR studies (ROESY, CIS), time-resolved and steady-state fluorescence spectroscopy, UV-absorption spectrophotometry, and induced circular dichroism were employed to determine the kinetics of inclusion (in the excited state), binding constants, and structural parameters, namely the depth of penetration of the guests into the cavity and their relative conformation.

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## ORGANIC PROCESSES INITIATED BY NONCLASSICAL ENERGY SOURCES

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Nonclassical energy sources such as microwave energy, ultrasound and triboenergy as well as their combination with UV/VIS-radiation are new tools in synthetic chemistry and chemical processing. Microwave heating has been used for a wide variety of purposes such as moisture analysis, acid decomposition of biological samples, dissolution of geological materials, rapid hydrolysis of peptides and proteins. Recently the use of microwave radiation has attracted the attention of organic chemists for use in synthesis and processing. Remarkable decrease in the time necessary to carry out reactions and in some cases cleaner reaction with easier work-up compared to conventional methods have been observed with microwave heating.<sup>[1,2]</sup>

In our lecture we describe the application of microwave treatment for selected organic reactions such as (i) enzymatic transesterification of optically active alcohols, (ii) mercury-sensitized gas phase photolysis of hydrocarbons in the microwave field and (iii) environmentally benign oxidations of olefins. The efficiency of enzyme-catalyzed organic synthesis has been observed to increase under the effect of microwave irradiation.<sup>[1d]</sup> It's a matter of interest to determine the conditions allowing to optimize enzyme activity and enantioselectivity. Our work will concentrate on substrates derived from renewable raw materials. The use of immobilized enzymes offers the advantageous possibility to work in quasi solvent-free systems. The catalyst can easily be separated from the reaction mixture and reused. However, it is necessary to examine the limits of catalyst recycling. The mercury-photosensitized reaction is known as a method to synthesize a wide variety of organic molecules with inexpensive and readily available starting materials by dehydrodimerization or cross-dehydrodimerization. In the present study we have tried to combine this synthetically useful method with electrodeless lamps, which irradiate a wide band UV – radiation initiated by a microwave field. For these MW – MWUV combination process we have developed reactors, and we analyzed the influence of several chemical and physical parameters. As an example the dehydrodimerization of cyclohexane was optimized and the mechanism determined. The oxidation of olefins to technical relevant products such as the oxidation of cyclohexene to adipic acid or of oleic acid to the corresponding 9,10-epoxide with an environmentally benign oxidation system<sup>[3]</sup> is described as the third example. In this oxidation hydrogen peroxide is used as oxidant and no organic solvent is necessary.

All discussed reactions with the non-classical energy source are faster, the yields are high and the energy consumption is lower compared to the conventional reactions.

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## The Novel Chromophore Crown Ethers and Cationic Recognition with Optical Spectroscopy and MM+ Calculations.

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The supramolecular role of ionophore macrocycles have become well known and quite practical for molecular and ionic recognition [1,2]. We have so far synthesized the chromophore derivatives of [12]crown-4, [15]crown-5, [18]crown-6 and [21]crown-7 bearing coumarin, anthraquinone and xanthone groups [3,4]. Macrocycles identified by high resolution EI-mass  $^1\text{H}$ ,  $^{13}\text{C}$  and 2D NMR spectroscopy were studied for the molecular recognition of  $\text{Zn}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  ions with steady state fluorescence spectroscopy as well as UV-VIS spectroscopy in acetonitrile. The observed complexing enhanced quenching fluorescence spectra, (CEQFS) as well as the complexing enhanced fluorescence spectra, (CEFS) of the chromophore macrocycles without isoemissive peaks exhibited the cationic behaviors [5-8]. The such results were recently initiated to be proved with molecular mechanical molecular dynamic methods with MM+ using the commercial software Hyperchem<sup>®</sup>. The conformations and strain energy of free and complexed macrocycle backbones examined with MM+ mostly in agreement with the supramolecular behavior of the macrocycles [9,10].

*Acknowledgment* ; TUBITAK is greatly acknowledged by the author due to its kind support of our serial work in this topic.

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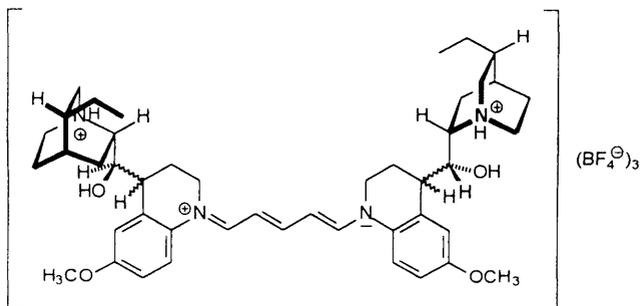
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**Chiral Polymethine Dyes**  
**Remarkable but Forgotten Conjugated  $\pi$ -Systems**

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Amongst compounds with conjugated  $\pi$ -systems such as aromatics and polyenes, polymethines constitute a third independent type of  $\pi$ -systems. Whereas chiral aromatics (e.g. helicenes) and chiral polyenes (e.g. carotinoids) are well known, chiral polymethines have been investigated only scarcely up to now.<sup>[1]</sup> This is in spite of the fact, that König reported on the first synthesis of chiral polymethine dyes already in 1928.<sup>[2]</sup>

Chiral polymethine dyes should exhibit particular new chiroptical properties, useful for their application as so-called functional dyes. For this reason, we have repeated and improved the preliminary work of König as well as synthesized a variety of new chiral polymethine cyanine dyes with heterocyclic end groups containing stereogenic centres.<sup>[3]</sup> For example, using naturally occurring Cinchona alkaloids such as (-)-quinine and (+)-quinidine as source of stereogenic centres with known absolute configuration, we have prepared for the first time pentamethine streptocyanine dyes with 1,2,3,4-tetrahydroquinoline end groups such as:



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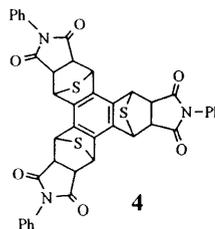
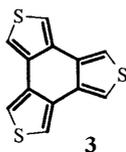
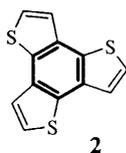
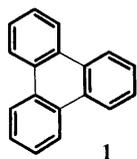
## SYNTHESIS, ELECTRONIC STRUCTURES AND CYCLOADDITIONS OF POLYCYCLIC HETARENES

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We have synthesized several polycyclic heteroaromatic compounds and studied their geometrical and electronic structures by X-ray crystal analysis,<sup>[1]</sup> UV photoelectron spectroscopy and quantum chemical calculations. The reactivity and stereochemistry of some compounds in Diels Alder reactions was investigated at high pressures. In tetracyclic compounds that are  $\pi$ -isoelectronic with triphenylene (**1**), [b]- or [c]-annellation of thiophene modifies the structure of the central benzene ring. **1** can be characterized as comprising three peripheral benzene rings connected by C-C single bonds.<sup>[2,3]</sup> The central ring is cyclohexa-1,3,5-triene-like. Alternation of the bond lengths in the central ring of **2** is rather small with C-C distances only little longer than in benzene. The central ring can thus be termed aromatic. **3** has a [6]radialene-like structure<sup>[4]</sup> in which the central six-membered ring is non-aromatic, and its six exocyclic C-C bonds have high double bond character. Extensive analysis of the PE spectra was accomplished by which all  $\pi$  and n(S) ionizations were identified.



c-Annellated thiophene rings such as in **3** show sufficient reactivity in cycloaddition reactions to afford tripod-shaped molecules like **4** which might be of interest in supramolecular chemistry. Based on the electronic structures of the hetarene, predictions regarding reactivity and reaction site are possible.

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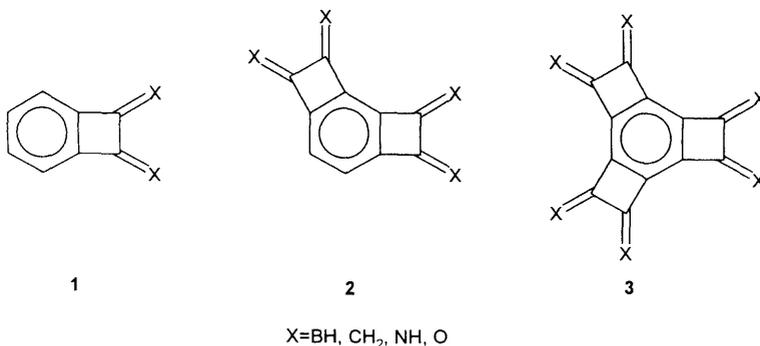
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SIBL IN STRAINED AROMATIC MOLECULES WITH EXTENDED  $\pi$  SYSTEMS.*Amnon Stanger*

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Strain Induced Bond Localization (SIBL) is a phenomenon that was introduced almost seventy years ago by Mills and Nixon, and is still intriguing today. There is no consensus about the role of strain and aromaticity – antiaromaticity factors in localizing aromatic system, and the reopening of the question of the nature of aromaticity by Shaik et. al. some fifteen years ago resubstantiate the SIBL issue as a probe for the study the importance of  $\sigma$  and  $\pi$  frameworks in aromatic systems.



In the last few years we have been engaged with the investigation of SIBL. Our theoretical and experimental findings suggest that strain can be manifested in either curved bond formation or in bond localization, and that  $\pi$  effects are relatively unimportant in SIBL. Others also verified these conclusions experimentally. Here we present some results concerning the systems 1-3, where the strained benzylic atoms are formally  $sp^2$  hybridized. Apparently, the localization found in these systems is small, and a rationalization will be presented.

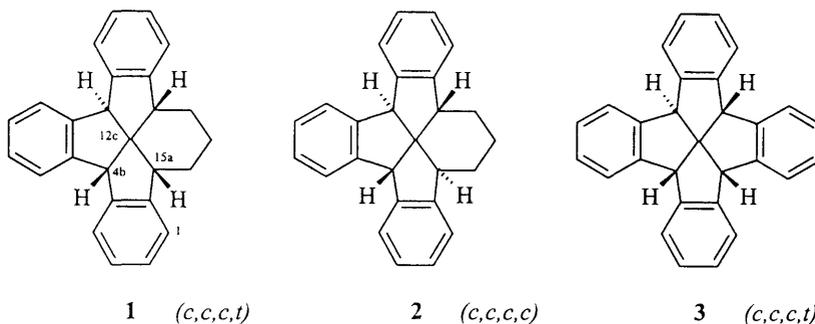
## Strained benzoannulated *cis,cis,cis,trans*-[5.5.5.6]Fenestranes: Synthesis and Properties

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The carbon frameworks of [m.n.o.p]fenestranes are not only defined by the characteristic mutual annellation of four rings in a “tetrafuso” manner but also, albeit less obviously, by the relative configuration of the four peripheral bridgehead positions.<sup>[1,2]</sup> As far as strained stereoisomers of the most stable all-*cis*-fenestranes are concerned, several small ring *cis,cis,cis,trans* isomers are known<sup>[1]</sup> within the [4.5.5.5]fenestrane series and only recently a complex derivative of *cis,cis,cis,trans*-[5.5.5.5]fenestrane has been reported.<sup>[3]</sup> However, extensive computational work has been published<sup>[1,2]</sup> demonstrating that the well-known strain of the *trans*-bicyclo[3.3.0]octane (*trans*-diquinane) unit is considerably enhanced by merging it with two additional rings in a *cis,cis,cis,trans*-[5.5.5.5]fenestrane skeleton. The calculations also point to a considerable increase of the non-bridged C-C-C-bond angles at the central bridgehead. Therefore, fenestranes bearing at least one *trans* fusion at the neopentane core are of considerable interest in the context of the planar-tetracoordinate-carbon problem.<sup>[4]</sup>



Here we report on the first directed synthesis as well as on the structure and reactivity of benzoannulated *cis,cis,cis,trans*-[5.5.5.6]fenestranes such as **1**,<sup>[5]</sup> which, according to semi-empirical calculations, are by ca. 10 kcal mol<sup>-1</sup> more strained than the respective all-*cis* isomers, e.g. **2**.<sup>[2]</sup> The extra strain of **1** gives rise to a strongly enhanced acidity of its “inverted” bridgehead C-H bond. This findings shed some light on the challenge to eventually synthesize the hypothetical *cis,cis,cis,trans*-tetrabenzo[5.5.5.5]fenestrane (“*epi*-fenestrindane”) **3**, which is predicted to be more highly strained by ca. 35 kcal mol<sup>-1</sup> as compared to all-*cis*-fenestrindane.<sup>[2]</sup>

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# Poster Presentations

## MICROWAVE-ASSISTED DEGRADATION OF PERSISTENT ORGANIC POLLUTANTS IN WATER

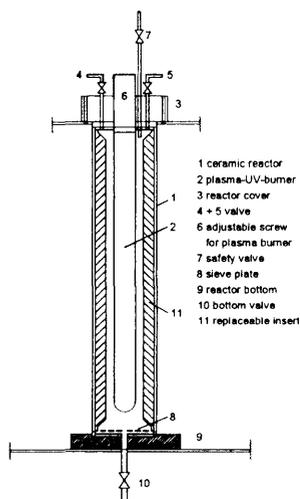
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The treatment of high contaminated waste water (CSB-level > 10000) in normal biological sewage disposal plants often impossible. The environmental disposal of this problem waste waters is a significant cost factor in many processes of the chemistry, pharmacy and food industry.<sup>[1]</sup> Innovative technologies could improve this situation. In a microwave field, particles are activated by dissipative energy. Polar molecules rotate and ions oscillate in the alternating electromagnetic field ( $f=2,45$  GHz). In this nonclassical manner energy is brought in chemical systems. Kinetic energy is transformed in thermal energy by "molecular" friction.<sup>[2,3]</sup>

The efficient heating of the mixtures accelerates chemical reactions. In this paper we describe the development and testing of a combined MW-MWUV reactor for batch and continuous reactions. Under defined conditions (pressure, temperature, materials) it is possible to ignite a nonthermal plasma in the microwave field [4]. This plasma is a source of UV/VIS-radiation, so there is the possibility to combine UV and microwave radiation. The electrodeless lamps are wear-resistant and the filling material is very variable. All stable elements of the periodic system are usable and so the emission of the lamps is adjustable. The effective degradation of water pollutants is demonstrated with some model substances. The results were determined with HPLC, TOC and ionselective electrodes. The intermediates and the reaction products were analyzed by chromatography (GC, HPLC, GC-MS). The results of our tests show, that the MW-MWUV process is faster in comparison to other "Advanced Oxidation Processes"

Scheme: MW-MWUV reactor



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DETERMINING CHEMICAL RATE COEFFICIENTS  
USING TIME-GATED FLUORESCENCE CORRELATION SPECTROSCOPY

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In recent years, fluorescence correlation spectroscopy (FCS) has become an important technique to determine kinetic coefficients of chemical reactions in solution without perturbing thermodynamic equilibrium. Fluorescent molecules are excited by laser light, and the emitted fluorescence from a small number of molecules in a volume of about 1 fl is collected using a high-NA microscope objective and sensitive detection. Number fluctuations, chemical reactions, and conformational changes of the molecules in the observation volume give rise to temporal correlations in the fluorescence intensity fluctuations. Autocorrelation analysis of the fluorescence emission allows one to extract diffusion coefficients as well as rate coefficients of chemical reactions.

Here we present a method to simplify the analysis of FCS measurements on samples containing multiple fluorescent species. Using pulsed laser excitation in conjunction with electronic gating in the detection channel, we suppress the emission from one of the components by fluorescence lifetime separation. The relaxation component of the autocorrelation function due to the reaction is thereby enhanced, and the reaction rate and equilibrium coefficients for unimolecular as well as bimolecular reactions can be determined. We have applied this technique to the binding reaction of the organic dye 1,8-anilino-naphthalenesulfonate (ANS) in the interior of the small globular protein apomyoglobin. In the hydrophilic environment of the aqueous solvent, the ANS fluorescence is strongly quenched, whereas in the more hydrophobic heme binding pocket of apomyoglobin, the fluorescence increases by more than a factor 100. ANS binding to apomyoglobin provides an excellent model system for investigating the effectiveness of gated FCS as well as an opportunity to investigate the dynamics of proteins in the native and partially denatured states.

## QUANTUM-MECHANICAL TUNNELING OF WATER IN HEME PROTEINS

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Quantum-mechanical tunneling plays an important role in the function of many proteins. Whereas the binding of small ligands to heme proteins at physiological temperature is governed by thermally activated barrier crossing, the reaction at low temperature ( $T < 50$  K) proceeds predominantly via quantum-mechanical tunneling, as shown by the presence of an isotope effect on the recombination rate coefficients. The ability to photodissociate ligands from the heme group makes these proteins excellent model systems for investigating tunneling in biological reactions. Indeed, there are only a few systems where the tunneling of entire molecules can be studied in depth.

Recently, we have shown that a photodissociable complex of myoglobin can be prepared, having a reduced heme iron ( $\text{Fe}^{2+}$ ) and water as a ligand<sup>[1]</sup>. This metastable complex is formed upon photoreduction of aquometmyoglobin ( $\text{Fe}^{3+}$ ) at low temperature. We have investigated the rebinding kinetics of the water ligand after laser flash excitation using transient absorption spectroscopy with monitoring in Soret band from 12 K to 150 K. To distinguish the effects of tunneling from other processes, the isotope effect was examined by measuring samples prepared with  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . Each sample was illuminated with x-rays for 48 hours at 80 K to achieve photoreduction. Since the oxidized species (aquometmyoglobin) is not photodissociable, we were not sensitive to any unreduced fraction of the sample. Above 60 K, ligand rebinding occurs by thermal excitation over enthalpy barriers, as seen from the temperature dependence which follows the Arrhenius law. Towards lower temperatures, the contribution of quantum-mechanical tunneling becomes more and more important. The kinetics are nonexponential, due to the heterogeneous nature of the protein ensemble investigated, and are described with a kinetic model involving energy barrier distributions. The parameters governing the tunneling rate coefficients are determined from the fits, and the results of normal and deuterated water are compared. Besides providing insights into the tunnel effect in ligand binding reactions, these experiments give the opportunity to investigate the dynamics of water ligands.

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## QUARTZ SURFACE MODIFICATION BY STILBENE: KEY TO NOVEL SENSOR FOR STUDY OF SURFACE PROPERTIES

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There are many important processes occurring on surfaces that depend on local microscopic properties (micropolarity, microviscosity etc.), e.g. heterogeneous catalysis, transplantation, fibreoptics transduction etc. Spin-labels, luminescent probes and Mossbauer spectroscopy have been proven to be very useful in the investigation of local molecular dynamics, micropolarity and conformational changes. But these methods can not be applied readily to the investigation of surface systems due to relatively low sensitivity.

According to our proposed method a number of stilbene derivative fluorescent labels were immobilized on the surface of the quartz plate in two steps:

1. immobilization of the protein spacer (lysozyme or human serum albumine) by means of two different immobilization techniques:
  - the surface activation by cyanogen bromide procedure.
  - the silanization technique.
2. covalent attachment of two stilbene labels (*trans*-4-dimethylamino-4*i*-aminostilbene and *trans*-4,4*i*-bis-brommethylstilbene) to immobilized protein by direct reaction or with cyanuric chloride as a cross-linker.

Thus for the first time the fluorescent photochrome labels suitable for the sensing were fixed by covalent bond at the definite distance from the surface.

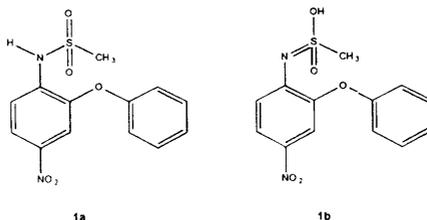
The kinetics of *trans-cis/cis-trans* photoisomerization of stilbene label in the immobilized and free state in different viscosity media (the water/glycerol mixture in different ratios) was monitored. As a result, a correlation between the media viscosity in the vicinity of the label and the apparent first-order rate constant of photoisomerization was observed. The proposed method can be used for analysis of both macro and microscopic properties of the media such as polarity or viscosity.

TAUTOMERIC EQUILIBRIUM IN NIMESULIDE,  
A SULPHONAMIDE PHARMACEUTICAL

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Nimesulide (**1a**) has been used as a painkiller, but more recently has shown promise in a number of other applications, including the prevention of miscarriage.<sup>[1]</sup> The sulphonamide could also exist as a sulphonic acid tautomer (**1b**); intra-molecular hydrogen-bonding is likely in both isomers. As the interconversion of the two forms involves only N → O proton transfer, the equilibrium should be rapidly established in e.g. water at ambient temperature<sup>[2]</sup>; essentially, there should be no barrier to reaction in the thermodynamically favoured direction, with the rate thus being diffusion-controlled. As well as being intrinsically interesting, the tautomerism may play a role in the drug's biological actions. Accordingly, the tautomerism is of particular interest in aqueous media.



We report initial studies in several solvents (water, acetone, DMSO, and chloroform)<sup>[3]</sup>. The equilibrium mixture is examined by <sup>1</sup>H- (300 MHz) & <sup>13</sup>C-NMR (75 MHz) at ~20 °C. Under these conditions, a set of peaks corresponding to the weighted average of the equilibrium ratio is observed, as tautomeric interconversion is rapid on the timescale of the NMR experiment. While the two tautomers are not expected to show substantially different *proton* spectra, we have observed significant differences in *carbon* NMR: comparison of the observed carbon signals with predicted spectra for **1a** and **1b** allows (tentative) assignment of the approximate tautomer ratio, which appears to show dramatic differences between solvents. The problem is also been tackled with low temperature NMR (which should 'freeze out' the individual tautomers), complimentary UV-Vis studies, pK<sub>a</sub> determination, molecular modelling, and the synthesis and characterisation of model compounds for each isomer.

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## KINETIC STUDY OF SOME PROTON TRANSFER CONTROLLED REACTIONS

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<sup>b</sup>Chemistry Department, University of Durham, Durham, UK.

The nitrosation of amines, ureas, amides has received much attention, owing in large part to the potencial carcinogenic properties of the N-nitroso products formed. Nitrosation of amines in acidic medium occurs with rate limiting attack of the nitrosating agent on the free base form of the substrate, while that of amides and ureas involves fast O-nitrosation followed by slow proton transfer from the substrate and a fast internal rearrangement to yield the N-nitroso products<sup>[1]</sup>.

We present a kinetic the results of a study in acid media of the nitrosation of N-methylformamide (MFA) and Dicyanoamide (DCA).

The obtained results are indicative of the first order term with respect to the substrate and to de acid and, show that the nitrosation of MFA is a non-equilibrium reaction while the nitrosation of CG and DCA are an equilibrium reactions.

We also have observed that contrary to the amines these reactions are subject to a general base catalysis, solvent isotope effects. All these fingers show that slow proton transfer is the rate determining step.

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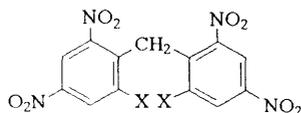
## Rapid Marcus Curvature Due to Extremely strong Solvational Imbalances in the Deprotonation of Polynitrobenzylic Carbon Acids by Oximate Bases.

François Terrier, Gilles Moutiers and Sandrie Pelet.

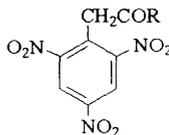
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Much attention has been paid to the reactivity of oximate ions in nucleophilic substitution and addition processes<sup>1</sup>. While oximate ions of  $pK_a \leq 8$  behave as  $\alpha$ -type nucleophiles, exhibiting a much higher reactivity than oxyanions of similar basicity, oximate ions of  $pK_a > 8$  have been found to suffer a dramatic saturation of their nucleophilic character in aqueous solutions. The proposal that the transition state of oximate reactions are subject to especially strong imbalances of solvational nature has been made to account for this behaviour. In this context it was of interest to study the behaviour of oximate ions as proton transfer catalysts in the ionization of carbon acids (a type of process where transition state imbalance effects play a major role in determining the intrinsic reactivity)<sup>2</sup>. A comparative kinetic study of the ionization of the carbon acids 1-5, by series of oximate ( $Ox^-$ ) and aryloxide ( $ArO^-$ ) ions has therefore been carried out in a 50%  $H_2O$ -50%  $Me_2SO$  (V/V) mixture.

While  $Ox^-$  and  $ArO^-$  ions define a linear Brønsted plot over a large  $pK_a$  range in the ionization of the less acidic compound 1, the catalytic efficiency of the oximate catalysts but not of the phenoxide catalysts levels off very rapidly in the ionization of 2-5. These systems add to the rare known examples of the occurrence of rapid levelling off in reactivity in proton transfer processes at carbon<sup>3</sup>. It is suggested that this behaviour results from a strong need for desolvation of the oximate ion prior to the actual proton transfer. The proposal that the situation may also be viewed as reflecting a large predominance of the work term ( $Wr$ ) over the intrinsic barrier term in the Marcus formalism will be made.<sup>4</sup>



1, X=H; 2, X=NO<sub>2</sub>



3, R=CH<sub>3</sub>; 4, R=C<sub>6</sub>H<sub>5</sub>; 5, R=C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>

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## ACIDITY OF CYCLOPROPANES: AB INITIO AND EXPERIMENTAL STUDIES

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Benzocyclopropenyl anion has been recently generated by deprotonation of the parent hydrocarbon (**1**) in the gas phase, and its proton affinity was measured by employing flowing afterglow technique.<sup>[1]</sup> Based on the results of *ab initio* calculations origin of its stability was rationalized by an interplay of two factors: (a) propensity of the aromatic ring to alleviate unfavourable antiaromatic interaction within the three-membered ring and (b) pyramidalization of the anionic center which minimizes interaction between the lone pair and the aromatic sextet. In this contribution we report on some of our recent work on the gas phase acidities of higher analogs of **1**, with particular emphasis on evaluation of the ring size effect on the intrinsic acidity of the benzylic position. In addition, a detailed analysis of the molecular and electronic structure of the corresponding anions based on high level *ab initio* molecular orbital and DFT calculations will be presented.

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## Acidity of Benzocyclobutene. *Ab initio* and Gas Phase Results

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Department of Chemistry, Ruder Bošković Institute, HR-10000 Zagreb, Croatia<sup>#</sup>

Gas phase acidities<sup>[1]</sup> of benzylic and aromatic ring positions in benzocyclobutene (**1**) will be presented and compared with results of the high level *ab initio* calculations. Special attention will be laid on the effect of the fused cyclobutene ring on the acidities of the aromatic ring protons. In addition, the effect of various  $\alpha$ - and  $\beta$ - substituents on the acidity of benzylic position in **1** will be discussed.

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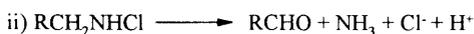
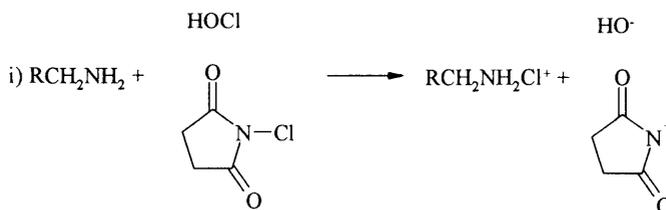
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KINETICS AND MECHANISM OF OXIDATION OF BENZYLAMINE BY AQUEOUS  
CHLORINE AND N-CHLOROSUCCINIMIDE

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Santiago de Compostela, SPAIN.

The reaction of oxidation of amines by aqueous chlorine or N-chlorosuccinimide (NCS) proceeds by a stepwise mechanism through an N-chloramine intermediate, which decomposes to give the corresponding aldehyde, ammonia and chloride ion as final reaction products.



Reaction i) is a fast process and has been studied using a stopped flow technique. The proposed mechanism consists in a nucleophilic attack of the amine on the chlorine atom of the chlorinating agent, resulting in a  $\text{Cl}^+$  transfer between the chlorinating agent and the amine. The rate constant for the reaction of benzylamine with NCS is  $7.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ , and for the reaction with hypochlorous acid  $1.01 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ .

Reaction ii) is much slower and a iodometric estimation of the stability of N-chlorobenzylamine at pH 9.5 gives a rate constant of  $1.70 \times 10^{-5} \text{ s}^{-1}$ .

ACID-BASE CATALYSIS IN THE DISPROPORTIONATION REACTION OF N-  
CHLOROTAURINE

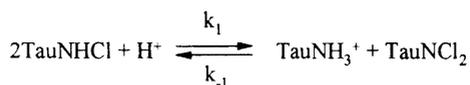
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Santiago de Compostela, SPAIN.

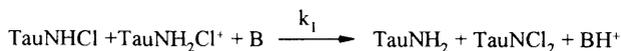
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Taurine, 2-aminoethanesulfonic acid, is one of the most abundant free amino acids in mammalian tissues. It has been implicated in various functions in the body, and one of them is to act as a trap for the HOCl produced by the myeloperoxidase-H<sub>2</sub>O<sub>2</sub>-Cl<sup>-</sup> system of leukocytes forming the long-lived oxidant N-chlorotaurine (TauNHCl) which is much less reactive and less toxic than HOCl. In acid media or in excess of hypochlorous acid, a second chlorine atom can be added to form the N,N-dichlorotaurine (TauNCl<sub>2</sub>). These reactions prevent the attack of cellular components by HOCl. Although the presence of TauNHCl in intact cells has been demonstrated, their chemical characteristics and complete functions are not fully understood. A better knowledge of the reactivity of taurine and taurine chloramines can help in our understanding of its physiological role.

N-Chlorotaurine disproportionates in acid media to give N,N-dichlorotaurine according to the equilibrium given below. We report the results obtained in the kinetic study of the forward and reverse reactions.

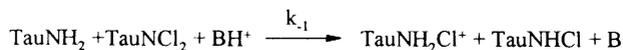


**Disproportionation reaction:** The forward reaction was found to be general base catalyzed:



A concerted mechanism is proposed in which proton removal from TauNHCl by a general base, and nucleophilic attack at the chlorine atom of TauNH<sub>2</sub>Cl<sup>+</sup> take place simultaneously in the transition state.

**Reaction of taurine with N,N-dichlorotaurine:** In alkaline media taurine reacts with N,N-dichlorotaurine to give N-chlorotaurine. This reaction is general acid catalyzed, as required by the microscopic reversibility principle:

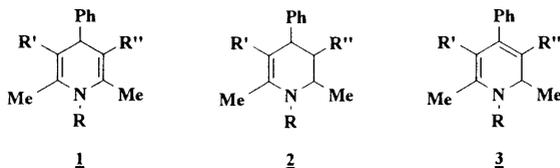


BASICITY OF PARTIALLY HYDROGENATED PYRIDINES  
AND ACID CATALYZED RECYCLIZATION OF 1,4-DIHYDROISOMERS

*Viesturs Lusis, Dzintra Muceniece and Ivars Turovskis*

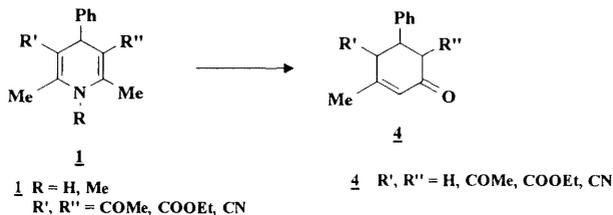
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Protonation of polysubstituted 1,4-, 1,2-dihydro- and 1,2,3,4-tetrahydropyridines **1**- **3** in CDCl<sub>3</sub>- CF<sub>3</sub>COOH solution was investigated by NMR. To compare basicity of the hydrogenated pyridines studied, an acidity  $H_o$  scale for chloroform-trifluoroacetic acid mixture was constructed based on the ionization of substituted anilines and  $pK_a$  values of protonated dihydro- and tetrahydropyridines were measured. The basicity of hydrogenated pyridines is arranged in the order **2** > **3** > **1**. Protonation of all these pyridine derivatives proceeds at  $\beta$ -carbon of the endocyclic enamine moiety  $-N-C_\alpha=C_\beta$ . Unexpected fast deuterium exchange in the 6-CH<sub>3</sub> group of 5-C-protonated 1,2-dihydropyridine **3** was observed.



**1**, **2** R = H, Me    **3** R = Me    **1** R', R'' = COMe, COOEt, CN    **2**, **3** R' = R'' = COOEt

The transformation of 1,4-dihydropyridines into the cyclohexenone derivatives proceeds as an acid catalyzed ring opening/ recyclization process where protonation is a rate determining step. Relationship between the dihydropyridine ring opening rate and the acidity of the reaction medium was studied in HCl / 50% EtOH solution.



**1** R = H, Me    **4** R', R'' = H, COMe, COOEt, CN  
R', R'' = COMe, COOEt, CN

Recyclization of dihydropyridines is affected by the substituents at 3 and 5 position and the increased acidity is required in the order: COMe < COOEt < CN. The structure of cyclohexenones **4** depends on acidity of reaction medium and substituents R', R''. In strong acidic medium the elimination of 3-acyl functions occurs simultaneously with recyclization.

## The Preparation and Kinetic Study of *N*-Nitrosohydroxylamines

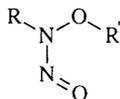
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A study into the kinetics of decomposition of *N*-nitrosohydroxylamines (**1**) is presented, together with their preparations.

Catalysis by  $\text{H}_3\text{O}^+$  having been identified,<sup>[1]</sup> possible catalysis by acetic, monochloroacetic, dichloroacetic and trichloroacetic acids for the compounds **1** was investigated. No catalysis was detected; indeed, these acids reduced rate constants. This observation was ascribed to a medium effect.



(1)

The effect of temperature on the specific acid catalysed decomposition was studied and activation parameters were determined. The results are shown in the table below.

Compound		Activation Parameter		$10^4 k_2(25^\circ\text{C})$ /mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>
R	R'	$\Delta H^\ddagger$ /kJmol <sup>-1</sup>	$\Delta S^\ddagger$ /JK <sup>-1</sup> mol <sup>-1</sup>	
MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	78	-37	6.94
Adamantyl	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	76	-32	27.8
C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> )	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	88	-14	1.99
(CH <sub>3</sub> ) <sub>2</sub> CH	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	87	-19	4.16
CH <sub>3</sub>	CH <sub>3</sub>	92	-27	0.21

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STRUCTURE - REACTIVITY EFFECTS ON THE PROTONATION EQUILIBRIA OF  
BENZOHYDROXAMIC ACID

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RAIPUR-492010 INDIA

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As part of our investigations on structure reactivity relationships in the hydrolysis (1) and protonation (2) behaviour of hydroxamic acids, we have now studied a series of benzohydroxamic acid ( $X.R(c=O).NHOH, X=H, 4-Me, 4-MeO, 4-NO_2, 4-Cl, 4-Br, 4-F$  &  $3-Cl$ ). The protonation constant,  $pK_{BH^+}$  and solvation parameters of these substituted benzohydroxamic acids have been calculated from UV-spectrophotometric data in aqueous solutions of sulfuric (0.0 to 16.2 mol dm<sup>-3</sup>) acid at 25 degree c. In the acidity range results obtained according to Hammett acidity function method, Bunnett-Olsen method, Marziano's Mc method and Cox-Yates excess acidity 'x' method are in good agreement. Structure reactivity relationships have been used to correlate molecular structural features of substrates. The Hammett and other equations have been applied to the data obtained. An attempt has been made to apply characteristic vector analysis to compensate the medium effect. In order to study the effect of various substituents the rate of hydrolysis and half - life periods of these compounds have also been investigated in sulfuric acid.

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DETERMINATION OF THE RATES OF FORMATION AND HYDROLYSIS  
OF THE SCHIFF BASES FORMED BY PYRIDOXAL 5'-PHOSPHATE  
WITH L-TRYPTOPHAN AND ITS METHYL ESTER.

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Pyridoxal 5'-phosphate (PLP) is one of the different forms of vitamin B<sub>6</sub> and plays an important role as the coenzyme of a wide range of different reactions such as transaminations, deaminations, decarboxylations and others.<sup>[1]</sup> Its action is by forming a carbinolamine intermediate by bonding its carbonyl group to the ε-amino group of L-lysine residue of the polypeptide chain.<sup>[2]</sup> The carbinolamine loses a molecule of water to yield the Schiff base in an acid catalysed process. The first step of all the PLP-dependent enzymes is a transimination reaction, namely, the conversion of the PLP-lysine imine to the substrate-PLP imine.

The interaction of PLP with L-tryptophan is essential for D-amino acid transferase (Trp 139) to exert an optimal catalytic function and also for aspartate amino transferase in the same respect (Trp 140).<sup>[3]</sup>

In this work, the stability and kinetics of formation and hydrolysis of the Schiff bases of pyridoxal 5'-phosphate with L-tryptophan (TRP) and L-tryptophan methyl ester (MTRP) were determined spectrophotometrically at various pH values, a temperature of 25°C and ionic strength of 0.1M, and the results were compared with those previously obtained for other amino group bearers.

Evidence on the formation of cyclic compounds by the Schiff bases formed in both cases (TRP and MTRP with PLP) in acidic media was found by different techniques.

*We thank "Fondo Nacional de Desarrollo Científico y Tecnológico"  
(FONDECYT) for financial support.*

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## KINETIC STUDY OF THE SCHIFF-BASE FORMATION BETWEEN PYRIDOXAL 5'-PHOSPHATE AND GABA. INFLUENCE OF TEMPERATURE.

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Pyridoxal 5'-phosphate (PLP) is one of the different forms of vitamin B-6 and plays an important role as coenzyme of a wide range of different reactions as transaminations, decarboxylations, deaminations and others.<sup>[1]</sup> In PLP-dependent enzymes, coenzyme (PLP) is bound to protein through a Schiff-base linkage with the  $\epsilon$ -amine group of a lysine (internal Schiff base) or is bound to  $\epsilon$ -amino group of amino acid substrate (external Schiff base). The first step of most the PLP-dependent enzymes is a transamination reaction, namely, the conversion of the internal Schiff base to the external Schiff base.  $\gamma$ -Aminobutyric acid (GABA) aminotransferase (EC 2.6.1.19, GABA-T) is a PLP-dependent enzyme that catalyses the conversion of the inhibitory neurotransmitter GABA and  $\alpha$ -ketoglutarate to succinic semialdehyde and the excitatory neurotransmitter L-glutamic acid.<sup>[2]</sup> Since GABA is the product of metabolism of L-glutamic acid, a reaction catalysed by the PLP-dependent enzyme L-glutamic acid decarboxylase, it is apparent that GABA aminotransferase is important in the regulation of brain neurotransmission of the mammalian.<sup>[2]</sup>

In this work, we report the stability and kinetics of formation and hydrolysis of the Schiff bases of PLP and GABA at different pH values and temperatures (20, 25 and 30°C), and constant ionic strength 0.1 M. The results obtained were compared with those found for Schiff bases of PLP and n-hexylamine,<sup>[3]</sup> and PLP and L-glycine.<sup>[4]</sup>

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METAL ION PROMOTED HYDROLYSIS OF RNA: GENERAL ACID CATALYSIS BY  
 $Zn^{2+}$  AQUO ION ON THE DEPARTURE OF THE LEAVING GROUP

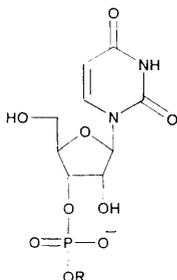
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Metal ion promoted cleavage of RNA and RNA model compounds has been extensively studied over the last two decades. It is hoped that detailed mechanistic understanding would enable a rational design of artificial RNA cleaving agents utilising metal ion chelates as their catalytically active function.

It is generally believed that metal ions enhance the cleavage of phosphodiester bonds of RNA by assisting the nucleophilic attack of the adjacent 2'-hydroxy function onto the phosphorus. Less attention has been paid to a possible catalysis on the departure of a leaving group, which, most probably, is the rate-limiting step of an uncatalysed reaction. The present work addresses this question by studying the  $Zn^{2+}$  promoted cleavage of series of uridine 3'-alkylphosphates (**1a-e**).

A  $\beta_{lg}$  value of the  $Zn^{2+}$  promoted cleavage of **1a-e** was determined, and the value obtained (-0.32) was compared to those reported previously for the cleavage promoted by hydronium and hydroxide ions,<sup>[1]</sup> and of the cleavage in buffer solutions.<sup>[2]</sup> The comparison suggests that in the presence of metal ions, the leaving group departs as an alcohol, and that the metal ion enhances its protonation. The results of comparative measurements with uridine 3'-arylphosphates (**2a-e**) support the conclusions. The present results suggest, hence, that in addition to enhancing the nucleophilic attack, metal ion assist also the departure of the leaving group.



**1a:** R=CH(CH<sub>3</sub>)<sub>2</sub>  
**1b:** R=CH<sub>2</sub>CH<sub>3</sub>  
**1c:** R=CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>  
**1d:** R=CH<sub>2</sub>CHCl<sub>2</sub>  
**1e:** R=CH<sub>2</sub>CCl<sub>3</sub>

**2a:** R=Phenyl  
**2b:** R=2-Chlorophenyl  
**2c:** R=4-Chlorophenyl  
**2d:** R=2,5-Dichlorophenyl  
**2e:** R=4-Nitrophenyl

*References:*

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## KINETICS AND MECHANISM OF THE AMINOLYSIS OF O-PHENYL 4-NITROPHENYL DITHIOCARBONATE IN AQUEOUS ETHANOL

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The reactions of the title substrate (**1**) with a series of secondary alicyclic amines are subjected to a kinetic investigation in 44 % ethanol-water, at 25.0 °C, ionic strength 0.2 (KCl). Under amine excess over the substrate, pseudo-first-order rate coefficients ( $k_{obs}$ ) are obtained. Plots of  $k_{obs}$  against  $[NH]$ , where NH is the free amine, are nonlinear upwards, except the reactions of piperidine, which show linear plots. According to the kinetic results and the analysis of products a reaction scheme is proposed with two tetrahedral intermediates, one zwitterionic ( $T_{\pm}$ ) and another anionic ( $T^{-}$ ), with a kinetically significant proton transfer from  $T_{\pm}$  to an amine to yield  $T^{-}$  ( $k_3$  step). By nonlinear least squares fitting of an equation derived from the scheme to the experimental points, the rate microcoefficients involved in the reactions are determined. Comparison of the kinetics of the title reactions with the linear  $k_{obs}$  vs.  $[NH]$  plots found in the same aminolysis of O-ethyl 4-Nitrophenyl dithiocarbonate (**2**) in the same solvent shows that the rate coefficient for leaving group expulsion from  $T_{\pm}$  ( $k_2$ ) is larger for **2** due to stronger push by EtO than PhO. The  $k_3$  value is the same for both reactions since both proton transfers are diffusion controlled. Comparison of the title reactions with the same aminolysis of phenyl 4-nitrophenyl thionocarbonate (**3**) in the water indicates that (i) the  $k_2$  value is larger for the aminolysis of **1** due to the less basic nucleofuge involved and the small solvent effect on  $k_2$ , (ii) the  $k_3$  value is smaller for the reactions of **1** due to the more viscous solvent, (iii) the rate coefficient for amine expulsion from  $T_{\pm}$  ( $k_1$ ) is larger for the aminolysis of **1** than that of **3** due to a solvent effect, and (iv) the value of the rate coefficient for amine attack ( $k_1$ ) is smaller for the aminolysis of **1** in aqueous ethanol, which can be explained by a predominant solvent effect relative to the electron-withdrawing effect from the nucleofuge.

KINETICS AND MECHANISM OF THE PHENOLYSIS AND THIOLYSIS OF  
O-ETHYL S-(2,4-DINITROPHENYL) THIOL AND DITHIOCARBONATES.

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The reactions of O-ethyl S-(2,4-dinitrophenyl) thiolcarbonate (EDNPTC) and the corresponding dithiocarbonate (EDNPDTC) with a series of benzenethiolates and the reactions of the latter substrate with a series of phenols, are subjected to a kinetic study in water at 25°C, ionic strength 0.2 M (KCl).

The kinetic law obtained for all the measured reactions is first order in the nucleophile. The results of the reactions of these title substrates are compared among them, and with those of the phenolysis of EDNPTC.<sup>[1]</sup>

The nucleophilic rate constants ( $k_N$ ) for the thiolysis of EDNPDTC are greater than those of EDNPTC, according to Pearson's hard and soft acids and bases; nevertheless the  $k_N$  values obtained for the phenolysis of EDNPDTC are closely similar to those for EDNPTC,<sup>[1]</sup> suggesting that the steric effect of the nitro group in position 2 is more important than the effect of the electrophile.

The Bronsted-type plots obtained for the reactions are linear with slopes in the  $pK_a$  range 0.6-0.9, suggesting concerted mechanisms for these reactions.

*We thank "Fondo Nacional de Desarrollo Científico y Tecnológico" (FONDECYT) for financial support.*

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*References:*

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## REACTIVITY OF THIOBENZOYL CARBAMATES

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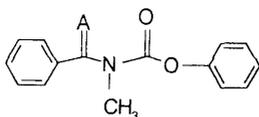
<sup>2</sup> CECF, Faculdade de Farmácia, Avenida das Forças Armadas, 1699, Lisboa, Portugal.

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Carbamates as well as their association with other moieties are known to have wide applications in medicinal and agrochemical fields and in the last few years our group has been interested in the development of new difunctional carbamates such as secondary and tertiary aroyl carbamates. For all the tertiary substrates (1) we have proposed a BAc2 type hydrolysis with general-base catalysis<sup>[1]</sup>.

Now we turned our attention to a new difunctional association involving thiobenzoyl instead of benzoyl together with the carbamate function (2). The first step of the synthesis was accomplished by obtention of thiobenzamide by treatment of N-methyl benzamide with Lawesson reagent<sup>[2]</sup>. Thiobenzamide was then made to react with NaH and phenyl chloroformate in dry DMF under nitrogen.



(1) A = O

(2) A = S

Once the new carbamate was obtained, its conversion to thiobenzamide and phenol was followed by UV spectroscopy. Reactivity was studied in several aqueous media including sodium hydroxide, and deuteroxide as well as non-hindered and hindered nitrogen and trifluoroethanol as an oxygen base.

The kinetic parameters under study will allow us to propose the sort of catalysis involved in the BAc2 type of hydrolysis of (2).

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2.-H. Fritz, P. Hug, S.O. Lawesson, E. Logemann, P.S. Pederson, H. Salter, S. Scheipye and T. Winkles, *Bull. Soc. Chim. Belg.*, **1978**, *7*, 87.

THE HOMOGENEOUS, UNIMOLECULAR GAS PHASE ELIMINATION KINETICS  
OF 2-SUBSTITUTED ETHYL DIMETHYLCARBAMATES. A TAFT CORRELATION WITH  
THREE SLOPES

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*Oswaldo Nuñez,<sup>b</sup> Norka Marcanob,<sup>b</sup> Suvighey Napolitano,<sup>b</sup> Armando Herize,<sup>b</sup> Henry  
Rodríguez,<sup>b</sup> Marianella Dominguez,<sup>b</sup> and Judany Ascanio<sup>b</sup>*

a) Centro de Química, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.), Caracas,  
Venezuela; b) Departamento de Química, Universidad Simón Bolívar, Sartenejas, Estado  
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The elimination kinetics of the title compounds have been studied over the temperature range of 269.0 – 430.0°C and pressure range of 24 – 220 Torr. The reactions, carried out in seasoned vessels, with the free radical inhibitor cyclohexene or toluene always present, are homogeneous, unimolecular and obey a first-order rate law. The process of elimination is described by the following general equation:  $(\text{CH}_3)_2\text{NCOOCH}_2\text{CH}_2\text{Z} \rightarrow \text{CH}_2=\text{CHZ} + (\text{CH}_3)_2\text{NH} + \text{CO}_2$  (Z = substituent). The use of Taft  $\sigma^*$  parameters was the only method to give a good correlation for substituents Z at the 2-position of ethyl dimethylcarbamates. Three good straight lines are originated at  $\sigma^*(\text{CH}_3) = 0.00$ . Each of these slopes appears to suggest that a small alteration in the polarity of the transition state may be due to changes of electronic transmission at the carbon reaction center. The unique substituent Z to assist anchimerically one of these elimination reactions is the phenyl group in 2-phenylethyl dimethylaminocarbamate. This result implies a mechanism in terms of a modest intimate ion-pair type of intermediate.

COMPLEXES OF N-HETEROCYCLIC COMPOUNDS WITH NITROSONIUM  
CATION: STRUCTURE AND DYNAMIC BEHAVIOUR

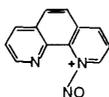
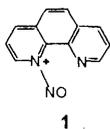
*Gennady I. Borodkina<sup>b</sup>, Rodion V. Andreeva<sup>b</sup>, Innokenty R. Elanova  
and Vyacheslav G. Shubin<sup>a</sup>*

Novosibirsk Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences<sup>a</sup>, and Novosibirsk State University<sup>b</sup>, Novosibirsk 630090, Russia

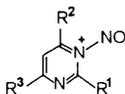
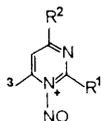
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Cationic complexes of heterocyclic compounds are well known to be key intermediates in numerous organic reactions. In this report some results of our studies on structure and dynamics of nitrosonium complexes of N-heterocyclic compounds are presented.

We have found the treatment of 1,10-phenanthroline (1,10-phen) with  $\text{NO}^+\text{BF}_4^-$  in  $(\text{CD}_3)_2\text{SO}$  at  $20^\circ\text{C}$  as well as that of 2-methyl-4,6-diphenylpyrimidine and 2-phenoxy-4,6-dimethylpyrimidine with  $\text{NO}^+\text{AlCl}_4^-$  in  $\text{SO}_2-\text{CD}_2\text{Cl}_2$  at  $-70^\circ\text{C}$  to result in formation of n-complexes (1-3, respectively), as determined from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.



$\text{R1}=\text{Me}, \text{R2}=\text{R3}=\text{Ph}$  (2)



$\text{R1}=\text{PhO}, \text{R2}=\text{R3}=\text{Me}$  (3)

The equivalence of the corresponding hydrogen and carbon atoms observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the complexes 1-3 suggests that the ions generated are dynamic complexes. The mechanism of the degenerate rearrangement is likely to involve intra- and/or intermolecular migration of the  $\text{NO}^+$  group from one nitrogen atom to another. On increasing the 1,10-phen :  $\text{NO}^+\text{BF}_4^-$  mole ratio from 1:1 to 1:2, additional downfield shifts of the signals in the NMR spectra are observed. This apparently results from the formation of the dicationic complex.

The results of MO calculations of the complexes will be discussed.

**NITROSO GROUP TRANSFER FROM SUBSTITUTED N-METHYL-N-NITROBECENESULFONAMIDES TO AMINES. INTRINSIC AND APPARENT REACTIVITY.**

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*Department of Physical-Chemistry, Faculty of Chemistry, University of Santiago*

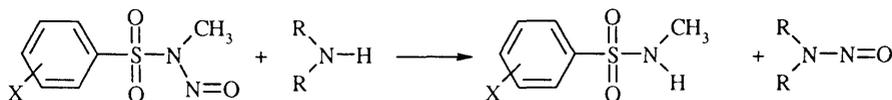
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We have studied the nitroso group transfer from substituted N-methyl-N-nitrosobecenesulfonamides to primary and secondary amines. The reaction rate is enhanced by the presence of electron withdrawing substituents in the nitrosating agents. From the rate constants of the nitroso group transfer,  $k_{tr}$ , we could achieve good Brønsted type relationships between  $\log k_{tr}$  and  $pK_a^{R_2NH_2^+}$  and  $pK_a^{leaving\ group}$ . The absence of correlation breakdown when  $\Delta pK_a = pK_a^{R_2NH_2^+} - pK_a^{leaving\ group} = 0$ , lead us to suggest a concerted reaction mechanism.



The obtained data for nitrosation/denitrosation of secondary amines catalyzed by  $SCN^-$ , and the equilibrium constant for  $ONSCN$  formation allowed us to calculate the equilibrium constant for  $NO^+$  loss from a protonated N-nitrosamine ( $pK_{NO}^{R_2N^+HNO}$ ). The  $pK_{NO}^{X-NO}$  values for  $NO^+$  losing from N-methyl-N-nitrosobecenesulfonamides have been obtained in a similar way. The calculated value of  $\Delta pK_{NO} = pK_{NO}^{R_2N^+HNO} - pK_{NO}^{X-NO}$  allow us to compute the equilibrium constants for  $NO$  transfer.

Brønsted type plots yielded  $\beta_{nuct}^{norm}$  and  $\alpha_{lg}^{norm} \cong 0.5$  showing a symmetrical transition state. In terms of Marcus Theory the intrinsic barrier for  $NO$  transfer is independent of the substituents on the N-methyl-N-nitrosobecenesulfonamides.

## ELECTROPHILIC SUBSTITUTION OF ARYLBORONIC ACIDS

*Stefan Salzbrunn, Jürgen Simon, G. K. Surya Prakash\**,

*Nicos A. Petasis and George A. Olah\**

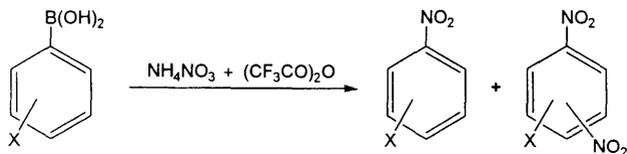
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Electrophilic nitrations of arylboronic acids with ammonium nitrate and trifluoroacetic anhydride were investigated at low temperatures. The reactions give the *ipso*-nitrated compounds, the desired regioselectivity, in good yields.

Competing nitration of the arylboronic acids at other ring positions was also observed. Dinitro compounds of activated and deactivated aromatic ring systems were obtained at  $-45^{\circ}\text{C}$  in moderate to good yields.

A mechanistic pathway for the nitration is proposed and the effects of the amount of nitrating agent employed on the product composition is shown.



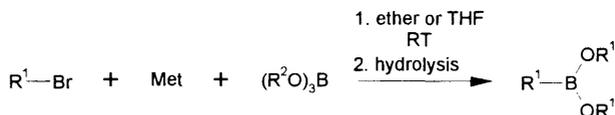
## A SIMPLE PROCEDURE OF OBTAINING OF ALKYL(ARYL)BORONIC ESTERS.

V.A.Bacherikov, V.V.Kuznetsov. A.I.Gren'.

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This procedure is modification of the traditional method<sup>[1]</sup> of obtaining of esters of alkyl(aryl)boric acids by reaction trialkoxyboranes with magnesium alkyl(aryl) halogenides or lithium alkyl(aryles).

A simplifity has been achieved by interaction of the metal and alkyl(aryl) halogenide at presence of trialkoxyborane in ether solution. The metalorganic reagent what was formed reacts with trialkoxyborane resulted after hydrolysis of reaction mixture alkyl(aryl)boric acid esters in 46-60% yields.


 $\text{R}^1 = \text{C}_2\text{H}_5, \text{C}_3\text{H}_5, i\text{-C}_3\text{H}_7, i\text{-C}_4\text{H}_9, \text{C}_6\text{H}_5;$ 
 $\text{R}^2 = n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, i\text{-C}_4\text{H}_9, i\text{-C}_5\text{H}_{11}, n\text{-C}_6\text{H}_{13}, n\text{-C}_7\text{H}_{15};$ 

Met = Mg or Li.

Proposed method contrary of traditional one is not required preliminary synthesis of metalorganic compound and the lower (-70oC ) temperature and in accordance with the inconvenient addition of metalorganic reagent.

As supplement the easy access to small scales lithium metal is reported.

*References:*

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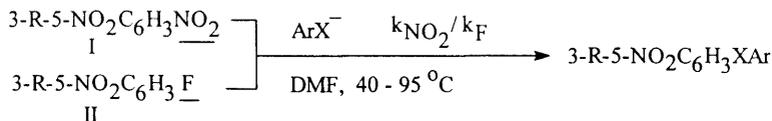
## REACTIVITY AND SELECTIVITY CONTROL IN THE NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS

V.M. Vlasov<sup>\*</sup>, I.A. Khalfina, A.A. Tabatskaya

N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry  
9, Lavrentjev Ave., Novosibirsk 630090, Russia

The comparison of soft and hard nucleophiles reactivity is a well known method to predict a leaving group mobility in  $S_NAr$  reactions [ 1 ].

The relative mobility of nitro group and fluorine  $k_{NO_2}/k_F$  in low activated arenes ( I, II ) under the action of both phenolate and thiophenolate ions has been studied. It is shown that the rise of a



R = H, CF<sub>3</sub>, CN, NO<sub>2</sub>. X = O, S. Ar = 2-C<sub>10</sub>H<sub>7</sub>; R'C<sub>6</sub>H<sub>4</sub>, R' = 4-MeO, 4-Me, H, 3-NO<sub>2</sub>, 4-Ac, 4-CN, 4-NO<sub>2</sub>.

substrate electrophilicity leads to a considerable rise of  $k_{NO_2}/k_F$  ratio. At the same time the sensitivity of sulfur nucleophiles for a nitro group substitution is higher than the one of oxygen nucleophiles when a substrate electrophilicity rises. The displacement selectivity of nitro group and fluorine depends on the nucleophile nature and is characterized by isokinetic ratios: the nitro group mobility grows relative to those of fluorine with the increase of the reaction temperature and the reduction of the nucleophile basicity. There are good correlations between Bronsted coefficient change  $\Delta\beta_{Nuc}$  and inverse temperature  $1/T$ , enthalpy ( $\Delta\Delta H^\ddagger$ ) and entropy ( $\Delta\Delta S^\ddagger$ ) change that suggested isokinetic ratios in these reactions. The isokinetic temperatures are lower than

For the competition reactions between  $ArO^-$  and compounds ( I, II ) ( R = CF<sub>3</sub> ):

$\lg k_{NO_2}/k_F = 0.52 - 0.03 \text{ pK ( at } 70^\circ\text{C )}$ ;  $\Delta\Delta H^\ddagger = 35.7 + 338 \Delta\Delta S^\ddagger$ ;  $\Delta\beta_{Nuc} = -0.44 + 141.7 / T$ .

For the competition reactions between  $ArS^-$  and compounds ( I, II ) ( R = CF<sub>3</sub> ):

$\lg k_{NO_2}/k_F = 3.28 - 0.22 \text{ pK ( at } 70^\circ\text{C )}$ ;  $\Delta\Delta H^\ddagger = -130.9 + 310 \Delta\Delta S^\ddagger$ ;  $\Delta\beta_{Nuc} = -1.83 + 554.1 / T$ .

the experimental temperature limit. Therefore, the displacement selectivity is controlled by entropy. The reasons of a peculiarities of sulfur nucleophiles reactivity are discussed.

[ 1 ] Bartoly G., Todesco P. Acc. Chem. Res. 1977, v. 10, N 4, p. 125 – 132.

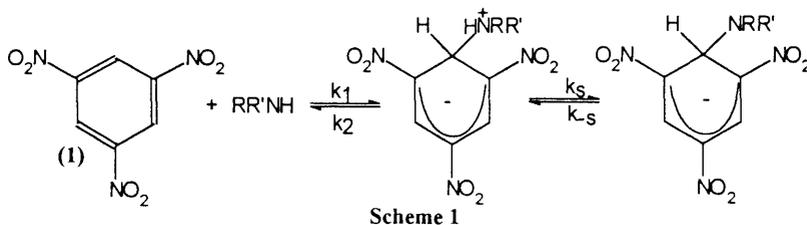
## Reaction of 4-Nitro-7-X-Benzofurazan Derivatives with Primary and Secondary Amines in Dimethyl Sulfoxide

Michael R. Crampton and Lynsey C. Rabbitt.

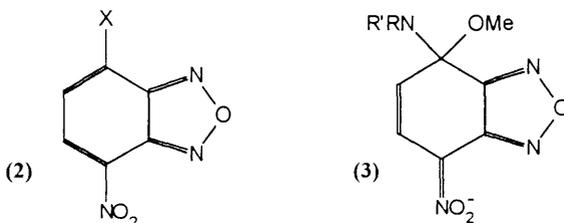
Department of Chemistry, Science Laboratories, University of Durham, South Road,  
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The reaction of 1,3,5-trinitrobenzene (**1**) with amines in dimethyl sulfoxide, leads to the formation of amine  $\sigma$ -adducts via zwitterionic intermediates as shown in scheme 1. Kinetic studies by Crampton have shown that the proton transfer step may be rate-determining.



We have studied the reaction of 4-nitro-7-X-benzofurazan (**2**) where X = Cl, OMe, OPh, with five different amines in dimethyl sulfoxide using conventional UV-Visible spectrophotometric and fast-reaction methods. These types of species are powerful inhibitors of nucleic acid synthesis and have an especially toxic effect on the metabolism of leukocytes *in vitro*.



The kinetically favoured reaction is nucleophilic attack by the amines at the 5-position to give anionic  $\sigma$ -adducts. This is followed by isomeric attack at the 7-position resulting in the formation of 7-amino derivatives by nucleophilic substitution. With (**2**) X = OMe, intermediates (**3**) on the substitution pathway are observable.

The present study has enabled a comparison of, i) the directing and leaving group ability of chloride, methoxide and phenoxide, ii) the relative nucleophilic reactivity of the amines, and iii) the reactivity of the furazan system with respect to trinitrobenzene.

## Mechanisms of nucleophilic substitution and elimination

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Traditionally, the mechanistic manifold of nucleophilic substitution and elimination reactions are explained by the concepts  $S_N1$ ,  $S_N2$ , E1 and E2, introduced by Hughes and Ingold.<sup>1</sup> With the extensions of Winstein<sup>2</sup> on the various possible variants of  $S_N1$  (intimate ion pair, solvent separated ion pair, and free carbocation) this is the common mechanistic scenario still adapted in journal articles and text books.

We have recently published work with experimental data and theoretical models of reactions between water and protonated alcohols;<sup>3</sup>

Substitution reactions:  $H_2^*O + R-OH_2^+ \rightarrow R^*OH_2^+ + H_2O$

Elimination reactions:  $H_2^*O + R-OH_2^+ \rightarrow (R-H) + (H_2O \cdot H_2^*O)H^+$

(R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CH and (CH<sub>3</sub>)<sub>3</sub>C; (R-H) = alkene, \* = <sup>18</sup>O)

The relative rates of the substitution reactions are (CH<sub>3</sub>)<sub>3</sub>C > (CH<sub>3</sub>)<sub>2</sub>CH > CH<sub>3</sub> > CH<sub>3</sub>CH<sub>2</sub>. The theoretical calculations are in good agreement. This is different from the situation in solution where the trend CH<sub>3</sub> > CH<sub>3</sub>CH<sub>2</sub> > (CH<sub>3</sub>)<sub>2</sub>CH > (CH<sub>3</sub>)<sub>3</sub>C traditionally is explained by the notion that increased methyl substitution at the α-carbon reduces the rate constant for  $S_N2$  reactions due to increased "steric hindrance".

Based on these and other data, we propose an easily conceivable mechanistic scheme where two competing elementary substitution mechanisms always operate in parallel:  $S_{N2B}$  (back side nucleophilic substitution), and  $S_{N2F}$  (front side nucleophilic substitution). This picture does not necessarily include the free cation  $S_{N1}$  mechanism, although it is realized that the carbocationic character becomes more prevalent upon increased alkyl or aryl substitution of the central carbon atom of given substrate molecule. In our interpretation  $S_{N1}$  illustrates the limiting situation, where  $S_{N2B}$  and  $S_{N2F}$  have collapsed into one single mechanism upon sufficiently increased carbocation stability. If this collapse ever takes place in reality is, however, uncertain.

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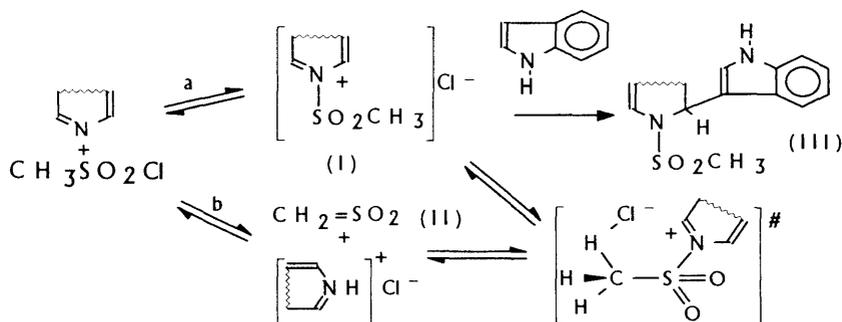
## HETEROARYLATION OF CH-ACIDS BY AZINES

*Yu.G.Skrypnik, N.V.Vasiljeva, S.N.Lyashchuk*

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By the use of synthetic and kinetic methods it has been shown that the heteroarylation of CH-acids (indole, pyrrole, dialkylanilines) by azines (pyridine, quinoline, isoquinoline) with promotion by sulfonyl chlorides  $\text{RSO}_2\text{Cl}$  (where R - Aryl, Alkyl) proceeds through the stage of sulfonylazinium salts (I) formation. The product of such reaction is corresponding sulfonamide heterocyclic derivative (III).

In the case of methanesulfonyl chloride (alkanesulfonyl chlorides) the sulfene route (b) with sulfene formation (II) may be realized. Probably, the sulfene (II) exists in the dynamic equilibrium with sulfonylonium salt (I).



New hetharyl products – sulfamoyl derivatives of (3'-indolyl)-1,2-dihydroisoquinoline have been synthesized by the reaction of isoquinoline and indole with N,N-dimethyl- and N,N-diethyl-sulfamoyl chlorides. The possibility of their existence in two isomeric forms has been shown by the semiempiric quantum-chemical approximation AM1.

By the use of theoretical methods (quantum chemistry, molecular mechanics, thermo-chemical calculations) the possibility of the mutual conversion  $\text{I} \rightarrow \text{II}$  has been studied. Structure, dynamics and energetics of I have been investigated. It has been determined that the conversion of N-mesylonium salts (I) in the sulfene (II) is an exothermic process ( $\Delta H = -244$  kJ/mol). The energy of ion bond has been examined ( $E = 220-235$  kJ/mol). It has been shown that (I) may be considered as stereochemically flexible molecules.

## Nucleophilic Catalysis in Oxidizing Activated Nucleophilic Substitution

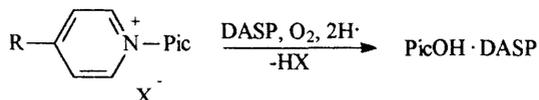
Gennadii D. Titskii, Tatyana S. Gaidash

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Molecular oxygen can change the rate of nucleophilic substitution reactions or act as a reagent in oxidizing nucleophilic substitution.

As evidenced from spectrophotometry data and studies on synthesis, N-picrylpyridinium salts [R = (CH<sub>3</sub>)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-CH=CH-; X<sup>-</sup> = I, Br, Cl, BPh<sub>4</sub>] in the presence of 4-[4-(dimethylamino)styryl]pyridine (DASP) at ambient conditions in acetonitrile give DASP picrate in quantitative yield according to irreversible process



The oxidation kinetics of onium salts was followed spectrophotometrically by DASP accumulation ( $\lambda$  455 nm) or disappearance of the salt cation ( $\lambda$  560 nm) at varying concentrations of molecular oxygen and DASP under concentration condition  $[\text{O}_2] \geq [\text{DASP}] \gg [\text{Salt}] = 2 \cdot 10^{-5}$  M in acetonitrile. The kinetic data fit a rate equation, first order in reagents (onium salt cation, molecular oxygen) and catalyst DASP concentrations. The reaction rate was unaffected by the salt anion.

The nucleophilic mechanism of catalysis by DASP involving generation of  $\sigma$ -adduct with salt anion followed by formation of picric acid by the reaction of the  $\sigma$ -adduct with molecular oxygen via a number of consecutive stages is discussed.

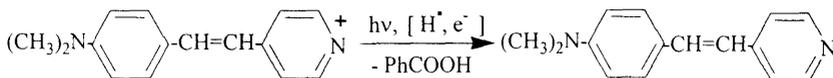
## Reaction of Photocleavage of N-O Bond in Acyloxypyridinium Salts

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UV and visible light irradiation of the solvents of 1-benzoyloxy-4-[4-(dimethylamino)-styryl]pyridinium chloride and tetrafluoroborate result in the break of N-O bond in 1-benzoyloxy-4-[4-(dimethylamino)styryl]pyridinium cation and in the quantitative formation of 4-[4-(dimethylamino)styryl]pyridine.



The kinetics of photoreaction followed by the decrease of 1-benzoyloxy-4-[4-(dimethylamino)styryl]pyridinium cation absorption has been studied in acetonitrile ( $\lambda_{\text{max}}$  515 nm;  $2.5 \cdot 10^{-5}$  mol / dm<sup>3</sup>; LUV 80,  $\lambda$  300 – 400 nm; quartz cuvette 1 cm; distance 15 cm; T 298 K). The reaction rate follows a first order kinetic law. The observed rate constant of the reaction doesn't depend of anion nature and is equal to  $(2.20 \pm 0.10) \cdot 10^{-2}$  s<sup>-1</sup>.

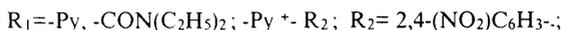
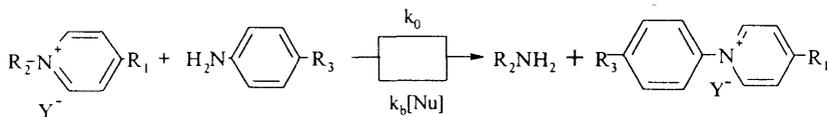
## Isoparametric Correlation of Charge-Charge Type in ANRORC Substitution

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Reactions of 4-R<sub>1</sub>-N-(2,4-dinitroaryl)pyridinium salts with arylamines in acetonitrile proceed according to ANRORC substitution mechanism and could be described by isoparametric correlation on the structure of the reagents, which are evaluated by traditional structure parameters (pK<sub>BH</sub><sup>+</sup>, σ<sup>o</sup>) [1].



The mechanism of rate determining stage block of the multi-step process studied is of the same type as base catalysed S<sub>N</sub>Ar substitution mechanism (slow decomposition of σ-adduct along the non-catalysed and catalysed pathways). Semiempirical quantum chemical method AM1 has been used to calculate charges on the reaction centres of the reagents (α -atom of pyridinium cation (q<sub>1</sub>) and nitrogen atom (q<sub>2</sub>) of arylamine). The isoparametric correlation between the charges and reactivity (lg k<sub>o</sub>) is observed:

$$\lg k_o = -(51 \pm 10) - (710 \pm 170)q_1 - (115 \pm 20)q_2 - (1770 \pm 400)q_1q_2$$

$$(R\ 0.956 \quad N\ 21 \quad S\ 0.298)$$

The calculated constant in isoparametric point (lg k<sub>o</sub> = -5.01) is coincide with the one experimentally found (lg k<sub>o</sub> = -4.96). The discovered correlation between the calculated charges of reaction centres of reagents and reactivity of salt cations in ANRORC substitution is discussed.

[1]. G.D. Titskii and E.S. Mitchenko. Mendeleev Commun. 1995, 162

## The Competition of $S_N$ and SET Mechanisms in the Reactions of Arene Carbonitrile Anionic Reduction Products with Alkyl Halides

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In the context of general problem of nucleophilic substitution ( $S_N$ ) and single electron transfer (SET) mechanisms competition in reactions of nucleophile + electrophile type, the possibility of the transition between  $S_N$  and SET pathways and factors governing it in the reactions of arene carbonitrile anionic reduced forms with alkyl halides has been studied as dependent upon the structure of both a substrate to be reduced and alkyl halide as well as the degree of reduction. The interaction of aromatic mononitriles such as benzonitrile, 1-naphthonitrile, 9-cyanoanthracene reduced by one or two equivalents of alkaline metal in liquid ammonia with primary alkyl halides has been found to result in the ipso-addition or the replacement of cyano group by alkyl one. Unlike this, the competition of both cyano group and hydrogen substitution occurs in alkylation of radical anions of 1,2- and 1,4-dicyanobenzene with negligible influence of alkyl halides nature upon the products ratio. By using cyclopropylmethyl bromide as testing "radical clock" reagent, for the alkylation of radical anions this change in alkylation regioselectivity has been revealed to result from the change of principal mechanism from  $S_N$  to SET. Thus, this change of mechanism is caused by the introduction of electron withdrawing substituent such as second cyano group into para- or ortho-position of aromatic ring of benzonitrile radical anion. Dianion of 1,4-dicyanobenzene displays dual nucleophilic and electron donating reactivity in dependence on alkyl halide nature. The tendency of mechanism change in the reactions of arenecarbonitrile reduced forms and the regioselectivity of alkylation are discussed on the ground of the results of quantum mechanical calculations of kinetic and thermodynamic reactivity indexes for competing mechanisms associated with electronic structure of reactive species and stability of their alkylation intermediates.

A KINETIC AND MECHANISTIC STUDY OF THE REACTION OF  
N-CHLOROSUCCINIMIDE WITH DIFFERENT ANIONS*Benito Agulla, Juan M. Antelo, Mercedes Parajó.*Dpto. Química Física. Fac. Química. Univ. of Santiago de Compostela.  
15706. Santiago de Compostela. Spain.

The rate of the reaction of N-chlorosuccinimide has been studied with iodide, hydroxide and bromide. In all three cases a Cl<sup>+</sup> transfer mechanism has been proposed to give ICl, ClOH and BrCl, respectively. In the case of iodide, the rapid formation of triiodide was measured at 287 nm, for the appearance of HOCl the reaction was measured at 292 nm and for bromide, the rapid formation of tribromide was measured at 265 nm.

The reaction kinetics were studied using the isolation method, the concentration of the anion being at least ten times that of the N-chlorosuccinimide. Owing the rapidity of these reactions, kinetic studies were carried out by means of the stopped-flow technique.

The rapidity of the reaction is attributed to the easy of valence shell expansion of chlorine and the strong nucleophilicity of anions.

The buffer-catalyzed rates for these reactions are proportional to the strength of the acids that are present in the solution, in accordance with the Brønsted-Pedersen <sup>[1]</sup> equation. The resulting values are  $0.10 \pm 0.01$  for the reaction with iodide and  $0.47 \pm 0.07$  for bromide. Rate constants for acid-assisted reactions of N-chlorosuccinimide with different anions increase with the anion nucleophilicity (n) in agreement with the Swain-Scott <sup>[2]</sup> relationship with an s value of 3.8. Thus, reactions at chlorine are much more sensitive to the nucleophilic strength than reactions at carbon.

The Brønsted values decrease as the nucleophilicity of anions increase. When the n values are large, the reactions are very favorable and the degree of proton transfer from the buffer acid (HA) is small because there is less need for acid assistance. On the other hand, if the nucleophilicity is small the reaction needs a larger degree of assistance by proton transfer as reflected by larger values. This is an interesting correlation between the role of general-acid assistance for proton transfer to oxygen and the role of the nucleophilicity of anions as it reacts with the adjacent chlorine in N-chlorosuccinimide.

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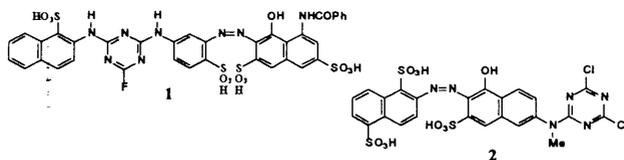
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- [2] Swain, C. G., Scott, C. B., *J. Am. Chem. Soc.*, 1953, 75, 141.

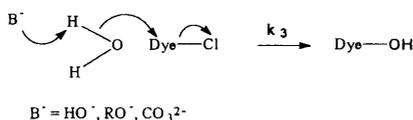
## Alkoxide- and carbonate-catalysed hydrolyses of a chloro-triazine in alcohol-water mixtures.

T. W. Bentley and P. J. Morris, University of Wales Swansea, Department of Chemistry, Singleton Park, Swansea, UK

Competing alcoholyses and hydrolyses of two reactive dyes (a monofluorotriazine **1** and a dichlorotriazine **2**) in water containing small amounts of added alcohols (methanol, and four poly-ols:  $\alpha$  or  $\beta$ -methylglucopyranosides, mannitol or sorbitol) at pH 11.2 have been used to model the chemical process of dye fixation to cellulose.[1]



In the presence of 0.044M polyol-water mixtures, an increase for  $k_{\text{DOH}}$  is observed for **2** [2] but not **1**. [1\*] These results are consistent with carbonate and/or alkoxide-catalysed hydrolysis of **2** via a third order, general base catalysed mechanism. Furthermore, hydroxide may catalyse in a similar manner.



Analysis of the data by the use of Bronsted theory and Kinetic Solvent Isotope Effects (KSIEs) has proved inconclusive. As a result, the same experimental procedure, dissecting observed first order rate constants into the separate contributions for hydrolysis and alcoholysis could be applied more generally to explore the scope of general base catalysed reactions at high pH and obtain data complimentary to Bronsted coefficients and KSIEs.

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2 T. W. Bentley, P. J. Morris and J. A. Taylor, unpublished observations

STATE AND REACTIVITY OF "NAKED" AND SPECIFICALLY SOLVATED  
NUCLEOPHILES IN PHASE TRANSFER CATALYSIS (PTC) CONDITIONS.

*Michael L. Kostrikin, Anatolii A. Afonkin, Alexander E. Shumeiko and Anatolii F. Popov.*

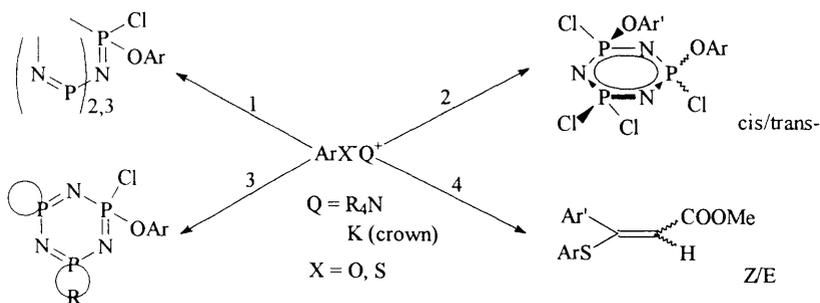
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The anion nucleophiles generated in PTC conditions as onium or crown-bonded salts take part in a number of equilibrium processes, e.g. extraction, dissociation, complex formation, etc.

For the model reactions of nucleophilic substitution in cylophosphasenes (1), their monoaryloxy (2) and carboranilen derivatives (3), and nucleophilic addition to activated triple bond (4)



the reactivity of ions ( $ArX^-$ ) and ion pairs ( $ArX^+Q^-$ ), their individual binding constants with proton-active components in organic phase and nucleophilicity of the most of specifically solvated species formed in PTC conditions were determined.

The solvent and structure effects both on the kinetic and thermodynamic parameters and on the stereo yield of reactions (2,4) are discussed.

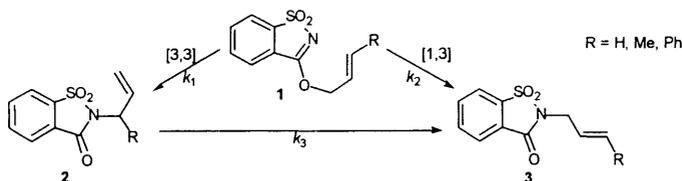
MECHANISTIC STUDIES ON SIGMATROPIC REARRANGEMENTS OF  
HETEROAROMATIC ALLYL ETHERS

*M. Lurdes S. Cristiano,<sup>1</sup> Amadeu F. Brigas,<sup>1</sup> and Robert A.W. Johnstone,<sup>1,2</sup>*

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<sup>2</sup> Department of Chemistry, University of Liverpool, Liverpool L69 3BX UK

Thermal isomerization of a range of 5-allyloxy-1-aryltetrazoles proceeds via concerted sigmatropic [3,3]-inversion of allyl during its shift from O to N, to give the tetrazolone product. Kinetic and cross-over experiments<sup>[1]</sup> indicated that the rearrangement was intramolecular and proceeded through a polar transition state. No products of [1,3]-migration, indicative of an ionic mechanism, were observed.



In contrast with these earlier results, a series of analogous 3-allyloxy-1,2-benzisothiazole 1,1-dioxides **1** formed products of both [3,3]- and [1,3]-rearrangement, the ratio of these depending on structure and reaction conditions. Thus, for the saccharyl heterocycle there appear to be two mechanisms of migration, one concerted and the other ionic.

On extended heating of the mixture of [1,3]- and [3,3]-products 2,3 (R=Me, Ph) the ratios of their respective amounts changed in favour of the [1,3]-isomer, indicating that there must have been a second rearrangement involving an allylic inversion from the [3,3]-product of a concerted shift to give the product of an ionic [1,3]-shift. This reversion of a concerted sigmatropic rearrangement to give the product of a similar ionic rearrangement appears to be highly unusual amongst the many known 'Claisen' type rearrangements. Rate constants for these reactions, in polar and apolar solvents, were determined<sup>[2]</sup> Electronic structure calculations were carried out on the rearrangement of compound **1** (R=H, CH<sub>3</sub> and Ph) through concerted and ionic mechanisms, in either ethanol or toluene as solvent. Results of kinetic measurements, X-ray structural analysis and theoretical calculations will be discussed.

*References:*

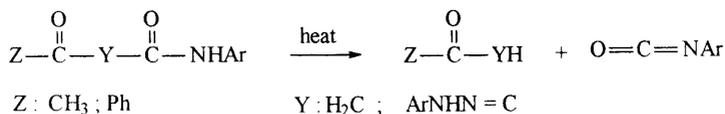
- [1] M.L.S. Cristiano and R.A.W. Johnstone, *J. Chem. Soc., Perkin 2*, **1997**, 489-494; *ibid.*, *J. Chem. Res. (S)*, **1997**, 164-165.
- [2] M.L.S. Cristiano A.F. Brigas, R.A.W. Johnstone, R. Loureiro and P. Pena, *J. Chem. Res. (S)*, submitted.

GAS-PHASE THERMOLYSIS OF KETOANILIDES,  
HYDRAZONES, AND RELATED SYSTEMS

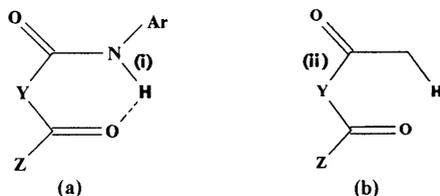
*Nouria A. Al-Awadi, Rana N. Malhas, and Osman M. E. El-Dusouqui*

Chemistry Department, University of Kuwait, P. O. Box 5969 Safat, Kuwait

The kinetics and product analysis of the thermal elimination reactions of twelve simple and hydrazone ketoanilides are described:



The kinetic studies were followed over  $51 \pm 6$  K temperature range to  $\geq 95\%$  reaction. Arrhenius  $\log A/s^{-1}$ ,  $E_a/kJ \text{ mol}^{-1}$ ,  $\Delta S^\ddagger/J \text{ K mol}^{-1}$ , and rates of reaction at 450 K have been obtained for the present substrates and compared with earlier results of related systems.<sup>[1]</sup> The products of complete pyrolysis of each compound were analyzed using GC-MS, FT-IR, and <sup>1</sup>H NMR, and the data amassed provided evidence for a rationalizable pathway (Scheme) in agreement with previous findings:



**Scheme.** Role of pre-assembly for a pathway involving H-bonding (a).

The present and earlier results allow the following important kinetic and structural comparisons to be made: (1) Replacement of the arylamino (-NHAr) group by a methyl substituent reduces molecular reactivity  $2.1 \times 10^3$  - fold (Y : ArNHN = C) to  $3.6 \times 10^6$  - fold (Y : H<sub>2</sub>C), in which case the H-bond donor acidity of (i) is deemed to control kinetics (a); (2) in absence of H-bonding and pre-assembly, the polarity of bond (ii) becomes a rate-controlling factor and the hydrazone moiety exerts a favourable rate-enhancing effect (eg.  $2.6 \times 10^2$  rate-factor for the simple dione); (3) where pathway (a) is suggested,  $\Delta S^\ddagger/J \text{ K mol}^{-1}$  values of approx. -10 to -70 have been recorded.

*References:*

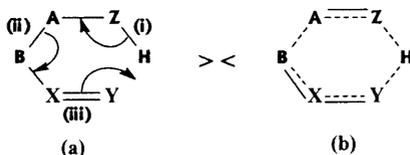
- [1] Al-Awadi et al, *Int. J. Chem. Kinet.*, 517 (1995); *ibid*, 457 (1998).

CONCERTED SIX-MEMBERED T. S. IN THERMAL ELIMINATION REACTIONS:  
STRUCTURE - REACTIVITY CORRELATIONS

*Nouria A. Al-Awadi and Osman M. E. El-Dusouqui*

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A large number of diverse organic compounds have been pyrolyzed under conditions conducive to unimolecular polar gas-phase elimination reactions free from catalytic surface effects and radical processes. The substrates included acids, esters, amides and diamides, oximes, alcohols, and amines with selective replacements involving the C, N, O and S atoms of key moieties in aliphatic or (hetero)aromatic systems. Typically, the elimination pathway involved a cyclic six-membered transition state (t.s.) either asynchronously (a) or synchronously (b) concerted:



Evidence for the t.s. has been obtained from reaction product analyses, kinetic investigations under conditions deemed reliable for polar elimination processes, Arrhenius energies and entropies of activation and A-factor, as well as Hammett  $\sigma/\rho$  linear and non-linear correlations.<sup>[1]</sup> Recent quantum mechanical investigations have lent support to the proposed mechanism<sup>[2]</sup>, and novel *quasi* 6-membered t.s. have been proposed.<sup>[1,3]</sup>

Besides, the communication analyzes and explains in terms of the proposed t.s. contribution to molecular reactivity from the H-bond donor acidity associated with bond (i), the relative bond polarity of (ii), and the protophilicity and  $\pi$ -bond lability of (iii). The structural effects of the A, B, X, Y and Z moieties on observed reactivities are likewise rationalized.

*References:*

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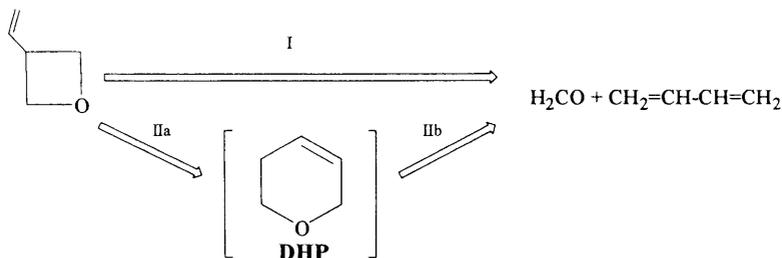
THE THERMAL DECOMPOSITION OF VINYLOXETANES:  
A THEORETICAL STUDY

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The pyrolysis of oxetanes seems important since these compounds are intermediates in the oxidation of hydrocarbons. Nevertheless, until recently scarce work<sup>[1-4]</sup> has been published on this topic which strongly contrasts with the large amount of data available on cyclobutanes. Kinetic studies<sup>[1,2]</sup> have shown interesting similarities between the thermal decompositions of cyclobutane and oxetane that can be extended to their simple alkyl derivatives.<sup>[1]</sup> Upon vinyl substitution the fragmentation rates of cyclobutanes and oxetanes are increased in large amount.<sup>[1]</sup> In these systems, an alternative reaction pathway (ring expansion) must be considered.

The thermal fragmentation of 3-vinyloxetane was investigated in the gas phase at MP2/6-31G\* and B3LYP/6-31G\* levels of theory. Relative energies were estimated performing single point calculations at higher theoretical levels. Two mechanisms were encountered (see Scheme): (I) a concerted reverse [2+2] cycloaddition and (II) a two-stepwise one as a result of a sigmatropic shift yielding 3,6-dihydro-2H-pyran (DHP) (IIa) followed by a concerted pericyclic [4+2] cycloreversion (IIb). Both mechanisms are compatible with the equimolar formation of formaldehyde and butadiene as major products of the reaction.<sup>[1]</sup>



*References:*

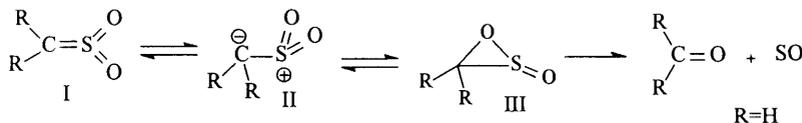
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QUANTUM CHEMICAL STUDY OF THIOFORMALDEHYDE-S,S-DIOXIDE  
STRUCTURE AND POSSIBILITY OF ITS IZOMERIZATION INTO YLIDE.

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Heterocumulenes of sulfene series (thioaldehyd-S,S-dioxides) are very high reactive molecules acting as intermediates of acylation, electrophilic and nucleophilic addition, cycloaddition.<sup>[1-3]</sup> The overwhelming majority of works devoted to chemistry of these compounds are focused on methods of their preparation and directions of it synthetic use. The aim of present work was the quantum chemical study of peculiarities of sulfene structure and it isomerization. By the use of semi-empirical MINDO/3, MNDO, AM1, PM3 approximations and ab initio MP2/4-31G and MP2/6-31G bases the structure, MO, stability and isomerization routes of sulfene under a change of angles /CSO and /HCSO have been studied.



It was established that the potential energy surface of sulfene has a polyextremal character. The existence of "planar" sulfene I is possible (Widberg's index of C-S bond is 1.30-1.60) but the change of /HCSO into 0.5-1.0 leads to isomerization of II into "ylide" II and sultine III. It was found that process I→II→III has a very low barriers (<20-30kJ/mol) Structural dynamism of sulfene is a cause of it very high reactivity. In our opinion, it would be more correct to consider the sulfene as non-classic heterocumulene. Being a binding link between heterocumulenes and ylides they can easily be "adapted" to specific situation arising as a result of chemical processes and lead to a wide range of existing reactions of these compounds.

*References.*

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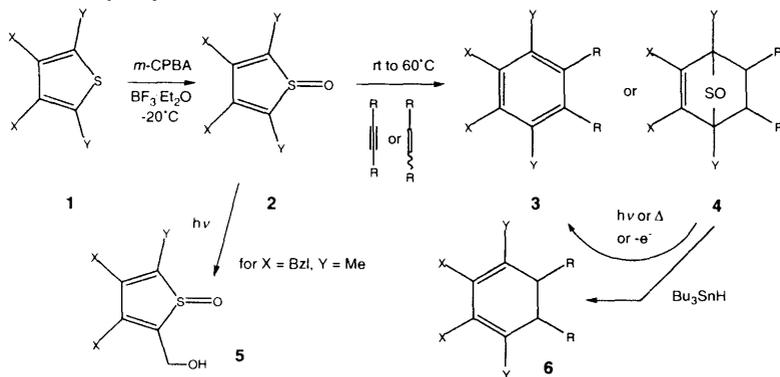
## Synthesis and Reactivity of Thiophene-*S*-Oxides

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Thiophene-*S*-oxides **2** can be prepared from thiophenes by oxidation with *meta* chloroperbenzoic acid in the presence of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . Thiophene-*S*-oxides can be isolated when the 2,5-positions carry alkyl substituents. Halo-substituents are also tolerated.



The thiophene-*S*-monoxides are reactive dienes in [4+2]-cycloaddition reactions. With alkynes substituted arenes **3** are the products, with alkenes the products are 7-thiabicyclo[2.2.1]heptane *S*-oxides **4**, which are precursors of arenes and cyclohexadienes **6**.

Photochemical irradiation leads to deoxygenation in the thiophene-*S*-oxides. In case of 3,4-dibenzyl-2,5-dimethylthiophene-*S*-oxide the 2-hydroxymethylthiophene **5** is formed.

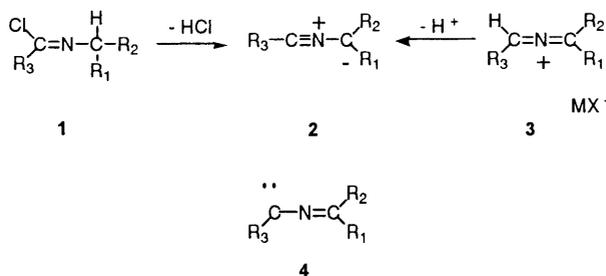
Electrochemical reduction of thiophene-*S*-oxides is possible. Chemically irreversible processes are observed by cyclic voltammetry in acetonitrile solution at carbon electrodes. In the presence of benzoic acid as a proton source a considerable change in the electrochemical characteristics occurs and the reduction process is associated with the cleavage of the S-O bond yielding the thiophene.

## FORMATION OF NITRILE YLIDES VIA 2-AZAALLENUM IONS

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Nitrile ylides (**2**) undergo a variety of reactions typical of 1,3-dipoles, including the well known cycloadditions and also reactions with nucleophiles and electrophiles. Of particular interest are those reactions in which they behave as "imine stabilised carbenes" (**4**), which then undergo carbon-carbon dimerisations.



Two possible routes to nitrile ylides have been examined in detail: 1,3-elimination of HCl from the corresponding imidoyl halide (**1**) and de-protonation of the corresponding 2-azaallenium ion (**3**). The latter reaction is reversible since it has recently been demonstrated that nitrile ylides also undergo rapid protonation in the presence of weak Bronsted acids yielding the corresponding azaallenium ions.<sup>[1]</sup>

When appropriately substituted (e.g.  $\text{R}_3 = p\text{-nitrophenyl}$ ,  $\text{R}_1 = \text{CF}_3$ ), the nitrile ylides (**2**) are relatively stable in basic solution and can be observed as highly coloured intermediates.

We also report on synthetic and kinetic studies of nitrile ylides and 2-azaallenium ions which are substituted by bulky groups (the presence of which slow both dimerisation and protonation).

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## Aryl Substituent Effects on Decarbonylation and Oxygen Scavenging of Carbon-Centered Radicals

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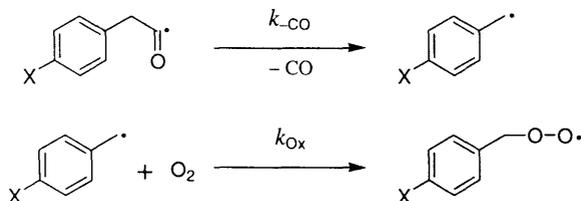
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Substituent effects in organic radical chemistry, in particular the interplay between radicals and polar effects, have been under intensive investigation. These substituent effects may affect the energies of the transition states<sup>[1]</sup> and, alternatively, the ground state energies of the reactants.<sup>[2,3]</sup> Substituent effects on the decarbonylation and oxygen scavenging of carbon-centered radicals have not been examined in detail.

In this work, the influence of aryl substituents on the fragmentation of phenacetyl radicals and on oxygen scavenging of benzyl radicals has been examined by laser flash photolysis, using dibenzyl ketones, peresters or Barton's esters as precursors. The kinetics of fragmentation and oxygenation was determined in acetonitrile and *n*-hexane, respectively.



The rate constants of the decarbonylation ( $k_{\text{CO}}$ ) in dependence on substituent (X) decreased in the order X = MeO > Me > H > CF<sub>3</sub> > Cl. The rate constants  $k_{\text{CO}}$  in *n*-hexane were three times larger than in acetonitrile. The rate constants of the oxygenation ( $k_{\text{Ox}}$ ) followed a similar trend X = MeO > Me > H > Cl > CF<sub>3</sub> > NO<sub>2</sub>, except that these values were larger in acetonitrile than in *n*-hexane. The two-parameter Hammett relationship<sup>[3]</sup> was employed to separate contributions from radical and polar substituent effects. A polar effect on oxygen scavenging of carbon-centered radicals in solution was observed for the first time.<sup>[4]</sup>

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## PHOTOCHEMISTRY OF ETHYL-9-FLUORENYLIDENAMINOOXALATE

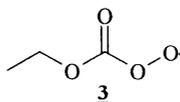
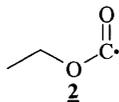
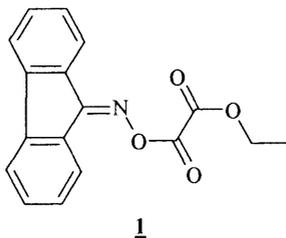
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The photochemistry of Ethyl-9-fluorenylideneaminoxalate **1** was investigated in carbon tetrachloride at room temperature by means of time resolved infrared spectroscopy using the step/scan technique and DFT calculations of the vibrational spectra.

Time resolved infrared spectra of the argon saturated solution of oxalate **1** after 355 nm irradiation (3rd harmonic of a Nd:YAG laser) showed within the rise time of our system (25 ns) the formation of carbon dioxide and a signal at 1770 cm<sup>-1</sup>, disappearing within 7\*10<sup>-6</sup> seconds, which was assigned to the ethoxycarbonyl radical **2**. An oxygen satured solution showed again the immediate formation of carbon dioxide and a blueshifted signal at 1846 cm<sup>-1</sup>, assigned to the ethoxycarbonylperoxyl radical **3**, which disappears within 12\*10<sup>-6</sup> seconds under our experimental conditions.

The vibrational spectra, calculated by the DFT method UBPW91 using the basis-set cc-pVDZ, are in good agreement with the experimental data.



5-FLUORO- AND 5-METHYL-1,3-DIDEHYDROBENZENE –  
A MATRIX ISOLATION STUDY

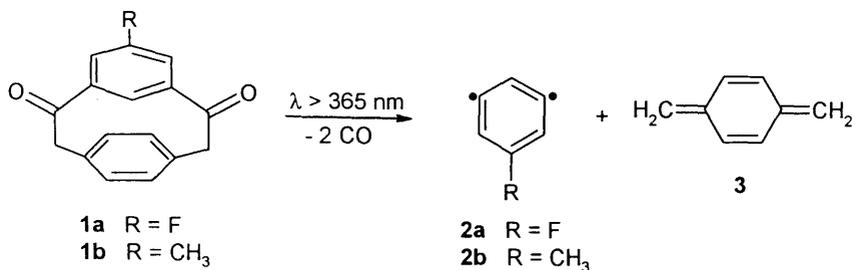
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The UV photolysis of [2.2]metaparacyclophanediketones **1** leads to  $\alpha$ -cleavage and formation of CO, *p*-xylylene **3**, and *m*-benzynes **2a** and **b** with a fluorine or methyl substituent in 5-position, respectively. The IR spectra of **2** were assigned by comparison with that of the parent *m*-benzyne and with spectra calculated at the BLYP/6-311G(d,p) level of theory. Both band positions and intensities of the experimental spectra are in excellent agreement with the DFT calculations. This method thus provides a reliable tool for the investigation of ground state properties of *m*-benzynes. The unsubstituted *m*-benzyne and **2** exhibit a very strong IR absorption at  $545\pm 2\text{ cm}^{-1}$  which is almost not effected by the substituents and therefore can be used to identify *m*-benzynes in product mixtures.



PHOTOCHEMISTRY OF 9,10-DICARBONYL-9,10-DIHYDROANTHRACENE:  
A SOURCE OF 9,10-DEHYDROANTHRACENE ?

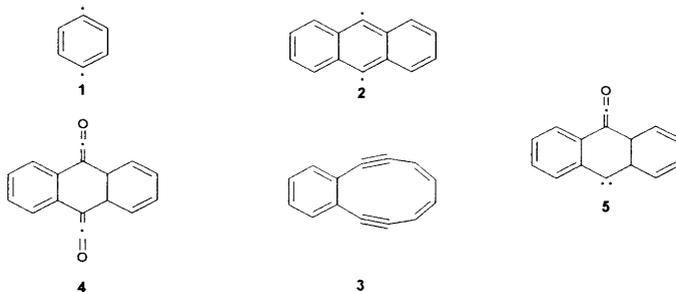
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Dehydrobenzenes are interesting reactive intermediates from an experimental as well as theoretical point of view. Of particular interest are *p*-benzynes **1** and its derivatives, which are key intermediates in cycloaromatization reactions.

In contrast to **1**, which could be observed in cryogenic matrices only recently in our laboratory, the isolation of 9,10-dehydroanthracene **2**, a derivative of **1**, in argon matrices was published by Chapman et al. as early as 1976. Recent laser flash photolysis studies by Chen et al. indicated that the species isolated by Chapman et al. was not dehydroanthracene **2**, but rather the ring-opened cyclic enediyne **3**. Since the photoproducts of **4** were only partially characterized in the original work, a reinvestigation of the photochemistry of 9,10-dicarbonyl-9,10-dihydroanthracene **4** in combination with DFT calculations should provide more detailed information.

9,10-Dicarbonyl-9,10-dihydroanthracene **4** is isolated in an argon matrix at 9 K. Irradiation with  $\lambda = 254$  nm results in a decrease of the IR bands of **4** and formation of CO and ketene-carbene **5** with an intense IR absorption in the ketene region at 2105.8  $\text{cm}^{-1}$ . **5** is labile towards broad band visible light irradiation ( $\lambda = 420\text{--}680$  nm) and decarbonylates to a species with a UV-spectrum similar to that described by Chapman et al. This species is assigned to cyclic enediyne **3** by comparison of calculated and experimental IR spectra. Thus, the isolation of 9,10-dehydroanthracene is still a challenge.



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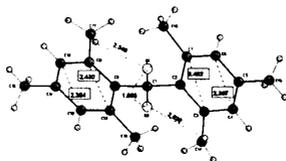
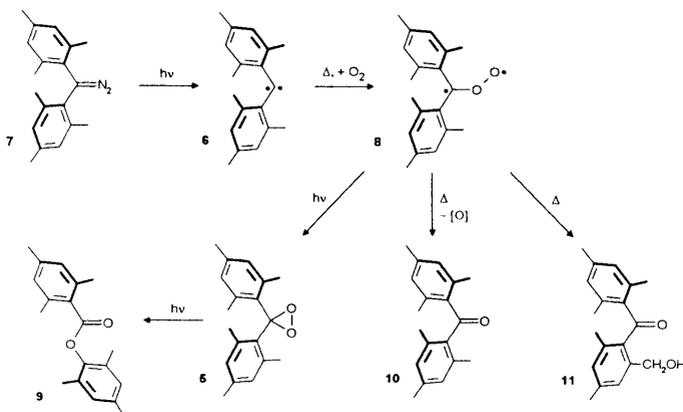
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A general route to carbonyl oxides and dioxiranes is the oxidation of triplet carbenes with molecular oxygen  $^3\text{O}_2$ . Carbonyl oxide **3a** is characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ - NMR spectroscopy and decomposes into two products: dimesitylketone **5a** and 2-hydroxymethyl-2',4,4',6,6'-pentamethyl-benzophenone **6a**. The ratio of products depends on reaction temperature. In freon ( $\text{CCl}_3\text{F}$ ) at room temperature the major product is **6a**, while in acetonitrile and n-hexane the major product at room temperature is **5a**. In freon, acetonitrile and hexane the decomposition follows first order kinetics. Carbonyl oxides rearrange to dioxiranes by photolysis with  $\lambda > 400$  to 475 nm depending on the reaction medium. The x-ray structure analysis of dimesityldioxirane **4a** is presented.

Irradiation of diazo compound **1b** with  $\lambda > 475$  nm in oxygen saturated  $\text{CCl}_3\text{F}$  at 176 K produces a new species with an intense, broad absorption at  $\lambda = 396$  nm which has been assigned to carbonyl oxide **3b**.



**4a**

## CARBENE PHILICITY

*Carsten Kötting and Wolfram Sander\**

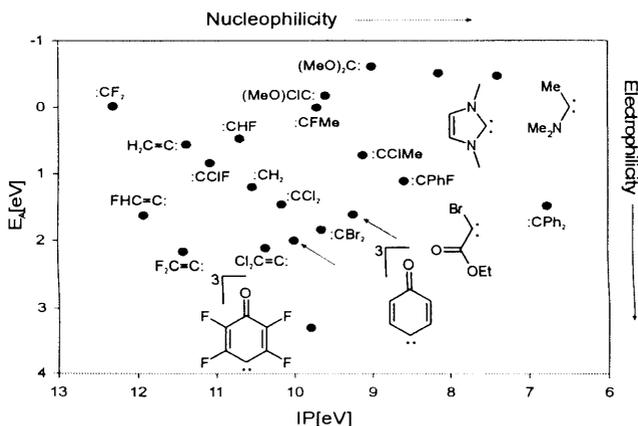
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The reactivity of carbenes mainly depends on the spin state and the philicity. Whereas spin is directly measurable by EPR spectroscopy, the quantification of philicity is less clear. Moss defined a carbene philicity index based on the selectivities of carbene additions to ethylenes.<sup>[1]</sup> However, kinetic data of highly reactive or unstable carbenes are not available. Alternatively, a Hammett equation or FMO theory was used to classify the carbene philicity.

According to FMO theory the reactivity depends on the differences of the HOMO and LUMO energies of the reaction partners. Thus, carbenes with energetically high lying HOMOs should be nucleophilic while those with low lying LUMOs should be preferentially electrophilic. Problems with HOMO and LUMO energies are that these are not directly measurable and the calculated values are highly dependent of the theoretical model used.

We therefore investigated the ionisation potentials IP and electron affinities  $E_A$  as measures for the nucleophilicity and electrophilicity of carbenes, respectively. The IP and  $E_A$  of a variety of carbenes was calculated at the B3LYP/6-311++G(d,p) level of theory and compared to experimental data, if available. From these data we constructed a two-dimensional philicity scheme which describes the nucleophilicity and the electrophilicity as independent entities.

*References:*

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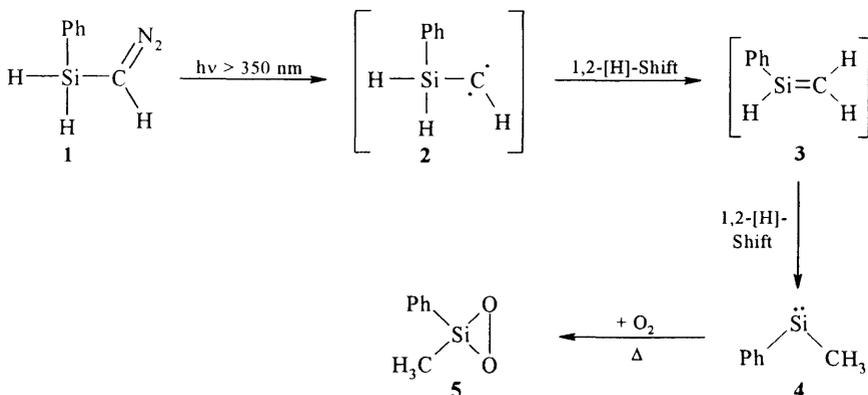
PHOTOCHEMICAL GENERATION AND OXIDATION OF  
METHYLPHENYLSILYLENE IN CRYOGENIC MATRICES

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Silylenes are among the most important basic intermediates in organosilicon chemistry, and therefore research has focused intensely on that class of compounds during the last three decades. Hitherto only a few methods were known to produce them without any byproducts. The short-wavelength irradiation of phenyl(diazomethyl)silane **1** in cryogenic matrices offers an adaptable way to generate the aryl-substituted methylphenylsilylene **4** in good yields. Silylene **4** was characterized by IR and UV/Vis spectroscopy and is probably formed via stepwise 1,2-H-shift of the silylcarbene **2** and the silene **3**, which both cannot be observed under these reaction conditions. The structure of **4** is proved on the one hand by comparison with a DFT-calculated spectrum, on the other hand by the reaction of the reactive intermediate with molecular oxygen.

Although the oxidation of the analogous carbenes is well investigated and is often used for their identification, sparse information about this reaction with respect to silylenes is available. Annealing of an oxygen-doped argon matrix containing methylphenylsilylene **4** leads to the formation of methylphenyldioxasilirane **5** and at least to a further product, which will be identified in the near future.



OPTIMIZATION OF MICELLAR CATALYSIS OF NUCLEOPHILIC SUBSTITUTIONS  
IN BUFFERED SOLUTIONS OF CETYLTRIMETHYLAMMONIUM SALTS

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Optimization of micellar catalysis of nucleophilic substitutions requires to enforce the micellar binding of the hydrophilic anionic nucleophile by exchange with the surfactant counter-ion, in the view of increasing its concentration at the water-micelle interface where it can react with the hydrophobic substrate. These reactions involve generally buffers to control the overall anionic nucleophile concentration. Now, the basic components of the buffers are in most cases organic anions which can also bind the micelles, in competition with the reactive nucleophile. It has, therefore, been suggested that very weakly bound buffers must be used to obtain significant micellar effects.

We present kinetic results on a model reaction, the p-nitrophenyldiphenylphosphate-butanedione monooximate reaction, in aqueous solutions of cetyltrimethylammonium salts, CTAX, with  $X^- = Br^-, Cl^-$  and  $AcO^-$ , in the presence of various buffers, carbonate, borate, glycine, ethanolamine and AMP (2-amino-2-methyl-1,3-propanediol) working in the 9-10 pH range.

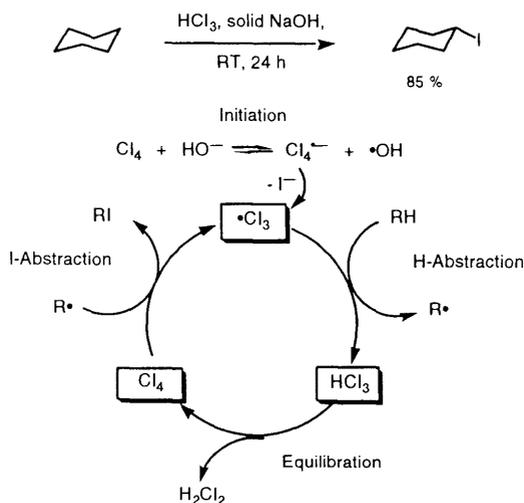
The PIE (pseudophase ion-exchange) model fails for analysing the corresponding rate-[surfactant] profiles in terms of  $k_m$ , the micellar rate constant, and  $K_X^{ox}$ , the counter-ion/oximate exchange constants. Nevertheless, the data can be fairly well interpreted when competitive binding of the three anions involved in the reactive system (surfactant counter-ion, the nucleophile and the buffer base) is considered. The results will be discussed in terms of efficiency of micellar catalysis and its critical dependence on the buffers and the counter-ions.

NO HEAVY METALS, NO ENZYMES, NO FUSS: ALIPHATIC HYDROCARBON  
HALOGENATIONS IN MULTI-PHASE SYSTEMS

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Recently, we reported a phase-transfer catalyzed method to transform even the simplest aliphatic hydrocarbons into their corresponding bromides.<sup>[1]</sup> We meanwhile also succeeded in developing the first efficient iodination of unactivated alkanes.<sup>[2]</sup> As these reactions offer new and general avenues for solving the long-standing problem of C-H-activation of paraffins, the scope and limitation as well as the mechanistic implications of these approaches are presented. Variants of this method may be applied to biomedically relevant compounds, for instance, in radio-iodinations, but are also valuable for the production of otherwise not as easily accessible alkyl iodides which may be useful for the pharmaceutical industry.



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- [2] Schreiner, P. R., Lauenstein, O.; Butova, E. D.; Fokin, A. A. submitted for publication.

## Microemulsion Promoted Mechanistic Changes. Solvolytic of Substituted Benzoyl Chlorides

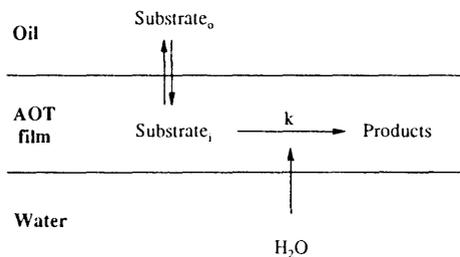
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Microemulsions are stable and transparent mixtures of water, oil, and surfactant, with or without a cosurfactant. Water properties are a function of the molar ratio of water to surfactant, defined as  $W=[H_2O]/[AOT]$  that is also related with the volume of the water droplet. An extension of the pseudophase model to microemulsions easily explain the kinetics of solvolysis of substituted benzoyl chlorides. Bearing in mind the poor solubility of substituted benzoyl chlorides in water it is safe to assume that the amount of these substrates in the water pseudophase is negligible and that the reaction should occur at the interface, where the water and benzoyl chlorides are both present as shown in the following scheme.



The change from a dissociative to an associative reaction path with increasingly electron-withdrawing substituents occurs much later in water than in AOT/isooctane/water microemulsions of  $W=50$ . This is due to the fact that the rate of associative reaction is independent of the leaving group, while the dissociative reaction is strongly dependent on the nature of the leaving group and on its solvation. When  $W$  decreases the associative pathway is favoured and benzoyl chlorides with electron donating substituents follow this mechanism.

## REACTIVITY IN MIXED MICELLES OF CTACI/OCTYLAMINE

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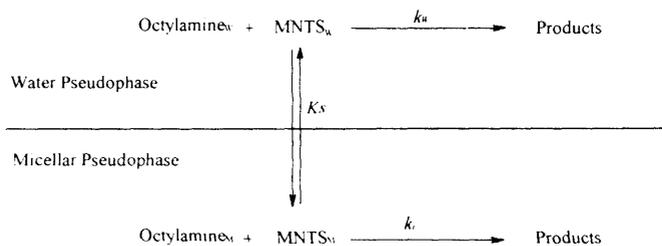
Transnitrosation between N-methyl-N-Nitroso-p-toluenesulfonamide (MNTS) and Octylamine in CTACI/Octylamine mixed micelles has been studied.

The Octylamine is a primary alkylamine, which by its structural characteristics drives to micellar aggregates. The mixtures of Octylamine (OA) and a cationic surfactant as CTACI (cetyl trimethyl ammonium chloride) are mixed micellar systems stable in the whole range of molar fractions.

Preliminary studies of transnitrosation between MNTS and OA under its critic micellar concentration, thus obtaining the reactivity constant in water ( $k_w$ ) were carried out.

A kinetic study for the several mixtures of CTACI/Octylamine ( $X_{OA}=0-1$ ). The simultaneous role of OA as reactant and surfactant must be underlined. In all the range of mixed system compositions a catalytic effect was observed. This behaviour is due to the concentration of both reactants in the small volume of the micelle.

The kinetic behaviour has been explained on the basis of the micellar pseudophase model. The binding constants of MNTS ( $K_S$ ) and the reactivity constants in the micellar pseudophase ( $k_i$ ) have been obtained.

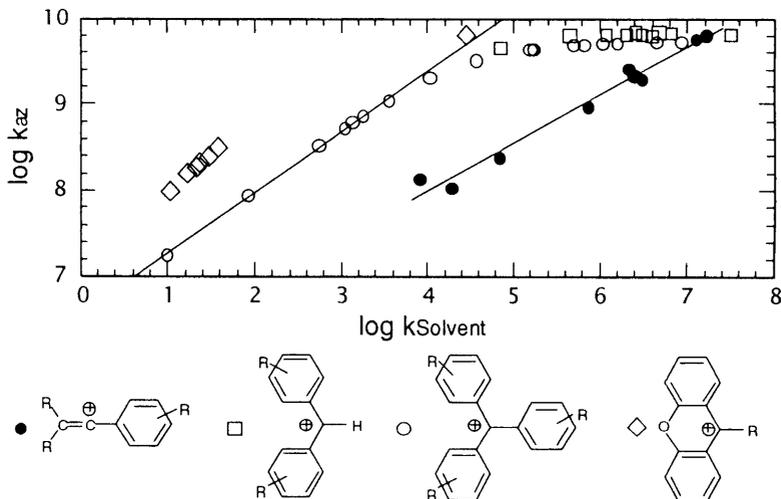


# STERIC EFFECT OF DIFFUSION LIMITED REACTIONS STUDIED BY LASER FLASH PHOTOLYSIS

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Laser flash photolysis is a new tool to investigate reactive intermediates under reaction conditions. It provide the rate constants of nucleophiles to unstable carbocations. McClelland et al studied on nucleophilic attack of azide ion and solvent to various di- and tri-aryl substituted carbocations in the 1:2 mixture (v/v) of acetonitrile and water as shown in the below figure.<sup>[1]</sup> The reactivity difference comes from the electronic effect of the substituents. We found a steric effect of the  $\beta$ -substituents of vinyl cations to a nucleophile.<sup>[2]</sup> Our recent work on vinyl cations provides another group in the figure as show as closed circles. The vinyl cations have a fixed p-methoxyphenyl group on the  $\alpha$ -position and various substituents on the  $\beta$ -positions. There is no large difference in the stability among the vinyl cations, but large steric effect on the nucleophilic attack to them. There seems to be large difference of nucleophilic attack between an anion, azide ion, and neutral molecule like solvent.



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REACTIONS OF N-CENTERED RADICALS DERIVED FROM  $\alpha$ -AMINO ACIDS; A  
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Time resolved methods (pulse radiolysis and laser flash photolysis) were used to investigate reactions of aliphatic  $\alpha$ -amino acids in anionic form with hydroxyl radicals ( $^{\bullet}\text{OH}$ ) and 4-carboxybenzophenone triplet ( $\text{CB}^*$ ) in aqueous solutions.

Besides H-atom abstraction from  $\alpha$ -C and/or side-chain C-H bonds,  $^{\bullet}\text{OH}$  radicals also readily undergo a one-electron transfer reaction from the free electron pair on nitrogen. The resulting aminium radicals,  $\text{H}_2\text{N}^{\bullet+}\text{-CR}_2\text{-CO}_2^-$  (R = H, alkyl), decarboxylate and transfer a proton to  $\text{OH}^-$ , which is still located within the solvent cage, at a ratio of ca 1:2. As products, strongly reducing  $\alpha$ -aminoalkyl and oxidizing aminyl radicals are respectively formed. The aminyl radicals further degrade via  $\beta$ -scission, yielding  $\text{CO}_2^{\bullet-}$  as another reducing species. In the presence of proton donors, they can also be re-protonated into the fast decarboxylating aminium radical, or may abstract H-atoms from, e.g.,  $\text{C}_{\alpha}\text{-H}$  bonds in the amino acid anions.

The quenching of  $\text{CB}^*$  by amino acid anions proceeds via the one-electron transfer mechanism, resulting in the formation of aminium radicals as the main initial product. Within the solvent cage, with  $\text{CB}^{\bullet-}$  as the counter ion, this radical either decarboxylates or deprotonates at a ratio of ca 9:1. Deprotonation into aminyl radicals by the  $\text{OH}^-$  ions in the bulk starts to be competitive at  $[\text{OH}^-] \geq 1$  M. This reaction enabled the determination of a rate constant of  $(1.0 \pm 0.3) \times 10^{11} \text{ s}^{-1}$  for the actual aminium radical decarboxylation process.

Specific scavenger methods were used to experimentally determine yields and rate constants of individual radical products from glycine, alanine and 2-aminoisobutyric acid.

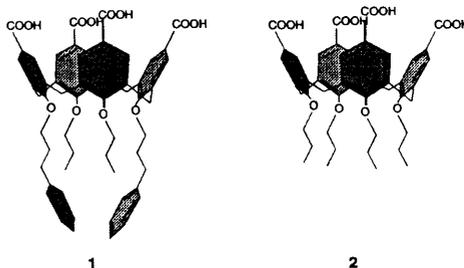


## BUILDING SUPRAMOLECULAR ASSEMBLIES OF CALIX[4]ARENE-BASED SURFACTANTS AND CYCLODEXTRINS

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Calix[4]arenes are known for their capabilities to act as host molecules in supramolecular chemistry. Especially calix[4]arenes occupying the cone conformation, which actually encompass a cavity, are able to accommodate guest molecules. In contrast, we envisaged that interesting



supramolecular systems would arise from using calix[4]arenes as *guest* molecules for binding into cyclodextrins. Moreover, the synthetic versatility of calix[4]arenes allows them to act as platforms on which several functionalities or guests for CDs can be combined. In order to quantitatively study the non-covalent interactions between calix[4]arenes and  $\gamma$ -cyclodextrin, water soluble calix[4]arene **1** was synthesized. The calix[4]arene lower rim is functionalized with two pendant phenyl groups, which act as a binding site for  $\gamma$ -cyclodextrin; this particular cyclodextrin is known for the ability to complex *two* aromatic rings strongly. Water soluble calix[4]arene **2**, which lacks a distinct binding site for  $\gamma$ -cyclodextrin, was synthesized as a reference compound for investigation of the influence of the aromatic groups.

The aggregation behavior of the calix[4]arene-based surfactants **1** and **2** in water was studied by UV spectroscopy and titration microcalorimetry. Critical micelle concentrations (CMCs) were determined. The experiments reveal that the increase in hydrophobicity caused by the pendant phenyl groups in the case of **1**, lowers the CMC of the surfactant significantly. The binding of **1** in  $\gamma$ -cyclodextrin was studied by NMR and titration microcalorimetry. A high complex stability was observed. Furthermore, the binding stoichiometry was determined to be 1:1 using a Job's plot analysis. The binding of **1** in  $\gamma$ -cyclodextrin is enthalpy-driven which, together with the confirmed 1:1 binding stoichiometry, suggests that indeed both phenyl rings are included in the  $\gamma$ -cyclodextrin cavity.

STRUCTURE, MOLECULAR DYNAMICS AND HOST–GUEST INTERACTIONS OF A  
WATER–SOLUBLE CALIX[4]ARENE

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By measurement of  $^2\text{H}$ ,  $^{13}\text{C}$  and  $^{14}\text{N}$  relaxation data the reorientational molecular dynamics for the following water–soluble calixarenes and host–guest systems were evaluated:

- calix[4]arene-p-sulfonic acid (**1**) and its pentasodium salt (**2**),<sup>[1]</sup>
- calixarenes **1** and **2** as hosts, tetramethyl-, trimethylphenyl- and trimethyladamantanyl-ammonium cations as guests in the corresponding host–guest systems.<sup>[2]</sup>

For the pure host systems the  $^{13}\text{C}$  spin–lattice relaxation times and nuclear Overhauser enhancements were measured in acidic and neutral aqueous (**1** and **2**) as well as methanolic (**1**) solutions. Furthermore, the  $^2\text{H}$  spin–lattice relaxation times of bulk  $^2\text{H}_2\text{O}$  were measured. From the temperature dependence the activation parameters for the reorientational motion were evaluated. The same data were obtained for the host–guest systems. Additionally,  $^{14}\text{N}$  relaxation data were determined for the guest molecules.

The reorientational molecular dynamics were compared for the different systems, and the influence of host–guest interactions on the molecular dynamics and thus the relaxation data was studied. While the effect of the host–guest interactions on the host dynamics was not very large, it was considerable for the guests. A proposal for the structure of the host–guest complexes in solution was made on the basis of the relaxation data.

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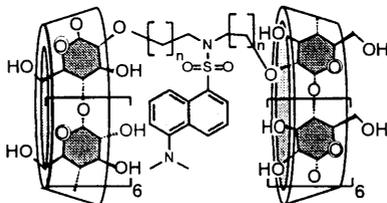
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FLUORESCENT WATER-SOLUBLE  $\beta$ -CYCLODEXTRIN-DIMERS AS SENSOR MOLECULES FOR THE DETECTION OF NEUTRAL ANALYTES*Menno R. de Jong, Jurriaan Huskens, and David N. Reinhoudt*Laboratory of Supramolecular Chemistry and Technology, MESA<sup>+</sup> Research Institute,  
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The complexation ability of cyclodextrins for organic species in aqueous solutions can be used for the development of fast responding, on-line sensing techniques for organic analytes in water. In the past, fluorescent cyclodextrins were prepared by appending a fluorophore to give fluorescent sensing molecules. Competition for the hydrophobic cavity between an analyte and the covalently linked fluorophore results in a change in the optical properties of the latter which is dependent on the concentration of the species to be detected. However, little attention has been paid to the alteration of the naturally given selectivity of cyclodextrins for complex formation with organic species.

The aim of this work is to improve the selectivity of cyclodextrin based sensing systems by changing the complexation properties. Earlier studies have shown that extending the cyclodextrin cavity leads to dramatically improved binding capabilities for large guests.<sup>[1]</sup>



In order to obtain a sensing molecule, we connected two cyclodextrin units via fluorophore containing spacers of varying lengths ( $n=1,2$ ). In aqueous solution, these molecules respond to the presence of steroids with an increase or decrease of the fluorescence intensity, depending upon the substitution pattern of the steroid. More remarkably, stabilities of the steroid complexes differ greatly for strongly resembling steroids. These differences in stabilities and the opposite fluorescence responses are studied by fluorescence lifetime measurements and isothermal titration calorimetry. In the presence of smaller organic analytes the fluorescence response was found to be less pronounced. As such, the selectivities of these novel fluorescent cyclodextrin dimers differ markedly from that of native  $\beta$ -cyclodextrin.

*References:*

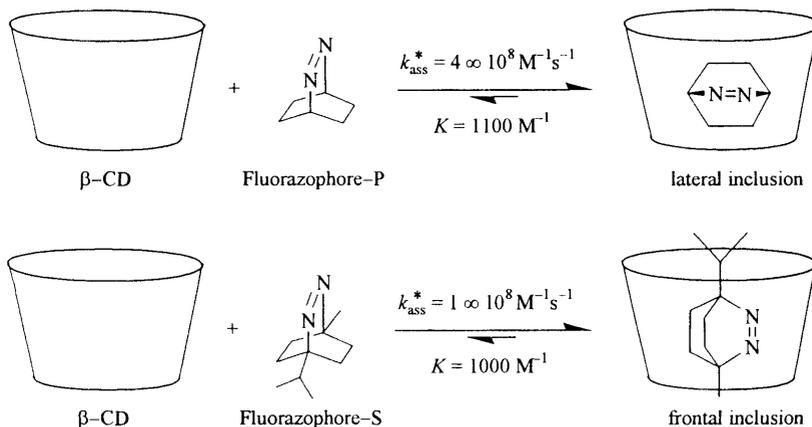
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A NOVEL STRUCTURAL AND DYNAMIC PROBE FOR THE INVESTIGATION OF  
SUPRAMOLECULAR ASSEMBLIES: AN EXPLORATORY STUDY OF CYCLODEXTRINS  
BY NMR, FLUORESCENCE, UV-ABSORPTION, AND INDUCED CIRCULAR  
DICHROISM

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The azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene and its derivatives have been introduced as the first fluorescent probes for monitoring antioxidant activity<sup>[1]</sup> and supramolecular kinetics.<sup>[2]</sup> When used as fluorescent probes, we refer to these compounds as fluorazophores.<sup>[3]</sup> In the present study, we have employed the parent compound, Fluorazophore-P, and compared the structural and kinetic data of its host-guest cyclodextrin complexes with those for the sterically elaborated, more selective derivative Fluorazophore-S.



NMR studies (ROESY, CIS), time-resolved and steady-state fluorescence spectroscopy, UV-absorption spectrophotometry, and induced circular dichroism were employed to determine the kinetics of inclusion (in the excited state), binding constants, and structural parameters, namely the depth of penetration of the guests into the cavity and their relative conformation.

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## ORGANIC PROCESSES INITIATED BY NONCLASSICAL ENERGY SOURCES

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Nonclassical energy sources such as microwave energy, ultrasound and triboenergy as well as their combination with UV/VIS-radiation are new tools in synthetic chemistry and chemical processing. Microwave heating has been used for a wide variety of purposes such as moisture analysis, acid decomposition of biological samples, dissolution of geological materials, rapid hydrolysis of peptides and proteins. Recently the use of microwave radiation has attracted the attention of organic chemists for use in synthesis and processing. Remarkable decrease in the time necessary to carry out reactions and in some cases cleaner reaction with easier work-up compared to conventional methods have been observed with microwave heating.<sup>[1,2]</sup>

In our lecture we describe the application of microwave treatment for selected organic reactions such as (i) enzymatic transesterification of optical active alcohols, (ii) mercury-sensitized gas phase photolysis of hydrocarbons in the microwave field and (iii) environmentally benign oxidations of olefins. The efficiency of enzyme-catalyzed organic synthesis has been observed to increase under the effect of microwave irradiation.<sup>[14]</sup> It's a matter of interest to determine the conditions allowing to optimize enzyme activity and enantioselectivity. Our work will concentrate on substrates derived from renewable raw materials. The use of immobilized enzymes offers the advantageous possibility to work in quasi solvent-free systems. The catalyst can easily be separated from the reaction mixture and reused. However, it is necessary to examine the limits of catalyst recycling. The mercury-photosensitized reaction is known as a method to synthesize a wide variety of organic molecules with inexpensive and readily available starting materials by dehydrodimerization or cross-dehydrodimerization. In the present study we have tried to combine these synthetically useful method with electrodeless lamps, which irradiate a wide band UV – radiation initiated by a microwave field. For these MW – MWUV combination process we have developed reactors, and we analyzed the influence of several chemical and physical parameters. As an example the dehydrodimerization of cyclohexane was optimized and the mechanism determined. The oxidation of olefines to technical relevant products such as the oxidation of cyclohexene to adipic acid or of oleic acid to the corresponded 9,10-epoxide with an environmentally benign oxidation system<sup>[3]</sup> is described as the third example. In this oxidation hydrogen peroxide is used as oxidant and no organic solvent is necessary.

All discussed reactions with the non-classical energy source are faster, the yields are high and the energy consumption is lower compared to the conventional reactions.

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## The Novel Chromophore Crown Ethers and Cationic Recognition with Optical Spectroscopy and MM+ Calculations.

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The supramolecular role of ionophore macrocycles have become well known and quite practical for molecular and ionic recognition [1,2]. We have so far synthesized the chromophore derivatives of [12]crown-4, [15]crown-5, [18]crown-6 and [21]crown-7 bearing coumarin, anthraquinone and xanthone groups [3,4]. Macrocycles identified by high resolution EI-mass  $^1\text{H}$ ,  $^{13}\text{C}$  and 2D NMR spectroscopy were studied for the molecular recognition of  $\text{Zn}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  ions with steady state fluorescence spectroscopy as well as UV-VIS spectroscopy in acetonitrile. The observed complexing enhanced quenching fluorescence spectra, (CEQFS) as well as the complexing enhanced fluorescence spectra, (CEFS) of the chromophore macrocycles without isoemissive peaks exhibited the cationic behaviors [5-8]. The such results were recently initiated to be proved with molecular mechanical molecular dynamic methods with MM+ using the commercial software Hyperchem®. The conformations and strain energy of free and complexed macrocycle backbones examined with MM+ mostly in agreement with the supramolecular behavior of the macrocycles [9,10].

*Acknowledgment ;* TUBITAK is greatly acknowledged by the author due to its kind support of our serial work in this topic.

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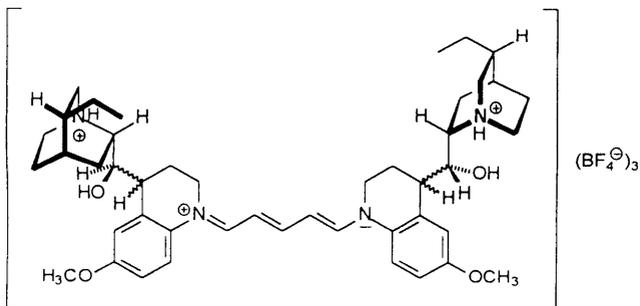
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**Chiral Polymethine Dyes**  
**Remarkable but Forgotten Conjugated  $\pi$ -Systems**

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Amongst compounds with conjugated  $\pi$ -systems such as aromatics and polyenes, polymethines constitute a third independent type of  $\pi$ -systems. Whereas chiral aromatics (e.g. helicenes) and chiral polyenes (e.g. carotinoids) are well known, chiral polymethines have been investigated only scarcely up to now.<sup>[1]</sup> This is in spite of the fact, that König reported on the first synthesis of chiral polymethine dyes already in 1928.<sup>[2]</sup>

Chiral polymethine dyes should exhibit particular new chiroptical properties, useful for their application as so-called functional dyes. For this reason, we have repeated and improved the preliminary work of König as well as synthesized a variety of new chiral polymethine cyanine dyes with heterocyclic end groups containing stereogenic centres.<sup>[3]</sup> For example, using naturally occurring Cinchona alkaloids such as (-)-quinine and (+)-quinidine as source of stereogenic centres with known absolute configuration, we have prepared for the first time pentamethine streptocyanine dyes with 1,2,3,4-tetrahydroquinoline end groups such as:



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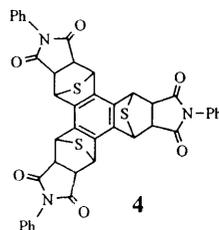
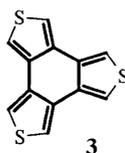
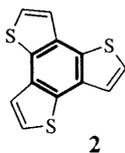
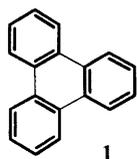
SYNTHESIS, ELECTRONIC STRUCTURES AND CYCLOADDITIONS  
OF POLYCYCLIC HETARENES

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We have synthesized several polycyclic heteroaromatic compounds and studied their geometrical and electronic structures by X-ray crystal analysis,<sup>[1]</sup> UV photoelectron spectroscopy and quantum chemical calculations. The reactivity and stereochemistry of some compounds in Diels Alder reactions was investigated at high pressures. In tetracyclic compounds that are  $\pi$ -isoelectronic with triphenylene (**1**), [b]- or [c]-annellation of thiophene modifies the structure of the central benzene ring. **1** can be characterized as comprising three peripheral benzene rings connected by C-C single bonds.<sup>[2,3]</sup> The central ring is cyclohexa-1,3,5-triene-like. Alternation of the bond lengths in the central ring of **2** is rather small with C-C distances only little longer than in benzene. The central ring can thus be termed aromatic. **3** has a [6]radialene-like structure<sup>[4]</sup> in which the central six-membered ring is non-aromatic, and its six exocyclic C-C bonds have high double bond character. Extensive analysis of the PE spectra was accomplished by which all  $\pi$  and n(S) ionizations were identified.



c-Annellated thiophene rings such as in **3** show sufficient reactivity in cycloaddition reactions to afford tripod-shaped molecules like **4** which might be of interest in supramolecular chemistry. Based on the electronic structures of the hetarene, predictions regarding reactivity and reaction site are possible.

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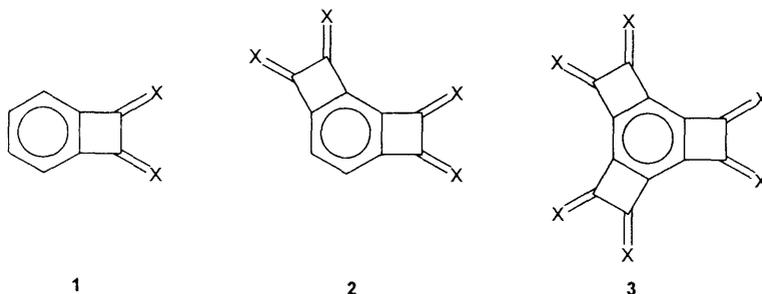
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SIBL IN STRAINED AROMATIC MOLECULES WITH EXTENDED  $\pi$  SYSTEMS.*Amnon Stanger*

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Strain Induced Bond Localization (SIBL) is a phenomenon that was introduced almost seventy years ago by Mills and Nixon, and is still intriguing today. There is no consensus about the role of strain and aromaticity – antiaromaticity factors in localizing aromatic system, and the reopening of the question of the nature of aromaticity by Shaik et. al. some fifteen years ago resubstantiate the SIBL issue as a probe for the study the importance of  $\sigma$  and  $\pi$  frameworks in aromatic systems.



X=BH, CH<sub>2</sub>, NH, O

In the last few years we have been engaged with the investigation of SIBL. Our theoretical and experimental findings suggest that strain can be manifested in either curved bond formation or in bond localization, and that  $\pi$  effects are relatively unimportant in SIBL. Others also verified these conclusions experimentally. Here we present some results concerning the systems 1-3, where the strained benzylic atoms are formally  $sp^2$  hybridized. Apparently, the localization found in these systems is small, and a rationalization will be presented.

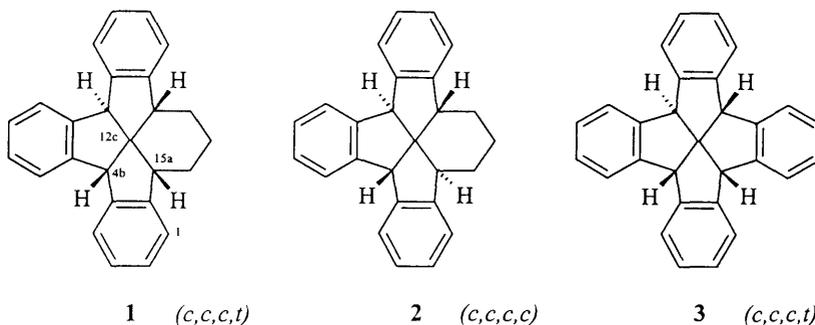
## Strained benzoannulated *cis,cis,cis,trans*-[5.5.5.6]Fenestranes: Synthesis and Properties

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The carbon frameworks of [m.n.o.p]fenestranes are not only defined by the characteristic mutual annellation of four rings in a “tetrafuso” manner but also, albeit less obvious, by the relative configuration of the four peripheral bridgehead positions.<sup>[1,2]</sup> As far as strained stereoisomers of the most stable all-*cis*-fenestranes are concerned, several small ring *cis,cis,cis*, *cis,cis,trans* isomers are known<sup>[1]</sup> within the [4.5.5.5]fenestrane series and only recently a complex derivative of *cis,cis,cis,trans*-[5.5.5.5]fenestrane has been reported.<sup>[3]</sup> However, extensive computational work has been published<sup>[1,2]</sup> demonstrating that the well-known strain of the *trans*-bicyclo[3.3.0]octane (*trans*-diquinane) unit is considerably enhanced by merging it with two additional rings in a *cis,cis,cis,trans*-[5.5.5.5]fenestrane skeleton. The calculations also point to a considerable increase of the non-bridged C-C-C-bond angles at the central bridgehead. Therefore, fenestranes bearing at least one *trans* fusion at the neopentane core are of considerable interest in the context of the planar-tetracoordinate-carbon problem.<sup>[4]</sup>



Here we report on the first directed synthesis as well as on the structure and reactivity of benzoannulated *cis,cis,cis,trans*-[5.5.5.6]fenestranes such as **1**,<sup>[5]</sup> which, according to semi-empirical calculations, are by ca. 10 kcal mol<sup>-1</sup> more strained than the respective all-*cis* isomers, e.g. **2**.<sup>[2]</sup> The extra strain of **1** gives rise to a strongly enhanced acidity of its “inverted” bridgehead C-H bond. This findings shed some light on the challenge to eventually synthesize the hypothetical *cis,cis,cis,trans*-tetrabenzo[5.5.5.5]fenestrane (“*epi*-fenestrindane”) **3**, which is predicted to be more highly strained by ca. 35 kcal mol<sup>-1</sup> as compared to all-*cis*-fenestrindane.<sup>[2]</sup>

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# Poster Presentations

DETERMINATION OF THE RATES OF FORMATION AND HYDROLYSIS  
OF THE SCHIFF BASES FORMED BY PYRIDOXAL 5'-PHOSPHATE  
WITH L-TRYPTOPHAN AND ITS METHYL ESTER.

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Pyridoxal 5'-phosphate (PLP) is one of the different forms of vitamin B<sub>6</sub> and plays an important role as the coenzyme of a wide range of different reactions such as transaminations, deaminations, decarboxylations and others.<sup>[1]</sup> Its action is by forming a carbinolamine intermediate by bonding its carbonyl group to the ε-amino group of L-lysine residue of the polypeptide chain.<sup>[2]</sup> The carbinolamine loses a molecule of water to yield the Schiff base in an acid catalysed process. The first step of all the PLP-dependent enzymes is a transamination reaction, namely, the conversion of the PLP-lysine imine to the substrate-PLP imine.

The interaction of PLP with L-tryptophan is essential for D-amino acid transferase (Trp 139) to exert an optimal catalytic function and also for aspartate amino transferase in the same respect (Trp 140).<sup>[3]</sup>

In this work, the stability and kinetics of formation and hydrolysis of the Schiff bases of pyridoxal 5'-phosphate with L-tryptophan (TRP) and L-tryptophan methyl ester (MTRP) were determined spectrophotometrically at various pH values, a temperature of 25°C and ionic strength of 0.1M, and the results were compared with those previously obtained for other amino group bearers.

Evidence on the formation of cyclic compounds by the Schiff bases formed in both cases (TRP and MTRP with PLP) in acidic media was found by different techniques.

*We thank "Fondo Nacional de Desarrollo Científico y Tecnológico"  
(FONDECYT) for financial support.*

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KINETIC STUDY OF THE SCHIFF-BASE FORMATION BETWEEN PYRIDOXAL 5'-  
PHOSPHATE AND GABA. INFLUENCE OF TEMPERATURE.

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Pyridoxal 5'-phosphate (PLP) is one of the different forms of vitamin B-6 and plays an important role as coenzyme of a wide range of different reactions as transaminations, decarboxylations, deaminations and others.<sup>[1]</sup> In PLP-dependent enzymes, coenzyme (PLP) is bound to protein through a Schiff-base linkage with the  $\epsilon$ -amine group of a lysine (internal Schiff base) or is bound to  $\alpha$ -amino group of amino acid substrate (external Schiff base). The first step of most the PLP-dependent enzymes is a transamination reaction, namely, the conversion of the internal Schiff base to the external Schiff base.  $\gamma$ -Aminobutyric acid (GABA) aminotransferase (EC 2.6.1.19, GABA-T) is a PLP-dependent enzyme that catalyses the conversion of the inhibitory neurotransmitter GABA and  $\alpha$ -ketoglutarate to succinic semialdehyde and the excitatory neurotransmitter L-glutamic acid.<sup>[2]</sup> Since GABA is the product of metabolism of L-glutamic acid, a reaction catalysed by the PLP-dependent enzyme L-glutamic acid decarboxylase, it is apparent that GABA aminotransferase is important in the regulation of brain neurotransmission of the mammalian.<sup>[2]</sup>

In this work, we report the stability and kinetics of formation and hydrolysis of the Schiff bases of PLP and GABA at different pH values and temperatures (20, 25 and 30°C), and constant ionic strength 0.1 M. The results obtained were compared with those found for Schiff bases of PLP and n-hexylamine,<sup>[3]</sup> and PLP and L-glycine.<sup>[4]</sup>

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METAL ION PROMOTED HYDROLYSIS OF RNA: GENERAL ACID CATALYSIS BY  
 $Zn^{2+}$  AQUO ION ON THE DEPARTURE OF THE LEAVING GROUP

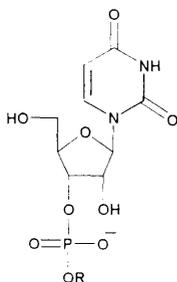
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University of Turku, Department of Chemistry, FIN-20014 Turku, Finland

Metal ion promoted cleavage of RNA and RNA model compounds has been extensively studied over the last two decades. It is hoped that detailed mechanistic understanding would enable a rational design of artificial RNA cleaving agents utilising metal ion chelates as their catalytically active function.

It is generally believed that metal ions enhance the cleavage of phosphodiester bonds of RNA by assisting the nucleophilic attack of the adjacent 2'-hydroxy function onto the phosphorus. Less attention has been paid to a possible catalysis on the departure of a leaving group, which, most probably, is the rate-limiting step of an uncatalysed reaction. The present work addresses this question by studying the  $Zn^{2+}$  promoted cleavage of series of uridine 3'-alkylphosphates (**1a-e**).

A  $\beta_{lg}$  value of the  $Zn^{2+}$  promoted cleavage of **1a-e** was determined, and the value obtained (-0.32) was compared to those reported previously for the cleavage promoted by hydronium and hydroxide ions,<sup>[1]</sup> and of the cleavage in buffer solutions.<sup>[2]</sup> The comparison suggests that in the presence of metal ions, the leaving group departs as an alcohol, and that the metal ion enhances its protonation. The results of comparative measurements with uridine 3'-arylphosphates (**2a-e**) support the conclusions. The present results suggest, hence, that in addition to enhancing the nucleophilic attack, metal ion assist also the departure of the leaving group.



**1a:** R=CH(CH<sub>3</sub>)<sub>2</sub>  
**1b:** R=CH<sub>2</sub>CH<sub>3</sub>  
**1c:** R=CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>  
**1d:** R=CH<sub>2</sub>CHCl<sub>2</sub>  
**1e:** R=CH<sub>2</sub>CCl<sub>3</sub>

**2a:** R=Phenyl  
**2b:** R=2-Chlorophenyl  
**2c:** R=4-Chlorophenyl  
**2d:** R=2,5-Dichlorophenyl  
**2e:** R=4-Nitrophenyl

*References:*

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## Condensation Reactions of Formaldehyde and Amines with and without the Presence of Sulfite

*Kathryn H. Brown<sup>#</sup>, Michael R. Crampton<sup>#</sup> and John H. Atherton<sup>§</sup>*

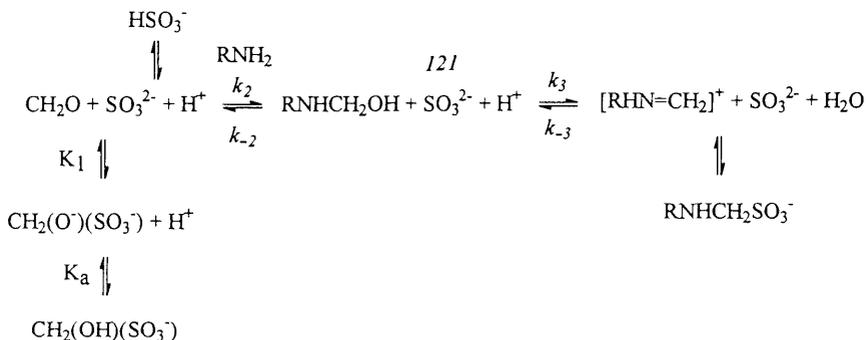
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Kinetics of the reaction of formaldehyde with aniline and seven aniline derivatives to give *N*-hydroxymethylamines, RNHCH<sub>2</sub>OH, have been investigated. Under certain conditions the reaction of amines with formaldehyde produces imines which are unstable and spontaneously polymerise. The formation of imine trimers and dimers and their stability in solution has been investigated for the reaction with aniline and its derivatives.

The presence of sulfite in the system has been examined by reacting amines with sodium hydroxymethanesulfonate, CH<sub>2</sub>(OH)(SO<sub>3</sub>Na). Here there is evidence for the processes shown in the scheme below. Individual steps, including the dissociation of hydroxymethanesulfonate, have been examined kinetically. Studies have utilised aniline and benzylamine and their derivatives. The nature of the rate determining step is thought to be pH dependent: at high pH it involves dehydration of the carbinolamine, *k*<sub>3</sub>, while at lower pH the reaction of formaldehyde and amine, *k*<sub>2</sub>, becomes rate limiting.



## KINETICS AND MECHANISM OF THE AMINOLYSIS OF O-PHENYL 4-NITROPHENYL DITHIOCARBONATE IN AQUEOUS ETHANOL

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The reactions of the title substrate (**1**) with a series of secondary alicyclic amines are subjected to a kinetic investigation in 44 % ethanol-water, at 25.0 °C, ionic strength 0.2 (KCl). Under amine excess over the substrate, pseudo-first-order rate coefficients ( $k_{obs}$ ) are obtained. Plots of  $k_{obs}$  against  $[NH]$ , where NH is the free amine, are nonlinear upwards, except the reactions of piperidine, which show linear plots. According to the kinetic results and the analysis of products a reaction scheme is proposed with two tetrahedral intermediates, one zwitterionic ( $T_{\pm}$ ) and another anionic ( $T^{-}$ ), with a kinetically significant proton transfer from  $T_{\pm}$  to an amine to yield  $T^{-}$  ( $k_3$  step). By nonlinear least squares fitting of an equation derived from the scheme to the experimental points, the rate microcoefficients involved in the reactions are determined. Comparison of the kinetics of the title reactions with the linear  $k_{obs}$  vs.  $[NH]$  plots found in the same aminolysis of O-ethyl 4-Nitrophenyl dithiocarbonate (**2**) in the same solvent shows that the rate coefficient for leaving group expulsion from  $T_{\pm}$  ( $k_2$ ) is larger for **2** due to stronger push by EtO than PhO. The  $k_3$  value is the same for both reactions since both proton transfers are diffusion controlled. Comparison of the title reactions with the same aminolysis of phenyl 4-nitrophenyl thionocarbonate (**3**) in the water indicates that (i) the  $k_2$  value is larger for the aminolysis of **1** due to the less basic nucleofuge involved and the small solvent effect on  $k_2$ , (ii) the  $k_3$  value is smaller for the reactions of **1** due to the more viscous solvent, (iii) the rate coefficient for amine expulsion from  $T_{\pm}$  ( $k_{-1}$ ) is larger for the aminolysis of **1** than that of **3** due to a solvent effect, and (iv) the value of the rate coefficient for amine attack ( $k_1$ ) is smaller for the aminolysis of **1** in aqueous ethanol, which can be explained by a predominant solvent effect relative to the electron-withdrawing effect from the nucleofuge.

KINETICS AND MECHANISM OF THE PHENOLYSIS AND THIOLYSIS OF  
O-ETHYL S-(2,4-DINITROPHENYL) THIOL AND DITHIOCARBONATES.

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The reactions of O-ethyl S-(2,4-dinitrophenyl) thiolcarbonate (EDNPTC) and the corresponding dithiocarbonate (EDNPDTC) with a series of benzenethiolates and the reactions of the latter substrate with a series of phenols, are subjected to a kinetic study in water at 25°C, ionic strength 0.2 M (KCl).

The kinetic law obtained for all the measured reactions is first order in the nucleophile. The results of the reactions of these title substrates are compared among them, and with those of the phenolysis of EDNPTC.<sup>[1]</sup>

The nucleophilic rate constants ( $k_N$ ) for the thiolysis of EDNPDTC are greater than those of EDNPTC, according to Pearson's hard and soft acids and bases; nevertheless the  $k_N$  values obtained for the phenolysis of EDNPDTC are closely similar to those for EDNPTC,<sup>[1]</sup> suggesting that the steric effect of the nitro group in position 2 is more important than the effect of the electrophile.

The Bronsted-type plots obtained for the reactions are linear with slopes in the pK<sub>a</sub> range 0.6-0.9, suggesting concerted mechanisms for these reactions.

*We thank "Fondo Nacional de Desarrollo Científico y Tecnológico" (FONDECYT) for financial support.*

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## REACTIVITY OF THIOBENZOYL CARBAMATES

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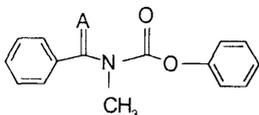
<sup>2</sup>CECF, Faculdade de Farmácia, Avenida das Forças Armadas, 1699, Lisboa, Portugal.

<sup>3</sup>Dpto. de Química e Bioquímica/CECUL, Faculdade de Ciências, Universidade de Lisboa 1749-016, Portugal.

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Carbamates as well as their association with other moieties are known to have wide applications in medicinal and agrochemical fields and in the last few years our group has been interested in the development of new difunctional carbamates such as secondary and tertiary aroyl carbamates. For all the tertiary substrates (1) we have proposed a BAc2 type hydrolysis with general-base catalysis<sup>[1]</sup>.

Now we turned our attention to a new difunctional association involving thiobenzoyl instead of benzoyl together with the carbamate function (2). The first step of the synthesis was accomplished by obtention of thiobenzamide by treatment of N-methyl benzamide with Lawesson reagent<sup>[2]</sup>. Thiobenzamide was then made to react with NaH and phenyl chloroformate in dry DMF under nitrogen.



(1) A=O

(2) A=S

Once the new carbamate was obtained, its conversion to thiobenzamide and phenol was followed by UV spectroscopy. Reactivity was studied in several aqueous media including sodium hydroxide, and deuteroxide as well as non-hindered and hindered nitrogen and trifluoroethanol as an oxygen base.

The kinetic parameters under study will allow us to propose the sort of catalysis involved in the BAc2 type of hydrolysis of (2).

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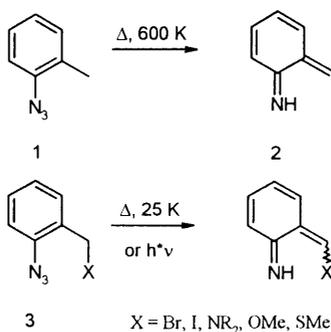
BENZYLIC SUBSTITUENTS INDUCE A 1,4-H-SHIFT IN *ORTHO*-TOLYLNITRENE:  
A MATRIX ISOLATION AND LASER FLASH PHOTOLYSIS STUDY

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The use of aryl nitrenes in organic synthesis has been hampered by their pronounced tendency to undergo ring expansion and by their reluctance to react in an intermolecular fashion. An alternative approach to make use of them could involve the use of a possible 1,4-H-shift in *ortho*-tolyl nitrene **1**, as *o*-iminoquinone methide **2** would represent a valuable reaction intermediate to be trapped in Diels-Alder reactions. Unfortunately, **1** does not undergo this 1,4-H-shift under ordinary conditions; flash vacuum pyrolysis is required. The work to be presented here has shown that certain substituents in benzylic position may induce such a 1,4-H-shift. In Ar-matrix, the reaction is a photochemical one if X = Br, OMe, SMe, and it proceeds thermally if X = NR<sub>2</sub> or I. The photochemistry of 2-diethylaminomethylazidobenzene **3** (X = NEt<sub>2</sub>) has also been investigated by laser flash photolysis. Two different iminoquinonemethides are detected (in *n*-hexane:  $t \sim 100$  ns /  $\lambda_{\max} = 640$  nm and  $t \sim 3$  ms /  $\lambda_{\max} = 450$  nm). The 450 nm – transient is quenched by 2-chloroacrylonitrile, dimethyl acetylene dicarboxylate, 1-octene and cyclohexene with  $k_q = 7.3 \cdot 10^6$ ,  $1.1 \cdot 10^7$ ,  $2.3 \cdot 10^6$ , and  $2.0 \cdot 10^6$  M<sup>-1</sup> s<sup>-1</sup>. Additionally, Stern-Volmer quenching of the 450 nm – transient is observed, indicating quenching of a precursor nitrene. This contribution will discuss scope and mechanism of the reaction.



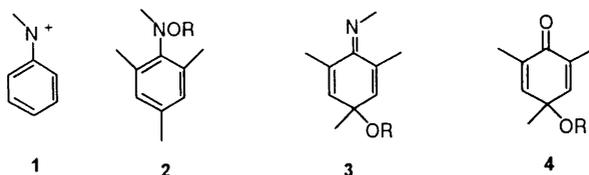
SYNTHESIS AND REACTIVITY OF STERICALLY HINDERED NITRENIUM IONS  
AND OXENIUM ION PRECURSORS

*Joseph Keogh and Anthony F. Hegarty,*

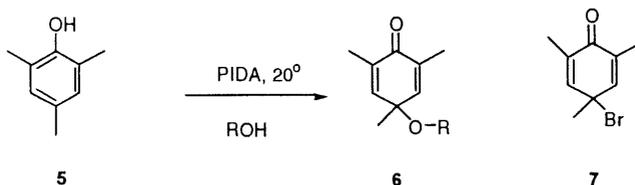
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Nitrenium ions **1** are the nitrogen analogues of carboocations (carbenium ions). Much work has been focussed on these intermediates since they are surprisingly stable and may react selectively with certain base sequences in DNA.



Initial work has focussed on the formation of mesityl and N-methyl mesityl hydroxylamines **2** as precursors. In acid these are converted quantitatively to the cyclohexadienones **3** via isolable imines **4**. Kinetic studies are reported on the formation of and the subsequent hydrolysis of the imine.



Parallel to this, aryloxenium ion precursors have also been prepared. These highly unstable ions have been previously generated by electrochemical methods, but are difficult to synthesise by chemical means. However they appear to be intermediates in the reaction of 4-methyl substituted phenols with phenyliododiacetate (PIDA) in the presence of primary alcohols or water. This gives the 4-methyl,4-hydroxy (or alkoxy) cyclohexadienones **6** in yields averaging 70%. The 4-methyl,4-bromo cyclohexadienone was also obtained by electrophilic substitution of bromine on mesitol at  $-20^\circ$ . Kinetic studies on **6** and **7** will be used to compare these with the corresponding nitrenium ion precursors.



## Unimolecular and Bimolecular Studies on the Ring Contraction of Gaseous Protonated 1,3,5-Cycloheptatriene and 7-Alkyl-1,3,5-cycloheptatrienes

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Dihydrotropylium ions **1** (protonated 1,3,5-cycloheptatriene) have been shown to be intermediates during the fragmentation of protonated toluene (toluenium ions) **2** in the gas phase.<sup>[1,2]</sup> In a study aimed at the elucidation of the isomerization behaviour of ions **1** and their 7-alkyl-(7-R-) substituted derivatives (R = Me, Et, Pr, iPr, etc.),<sup>[3]</sup> we have found that metastable alkylidihydrotropylium ions undergo, in part, ring contraction to the corresponding alkyl-(RCH<sub>2</sub>-) substituted benzenium and alkyl (R-) substituted toluenium ions. With R ≥ Et, other (non-arenium ion) rearrangements start to compete. Some examples of this unimolecular chemistry will be presented.

In agreement with these findings, gas-phase titration<sup>[4]</sup> experiments of C<sub>7</sub>H<sub>9</sub><sup>+</sup> ion mixtures generated by CI(methane) reveal that at least three populations of constitutional isomers are formed, presumably ions **2** and **1** as well as protonated 6-methylfulvene **3** (given in order of decreasing acidity). This is confirmed by the determination of the previously unknown gas-phase basicities (GB) and proton affinities (PA) of 1,3,5-cycloheptatriene and 6-methylfulvene using the thermokinetic method developed recently by Bouchoux et al.<sup>[5]</sup> Together with the known PA of toluene, this has allowed us to construct an (experimentally supported) energy hypersurface for the unimolecular reactions of dihydrotropylium ions **1**.

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## Steric Strain and Reactivity. The Electrophilic Bromination of *trans*-1-Methyl-2-adamantylidene-1-methyladamantane

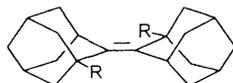
Cinzia Chiappe,<sup>a</sup> Antonietta De Rubertis,<sup>a</sup> Peter Lemmen<sup>b</sup> and Dieter Lenoir<sup>c</sup>

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Electrophilic bromination of olefins is one of the classic reactions in organic chemistry whose mechanism is documented by a large number of investigations. Recent works in this field have been mainly directed to the early steps of the reaction and fruitful approach to obtain informations has been that to use sterically crowded olefins. The first olefin investigated to this purpose was adamantylideneadamantane (**1a**) whose highly congested structure absolutely impedes the progress of Br<sub>2</sub> addition beyond the stage of bromonium ion formation. **1a** is a tetrasubstituted olefin bearing bulky „cage“ substituents in which, however, no significant twisting or pyramidalization of the double bond is present. The introduction of two *trans*-alkylsubstituents at the allylic carbon atoms considerably increases the strain of the system and induces significant torsion and out-of-plane bending of the double bond.



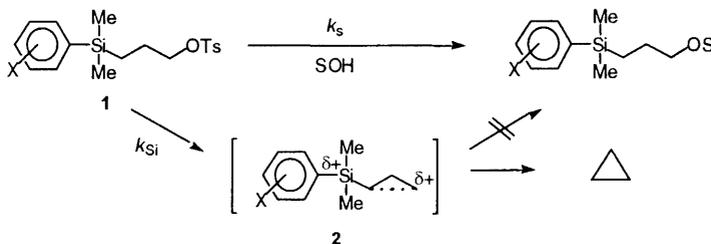
**1a:** R = H  
**1b:** R = CH<sub>3</sub>

*Trans*-1-Methyl-2-adamantylidene-1-methyladamantane (**1b**) reacts with Br<sub>2</sub> in chlorinated hydrocarbon solvents to give, depending on bromine concentration, a bromonium polibromide ion pair, or a substitution compound. The first product of the interaction of **1b** and Br<sub>2</sub> is a 1:1 π-complex having  $K_f = 1.85 (0.19) \times 10^3 \text{ M}^{-1}$  at 25 °C, which rapidly evolves to the bromonium tribromide ion pair. In the presence of a relatively high Br<sub>2</sub> concentration a stable bromonium ion unable to undergo to products is formed. When the reaction is carried out using a very low Br<sub>2</sub> concentration, no ionic intermediate is detected and the reaction rapidly yields a substitution product. Under these conditions the disappearance of the π-complex follows a first order rate law and the observed rate constant increases with increasing olefin concentration, showing that the product formation implies Br<sup>-</sup> as counter anion of the ionic intermediate whose formation is a reversible process.

The comparison of the results reported here about the bromination of **1b** with those previously found for the parent olefin, **1a**, show that steric strain markedly affect the reactivity of the double bond.

THE  $\gamma$  SILICON EFFECT ON THE CARBOCATIONIC SOLVOLYSES*Mizue Fujio, Tohru Nakashima, Ryoji Fujiyama, and Yuhō Tsuno*Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki,  
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Solvolysis rates of 3-(aryldimethylsilyl)propyl *p*-toluenesulfonates were determined in various solvents and the reaction mechanism of this simple  $\gamma$ -silyl compound was clarified based on the solvent effect and the substituent effect analyses. The solvent effect on this system clearly showed the nucleophilic assistance of solvent but failed to correlate linearly with the extended Winstein-Grunwald Eq., providing evidence for that the reaction should not proceed through either the formation of the cation intermediate or the  $S_N2$  mechanism. This suggests that the reaction takes place in competition between  $\gamma$ -silyl-assisted ( $k_{Si}$ ) and solvent-assisted ( $k_S$ ) pathways, and the ratio varies with solvents and with aryl substituents. Product analysis revealed that the former gave only cyclopropane and the latter gave only the substitution products. Overall  $k_t$  could be dissected into the partial rate constants  $k_{Si}$  and  $k_S$  for the two pathways using product ratios. The effects of aryl substituents at the  $\gamma$ -silyl atom on  $k_{Si}$  pathway were correlated with unexalted  $\sigma^0$  parameter, giving the  $\rho$  values of  $-1.0$  in 60E and  $-1.36$  in 97Tw, and reflected the delocalization of incipient carbocationic charge by participation of the Si-C $\gamma$  bond. The effects for  $k_S$  were negligibly small, which are in line with the remote reaction center in the concerted  $S_N2$  mechanism.



HYPERCONJUGATION IN CARBOCATIONS - EXPERIMENTAL AND  
COMPUTATIONAL INVESTIGATION OF STABILIZATION IN  $\beta$ -SUBSTITUTED  
CYCLOPROPYLMETHYL CATIONS

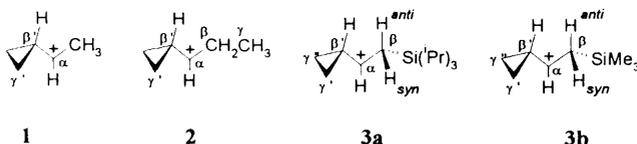
*Alexander Christian Backes, Hans-Ullrich Siehl*

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Positive charge in carbocations can be stabilized by various mechanisms. In alkyl cations, only  $\sigma$ -bonds are present, and hence delocalization of the positive charge is possible by hyperconjugation or hypercoordination. In silyl substituted carbocations, the stabilizing effect of silicon in  $\beta$ - and  $\gamma$ -position to a positive charge by means of C-Si-hyperconjugation is very well known for a variety of alkyl and benzyl cations and also for vinyl cations.<sup>[1-5]</sup>

Quantum chemical ab-initio calculations of carbocations on high level of theory allow the investigation of structure and energies and also of properties that are experimentally observable. Since NMR-spectroscopy is a powerful tool for the investigation of carbocations in superacidic solution, the calculation of NMR chemical shifts and spin-spin coupling constants provides a direct link between experiment and theory.<sup>[1-3]</sup>

In this contribution we compare differently  $\beta$ -substituted cyclopropylmethyl cations with regard to the ability of the  $\beta$ -substituent in stabilizing positive charge. *E*-1-(Cyclopropyl)ethyl cation (**1**), *E*-1-(Cyclopropyl)propyl cation (**2**) and *E*-1-Cyclopropyl-2-(triisopropylsilyl)ethyl cation (**3a**) have been prepared in superacidic solution and their <sup>1</sup>H- and <sup>13</sup>C-NMR spectra have been recorded at low temperatures. Additionally, **1**, **2** and the model structure *E*-1-Cyclopropyl-2-(trimethylsilyl)ethyl cation (**3b**) have been optimized at the correlated MP2/6-31G(d) level. The NMR chemical shieldings have been calculated at the GIAO-DFT(B3LYP)/6-311G(d,p) level, to compare the stabilizing influence of the  $\beta$ -substituent onto the chemical shieldings of the cyclopropane ring atoms. Additionally, ab-initio calculations have been performed on the transition state of rotation around C $_{\alpha}$ -C $_{\beta}$ '-bond to yield quantitative information about the stabilization energy in **1** - **3**.



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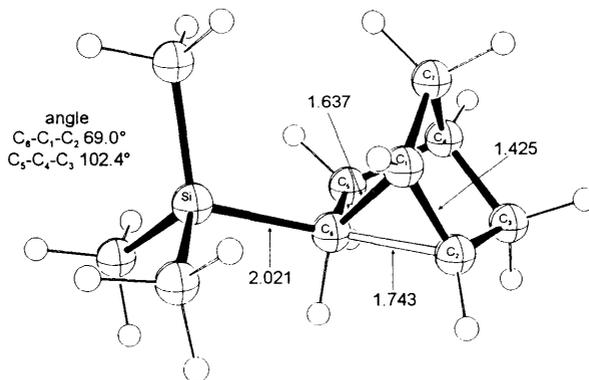
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SILYL-STABILIZATION IN THE 2-NORBORNYL CATION  
 NMR SPECTROSCOPIC AND QUANTUM CHEMICAL INVESTIGATIONS

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Experimental NMR investigations and accompanying quantum chemical *ab initio* calculations of NMR chemical shifts are presented for a  $\gamma$ -silyl substituted 2-norbornyl cation. The 6-*exo*-Trimethylsilyl-2-norbornyl cation is generated by protonation of 6-*exo*-Trimethylsilyl-2-norbornene with  $\text{FSO}_3\text{H}/\text{SbF}_5$  at  $-125^\circ\text{C}$ . The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra in  $\text{SO}_2\text{F}_2/\text{SO}_2\text{ClF}$  were recorded at  $-121^\circ\text{C}$ . *Ab initio* calculations of NMR chemical shifts were performed using GIAO-methods for the MP2/6-31G(d) optimized geometry of the 6-*exo*-Trimethylsilyl-2-norbornyl cation. A comparison between the theoretical values and the experimental data indicates that the experimentally observed carbocation can be described as a  $\gamma$ -silyl substituted dynamic carbocation undergoing a fast 1-2-6 H-shift.



6-*exo*-Trimethylsilyl-2-norbornyl cation

MP2/6-31G(d) optimized geometry

References:

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HYPERCOORDINATED BICYCLOBUTONIUM - CATIONS  
EXPERIMENTAL AND QUANTUM CHEMICAL NMR STUDIES

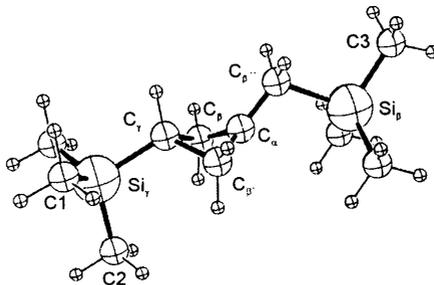
*Mato Knez, Hans-Ullrich Siehl*

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The parent  $[C_4H_7]^+$  cation is best described as system of bicyclobutonium and cyclopropylmethyl cations undergoing a fast methylene rearrangement process which cannot be frozen out at the lowest accessible temperatures in solution.<sup>[1]</sup> The corresponding 1-methyl substituted cation  $[1-CH_3-C_4H_6]^+$  is best described as a threefold degenerate 1-methylbicyclobutonium for which the methylene rearrangement but not the conformational averaging of geminal protons can be stopped at very low temperatures.<sup>[2]</sup> Cyclobutylcation with better electron donating substituents such as the 1-phenylcyclobutyl cation no longer show any significant  $\gamma$ -bridging.<sup>[3]</sup>  $\gamma$ -silyl groups stabilise the positive charge in bicyclobutonium ions and the strong bridging results in a bicyclobutonium ion structure which is static on the NMR time scale.<sup>[4,5]</sup>

We have now investigated the 1-(trimethylsilylmethyl)-3-*endo*-trimethylsilyl bicyclobutonium cation which combines the stabilising effect of silyl-substituents in  $\beta$ - and  $\gamma$ -position to the formal cationic centre. Experimental and calculations NMR chemical shifts show that this cation structure can be described as a static hypercoordinated bicyclobutonium cation.<sup>[6]</sup>



1-(Trimethylsilylmethyl)-3-*endo*-trimethylsilyl bicyclobutonium cation –  
B3LYP/6-31G(d) optimized geometry

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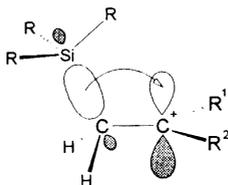
# QUANTUM CHEMICAL INVESTIGATION OF $\beta$ -SILYLSUBSTITUTED CARBOCATIONS

*Christoph Freudenberger, Hans-Ullrich Siehl*

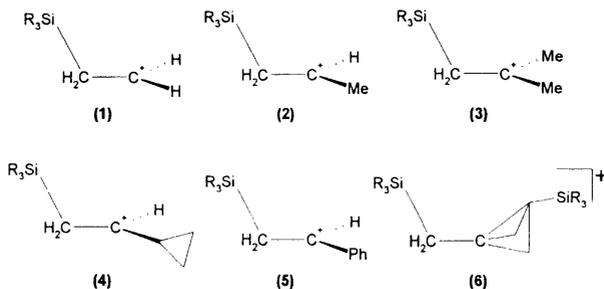
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Silylgroups in  $\beta$ -position to a cationic carbon atom are stabilizing the positive charge by shifting electron density from the  $C_\beta$ -Si- $\sigma$  bond to the positive center at  $C_\alpha$ . This hyperconjugative effect is known as the " $\beta$ -silyleffect".



In this contribution we compare the energies and geometries of several  $\beta$ -silylsubstituted carbocations (**1-6**) calculated with *ab initio* methods (B3LYP/6-31G(d) and MP2/6-31G(d)). The extend of the  $\beta$ -silyl-effect is measured in terms of the  $C^+$ -CH<sub>2</sub> and the CH<sub>2</sub>-Si bond length as well as the  $C^+$ -CH<sub>2</sub>-Si bond angle. We will investigate how these geometric parameters depend on the electron demand of the cationic center, which should be determined by the stabilisation effects arising from the different substituents  $R^1$  and  $R^2$ .



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NONDEGENERATIVE EQUILIBRIUM IN ISOPROPYLCYCLOALKYL CATIONS;  
COMPARISON OF THE ISOPROPYLCYCLOHEXYL AND  
ISOPROPYLCYCLOPENTYL CATIONS

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In order to find out how does the ring size and its conformation influence the rearrangement processes that take place in isopropylcycloalkyl cations, the temperature dependent <sup>13</sup>C NMR spectra of cations **1A/1B** and **1B/2B** were recorded, respectively. Geometries of all species involved in the rearrangements were optimized on the B3LYP/6-31G(d) level, both in vacuum and in SO<sub>2</sub>Cl<sub>2</sub> (ε=10) using the IPCM model at the B3LYP/6-31G(d) level of theory. Experimental and theoretical results revealed that equilibrium favors the isomer **1B** which has the charge located on endocyclic carbon atom. On the other hand, when the cyclopentyl ring is replaced with cyclohexyl, the direction of the equilibrium is switched, and the more stable isomer was found to be **2A**, which has a charge on exocyclic carbon atom. It was demonstrated that hyperconjugative interactions, angle strain, torsional strain and solvation effects contribute in a way to stabilize the structure **1B**. In contrast to this, the relative energy difference of cyclohexyl derivatives is mostly determined with the exceptional stability of the cyclohexyl ring, in which the torsional strain is almost completely avoided and the result is that structure **2A** is more stable. Even though the equilibrium is shifted in opposite direction for the cations compared, the overall hydride shift mechanism with both cations are the same, i.e. the hydride shift occurs through the nonsymmetric hydrido-bridged structures 1TS and 2TS.



$$\Delta H^\circ = -1.8 \text{ kcal/mol}$$

$$\Delta S^\circ = 5.7 \text{ cal/Kmol}$$



$$\Delta H^\circ = 2.5 \text{ kcal/mol}$$

$$\Delta S^\circ = 7.0 \text{ cal/Kmol}$$

KINETIC STUDIES OF THE REACTION OF HALOGEN ACIDS  
(HX, X=CL, BR) WITH MONOALCOHOLS

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The reactions of HX (X = Cl, Br and I), with alcohols have been scarcely studied although many qualitative analysis have been presented in the last decades.<sup>[1]</sup> It has been proposed<sup>[2]</sup> a general mechanistic scheme for the reactions of *tert*-butyl halides with alcohols which points out towards the coexistence of several kinetically significant steps, of which the second one is the reaction of the produced acid, HX with the solvent. It is therefore relevant, in this context, to characterize these reactions in terms of accurate rate coefficients. Although the conductometric technique is adequate to follow the change in acid concentration over time, preliminary studies<sup>3</sup> have shown that calibration curves ( $G = f(c)$ ) were needed in order to apply either integrated or differential rate laws, since time-lag methods could not be used in most cases. Nevertheless, the use of those laws showed that the  $c = f(t)$  curves could not be fitted by a first or second order rate equation. Further analysis revealed the importance of considering the degree of ionization ( $\alpha$ ) of the acids in the reaction media to overcome this problem. In this work the reactions of HX with several primary, secondary and tertiary alcohols were followed at temperatures ranging from 60.00 to 95.00 °C, depending on the alcohol. Rate constants were obtained conductimetrically and calibration curves were determined for each system. The Arrhenius-Ostwald equation was shown to be appropriate to calculate  $\alpha$  values for the acid concentration in all alcohols except in methanol. Integrated and differential rate equations were then successfully applied to the variation of free acid concentration with time.

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KINETIC AND SOLVATOCHROMIC STUDIES OF 1-BROMO-ADAMANTANE IN  
ETHANOL-WATER MIXTURES

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<sup>2</sup>Department of Chemistry, Faculty of Sciences, University of Lisbon, GERQ, Cç. Bento da Rocha Cabral, 14, 1200 Lisboa, Portugal

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Adamantyl-X substrates have been considered alternative model compounds to define scales of solvent ionizing power<sup>[1]</sup> thus permitting kinetic studies of a wide range of solvents and leaving groups. The solvolyses of adamantane compounds have been studied in the past,<sup>[2]</sup> in some pure and mixed hydroxylic solvents and have been taken as good examples of pure S<sub>N</sub><sup>1</sup> behaviour. However some solubility problems arise in highly aqueous media. In addition these solvolyses are generally slow at 25 °C leading to the need of extrapolations based on a reduced data set and often assuming, without testing, an Arrhenius-type behaviour.

In this work, the solvolysis of 1-bromoadamantane in the standard mixture 80% aqueous ethanol, has been studied at temperatures ranging from 10.00 to 75.00 °C. The rate coefficients have also been determined for the same mixture for mole fractions from pure to 20% ethanol, at 50.00 °C. The conductimetric technique has been used and the reactions were followed to 90-95% of the apparent plateau. Experimental values of E<sub>T</sub> were obtained for the same temperature interval.

The rate coefficients were calculated using the Swinbourne time-lag method optimized by the use of a computer program specifically written for this purpose. Several temperature equations based both on the Clarke and Glew<sup>[3]</sup> and the Wold and Ahlberg<sup>[4]</sup> approaches were tested to derive the activation parameters for this system. On the other hand, different LSER equations have been used to correlate ln (k) with various solvent descriptors.

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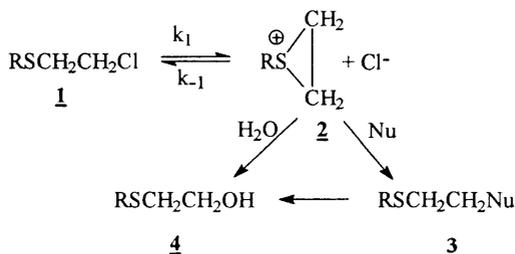
HYDROLYSIS OF YPERITE ANALOGUES IN PRESENCE OF OXIMATE IONS AND  
 AQUEOUS SURFACTANTS : A KINETIC STUDY USING A  
 CHLORIDE ION SELECTIVE ELECTRODE

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Yperite (HD) **1** is a chemical blistering vesicant agent, damaging skin, eyes and the respiratory track. Its destruction is a matter of great concern because of its high toxicity, its environmental persistency and the large stockpile quantities.<sup>[1]</sup> Nowadays, yperite detoxification exemplifies an extremely interesting and general problem in organic reactivity because of its failure to react in aqueous media, due mainly to its poor solubility. In water it reacts readily with the solvent at its interface to form a set of ionic products which can then diffuse rapidly to the bulk water phase. The rate of dissolution of **1** is so slow that these ionic products are produced at the interface even before **1** is dissolved.<sup>[2]</sup> From these instances, it results that the hydrolysis of yperite (or its substitution to produce a non toxic derivative) can be improved taking into account three main conditions : (1) to increase the solubility of the substrate ; (2) to ease the ionisation of **1** into episulfonium ion ; (3) to minimize the return reaction pathway. We will show in this poster that these conditions can be achieved by the use of oximate ions as nucleophiles (conditions (2) and (3)) and aqueous anionic surfactants (conditions (1) and (2)), in buffered aqueous solution, allowing, thus, a mild detoxification. The kinetic parameters have been obtained by the use of a chloride ion selective electrode and are discussed.



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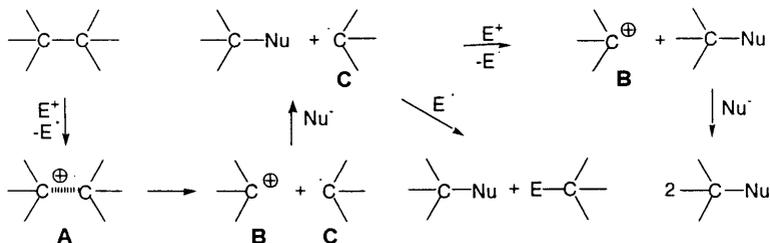
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COMMON RADICAL CATION INTERMEDIATES IN SATURATED HYDROCARBON  
ACTIVATIONS

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Electrophilic attack on single C-C bonds is believed to proceed through three center - two electron (3c-2e) species.<sup>[1]</sup> We show here that single electron transfer (SET) involving oxidants like  $\text{NO}_2^+\text{Nu}^-$ ,  $\text{NO}^+\text{Nu}^-$ ,  $\text{I}^+\text{Nu}^-$ , and metal-oxo reagents like  $\text{CrO}_2\text{Nu}_2$ ,  $\text{VO}(\text{Nu})_3$  ( $\text{Nu}=\text{nucleophile}$ ) is an important pathway for alkane activation with oxidizing electrophiles. Double nucleophilic addition to the cationic intermediates A and B is observed in this stepwise oxidation process.<sup>[2]</sup> Intermediate radical C is likely to be captured by the reduced form of the reagent or by other radical scavengers.<sup>[3]</sup>



Some model processes for non-electrophilic C-C bond activations, *e.g.*, oxidations with photoexcited aromatics (1,2,4,5-tetracyanobenzene) and electro-oxidation were also studied; similar products were observed. These findings can also be extended to hydrocarbon C-H bond activations. Analogous SET pathways may be followed in the activation of cage compounds with low oxidation potentials like adamantane derivatives. Supporting *ab initio* computations on relevant hydrocarbon radical cations are also presented.

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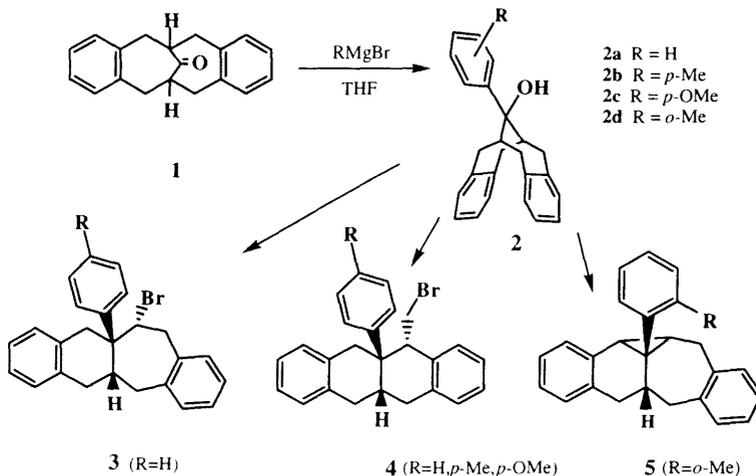
## Novel Rearrangement of Conformationally Restrained [3.3]Orthocyclophanes

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Grignard reaction of bisarenobicyclo[4.4.1]undecanone **1** with arylmagnesium halides yields layered [3.3]orthocyclophane carbinols **2**. Depending on the substituent *R* on the newly introduced aryl moiety, acid catalysed rearrangement can lead to any of three products. Upon treatment with HBr in dioxane, phenyl-substituted orthocyclophane-alcohol **2a** gives two rearrangement products, **3** and **4a** (*R*=H), which can be explained by *Wagner-Meerwein* type rearrangements. Carbinols carrying an electron rich, *i.e.* donor substituted, phenyl group or a 2-naphthyl group rearrange exclusively to form *cis*-configured dibenzo-annulated bromomethyldecalin **4**. The mechanism of the formation of these products is thought to involve the participation of one of the annelated benzo-units via its intramolecular alkylation by the secondary cation produced by the *Wagner-Meerwein* rearrangement. Carbinols with bulky substituents *R* on the aryl-group rearrange exclusively to tricyclo[5.4.0.0<sup>2,11</sup>]undecanes **5**. The pathway to these molecules, the structure of which has been verified by X-ray crystal structural analysis, has been investigated by various methods.



## Solvent Effects on Redox Properties of Radical Ions

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### Abstract

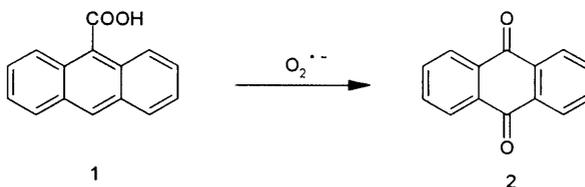
The one-electron reduction potentials of the radical cations of 1,4-diazabicyclo[2.2.2]octane (DABCO) and *N,N,N',N'*-tetramethyl-1,4-phenylenediamine (TMPD) in 2-propanol, ethanol, methanol, acetone, acetonitrile and dimethylsulfoxide have been measured by cyclic voltammetry. Furthermore, the one-electron reduction potentials of 1,4-benzoquinone, 1,4-benzoquinone radical anion, methyl viologen dication and methyl viologen radical cation also have been measured in a number of solvents. The present results, together with previously published data on radical anions, have been used to evaluate solvent effects in view of the Kamlet-Taft relationship. The main factors affecting the magnitude of the solvent effects are the gas-phase redox properties of the corresponding neutral molecule (ionization potential and electron affinity) and the charge. In general, the magnitude of the solvent effects on solution redox properties of radical ions decrease with increasing redox stability of the radical ion reflected by low ionization potential of the corresponding neutral molecule for radical cations and by high electron affinity of the corresponding molecule for radical anions.

INDIRECT GENERATION OF THE ELUSIVE RADICAL ANIONS  
OF ALKYL ANTHRACENE-9-CARBOXYLATES

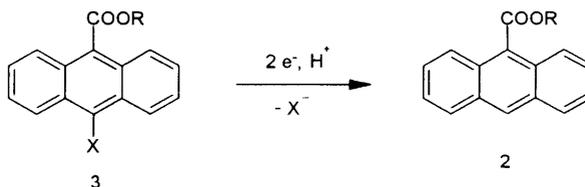
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Electroreduction of dioxygen in aprotic media yields superoxide anions  $O_2^{\bullet -}$ . These highly reactive radical anions easily attack sensitive arenes. It is, therefore, not possible to generate the radical anions of anthracene-9-carboxylic esters (**1**) by direct *in-situ* electroreduction because traces of oxygen cannot be completely excluded and unavoidably lead to the formation of anthraquinone **2** and eventually to its extremely stable radical anion **2 $\bullet$ -**.



Since we were interested in the spin density distribution of **1 $\bullet$ -** we had to overcome this difficulty in order to be able to measure its EPR spectrum. – The radical anion **1 $\bullet$ -** was therefore generated indirectly. First we electrolysed the 9-haloderivatives **3** in dry DMF at -0.5 V (*vs* Ag/AgBr) until the complete consumption of traces of oxygen. Then electroreductive dehalogenation of **3** (X = Br, Cl) to form **1** was achieved at -0.8 V and finally the radical anion **1 $\bullet$ -** was generated at -1.1 V, which proved to be persistent enough. Its EPR spectrum could be recorded, the proton HFS coupling constants were determined and related to spin densities by McConnells equation.



In a series of EPR experiments we were able to study the influence of various substituents on both the stability of the anthracene derivatives against superoxide and the spin density distribution.

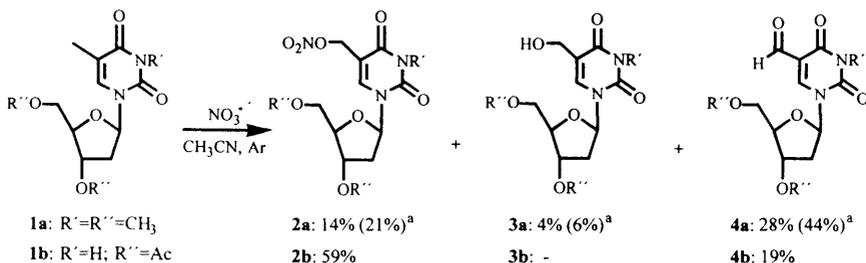
## Thymidine and Guanosine Selective Oxidative DNA Damage? Reactions of Purine and Pyrimidine Nucleosides with NO<sub>3</sub> Radicals

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Oxidants with free radical character are well-known intermediates causing DNA and RNA damage which leads to mutation, cancer and cell desactivation. This group includes certain activated antibiotics, metal complexes, redox-active metalloenzymes, oxygen metabolites, and molecules ionized by high-energy radiation (e.g. OH<sup>•</sup> originating from water). Interestingly, whereas the reactions of the strong oxidizing radicals OH<sup>•</sup> and SO<sub>4</sub><sup>-•</sup> (the latter can be generated by enzymatic oxidation of sulfites) with DNA are well known,<sup>[1-4]</sup> the reaction of NO<sub>3</sub><sup>•</sup>, which is the most important oxidant in the nighttime atmosphere, with DNA has not been investigated up to now.

Methyl and acetyl protected 2'-deoxyribo- and ribonucleosides were treated with NO<sub>3</sub> radicals, which were generated by photolysis of cerium(IV) nitrates. In neither case a primary reaction of the radicals with the sugar moiety was found. In the case of the pyrimidines an exclusive reaction at the methyl side chain of thymidine (**1a**, **1b**) was observed. With purine nucleosides an extremely fast electron transfer occurred only in the reaction with guanosine. In some cases a fast NO<sub>3</sub><sup>•</sup> induced electron transfer reaction with nucleosides, which were methylated at the heterocyclic base (these species can be formed in the DNA by toxic methylating agents, i.e. methyl iodide), lead to cleavage of the bond between the sugar moiety and the base. In the DNA this reaction might lead to the creation of abasic sites. This serious damage could result in mutations due to base pair mismatches.



<sup>a</sup> with respect to consumed starting material

[1] W.K. Pogozelski, T.D. Tullius, *Chem. Rev.* **1998**, *98*, 1089. - [2] W.F. Ho, B.C. Gilbert, M.J. Davies, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 2533. - [3] D. Schulte-Frohlinde, K. Hildenbrand, in: *Free Radicals in Synthesis and Biology* (Ed. F. Minisci), NATO ASI Series, **1989**, p. 31. - [4] J.G. Muller, R.P. Hickerson, R.J. Perez, C.J. Burrows, *J. Am. Chem. Soc.* **1997**, *119*, 1501.

## THE INFLUENCE OF SOLVENTS ON THE HYDROGEN PEROXIDE DECOMPOSITION INHIBITED WITH QUINONE

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Mechanism of hydrogen peroxide (HP) cleavage and its reactivity in different solvents have a significant meaning for the bulk and fine chemistry, as well as medicine. The importance of these reactions is connected with the ability of  $\text{H}_2\text{O}_2$  to generate of highly-active free-valent species.

Performed research is devoted to the investigation of influence of quinone (InH) and some solvents of different nature - *t*-butanol (*t*-BuOH), acetonitrile (ACN), morpholine (Morph), acetic acid (HOAc), *a.o.* at the kinetics and mechanism of catalyzed by Co(II)acetate cleavage of HP. Has been established that during the titration of analyzed probes the molecules of InH also oxidized with  $\text{MnO}_4^-$ -anions and what's more the rate of  $\text{KMnO}_4$  consumption no depends on the nature of solvents in which have been carried out the experiments.

Controlled experiments showed that in the titration conditions oxidation of solvents weren't occurred. Verified that inhibitor depressed the  $\text{H}_2\text{O}_2$  decomposition in the experiments' conditions both in the absence and in presence of catalyst. The strength of the InH influence at the rate of HP decay correlates with the physico-chemical constants of solvents (Table). The mechanism of this phenomenon is proposed.

Table

The kinetics of 0.02 N  $\text{KMnO}_4$  consumption for titration of 1 mL' probes ( $t = 30^\circ\text{C}$ ,  $[\text{H}_2\text{O}_2]_0 = 1.0$  wt. %,  $[\text{InH}]_0 = 0.2$  wt. %,  $[\text{Co}^{+2}]_0 = 0.015$  wt.%, solvent = 10.0 mL).

Solvent	Time of probes withdrawing for titration by $\text{KMnO}_4$			
	0	30 min	60 min	24 hr
HOAc	11.8	10.4	9.4	2.1
<i>t</i> -BuOH	11.7	10.9	10.2	6.2
Morph	9.1	8.1	7.6	3.1
ACN	13.7	13.6	13.4	10.5
$\text{H}_2\text{O}$	7.2	7.0	6.8	0.2

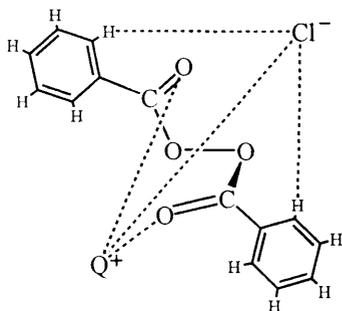
$[\text{InH}]_0 = 0$

REACTIVITY OF ONIUM HALOGENIDES IN THE REACTIONS OF THE ORGANIC  
PEROXIDE DECOMPOSITION

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The reaction of the benzoyl peroxide (BPO) decomposition activated by  $\text{Et}_3\text{HN}\cdot\text{Cl}$  and  $\text{Et}_4\text{N}\cdot\text{Cl}$  has been studied. It was found, that the rate of the peroxide decomposition in the presence of  $\text{Et}_3\text{HN}\cdot\text{Cl}$  is 100 times lower, than in the case of  $\text{Et}_4\text{N}\cdot\text{Cl}$ . The lower reactivity of the tertiary salt in comparison with the quaternary one may be explained by lower dissociation constant for  $\text{Et}_3\text{HN}\cdot\text{Cl}$   $5.2 \cdot 10^{-5}$  than  $5.1 \cdot 10^{-3}$  mol/l for  $\text{Et}_4\text{N}\cdot\text{Cl}$  in the acetonitrile solution. The calculation by AM1 method of peroxide decomposition when BPO is in the substratum separated ion pair :  $\text{Q}^+ \cdots \text{R}-\text{O}-\text{O}-\text{R} \cdots \text{Cl}^-$  ( $\text{Q}^+ = \text{Et}_3\text{N}^+\text{H}$ ,  $\text{Et}_4\text{N}^+$ ) show that the transition state on the reaction



coordinate for  $\text{Et}_3\text{HN}\cdot\text{Cl}$  lays later as compared to  $\text{Et}_4\text{N}\cdot\text{Cl}$ . Energy barriers of BPO decomposition are equal to 73.6 and 99.2 kJ/mol respectively. Stereochemical complementarity of the cation and peroxide was found in the  $\text{Cl}^- \cdots \text{BPO} \cdots \text{H}^+\text{NEt}_3$  which is due to the formation of the hydrogen bonds ( $\text{N}-\text{H} \cdots \text{O}$ ) with participation of one of two carbonyl oxygens and one oxygen atom of  $-\text{O}-\text{O}-$  bond. These interactions may be the main cause of the later transition state in case of the tertiary salt.

Electron transfer from the  $\text{Cl}^-$  to the  $\text{O}-\text{O}$  bond occurs after transition state. It allows to assume that the single electron transfer is not a cause of the peroxy bond activation and rupture.

The research described in this paper was made possible in part by Grant <sup>1</sup> U1H000 from the International Science Foundation and it also was supported , in part, by International Science Education Program (ISSEP) through Grant <sup>1</sup> APU053101.

THE KINETICS AND MECHANISM  
OF 1,3-DIOXACYCLANES OXIDATION BY DIMETHYLDIOXIRANE

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Dioxiranes are cyclic peroxides which are more and more often used as efficient oxidative reagents. Reactions with participation of these substances proceed in mild conditions, very quickly and selectively.

We have studied kinetics of dimethyldioxirane reaction with 2,2,4-trimethyl-1,3-dioxane, 2-isopropyl-4-methyl-1,3-dioxane, 2-phenyl-4-methyl-1,3-dioxane (RH).

Reaction kinetics was studied on the base of dimethyldioxirane (DMDO) consumption. Monitoring of changes of dioxirane concentration was made by spectrophotometric method, when  $\lambda_{\max} = 335\text{nm}$  ( $\epsilon = 101/\text{mole}\cdot\text{cm}$ ). The experiments were held at temperature 10-40°C. Reagents concentration was  $[\text{RH}]_0 = 0.125 - 2.500 \text{ mole/l}$ ,  $[\text{DMDO}]_0 = 0.025 \text{ mole/l}$  correspondingly.

In excess of substrate kinetics curves of dioxirane consumption are described by a first-order equation. By curves rectification we found the effective rate constants  $k' = k \cdot [\text{RH}]_0^n$ . Effective constant  $k'$  is in linear dependence on RH concentration.

On the base of dependence of the second order rate constant  $\lg k = \lg A - E/(2.303 \cdot R \cdot T)$  on temperature we found activation energy  $E$  and pre-exponential multipliers  $A$ .

The results obtained are represented in the table.

Table

Kinetics of 1,3-dioxanes oxidation by dimethyldioxirane

N	Compound	$k \cdot 10^3$ l/mole sec*	E kcal/mole	lgA
1.	2,2,4-trimethyl- 1,3-dioxane	0,41	13,06	6,4
2.	2-isopropyl-4-me- thyl-1,3-dioxane	1,36	11,03	5,6
3.	4-methyl-1,3-di- oxane	0,59	13,84	7,2
4.	2-phenyl-4-methyl- 1,3-dioxane	7,07	12,87	7,4

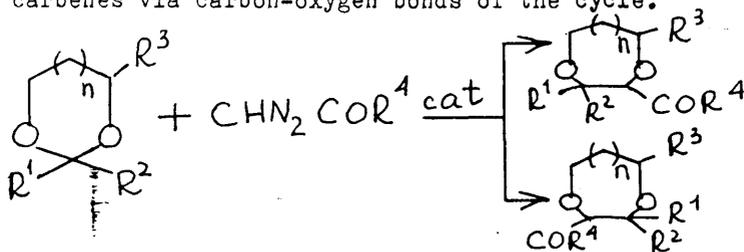
\* temperature = 20°C

THE MECHANISM OF CYCLIC ACETALS CATALYTIC INTERACTION  
WITH DIAZOCARBONYL COMPOUNDS

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Catalytic decomposition of diazocarbonyl compounds in the media of cyclic acetals results in introduction of the corresponding carbenes via carbon-oxygen bonds of the cycle.



R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = H, alk; R<sup>4</sup> = alk, Oalk; n = 0, 1;  
cat = Rh(II), Cu(II), BF<sub>3</sub> OEt<sub>2</sub>

It was shown that the reaction proceeds with ylides formation as intermediates. When R<sup>3</sup> ≠ H both possible isomers are formed and their proportion depends on the conditions, R<sup>3</sup>, R<sup>4</sup> substituents and catalyst nature. In 1,4-dioxacyclohexanes when R<sup>2</sup> = H groups R<sup>1</sup> and COR<sup>4</sup> have preferable equatorial position.

By methods of competitive kinetics the relative activity of substituted cyclic acetals was evaluated as regards diazocompounds of various structure.

Activity of the latter was studied in the reactions of cycle expansion and introduction via X-H bonds (X = RO, RCOO, RS, R<sub>2</sub>N). On the base of the results obtained the mechanism of 1,3-systems transformation into 1,4-dioxacyclanes under influence of diazocarbonyl reagents has been proposed.

# FREE RADICAL CHAIN REACTIONS IN RADIATION-INDUCED PEROXIDATION OF NEAT AND ADSORBED OLEIC ACID

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Reliable data on the absolute values of the rate constants of individual reaction steps in the peroxidation of unsaturated fatty acids are scarce. Relatively more attention was paid to polyunsaturated fatty acids (LH) as compared to oleic acid (OIH) due to the availability of suitable analytical methods. Our previous investigation of radiation-induced peroxidation of neat unsaturated fatty acids include the series: oleic, linoleic, linolenic and arachidonic acid.<sup>[1]</sup>

In this paper we report on radiation-induced peroxidation of oleic acid adsorbed on silica gel in comparison with peroxidation of bulk oleic acid. The measured radiation chemical yields of oleic acid hydroperoxides, G(OIOOH), were inversely proportional to the square root of dose rate P in both systems, indicating a chain mechanism with bimolecular termination of propagating radicals:

$$G(\text{OIOOH}) = \frac{k_p}{\sqrt{2} k_t} (\text{OIH}) \sqrt{\frac{G(\text{OI}\cdot)}{P}}$$

where  $k_p$  and  $k_t$  are propagation and termination rate constants, respectively, and  $G(\text{OI}\cdot)$  is the radiation chemical yield of initiated alkyl radicals ( $\text{OI}\cdot$ ).  $G(\text{OI}\cdot)$  was determined by the inhibitor method using  $\alpha$ -tocopherol ( $\alpha$ -toc) and measuring inhibition dose,  $D_{\text{inh}}$ :

$$G(\text{OI}\cdot) = 2[\alpha\text{-toc}]D_{\text{inh}}$$

From these measurements the respective oxidizabilities ( $k_p / \sqrt{2k_t}$ ) and kinetic chain lengths  $\nu = G(\text{OIOOH}) / G(\text{OI}\cdot)$  could be calculated.

However, individual values of  $k_p$  and  $k_t$  could not be determined from steady-state radiolysis data alone. Therefore a variant of the rotating sector method was applied, using a specially built apparatus for intermittent irradiation. Lifetime of peroxy radical  $\tau(\text{OIOO}\cdot)$  was thus obtained, which was related to  $k_t$ :

$$\tau(\text{OIOO}\cdot) = (k_t G(\text{OI}\cdot) P)^{-1/2}$$

Absolute rate constants of all individual reaction steps could then be calculated.

The proximity of molecules adsorbed on silica gel caused the acceleration of both propagation and termination reactions, increasing  $k_p$  and  $k_t$  values, but on the other hand, the kinetic chain length was shortened in the heterogeneous system. Due to restricted mobility,  $k_{\text{inh}} = 5.8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was two orders of magnitude lower than in neat fatty acids.

## References

- [1] B. Katusin-Razem, D. Razem, Absolute Rate Constants of Elementary Reaction Steps in Radiation-Induced Peroxidation of Unsaturated Fatty Acids, *J. Phys. Chem.*, submitted.

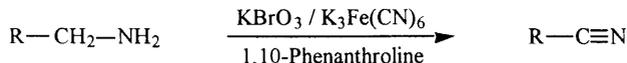
CATALYTIC OXIDATION OF PRIMARY ALIPHATIC  
AMINES BY POTASSIUM BROMATE

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Bromate salts are known as oxidizers, which exhibit very strong activity in acidic aqueous solution usually followed by bromine evolution. Under neutral conditions they also show moderate oxidizing activity only in the presence of metal complexes as catalysts. Oxidation with bromates is friendly to the environment, as only bromide (or minor quantities of bromine) is produced. Thus, it might substitute in the future metallic oxidizing agents as chromates, permanganates and others.

We have shown that potassium bromate participates in oxidation of primary aliphatic amines under weak basic conditions (pH 9-10.5) in presence of catalytic amounts of potassium hexacyanoferrate(III) and 1,10-phenanthroline. Under these conditions a mild oxidation process takes place with no bromine evolution. The reactions proceed to yield selectively the corresponding nitriles:



Aldehydes and the corresponding carboxylic acids are found as minor by-products of this reaction.

We propose a mechanism for this oxidative dehydrogenation, which includes ligands exchange, interaction between N and Fe atoms followed by imine formation (first stage) and nitrile formation by the same way (second stage). We will analyse the behaviour of benzyl amines under different set of conditions and compare with results obtained using other aliphatic amines.

## HOCl vs N-Cl-Taurine Chlorination of Aminoacids

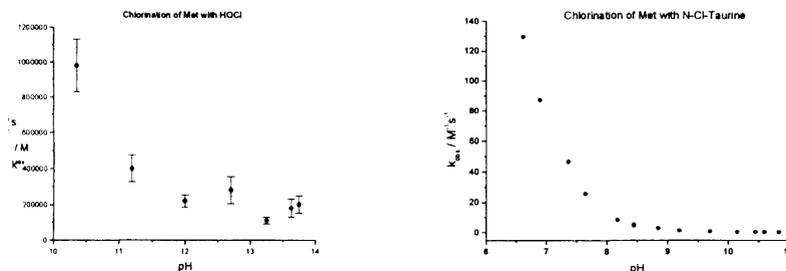
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It is well-known that HOCl can react with aminoacids, peptides and amines and produces N-Cl-compounds<sup>[1]</sup> or S-Cl-compounds<sup>[2]</sup> depending on the functional groups in the molecule.

By the way, Taurine is one of the most abundant free amino acids in mammalian tissues and appears to act as a trap for HOCl produced by the myeloperoxidase-H<sub>2</sub>O<sub>2</sub>-Cl<sup>-</sup> enzymatic system of leukocytes forming the oxidant taurine monochloramine.<sup>[3]</sup> Therefore N-Cl-Taurine can act as oxidant like HOCl, but is much less reactive and less toxic.

N-Cl-Taurine was formed by a not enzymatic reaction with HOCl, not decomposes at neutral pH and it can be used like HOCl for forming N-Cl- or S-Cl- compounds.



The processes of chlorination of aminoacids with both chlorinating agents are always bimolecular, the halogen atom being transferred from the HOCl or N-Cl-Taurine to a nucleophilic position (either a N- or S-containing group) of the amino acid. The reactions are followed by using a stopped-flow spectrophotometer, monitoring the absorbance decrease at 292 (maximum absorbance for HOCl) or 255 nm (maximum absorbance of N-Cl-Tau). The dependence of rate constant with the pH are in the following figures.

## References:

- [1] X. L. Armesto, M. Canle L., M. V. García, J. A. Santaballa, *Chem. Soc. Rev.*, 1998, 7, 453
- [2] X. L. Armesto, M. Canle L., M. I. Fernández, M. V. García, J. A. Santaballa, submitted for publication
- [3] Leah A. Marquez, H. Brian Dunford, *J. Biol. Chem.*, 1994, 269, 7950

## PHOTO- AND RADIATION CHEMICAL OXIDATION OF S-TRIAZINE-BASED HERBICIDES.

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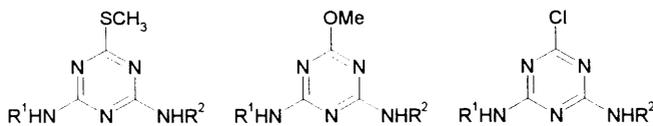
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s-Triazine derivatives are extensively used as herbicide<sup>[1]</sup> since they are able to inhibit photosynthesis and interfere with other enzymic processes that are fundamental for plant metabolism. Their degradation takes place through dealkylation of the amino groups and hydroxylation in the sixth position. It seems that photodegradation processes may occur in a similar way.<sup>[2]</sup>

This work is focused on the study of the mechanism of photodegradation of s-triazine-based herbicides in aqueous solution, using the laser flash photolysis technique. The structures of the s-triazine-based herbicides used are shown below.



Photolysis experiments were carried out using exciting light of 193 and 248 nm. Low percentages of photoionization were observed in both cases. Photoionization at 193nm is a monophotonic process, and the corresponding quantum yield values have been determined. In turn, the optical density measured for the  $e_{aq}^-$  when 248nm was used, was so low that the photoionization quantum yield could not be obtained.

The results available so far are indicative that these triazine-based herbicides are not photodegraded to a reasonable extent by sunlight.

As an alternative method of degradation, and as a tool to understand the laser flash photolysis results, we have also studied by pulse radiolysis the reactivity of these herbicides toward several oxidizing radicals:  $SO_4^{\cdot-}$ ,  $OH^{\cdot}$ ,  $O^{\cdot-}$  and toward the  $e_{(aq)}^-$ .

#### References:

- [1] Tomlin, C.; *The Pesticide Manual*, 10<sup>th</sup> ed., British Crop Protection Council, Surrey (U.K.) and The Royal Society of Chemistry, Cambridge (U.K.), 1994.
- [2] Burkhard, N. and Guth, J. A.; *Pestic. Sci.*, 1976, 7, 65

## MECHANISM OF PHOTODEGRADATION OF UREA-BASED PESTICIDES

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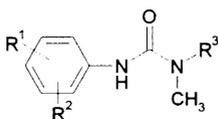
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In the framework of a wide project aiming to clarify the mechanism and products of photodegradation of different kinds of pesticides in aqueous solution, we have studied the laser-flash photolysis of commercially available urea-based pesticides, like linuron, isoproturon, etc, with the type of structure shown below. These compounds are used as herbicides, since they are able to inhibit photosynthesis.<sup>[1]</sup>



The photoionization quantum yields observed for these processes were very low (<10%). The process was monophotonic when the excitation was carried out at 193 nm and biphotonic when it was performed at 248 nm or 266 nm. These observations imply that the studied urea-based pesticides are not photodegraded by sunlight.

As an alternative method of degradation, and as a tool to understand the laser-flash photolysis results, we have also studied by pulse radiolysis the reactivity of these herbicides toward different oxidising radicals, and their affinity to reduction by e<sup>-</sup><sub>aq</sub>.

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### References

- [1] C. Tomlin (editor) „The Pesticide Manual“ Crop Protection Publications, Tenth edition, 1994.

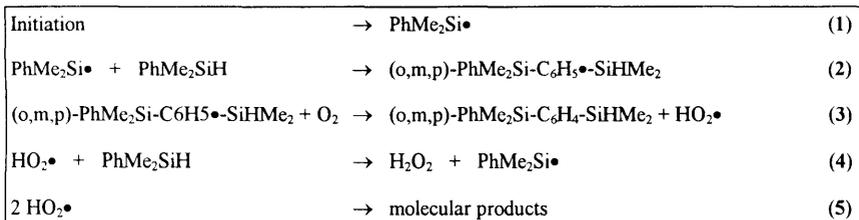
## PECULIARITIES OF DIMETHYLPHENYLSILANE OXIDATION

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Processes of free-radical oxidation of silicon-containing compounds permit obtain new materials with usable physical, electrical and photochemical properties and also improve our knowledge in the fields of organic compounds reactivity.<sup>[1]</sup>

We have carried out quantum-chemical simulation of dimethylphenylsilane (DMPS) oxidation using unrestricted Hartree-Fock method with PM3 hamiltonian, realized in MOPAC 6 program. This process is of a great interest, because initiated by AIBN oxidation of DMPS by molecular oxygen leads to formation of hydrogen peroxide with approximately full yield. In contrast, main products of oxidation of the DMPS carbon analogue (cumene) is cumene hydroperoxide. In our opinion, HO<sub>2</sub>• is the main agent in the reaction of the chain propagation. We have considered few possible trends of formation of HO<sub>2</sub>• radical. Based of the results of quantum-chemical calculations we propose the scheme of the DMPS oxidation as follow:



The main characteristic feature of proposing scheme is joining of dimethylphenylsilyl radical to substrate molecule with following abstraction of hydrogen atom from substituted cyclohexadienyl radical with formation of HO<sub>2</sub>•. Such reactions are widely known and are described in many works.<sup>[2]</sup> The results of quantum-chemical calculations of energy barriers for reactions 2 and 3 give the values 2.50 and 8.98 kcal/mole, respectively. The obtain value for reaction 2 is commensurate with the energy of heat movement of molecules, and, because, its rate must be limited predominantly by the diffusion. So far as the ratio [DMPS]/[O<sub>2</sub>] is about 700, the rate of joining of O<sub>2</sub> to PhMe<sub>2</sub>Si• must be lower compare to the rate of reaction 2.

*References:*

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## THE ROLE OF ASCORBATE IN THE DECOMPOSITION OF S-NITROSO THIOLS (RSNO)

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S-Nitrosothiols have the potential to release the biologically important molecule nitric oxide (NO) during their decomposition, and could therefore have applications as medicinal sources of NO. The role of ascorbic acid (Vitamin C) in S-nitrosothiol decomposition was investigated because of its relevance to physiological processes.

Studies carried out at physiological pH (7.4) have shown that there are two pathways for ascorbate to promote S-nitrosothiol decomposition.<sup>[1]</sup> Ascorbate can act as a reducing agent for  $\text{Cu}^{2+}$  in the well known  $\text{Cu}^+$  catalysed reaction,<sup>[2]</sup> yielding NO and the disulfide, which requires only low concentrations of ascorbate. It can also promote S-nitrosothiol decomposition through a metal ion independent process (shown by the addition of the metal ion chelator EDTA), the products being NO and free thiol.

The metal ion independent pathway exhibits a first order kinetic dependence upon both the concentration of S-nitrosothiol and ascorbate. This has been interpreted in terms of rate limiting transnitrosation between ascorbate and the S-nitrosothiol, resulting in the formation of O-nitroso ascorbic acid (which immediately decomposes with loss of NO to monodehydroascorbic acid) and thiolate. The rate of the reaction increases towards higher pH, indicating that the ascorbate di-anion is more reactive than the mono-anion and the neutral form of the acid.

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## Charge-Transfer-Induced Quenching of $n,\pi^*$ -Excited States by Amines

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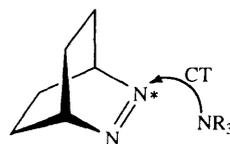
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The mechanistic understanding of the transfer of electrons, protons or hydrogen atoms is vital to the understanding of many photochemical and photobiological processes. The quenching of  $n,\pi^*$ -excited ketones by amines, which usually leads to the formation of photoreduction products, is a prototypal reaction since it involves all the mentioned primary steps.<sup>[1-3]</sup> While a „direct“ hydrogen abstraction competes in some cases, the dominant photochemical reaction is generally assumed to involve electron transfer.<sup>[2]</sup> In addition, excited charge-transfer intermediates have been proposed to be of mechanistic importance.<sup>[1,3]</sup>

In the present study the azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene was examined as an alternative chromophore, which has an exceedingly long-lived singlet state (up to 1  $\mu$ s) with  $n,\pi^*$  character, a singlet excitation energy of 76 kcal mol<sup>-1</sup>, and a very low-lying reduction potential ( $E_p = -2.8$  V versus SCE).<sup>[1,4]</sup> This azoalkane is a much weaker acceptor than, for example, triplet-excited benzophenone.<sup>[1]</sup>

According to the well-known Rehm-Weller equation the quenching rate constants fall far below the diffusion-controlled limit and offer therefore the possibility to investigate mechanistic details like the competition of charge transfer and „direct“ hydrogen abstraction. Different classes of amines, namely primary, secondary and tertiary aliphatic ones, which are known to act as so-called lone pair or n-donors as well as aromatic amines, which donate charge from their  $\pi$ -systems, were investigated.<sup>[3,5]</sup> The quenching rate constants depend on the ionization potential of the amine and its propensity to donate hydrogen atoms from C–H or N–H bonds. The involvement of exciplexes is discussed.



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QUENCHING OF THE CASCADE REACTION BETWEEN TRIPLET AND PHOTOCHROME  
PROBES BY NITROXIDE RADICALS

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A cascade of photochemical reactions between the triplet sensitizer Erythrosin B and the photochrome stilbene-derivative probe exhibiting the phenomenon of *cis-trans* photoisomerization has been investigated. The cascade triplet *cis-trans* photoisomerization of the excited stilbene chromophore was sensitized with the excited triplet Erythrosin B and depressed with nitroxide radicals that quench the excited triplet state of sensitizer. The rate of the cascade photoisomerization is sensitive to the molecular dynamics of media and radicals' concentration.

The proposed method enables the measurement of a product of the quenching rate constant and the sensitizer's triplet lifetime. Calibration of the „triple“ system permits a quantitative detection of the nitroxide radicals in a vicinity of the stilbene-derivative photochrome and sensitizing triplet probes. The experiment was carried out using the constant-illumination fluorescence technique. Sensitivity of the method using a standard commercial spectrofluorimeter is about  $10^{-12}$  mole of fluorescence molecules per sample and can be improved using an advanced time-resolved fluorescence technique. The minimal local concentration of the nitroxide radicals or any other quenchers being detected is about  $10^{-5}$  M. This method enables the investigation of any chemical, biological objects and surface processes of microscopic scale when the minimal volume is about  $10^{-3}$   $\mu$ l or less.

## THE KINETICS OF THE THREE-DIMENSIONAL RADICAL PHOTOPOLYMERIZATION OF DIACRYLATES

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The process of three-dimensional radical photopolymerization of diacrylates is characterized by peculiarities, which are qualitatively explained by the microheterogeneous model. The quantitative interpretation of these processes was introduced in paper<sup>[1]</sup> under the following assumption:

- The rate of the three-dimensional polymerization is the sum of the rates of homophase and heterophase process. Homophase process is running in the volume of liquid oligomer, and heterophase process is running in the interphase layer in the regime of the gel-effect;
- The initiator is uniformly distributed between the phases and the interphase layer;
- Clusters of the solid polymer in liquid oligomer phase and clusters of the liquid oligomer in solid polymeric matrix have the fractal structure.

The kinetics of photopolymerization of diacrylates: diethylene glycol(DEGDA)-, 1,4-butanediol-, 1,6-hexanediol- and dipropylene glycol diacrylate at the wide range of photoinitiator concentration and thickness of the layer of the polymerization composition was investigated. We found the dependences between the maximum rate of the process and of the thickness of photocomposition layer and kinetic parameters. Experimental data were compared with kinetic model of the photoinitiated three-dimensional radical photopolymerization. It was determined that kinetic model allows us to describe the process of three-dimensional photopolymerization in the whole range conversions. Molar extinction coefficient of photopolymerization ( $\epsilon$ ) and quantum yield of the photoinitiator decomposition ( $\gamma$ ), rate constants of homo ( $k_1$ )- and heterophase ( $k_2$ ) process were estimated. It was determined that constants  $k_1$  and  $k_2$  of investigated diacrylates are one order, and the constants of rate  $k_1$  of the homophase process practically does not depend from the nature of diacrylates, but increases with the decrease of the molecular mass of monomer. Quantum yields ( $\gamma$ ) of the decomposition of photoinitiator are about the one.

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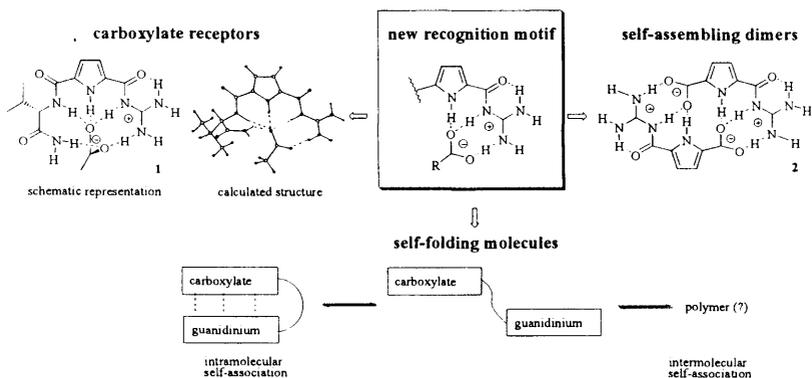
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THE 2-(GUANIDINIOCARBONYL)-1H-PYRROLE/CARBOXYLATE INTERACTION IN THE  
DESIGN OF NOVEL SUPRAMOLECULAR ASSEMBLIES

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We recently found that 2-(guanidiniocarbonyl)-1H-pyrroles like **1** bind carboxylates by ion pairing in combination with multiple hydrogen bonds even in highly polar solvents ( $K \approx 10^3 \text{ mol}^{-1}$  in 40% water in DMSO).<sup>[1]</sup> This new and hitherto unexplored recognition motif can be used for the design of efficient receptors for the stereoselective recognition of amino acid carboxylates in polar solvents. Through a systematic variation of the receptor structure, the energetical contributions of the individual binding interactions could be estimated. These data show that the various hydrogen bonds are not equally important for the binding but differ significantly in their energetical contribution to the overall complexation process.<sup>[2]</sup> Furthermore based on this 2-(guanidiniocarbonyl)-1H-pyrrole/carboxylate interaction novel supramolecular structures can be designed. The zwitterion **2**, for example, forms extremely stable dimers in DMSO (estimated  $K \approx 10^{12} \text{ mol}^{-1}$ ), though this dimerization can be completely disrupted by protonation.<sup>[3]</sup> Finally, self-folding molecules might open the way to new non-covalent, supramolecular polymers. This presentation describes the synthesis of such systems and the evaluation of their binding properties using NMR titration studies and computational chemistry.



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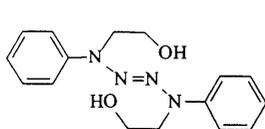
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## HYDROGEN BONDING OF HYDROXYALKYL-SUBSTITUTED 2-TETRAZENES

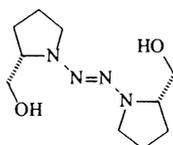
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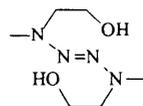
Three members of previously unknown hydroxyalkyl-2-tetrazenes (**1** - **3**) have been synthesized and hydrogen bonding of these novel bifunctional compounds has been investigated by spectroscopic (IR,  $^1\text{H-NMR}$ ,  $^{15}\text{N-NMR}$ ) and theoretical methods.



1,4-Bis(hydroxyethyl)-  
1,4-diphenyl-2-tetrazene (**1**)



N,N'-Bis(2-hydroxymethyl)-  
pyrrolidiny-2-diazene (**2**)



1,4-Bis(hydroxyethyl)-  
1,4-dimethyl-2-tetrazene (**3**)

Alkylated 2-tetrazenes show a strong intrinsic basicity as evidenced by their high absolute proton affinities.<sup>[1]</sup> Therefore, 2-tetrazenes should react as good acceptors in hydrogen bonding and this property should render them suitable as building blocks in supramolecular chemistry. The structures of **1** and its bis(trimethylsilyl) derivative were determined by X-ray analysis. In the crystalline state, molecules **1** are associated by O-H...O hydrogen bonds that form a three-dimensional network. The intramolecular O-H...N hydrogen bonds of hydroxyalkyl-2-tetrazenes **2** and **3** were investigated by quantum chemical calculations. As a model system, complexes of 1,1,4,4-tetramethyl-2-tetrazene with methanol were studied. The results indicate that O-H...N hydrogen bonds of 2-tetrazenes are medium strong. Hydrogen bonding causes only minor perturbations in the geometrical parameters of the 2-tetrazene unit whereas systematic effects on the electronic structure are more distinct.  $\delta\text{-}^{15}\text{N}$  data and quantum chemical calculations indicate that the amino-nitrogen atoms of a 2-tetrazene are involved in intermolecular hydrogen bonding to a larger extent than the azo-nitrogen atoms, the corresponding energy difference of the two types of hydrogen bonds is about  $3\text{ kJ mol}^{-1}$ .<sup>[2]</sup>

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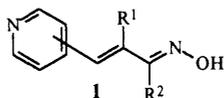
## Molecular Self-Assembly of Pyridinyl $\alpha,\beta$ -Unsaturated Ketoximes

**Monika Mazik,<sup>a</sup> Dieter Bläser<sup>b</sup> and Roland Boese<sup>b</sup>**

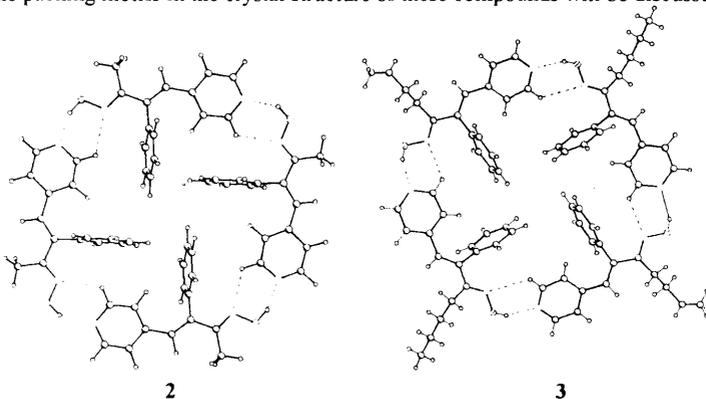
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Programmed self-assembly of small building blocks via noncovalent interactions is a promising alternative to covalent synthesis, which can provide numerous functional materials. The advantages of the biomimetic strategy are the simple synthesis of small subunits, economy in the construction of structures with nanometer dimensions, and reversible formation of complex structures with specific architectural functional features. Particularly hydrogen bond-mediated self-assembly is a promising approach to new, interesting assemblies both in solution and in the solid state. The present study concerns the aggregation behaviour of simple molecules including the pyridine and  $\alpha,\beta$ -unsaturated ketoxime subunits (**1**).



Small changes in the molecular structure of these compounds lead to formation of a variety of different aggregates in the solid state, such as discrete cyclic tetramers (**2** and **3**),<sup>[1]</sup> helical structures,<sup>[2]</sup> infinite one-dimensional chains, chains linked via  $\text{CH}\cdots\text{Cl}$  contacts, and others. The packing motifs in the crystal structure of these compounds will be discussed.



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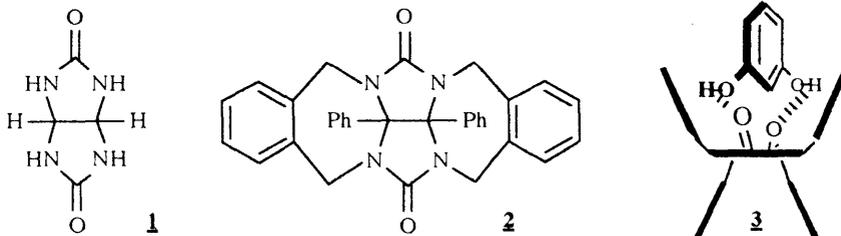
## MOLECULAR RECOGNITION of DIHYDROXYAROMATICS: DEVELOPMENT of SWITCHABLE and WATER-SOLUBLE MOLECULAR CLIPS

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Glycoluril **1**, a V-shaped structure with convergent carbonyls which can act as hydrogen-bond acceptors, has been incorporated into an increasing variety of host molecules, such as the 'pumpkin'-shaped cucurbituril (a dimethanoglycoluril cyclohexamer) [1], Rebek's bis(glycoluril)durene which forms a 'tennis ball' dimer [2], and Nolte's 'molecular clip' **2** [3], shown - in stylised form - in its 1:1 complex **3** with resorcinol, in which its xylylene walls provide an aryl-stacking 'sandwich' with the aromatic surface of the guest. Recognition of (di)hydroxyaromatics can be a stepping stone towards recognition of a wide variety of drug and hormonal substances: dopamine, DOPA, (nor)adrenaline, etc.



We have extended the range of such molecular clips, improved their syntheses, and studied their binding to guests such as resorcinol and catechol by NMR, IR and phase transfer experiments [4].

We now report a number of refinements of the basic molecular clip, including redox- and pH-switchable versions, water-soluble clips, and receptors designed for attachment to solid supports such as silica.

Binding studies to guests such as resorcinol have also been extended over a wide temperature range, yielding values for the enthalpy and entropy of 1:1 complexation.

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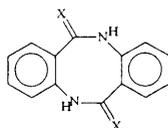
SUPRAMOLECULAR SELF-ASSEMBLY OF DIANTHRANILIDE AND  
DITHIODIANTHRANILIDE

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The *cis*-amide group promoting two-point hydrogen-bond interaction plays important role in the design of self-assembling supramolecular structures.<sup>[1]</sup> Particularly, cyclic diamides are well suited for preparation of tape arrangements in the solid state.<sup>[1,2]</sup>



1 X = O  
2 X = S

Here we report supramolecular architectures formed by dianthranilide (**1**) and its dithio analogue (**2**). The crystal structure of the racemate **1**, grown from MeCN solution, revealed the diamide molecules in a boat conformation assembled via the  $R_2^2(8)$  hydrogen bond motif<sup>[3]</sup> into infinite undulating chains of the alternating enantiomers. The empty spaces between the adjacent chains are filled with the MeCN molecules.

Chain-type aggregates have also been found in the crystal structure of **2**. Here, however, the dithioamide molecules are connected by the N...H...S hydrogen bonds with the  $R_2^2(8)$  and  $R_2^2(12)$  motifs. Only one thiocarbonyl group acts as the hydrogen bond acceptor. These chains form closely-packed crystals with no solvent molecules included. The packing arrangement of the chains is determined by  $\pi$ -stacking interactions between the phenyl rings of the neighbouring units of **2**.

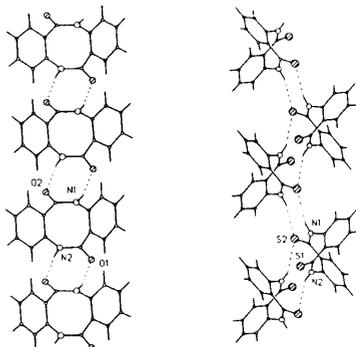


Fig. Chain-type hydrogen-bonded aggregates in **1** and **2**

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## SELF-ORGANIZED MOLECULAR CAPSULES IN WATER

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Chemists have recently imitated Nature by designing molecular capsules which self-assemble from smaller components by virtue of multiple noncovalent interactions.<sup>[1]</sup> However, most of these model systems rely on weak directed hydrogen bonds, and are hence restricted to unpolar solvents. We now report on a simple and versatile access to such complexes, which also strongly hold together in water. These are composed of highly charged complementary building blocks based on ammonium and phosphonate ions.<sup>[2]</sup>

Molecular dynamics calculations reproducibly lead to the same  $C_{3v}$ -symmetrical cyclic arrangement of alternating positive and negative charges linked by a network of ideal, linear hydrogen bonds, if trisphosphonate 1 approaches triammonium ion 2 (Figure 1.a). These structures are calculated to be far more stable than the respective simple ion pairs by  $\sim 30$  kcal/mol. The alternating order of molecular arms coming from the top and bottom unit generates a compact ball-like structure with a small cavity inside (Figure 1.b and 1.c).

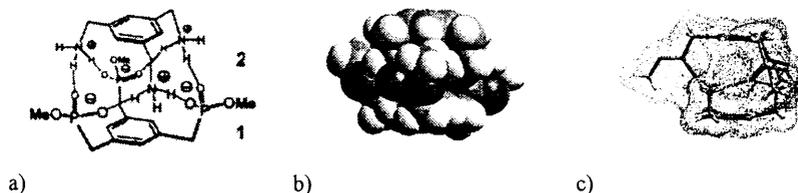


Figure 1. Force-field-optimized structure of the complex from 1,3,5-trisphosphonate 1 and its analogous triammonium salt 2; a) Lewis structure; b) Front view of a CPK-model; c) Calculated van der Waals surface shown as Connolly surface (dotted area around the complex) with internal cavity.

Complexes between 1 and various  $C_3$ -symmetrical triammonium und trisamidinium compounds give rise to sharp signals in  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra and according to Job-Plots show a perfect 1:1 stoichiometry. Evaluation of their NMR titration curves with nonlinear regression methods reveals their large thermodynamic stability, reaching  $106 \text{ M}^{-1}$  in methanol. The transport of drugs, sensors, markers or reagents by such artificial container molecules would, especially in physiological solution, open the door for a wide range of possible applications.<sup>[3]</sup>

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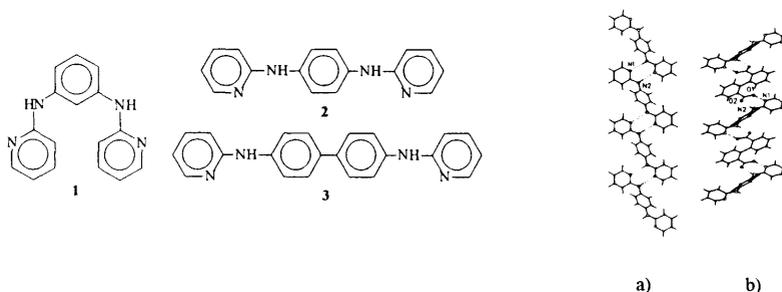
MOLECULAR RECOGNITION AND SELF-ASSEMBLY OF  
N-ARYLAMINOPYRIDINES

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The preparation of new solids, with specific properties, is a main goal of crystal engineering. It requires the design of mutually complementary molecules capable of self-assembling into an organized molecular framework. Directed hydrogen-bonding interactions are of primarily importance in controlling intermolecular orientations in crystals.



We expected that the bis(2-aminopyridine) derivatives 1–3, containing two equivalent proton donors and two proton acceptors, should form linear tapes in the solid state. However, the X-ray structure analysis revealed the tapes with the expected  $R_2^2(8)$  hydrogen bond motif<sup>[1]</sup> only in the less stable polymorphic forms of 2 (Fig. a) and 3. Conformations adopted by these diamine molecules in the solid state disfavour formation of the linear tapes of this type. Since 2-aminopyridine derivatives are known to form strong hydrogen bonds with carboxylic acids,<sup>[2,3]</sup> we obtained several 1:1 complexes of 1–3 with aromatic dicarboxylic acids. Their highly ordered crystal structures showed infinite chains of the alternating diamine and dicarboxylic acid molecules joined via hydrogen bonds with the  $R_2^2(8)$  motif (Fig. b).

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## EXPERIMENTAL AND THEORETICAL STUDY OF SUPRAMOLECULAR COMPLEXES OF BIOMOLECULES IN THE FRAMES OF MOLECULAR RECOGNITION

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Investigations of interactions in simple model systems are of fundamental importance for understanding of the formation of supramolecular complexes and mechanisms of molecular recognition. Studies of small clusters which model interactions between nucleic acids and proteins on monomer level allow us to evaluate the role of particular atomic groups in protein - nucleic acid complex formation and, therefore, predict a variation in stability of the complex caused by a change in a biopolymer primary structure. Present report is an overview of a series of our works, in which the elementary interactions between the monomers of nucleic acids and proteins were studied on the model systems consisting of various nitrogen bases and acrylamide as a model of the side chains of Asparagine and Glutamine amino acids. Thermodynamic parameters of interactions between the acrylamide and methyl derivatives of the bases were obtained using a method of temperature-dependent field ionization mass spectrometry. Energies of formation and most favourable structures of such complexes were studied using the *ab initio* and Density Functional Theory (DFT) calculations. Under the mass spectrometric conditions the associates of the molecules were formed in the gas phase. The variation of temperature allowed to obtain relative association constants for complexes of these molecules and to calculate the enthalpies of associates formation ( $\Delta H$ , kcal/mole) using Vant-Hoff plots. The enthalpy values for all complexes are presented in the following Table.

Base	$m_2^{1,4}$ Cyt	$m^1$ Cyt	$m_3^{1,4,4}$ Cyt	$m^9$ Ade	$m^9$ Gua	$m_2^{1,3}$ Thy	$m^1$ Ura
$-\Delta H$ , kcal/mole	14.0	13.6	10.9	12.4	14.2	6.8	9.7

The data obtained allowed us to construct the order of stability for base-acrylamide dimers:



A good correlation exists between this order and the sequence obtained in a number of studies of complexes formation in solutions by some other experimental techniques. A good agreement between experimental data and theoretical calculations by the various semiempirical and nonempirical methods for the studied complexes was observed as well. The data obtained can be used for determination of the mutual positions of amino acids and bases in naturally occurring recognition complexes and for quantitative estimates of the probability of recognition of the nucleic acid bases in single or double stranded DNA by amino acids Glutamine and Asparagine.

HYDROPHOBIC INTERACTIONS COMPUTED WITHIN  
THE CONTINUUM APPROACH OF THE SOLVENT

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The hydrophobic interaction term is used to describe the tendency of nonpolar groups or molecules to aggregate in water solution, being the potential of mean force (PMF) the physical magnitude related to it. Hydrophobic interactions are believed to play a very important role in a variety of processes, especially in the behavior of proteins in aqueous media. The origin of these solvent-induced interactions is still unclear.

In this work we compute the PMF as a sum of the interaction energy of the particles in vacuum plus the solvation energy. The first term is calculated with ab-initio quantum mechanics methods. The solvation term may be divided in three contributions: electrostatic, dispersion-repulsion and cavitation energy. The first and second term of solvation energy are computed using the continuum model developed by the group of Prof. Tomasi in the University of Pisa. The third term is computed using the area of the solvent-excluding surface of the solute and the surface tension of water. The systems studied are the benzene-benzene and neon-neon in water.

The results show that electrostatic and dispersion-repulsion do not play a relevant role. The cavitation free energy determine the existence of an energy barrier between the contact minimum and the separated monomers. This barrier can only be reproduced using the solvent-excluding surface and not with the solvent-accessible surface.

**PSEUDOPHASE APPROACH TO REACTIVITY OF SECONDARY AMINES TOWARDS MNTS IN PRESENCE OF QUATERNARY W/O MICROEMULSIONS OF AOT/SDS/ISOOCTANE/WATER**

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Reactivity of three secondary amines (morpholine –MOR–, piperazine –PIP– and N-methyl benzyl amine –NMBA–) towards N-methyl-N-nitroso-*p*-toluenesulfonamide –MNTS– was studied for a large range of composition of AOT/SDS/isooctane/water microemulsions.

The amines were chosen because their different hydrophobicity and their different solubility in the domains of the microheterogenous medium. PIP is a high water soluble and NMBA is a high isooctane soluble, while MOR presents a halfway behaviour. For these reasons PIP will be located in the water pool of the microemulsion and in the surfactant film, NMBA will be placed in the isooctane and in the surfactant film and MOR will be share out the three possible locations (water, isooctane and surfactant film).

Taking into account, the distribution of the three amines and the MNTS in the microemulsion, the pseudophase model extended to microemulsions allows us to rationalise the observed behaviour. The rate constant of the tree amines was calculated and the results were compared with the corresponding kinetic coefficients for the same reactions in ternary AOT/isooctane/water microemulsions.

Effects of different rigidity and polarity of the surfactant film and changes in the molar volume of the interphase were used to explain the kinetics in these media.

## ACID HYDROLYSIS IN $\beta$ -CYCLODEXTRIN/SURFACTANTS MIXED SYSTEMS

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<sup>2</sup> Dpto. de Química Física e Química Orgánica, Universidade de Vigo, Vigo, SPAIN.

The kinetics of the acid hydrolysis of N-methyl-N-nitroso-*p*-toluene sulfonamide (MNTS) were studied in media containing different cationic micelles and  $\beta$ -cyclodextrin (CD). The experimental kinetic behaviour depends of the possibility of CD acting or not as catalyst for acid hydrolysis of MNTS.

The experimental results have been interpreted in terms of a pseudophase model which takes into account the formation of both CD-surfactant and CD-MNTS complexes. Kinetic behaviour does not shows evidences of interactions of the micellar aggregate and the CD after the micellization process. Nevertheless, big effects on cmc were observed. Complexation of surfactant by CD makes the cmc dependent on CD concentration because cmc is now the sum of the concentrations of free and complexed surfactant; increasing [CD] reduces the former quantity but increases the latter to a greater extent. At surfactant concentrations above the cmc, competition between micellization and complexation processes leads to the existence of a significant concentration of free CD.

From the analysis of the observed rate constant in presence of micelles and in presence of micelles-CD mixed systems can be proved: (1) the absence of interactions between the micellar aggregate and the CD, (2) the presence of a important quantity of free CD after the micellization process, and, (3) the concentration of free CD reminds constant after the micellization process.

INTERFACIAL BINDING OF BUFFERS IN AQUEOUS SOLUTIONS OF  
CETYLTRIMETHYLAMMONIUM SALTS AND ITS ROLE IN MICELLAR CATALYSIS

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The dependence of the micellar kinetic effect on a model nucleophilic substitution (paranitrophenyldiphenylphosphate, PNDPP, -butanedione monooximate Ox<sup>-</sup> reaction) on the surfactant counter-ion, X<sup>-</sup>, and the buffer is investigated in buffered (pH 9-10) aqueous solutions of cetyltrimethylammonium salts. It is observed that the micellar effect increases with X<sup>-</sup> and the buffer in the following orders:

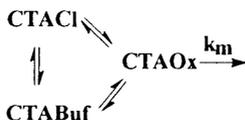


**Carbonate << Borate << Glycine ≤ Ethanolamine ≈ AMP**

(AMP = 2-amino-2-methyl-1,3-propanediol)

These results cannot be straightforwardly interpreted in terms of competitive micellar bindings of the three anionic or basic species (Ox<sup>-</sup>, Buffer base and X<sup>-</sup>) involved in the investigated system. On one hand, as regards the surfactant counter-ion, X<sup>-</sup>, acetate is known to be bound to CTA<sup>+</sup>-micelles markedly less strongly than chloride. On the other hand, as regards the buffer, the dependence of the pH of the correspondingly buffered water on the surfactant concentration which can be considered as estimates of the relative affinities of the buffer bases, is not parallel to the reactivity trend.

The two series of kinetic and pH metric data will be discussed in the relative abilities of the buffer and the counter-ion to exchange the nucleophile within an original 3-equilibrium exchange scheme.



MICELLE CATALYSIS: HOW TO ACCOUNT FOR CHANGES IN THE CONCENTRATION  
OF UNMICELLIZED AMPHIPHILE  
WITH SALT AND SURFACTANT CONCENTRATIONS?

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Ionic micelles have been shown to be very efficient for catalysing reactions between ionic reagents, e.g. a nucleophile, and fairly lipophilic substrates. Catalysis is thought to stem mainly from an increase in the frequency of the encounters between the substrate incorporated into the micelles and the reactive counterions located at the bulk/micelle interface. According to the pseudophase-ion-exchange (PIE) model, the observed first-order rate constants are related by Equation 1 to the mole fraction,  $F_s$ , of the micelle-incorporated

$$k_{\psi} = \frac{k_{2m}}{V_m} \theta_r F_s + k_{2w} (1 - F_s) [\text{Nu}^-]_w \quad (1)$$

substrate and to the fraction  $\theta_r$  of the reactive ions at the interface, relative the aggregation number. Here,  $k_{2m}$  is the second-order rate constant in the micelle pseudophase,  $V_m$  is the mole volume of the amphiphiles within the micelles and  $F_s$  is given by Equation 2 in terms of

$$F_s = \frac{K_s (c - c_1)}{1 + K_s (c - c_1)} \quad (2)$$

substrate incorporation constants,  $K_s$ , and micellized amphiphile concentrations. In this latter equation,  $c$  is the surfactant concentration and  $c_1$  is the concentration of the amphiphilic monomers in the water phase in equilibrium with the micelle aggregates. This  $c_1$  concentration in complex solutions containing the ionic surfactant and the ionic nucleophiles is usually unknown, but has been shown in many instances to depend fairly markedly on electrolyte concentrations, including nucleophile, surfactant and common-ion salt concentrations. For the sake of simplicity, it is usually assumed that  $c_1$  equals cmc, the critical micelle concentration, but this hypothesis is usually rather crude and sometimes misleading. It follows that accurate analysis of kinetic data requires experimental data for  $c_1$  or estimates. Based on cmc data for counterion-mixed surfactants and on thermodynamics considerations, this communication deals with a fairly general method for evaluating  $c_1$  whatever the experimental conditions. Examples related to the reaction of oximate ions with phosphoric triesters are given.

## STRUCTURE ACTIVITY RELATIONSHIP OF ENZYME MODELS

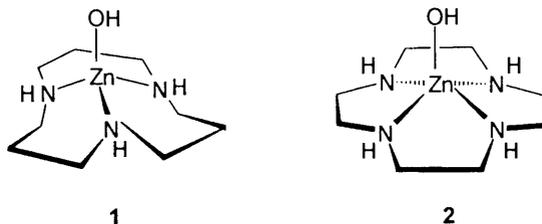
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Carbonic anhydrase (CA) is a zinc-containing enzyme which catalyses the reversible hydration of  $\text{CO}_2$ , i.e.:



This enzyme is ubiquitous in nature, occurring in animals, plants and bacteria and it is known to act very efficiently (turnover numbers  $10^4 - 10^6$ ). Using *ab initio* and DFT methods we performed a theoretical investigation on the influence of the coordination at zinc on the activity of model complexes. Special attention is paid to the control of nucleophilicity of the OH group as well as to the stability of the intermediate bicarbonate complex. A quantification of the effects of the ligands on the reactivity of the enzyme is an aim of this study. For this purpose we explored the potential energy surface of several model systems and derived structure activity patterns from geometrical and electronic data. As models we chose bare zinc hydroxide, Zinc(II)trisamine(OH) model



and the equivalent model using imidazole ligands as the model which is closest to the experimentally resolved structure. Furthermore, we investigated the complexes **1** and **2** in more detail since they have proved to be the most efficient synthetic analogues of CA so far investigated.<sup>[1,2]</sup>

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**Higher and Smaller Fullerenes - Isomerism and Relative Stabilities:****A Profound Enthalpy/Entropy Interplay**Zdeněk Slanina, Xiang Zhao, and Eiji Ōsawa

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Early results from the eighties for small carbon clusters like  $C_4$  or  $C_6$  have suggested that the combined quantum-chemical and statistical-mechanical computations could show some interesting temperature effects also for isomeric fullerenes. This feature was first demonstrated on some  $C_{50}$  isomers. The fullerene research has indeed supplied several sets of isomeric higher fullerenes. At present over twenty stable fullerenes  $C_n$  have been identified with  $n$  varying from 60 to 96. Several such mixtures of fullerene isomers have been computed ( $C_{76}$  till  $C_{94}$ ) and an agreement with observations found. Hence, the computations have demonstrated that the presumption of partial, inter-isomeric thermodynamic equilibrium is actually well working. One of the biggest system computed within the partial thermodynamic-equilibrium treatment so far is  $C_{92}$  with 86 IPR isomers. The reported computations are based on semiempirical (SAM1), *ab initio* SCF (HF/4-31G), and DFT (B3LYP/6-31G\*) approaches and RRHO partition functions. The entropy considerations also indicate an interesting way for non-IPR structures stabilization, illustrated on  $C_{72}$  and  $C_{74}$ . The approach is also applied to smaller fullerenes like  $C_{36}$ . As fullerenes are formed at high temperatures, entropy effects should be important owing to the temperature enhancement. It turns out for  $C_{36}$  that in the most sophisticated computational approximation used, B3LYP/6-31G\*, just two structures are controlling the region of higher temperatures: the conventional fullerenes  $D_{6h}$  and  $D_{2d}$ . Although the  $D_{2d}$  ground state has to prevail at low temperatures, the stability order is reversed by entropy effects already at a temperature of 1500 K.

## [2+2] Photocycloadditions of Acyclic Enones to C<sub>60</sub>. Regio- and Stereoselectivity.

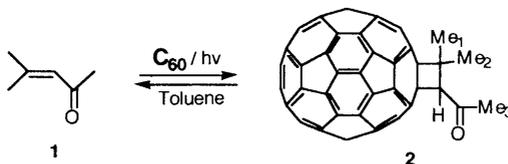
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Fullerene C<sub>60</sub> is an electrophile and undergoes a large variety of chemical reactions. The preparation of synthetically useful monoadducts of C<sub>60</sub>, continues to be the prime effort in the area of fullerene chemistry.<sup>[1]</sup> Many [4+2]<sup>[2]</sup> and [3+2]<sup>[3]</sup> cycloadditions have been reported and their monoadducts have been well characterized. However the [2+2] cycloadditions are less common<sup>[4]</sup> and only a few examples with electron rich unsaturated molecules have been reported. Furthermore, [2+2] photocycloaddition of electron poor alkenes (cycloenones) to C<sub>60</sub> have been also reported recently, however in this case the reaction proceeds through the excited state of the enone.<sup>[5]</sup> Although most of the efforts have been focused mainly on [2+2] product isolation and characterization, little is known about the mechanism of this reaction.

In this presentation we report the regio- and stereoselectivity as well as the secondary isotope effects of the [2 + 2] photocycloaddition of acyclic enones and dienones to C<sub>60</sub>. The results are in agreement with a mechanism that includes the formation of a biradical intermediate between the triplet excited states of dienones and the ground state of C<sub>60</sub>.



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## Mechanistic Studies on the [4+2] Cycloaddition Reaction of Rigid *s-cis* Dienes to C<sub>60</sub>

*Nikos Chronakis<sup>a</sup>, Michael Orfanopoulos<sup>a</sup>*

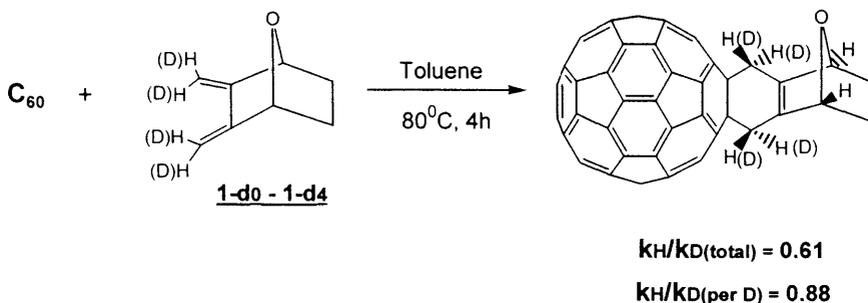
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Buckminsterfullerene C<sub>60</sub> was named "Molecule of the Year" by *Science* (Dec 20, 1991). It is hard to imagine any area of chemical research in recent history that has attracted more attention than C<sub>60</sub> and the related fullerene family.

Buckminsterfullerene exhibits electrophilic behaviour<sup>[1]</sup>, reacting with alkenes and dienes to afford [4+2],<sup>[2]</sup> [2+2]<sup>[3]</sup> and "ene" adducts.<sup>[4]</sup> Most work has been focused on adduct isolation and characterization, and less emphasis has been given to reaction mechanisms.

We present here a mechanistic study of the [4+2] cycloaddition reaction of rigid *s-cis* dienes to C<sub>60</sub>. For this purpose,  $\alpha$ -secondary kinetic isotope effects (KIE) were utilized in order to determine whether the mechanism is concerted or stepwise.



The  $\alpha$ -secondary KIE  $kH/kD$  was obtained from the equimolar 1-d<sub>0</sub> vs 1-d<sub>4</sub> competition for C<sub>60</sub>. Determination of the isotope effect was possible by integration of the appropriate signals in the <sup>1</sup>H-NMR spectrum of the purified reaction products. The measured intramolecular product isotope effect was  $kH/kD(\text{total}) = 0.61$ , i.e.,  $kH/kD(\text{per D}) = 0.88$ . This value supports a concerted mechanism in which new bonds are formed in one step. The measured value of the isotope effect excludes a stepwise mechanism, which would occur through an open intermediate. In this case, a very small or no isotope effect would be expected.

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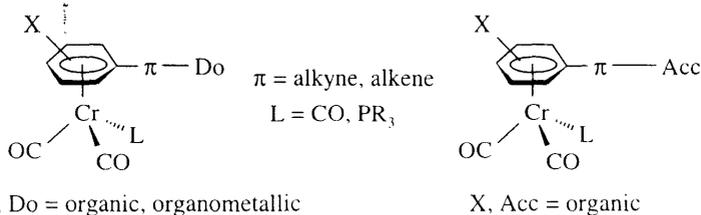
## Alkynylated and Alkenylated Arene Chromiumcarbonyl Complexes – Syntheses, Structures and NLO-Properties of Electronic Amphoters

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The peculiar ability of areneCr(CO)<sub>3</sub>-complexes to behave as an electronically amphoteric functional group, i.e. electron withdrawing and donating, has set the stage for chromium-carbonyl complexes in numerous synthetic applications, namely sidechain functionalizations.<sup>[1]</sup> Since there is a rapidly increasing demand for novel organometallic chromophores for electronic and photonic applications<sup>[2]</sup> the question arises whether this remarkable electronic effect can be extended to electronically ambident chromophores. Do chromium-carbonyl arene complexes behave amphoteric in push-pull chromophores as well?



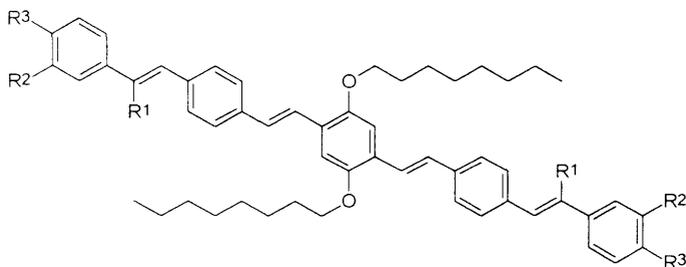
Recently, we could show that our methodology allows a facile, selective and very broad access to areneCr(CO)<sub>3</sub>-complexes with alkynyl<sup>[3]</sup> and alkenyl<sup>[4]</sup> substituents. In first measurements (HRS = Hyper-Rayleigh-Scattering) the NLO-properties, i.e. the static hyperpolarizabilities  $\beta^0$  of simple  $\eta^6$ -phenylCr(CO)<sub>3</sub>-complexes with conjugated sidechains were found to  $30\text{-}50 \times 10^{-30}$  esu,<sup>[5]</sup> i.e. comparable to those of ferrocenyl derivatives.<sup>[2b]</sup> However, the rich chemistry of chromium arene complexes allows multiple strategies for optimizing the amphoteric effect. Here, the syntheses, the structures and the electrical properties (optical nonlinearities) of these novel polyfunctional complexes with extended  $\pi$ -conjugation will be presented and discussed.

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## SYNTHESIS, ELECTRONIC SPECTRA AND PHOTOCHEMICAL BEHAVIOUR OF OLIGO(PHENYLENEVINYLENE)S WITH ELECTRON-WITHDRAWING SUBSTITUENTS

Heiner Detert and Erli Sugiono

The use of Poly(phenylenevinylene) (PPV) as emitting material in Light Emitting Diodes is well established.<sup>[1]</sup> PPV and its soluble, alkoxy-substituted derivatives are hole conducting materials with high energy levels of the conduction and valence bands<sup>[2]</sup>. Oligomers of the PPV-type are interesting as model compounds for studying degradation processes as well as as luminescent materials due to their high fluorescence quantum yields.<sup>[3]</sup> We present the synthesis of a series of monodisperse, highly soluble oligo(phenylenevinylene)s with a variety of substituents with electron accepting character (i.e. sulfonyl, cyano, 1,3,4-oxadiazolyl) in order to improve electron injection and conduction by lowering the energy levels. The influences of different substitution types on the absorption and emission spectra will be presented and the photochemical behaviour by UV-irradiation in neutral solution and in the presence of acids and bases is studied. Whereas the OPVs are highly stable towards  $\lambda = 366$  nm, different processes, depending on the environment, are observed by irradiation with hard UV-light ( $\lambda = 254$  nm).



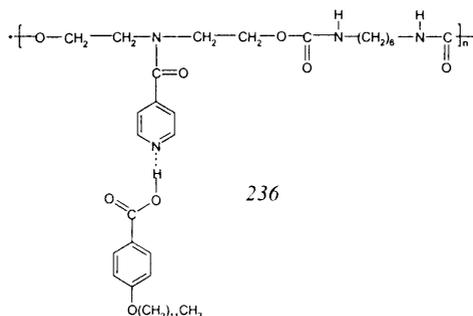
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## Novel supramolecular liquid-crystalline polyurethane

Gabriela Ambrožič, Aneta Mirčeva, Majda Žigon

In the supramolecular liquid crystal polymers, the mesogenic properties are tailored via noncovalent interactions. The most common type of supramolecular liquid-crystalline (LC) polymers are the side-chain LC polymers (SCLCP), in which a low molar mass molecule is attached to the polymer backbone through hydrogen bonding. One of the most studied supramolecular associations in this regard is the carboxylic acid-pyridine molecular complex<sup>[1]</sup>. There are a few examples of supramolecular SCLCP that contain hydrogen bonds located in the vicinity of the polymer backbone without the flexible spacers<sup>[2,3]</sup>. A novel supramolecular liquid-crystalline polyurethane (Figure) was prepared by mixing the polyurethane containing pendant pyridyl unit as H-bond acceptor and 4-dodecyloxybenzoic acid as H-bond donor. Intermolecular hydrogen bond formation was confirmed by Fourier transform infrared spectroscopy. The liquid-crystalline behavior of the complex formed was established by differential scanning calorimetry, polarizing optical microscopy and X-ray diffractometry. The complex exhibited highly ordered smectic and nematic phases. The smectic–nematic and nematic–isotropic transitions were observed at 89 °C and 120 °C, respectively.



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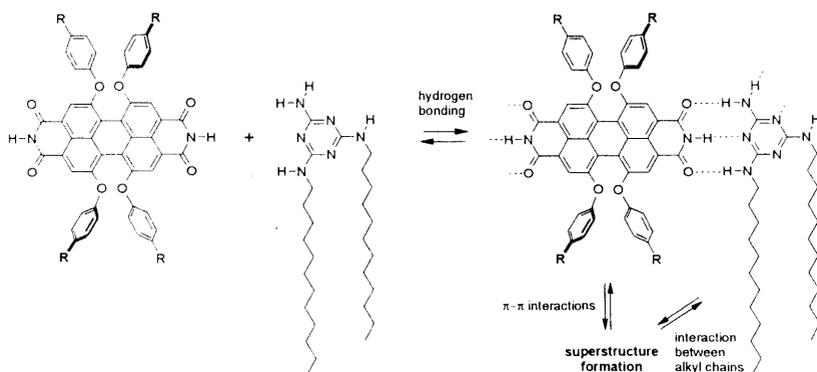
## SUPRAMOLECULAR ORGANIZATION OF FUNCTIONAL PERYLENE DYES TO HIGHLY FLUORESCENT MESOSCOPIC FIBERS

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The controlled arrangement of functional units in space is demonstrated by numerous complex systems given in nature. Spontaneous self-assembly could also provide a powerful tool for supramolecular chemistry to achieve architectural control and functional specificity. Our approach is to use different, e.g. "orthogonal" intermolecular interactions to achieve ordering of functional building blocks on a molecular and supramolecular level.



Our recent work on the selforganization of highly fluorescent perylene dyes indeed demonstrated the versatility of this concept. Thus a hierarchical structure formation process involving hydrogen bonding and  $\pi$ - $\pi$  stacking was unambiguously demonstrated by means of NMR titration studies and UV/vis and fluorescence dilution experiments in various solvents. Moreover, in aliphatic solvents additional organizational forces come into play and superstructures of nano- and mesoscopic dimensions appear as visualized by electron microscopy.<sup>[1]</sup> The intensive emission of the perylene dyes within these aggregates could be of great interest for future studies on energy transport phenomena in artificial assemblies related to the example of the light harvesting complex of natural photosynthesis.

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RECEPTOR-SUBSTITUTED PERYLENES: NEW FUNCTIONAL BUILDING BLOCKS FOR  
METALLOSUPRAMOLECULAR CHEMISTRY

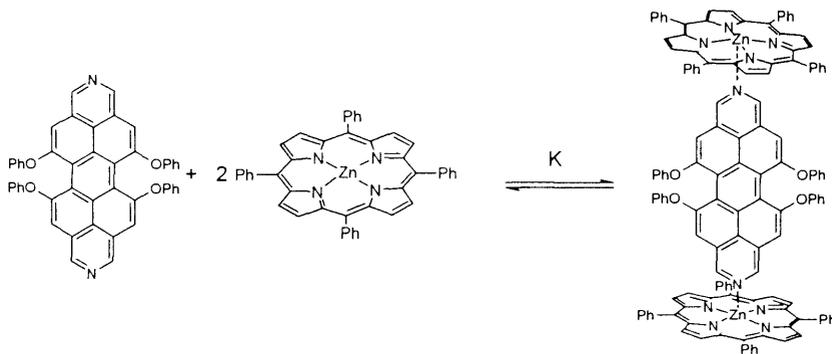
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Supramolecular chemistry designs structures of ever increasing complexity and size which are already comparable to natural systems.<sup>[1]</sup> However, all those artificial supramolecular structures are far from nature's capabilities with respect to functionality. One reason for this is a lack of suitable building blocks which exhibit optical or electrical functionality as well as receptor groups positioned in the way demanded for self-assembly.

In our contribution we present the synthesis of tetraaryloxy-substituted perylene dyes and their functional and coordination properties.<sup>[2]</sup> Structural properties were revealed by x-ray crystallography and NMR investigations, and functional properties are demonstrated by high fluorescence quantum yields and reversible oxidations and reductions according to cyclic voltammetry. Coordination to carboxylic acids, zinc porphyrins<sup>[3]</sup> and metal ions was examined including the determination of binding constants as well as the optical properties for a functional assembly of diazadibenzoperylene with zinc tetraphenylporphyrin.



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ELECTROOPTICAL CHROMOPHORES: MOLECULAR PROPERTIES, AGGREGATE  
FORMATION AND PHOTOREFRACTIVE HOLOGRAPHIC APPLICATIONS

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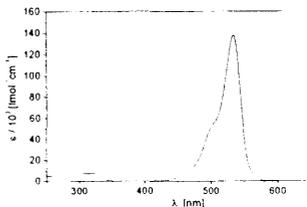
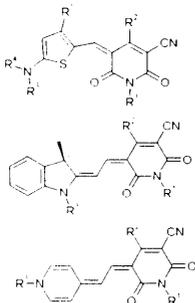
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Polymers for nonlinear optical and photorefractive applications rely on chromophores which exhibit high first and/or second order polarizabilities and suitable optical properties for a given laser wavelength. Beyond these molecular properties aggregation and phase separation processes are of primary importance for the given applications because of high dye concentrations in the polymeric binder.



UV/vis spectrum showing the highly brilliant  
chromophoric system of the given merocyanine dyes.

In this contribution we will show our results on the optimization of the electronic system of merocyanine dyes for photorefractive holographic applications<sup>[1]</sup> as well as our recent progress towards the control of supramolecular interactions in amorphous polymeric materials. The formation of dimer aggregates between the highly dipolar dyes was shown to compete with the poling process induced by applying external electric fields. Sterically demanding groups proved to be suited for a better poling efficiency by preventing this undesired intermolecular interaction. Interestingly, our work lead us to glass-forming chromophores which are highly desired to achieve homogeneous films of high optical quality because of their low crystallization tendency.<sup>[2]</sup> Finally photorefractive materials with unprecedented refractive index modulation efficiencies could be obtained.<sup>[3]</sup>

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## SYNTHESIS AND CHARACTERIZATION OF OLIGOTHIOPHENE TRIBLOCKCOPOLYMERS

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Well defined triblockcopolymers (Fig. 1) are synthesized in such a way, that the conjugation between the thiophen units is guaranteed. The polystyrene was synthesized via anionic polymerization, so that the molecular mass and the polydispersity is controlled. With the use of the Stetter reaction a tetraketone is made from substituted  $\alpha$ -terthiophenes which can undergo a ring closure using Lawesson's reagent.

Using the described procedure we made three triblockcopolymers with different lengths of the outer blocks. They were characterized (SEC, NMR) and investigated with respect to the formation of microstructures (UV-VIS, TEM, AFM).

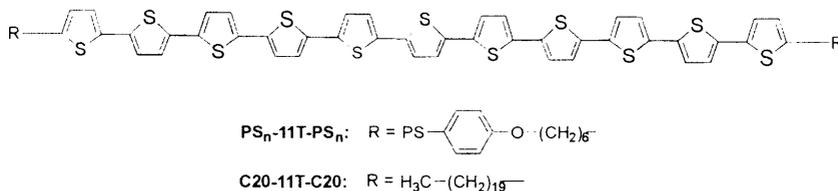


Figure 1: Synthesized oligothiophene triblockcopolymers

## BLOCK COPOLYMER MICELLES AS TEMPLATES FOR THE CONTROLLED SYNTHESIS OF NANOSCALED MAGNETIC PARTICLES – A COLLOID CHEMICAL APPROACH

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Block copolymers with two incompatible blocks undergo micellation in selective solvents. These associates have been used in the past for the controlled uptake of inorganic compounds, which can be subsequently transformed inside the micellar cores. Polystyrene-*block*-poly(2-vinylpyridine)-copolymers (PS-*b*-P2VP) form inverse micelles in toluene with the vinylpyridine units as the core building block. Noble metal salts can be incorporated in the core region either by complexation or by simple acid-base reactions. Reduction of these compounds e.g. with anhydrous hydrazine is well suited for the generation of nanoscaled noble-metal particles usually in the size range of 3-20 nm. Casted films of these colloidal solutions are arranged in highly ordered two-dimensional patterns.

The present contribution deals with the controlled confinement of the magnetic transition elements following the "nanoreactor approach" with emphasis on Iron and Cobalt. This is done by solubilization of iron- and cobalt salts followed by reduction or thermal decomposition of the respective compound. Also the special magnetic properties of the nanosized particles are taken into account. The variation of numerous parameters is presented in order to optimize the approach.

## SEMIFLUORINATED COMPOUNDS AT INTERFACES

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Semifluorinated compounds exhibit very low surface energies and low adhesion to both aqueous and organic media. Since the fluorinated chains tend to orient on various substrates, these substances are valuable candidates for surface modification. Semifluorinated monomeric and polymeric isocyanates were coated reactive onto cellulose films in sc CO<sub>2</sub>. The excellent water and oil repellent properties were proved by means of contact angle measurements using the sessile drop method. Preliminary studies of semifluorinated alkanes F-(CF<sub>2</sub>)<sub>12</sub>-(CH<sub>2</sub>)<sub>m</sub>-H using x-ray reflectivity and surface tension measurements already showed specific ordering, the so-called surface freezing effect, which is the formation of a solid layer at the surface of the melt.

## CONTROLLED GRAFTING OF HYPERBRANCHED POLY(METHYLBIS-UNDECENYLSILANE) FROM CHEMICAL MODIFIED GLASS SURFACES

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In various applications like catalysis, photoimaging and sensor technology the surface is the real functional unit.

Polymer materials are interesting for coating because of their simple synthesis, manifold functional groups and their specific adjustable layer thickness on special materials.

Here we describe the growing of hyperbranched polymers from suitable surfaces. The polyundecenylsilane is "grafted from" by attaching alkenylalkoxysilanes on the substrate and starting the hydrosilylation reaction with a platinum-catalyst.

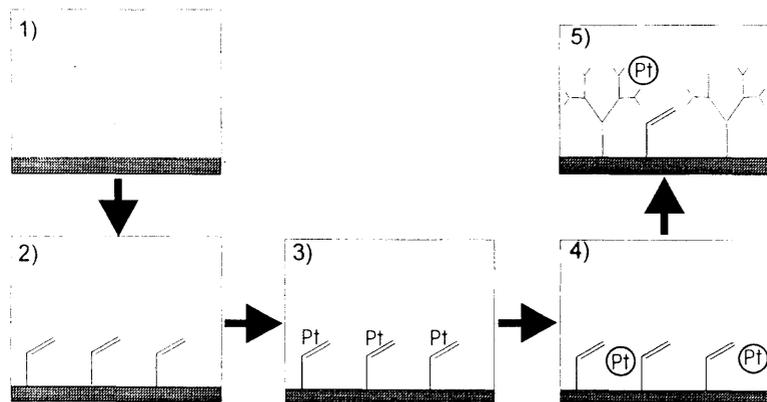


Figure: Schematic description of the "grafting from" concept with polyundecenylsilane

## NANOSTRUCTURED SURFACES WITH DIFFERENT METAL / METAL OXIDE CLUSTERS

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The formation of A-B functionalized surfaces, where nanometer sized A and B patches are distinguished for their different physical and chemical properties, represent a rather virgin field of research. We will present a techniques for generating nanosized chemical heterogeneous surfaces by combination of specific interaction of diblock copolymers with substrates, self-organization of metal particle containing diblock copolymer micelles, and conventional semiconductor etching techniques.

Polystyrene-block-poly(2-vinylpyridine) diblock copolymers form reverse micelles in toluene. Such nanocompartments are used for generating metal or semiconductor particles of equal size in each single micelle. The micelle stabilized particles can be cast to mono micellar films, forming quasi hexagonal arranged lattices. The particle to particle distance is controlled by the polymer shell and the particle size by the micellar compartment. After film formation the polymer shell can be removed totally using gas plasma techniques resulting in the deposition of 'naked' clusters on different substrates without destroying the former particle organization. These highly regular metal nanopatches can cover macroscopic areas up to several  $\text{cm}^2$ .

SYNTHESIS OF HYPERBRANCHED POLYHYDROXYSILOXANES

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Hyperbranched polyhydroxysiloxanes are synthesized via ammonia catalyzed polycondensation of triethoxysilanol. Subsequent hydrolysis of the received hyperbranched polyethoxysiloxanes yields products soluble in absolute tetrahydrofurane. The solutions can be stored without precipitation over several weeks. Silica particles can be precipitated by adding nonpolar organic solvents. The intermediates and products were characterized by IR, GC-MS, NMR and SEC.

The polyhydroxysiloxanes can be used either for making new ceramic materials or for the preparation of organic-inorganic composite materials. For this purpose a device for biaxial drawing of ultrahigh molecular weight polyethylene was developed.

## FUNCTIONAL STAR POLYMERS - MODEL COMPOUNDS FOR COATINGS

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Although the surface modification of textiles is of great industrial relevance, for these complex systems it is rendered difficult to find the correlations between the polymer structure, the coating conditions and the final coating properties. We focus on new multifunctional coating agents which are based on functionalized star polymers. The applied star polymers consist of a sorbitol core bearing poly(alkylene oxide) arms which can be easily functionalized due their terminal alcohol moiety. Variation of the arm length and hydrophilicity provides a smart method to optimize coating properties. In order to determine the homogeneity of the coatings, the star polymer arms are terminated partially with perfluoroalkyl moieties. The remaining star polymer arms are terminated with protected isocyanate groups to bind the star polymer molecules covalently to regenerated cellulose, which serves as a flat and uniform model substrate for cotton. Furthermore, the variation of the ratio of fluorinated and reactive arms can also be optimized for the coating. In the present work the degree of surface coverage and ordering of fluorinated ends is determined by contact angle and scanning force microscopy measurements. In particular, the effect of star polymer arm length and fluorocarbon chain end length were investigated. In addition, the competing factors of the thermally driven ordering of perfluoroalkyl moieties and the crosslinking on the substrate were examined. The results suggest that if all contributing factors in coating preparation are considered, homogeneous coatings with the desired properties can be prepared.

## PERSISTENT MOTION OF MOLECULAR BRUSHES AT INTERFACES

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<sup>2)</sup>Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA

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Significant progress in polymer chemistry has been made towards preparation of three dimensional molecules with a well defined shape, interior, and surface structure. The most prominent examples are dendrimers and cylindrical brushes. These molecular particles have been discussed as perspective materials for photonic applications (optical filters, switches, photonic band gaps), lithography (molecular masks), membrane technology (templates), chemistry (catalysts, initiators), and biomedical applications (carriers, containers, sensors). We are interested in interfacial ordering and dynamics of cylindrically shaped molecules in thin films to prepare ordered films and patterned surfaces with a long range coherence on the nanometer scale. Conformation and motion of single macromolecules have been investigated by scanning force microscopy. Due to the high branching density, this type molecules could be observed as individual species adsorbed on solid surfaces. Resolution of single molecules made SFM a powerful analytical tool for direct characterisation of the molecular properties such as absolute molar mass, mass distribution, length per monomer unit, and persistence length.

We have also succeeded in monitoring of motion of individual macromolecules as a function of temperature. Remarkably similar to biological objects, e.g. cells, small clusters of monodendron jacketed linear chains demonstrated an amoeboid-type motion. The most unusual observations in this case were the persistent character of the motion and periodic variations of the cluster shape.

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## WATER SOLUBLE BOTTLEBRUSHES WITH POLY(ETHYLENE GLYCOL) SIDE CHAINS

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Polymers with stretched backbone, the stretching being caused by sterical overcrowding of large, space demanding side groups, are called "cylindrical brushes" or "bottle brushes". A possibility of the preparation of such brushes is the radical homopolymerization of macromonomers. High degrees of polymerization are obtained at high concentrations of the polymerisable end groups only. Extremely high local concentrations can be achieved by micellation of the macromonomers. Poly(ethylene glycol) (PEO) macromonomers with a sufficiently hydrophobic alkylstyrene end group self-assemble in water into micelles, and polymerization inside these aggregates proceeds rapidly to high conversion. Amphiphilic Polymers of very high molecular weight possessing the unique regular structure of a hydrophobic backbone surrounded by a shell of hydrophilic PEO chains.

PEO macromonomers with hydrophobic segments of different length and a maleimide end group were synthesized and characterized by MALDI-TOF mass spectrometry and NMR. Moreover, first experiments to determine the critical micell concentration were carried out.

The PEO macromonomers were copolymerized with styrene in toluene and water, to receive water soluble brushes with a styrene-maleimide backbone and poly(ethylene glycol) side chains.

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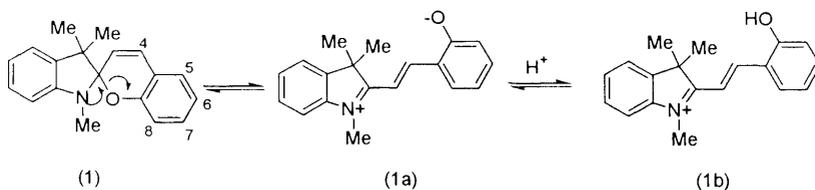
THERMAL RING OPENING OF SUBSTITUTED INDOLINO AND  
DIBENZOSPIROPYRANS IN ACIDIC MEDIA.

*Christine Lumsden, Brian Lambert, Rory More O'Ferrall.*

University College Dublin, Belfield, Dublin 4.

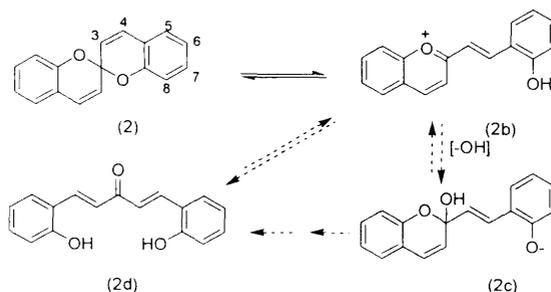
Rate constants and equilibrium constants have been measured for the ring opening of substituted 1',3',3'-trimethylindolinospiropyrans (1) and 2,2'-spiropi[2H-1]benzospiropyrans (2).

Ring opening is effected by trapping a zwitterionic intermediate (1a) by protonation on a phenolic oxygen atom in the acid dependent equilibrium shown in Scheme 1.1.



Scheme 1.1

For the dibenzospiropyrans, reaction in acid yields a benzopyrilium ion (2b) analogous to the indolenium ion (1b)



Scheme 1.2

Interestingly the 7,7'-dimethoxybenzospiropyran not only formed the benzopyrilium ion, but was found to undergo a second ring opening to form the *trans-trans* chalcone at mildly acidic pHs. This is shown in the dotted pathway in Scheme 1.2.

For each compound pH-rate profiles were constructed. Substituent effects on reaction rates and equilibria will be discussed.

SYNTHESIS OF A NOVEL RIGID TTF-S-P-BENZOQUINONE DIAD WITH INHERENT  
STRUCTURAL CONFIGURATION SUITABLE FOR INTRAMOLECULAR CHARGE  
TRANSFER.

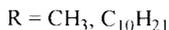
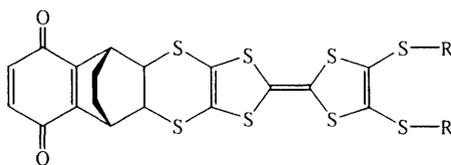
*Evgeny Tsiperman, Vladimir Khodorkovsky, James Becker, Arkady Ellern, Lev Shapiro*

Department of Chemistry, Ben-Gurion University of the Negev, 84105, Beer-Sheva, Israel

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Although tetrathiafulvalene (TTF) and its derivatives have been extensively studied for more than 25 years as p-electron donors in intermolecular charge transfer materials, the intriguing potential of TTF as a donor in an intramolecular sense has only recently been developed. Many versatile functionalized TTF building blocks are now readily available for donor-acceptor diads. In order to control the stoichiometry of the D and A components and the degree of charge transfer in such intramolecular CT complexes the concept of a rigid bicyclic non-conjugated spacer was developed.<sup>[1]</sup>

The compounds (I) which have been prepared in the course of the present work are the first examples of rigid donor-acceptor diads with inherent intramolecular through space charge transfer properties. They have been investigated by UV-VIS, X-ray diffraction, and Cyclic Voltammetry.



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*References*

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SYNTHESIS AND INVESTIGATION OF STABLE METAL DERIVATIVES OF  
TETRAPHENYLPORPHINE AS COMPOUNDS FOR NEW ORGANIC MATERIALS

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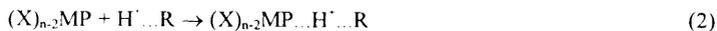
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Synthesis and reactivity of the so called super stable metal derivatives of aromatic macrocyclic compound - mezo(tetraphenyl)porphine with metal-nitrogen and metal-element (halogen, oxygen) bonds with composition  $(X)_{n-2}MP$ , where  $X =$  anion (charge = -1),  $n =$  formal charge of M atom,  $P =$  porphyrin, are examined. The destruction ability of the compounds in 100% sulphuric acid at 298 K is equal zero. Derivatives of p-metals of Al and Si sub-groups of Periodic system and of d-metal cations ( $n > 2$ ) with significant dative  $M \rightarrow N$  bond contribution regard to super stable porphyrin complexes. There is a peculiarity of  $(X)_{n-2}MP$  synthesis from the porphyrin and metal salt or oxide:  $M^{n+}$  cation during synthesis can undergo oxidation or reduction to form the metal compound with definite, often unusual oxidizing degree, which is stabilized by the aromatic part of the molecule.

The rates of elementary stages or equilibrium constants of the reactions of the metal derivatives in different reaction centers (M-X, M-N, mezo-atom C) were measured. Equilibrium reaction (1) is suitable for selection of compounds with optimum properties for creation sensors and membrane activators for division  $H_2S$  containing gas mixtures. Proper recommendations are given in the report.



Reaction (2)  $(X)_{n-2}MP$  with solvent protons in concentrated sulphuric acid with high concentration of  $H_3O^+$  and non-ionized  $H_2SO_4$ , where the mezo(tetraphenyl)porphine metal derivative acts as C-base, was studied.



PM3 calculation showed that H-bond forms with mezo carbon atom. Properties of mezo-protonated forms of  $(X)_{n-2}MP$  are examined.

High stability, ability to polarization and aromaticity spread to d-metal atom make the compounds perspective materials for practical use in different areas of technics.

REACTIVITY OF CHLORO DERIVATIVES OF PHTHALOCYANINES OF COPPER AND ALUMINIUM IN DESTRUCTION REACTIONS

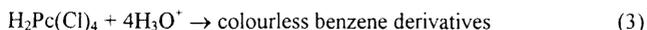
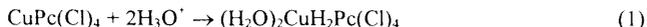
*Tatjana N.Lomova<sup>1</sup>, Tatjana N.Sokolova<sup>1</sup>, Elena E. Suslova<sup>1</sup>, Vladimir E.Mayzlish<sup>2</sup>, Gemady P.Shaposhnikov<sup>2</sup> and Marija E. Klueva<sup>1</sup>*

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Reactivity of halogen and halogen, nitro-derivatives of phthalocyanines of copper(II) and aluminium(III) with substituents R in positions 3, 4 and 4,5 of benzene rings: CuPc(3-Cl)<sub>4</sub>, CuPc(4-Cl)<sub>4</sub> and (OH)Al(4-Cl)<sub>4</sub>(5-NO<sub>2</sub>)<sub>4</sub> was investigated in hot concentrated sulfuric acid.

Copper phthalocyanines are in the form of (CuPc(Cl)<sub>4</sub>H)<sup>+</sup> in the mixed H<sub>2</sub>SO<sub>4</sub> – H<sub>2</sub>O solvent for different H<sub>2</sub>SO<sub>4</sub> concentrations. State of the phthalocyanine derivative of aluminium(III) differs while H<sub>2</sub>SO<sub>4</sub> concentration increases. Gradual long wave shift of the band of π→π\* transition in electron absorption spectra is observed. Rate of the destruction of copper phthalocyanines in concentrated H<sub>2</sub>SO<sub>4</sub> with limiting stage (1) was measured at T > 380 K.



Destruction reaction has the first order on metallophthalocyanine for all studied compounds (M = Cu, Al).

The rate law for copper phthalocyanines is:

$$-dC_{\text{CuPc(Cl)}_4} / dt = k_v \cdot C_{\text{CuPc(Cl)}_4} \cdot C_{\text{H}_2\text{SO}_4}^2 \quad (4)$$

Destruction of (OH)Al(4-Cl)<sub>4</sub>(5-NO<sub>2</sub>)<sub>4</sub> is the first example of the processes of this type the rate of which does not depend on H<sub>2</sub>SO<sub>4</sub> concentration. Perhaps it is connected with changing of the state of the compound while H<sub>2</sub>SO<sub>4</sub> concentration increases because of additional bonding of aluminium atom with OH-group.

Using earlier received data for NO<sub>2</sub>- and COOH- derivatives of copper phthalocyanines mechanism of the electron and steric influence of the substituents onto reaction center of transformations (1-3) is discussed.

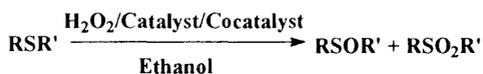
METALLOPORPHYRIN-CATALYSED OXIDATION OF SULFIDES BY HYDROGEN-  
PEROXIDE

*Antonio Marques, Marie-Françoise Ruasse*

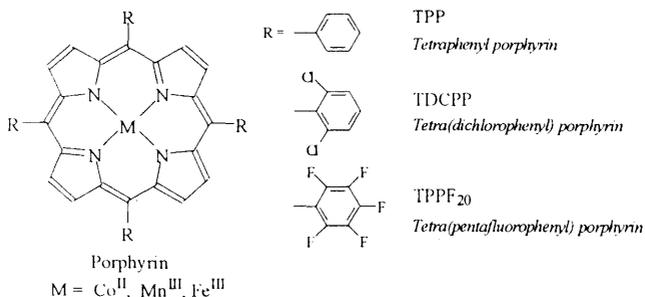
Institut de Topologie et de Dynamique des Systèmes de l'Université Paris 7-Denis Diderot,  
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Toxicity of some organic sulfides is strongly decreased, or even disappears, by oxidation into sulfones. In the view of obtaining cheap decontamination procedures which oxidize sulfides rapidly, quantitatively and under mild (room temperature, neutral pH, non-pollutant by-products) reaction conditions,



we investigated the catalysis of the hydrogen peroxide oxidation of typical sulfides (simulant of mustard gas) by biomimetic organometallic complexes such as metallo-porphyrins.



The best catalytic system which converts quantitatively sulfide into sulfone in less than 2s after the addition of 2 equivalents of H<sub>2</sub>O<sub>2</sub>, and without significant destruction of the porphyrin at room temperature is :



**1                      900                      420**

In contrast with experiments involving Mn<sup>III</sup> or TPP, the presence of a cocatalyst is not necessary. On the contrary this catalyst, quite robust in the above conditions, is fastly destroyed when imidazol or ammonium acetate is added to the reaction mixture. These results will be discussed in terms of the nature of the active catalytic species and of the mechanism of their oxygen transfer to sulfides.

## NMR SPECTRA OF 5,15-DIPHENYLPORPHYRIN ATROPISOMERS.

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By condensation of 5,5'-dicarboxy-4,4',3,3'-tetraalkyl-2,2'-dipyrrolylmethane with 2-methoxybenzaldehyde and 1,4-di(2-formylphenoxy)buthane in pyridine in presence of zinc acetate are synthesized monomeric and dimeric 5,15-diphenylporphyrin atropisomers which differs by orientation of aryl- fragments rather tetrapyrrolic macrocycle. All isomeric structures differs by chromatography mobility, that has allowed to divide them into individual substances.

The research of 5,15-di(2-methoxyphenyl)octaalkylporphyrin atropisomers (A and B) has shown, that NMR spectra of these substances differs by a multiplicity of phenyl protons signals. In atropisomer A there are two doublets of *ortho*- and *meta*-protons both two triplets of *meta*- and *para*-protons. In atropisomer B there are a doublet of *meta*-protons, triplet of *para*-protons both multiple of *ortho*- and *meta*-protons. As against monomeric porphyrin, which is easily plunged by atropisomerisation (in boiling *ortho*-xylol from one isomer the mixture of two in the ratio 1:1 will be derivated), dimeric porphyrin to rotation of phenyl fragments is not capable. At atropisomer C, which is characterized by the greater equivalence of protons, the doublet of *ortho*-protons and triplet of *para*-protons is exhibited. In NMR-spectra of D- and F-atropisomers there are a precise triplet of *para*-protons and doublet of a part of *meta*-protons. Other part of *meta*-protons and the *ortho*-protons merge in a multiple.

## MULTIMOLECULAR PORPHYRIN ASSEMBLIES: DESIGN AND PHOTOPHYSICS

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Stimulated by biophysical investigations in vivo, the majority of model supramolecular porphyrin-type arrays have been used quite intensively in order to better understand factors and mechanisms which control the efficiency and directionality of the electronic excitation energy transfer (ET) and charge transfer (CT) reactions taking place without diffusional limitations. Within last two years, our main strategy in the creation of well-defined highly organised multimolecular tetrapyrrolic assemblies with controllable number and photophysical properties of porphyrinic subunits is based on the combination of two fundamentally different approaches: i) chemical synthesis of covalently linked Zn-porphyrin or Zn-chlorin dimers and trimers (having spacers of various nature and structure) with or without quinone (or anthraquinone) and ii) self-assembling non-covalent interactions with pyridyl substituted tetrapyrrolic extra-ligands (two-fold extra-ligation effect with "key-hole" principle, complexation constant  $K_c \approx 106-107 \text{ M}^{-1}$ ) [1,]. In non-polar or small polar solutions, for these systems ET and /or CT processes play the dominant role in the nonradiative deactivation of the locally excited states.

In this report we analyse ET and CT (electron transfer) processes governed by the structure of the arrays, redox and optical properties of interacting subunits, obtained on the base of steady-state, picosecond time-resolved fluorescence spectroscopy (system response  $\Delta t = 30 \text{ ps}$ ) and femtosecond pump-and-probe kinetic data (system response  $\Delta t = 350-400 \text{ fs}$ ) in methylcyclohexane and toluene solutions in a temperature range of 77-300 K.

The obtained results reveal that the strong fluorescence quenching found for Zn-dimers and Zn-trimers in multimolecular arrays is due to the fast (within  $\leq 10 \text{ ps}$ ) effective ET to non-fluorinated extra-ligands or due to the CT ( $k_{CT} \approx 1.4 \times 10^{12} \text{ s}^{-1}$ ) in the case of pentafluorinated extra-ligands). The main feature of the systems is that CT remains still effective ( $k_{CT} \approx 10^{11} \text{ s}^{-1}$ ) in glassy matrices at 77 K being the electron tunnelling by nature. In multimolecular assemblies containing covalently linked p-benzoquinone the effective fluorescence quenching of the (ZnOEP)Ph(ZnOEP) dimer ( $\tau_S < 10 \text{ ps}$ ) is attributed to ET from the dimer to an extra-ligand and to CT from the dimer to quinone. In addition, the fluorescence lifetime shortening is observed for extra-ligands:  $\tau_S = 464 \text{ ps}$  for porphyrin ( $\tau_{S0} = 11 \text{ ns}$ ),  $\tau_S = 690 \text{ ps}$  for chlorin ( $\tau_{S0} = 3.7 \text{ ns}$ ). The extra-ligand fluorescence quenching is explained in terms of photoinduced electron transfer via the "superexchange" mechanism.

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## EXCITONIC EFFECTS AND ENERGY TRANSFER IN POLYMERIC AGGREGATES OF PHOTOSYNTHETIC PIGMENTS

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At the moment, from investigations of the primary light-harvesting reactions for natural objects (green plants and photosynthetic bacteria), mainly by steady-state and time-resolved fluorescence and absorption spectroscopy, some insight into primary events of photosynthesis has been gained. In this respect the growing interest has been devoted to the investigation of dimers and higher oligomers of porphyrins and chlorophylls suited for the modelling photoinduced excitation energy transfer and excitonic interactions. Our strategy was to use the principles of the formation of chlorophyll "a" (Chl) or bacteriochlorophyll "a" (BChl) polymeric ordered aggregates in binary mixtures of solvents (water-dioxane 4:1 and 3-methylpentane-dioxane 1000:1 mixtures) where monomeric molecules are cross-linked by bifunctional ligand dioxane via central Mg atoms of Chl or BChl.<sup>[1]</sup>

In the present report we will discuss the excited states dynamics for individual ordered oligomers ( $n \approx 100-300$ ) of Chl and BChl in binary water-dioxane (4:1) and 3-methylpentane-dioxane (1000:1) mixtures obtained by use of femtosecond time-resolved emission spectroscopy (the instrument function of the system is 50 ps) as well as by steady-state polarised fluorescence and circular dichroism measurements at 293-77 K. The main idea is to find the correlations of spectral, photophysical and optical activity parameters of these aggregates with their structural organization as well as to elucidate the possible mechanisms of the energy transfer in these systems.

These aggregates are characterised by the high optical activity, the conservative excitonic splitting ( $\Delta E \approx 40-70 \text{ cm}^{-1}$ ) of circular dichroism bands into two components of opposite signs and highly polarised emission. On the base of experimental results (a three-component global analysis of time-resolved isotropic emission kinetics measured as a function of temperature) and theoretical estimations (theory of the „hot transfer“ or „localised exciton“) it has been shown that for- and backward energy transfer processes in dioxane-coordinated ordered Chl or BChl aggregates are realised in picosecond time scale (50-850 ps) and may take place during the vibrational relaxation of excited S-states. In addition, single-colour isotropic transient absorption kinetics with 250 fs resolution measured at two wavelengths with two experimental time windows reveal that the composition of BChl aggregates differs from that found for Chl complexes at the same conditions.

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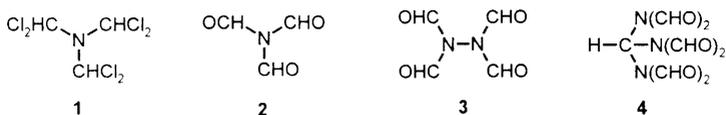
NEW FORMYLATION REACTIONS FOR AROMATIC AND  
HETEROAROMATIC COMPOUNDS

*Prof. Dr. Willi Kantlehner, Dr. Michael Ciesielski, Dr. Oliver Scherr, Dr. Markus Wezstein,  
Dipl.-Ing. (FH) Richard Haas, Dipl.-Ing. (FH) Georg Ziegler*

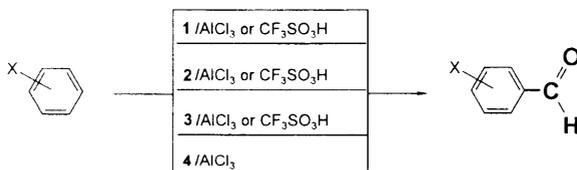
Fachbereich Chemie/Organische Chemie, Fachhochschule Aalen

Only a few stable formic acid derivatives are known which can act as direct formylation reagent for aromatic compounds, e.g. formylfluoride and dichloromethylether are used for such purposes. In other synthesis for aromatic aldehydes the electrophilic reagents are produced in situ as it is the case in the well known reactions introduced by Gattermann, Gattermann-Koch and Vilsmeier-Haack.

We were able to demonstrate that the stable formic acid derivatives tris(dichloromethyl)amine (1), triformamide (2), tetraformylhydrazine (3) and tris(diformylamino)methane (4) can be used for the formylation of aromatic and heteroaromatic compounds.



The formylation reagents 1-3 can be activated by Lewis-acids e.g.  $\text{AlCl}_3$  and by superacids e.g. trifluoromethansulfonic acid as well. The orthoamide derivative 4 hitherto could be reacted only under the activation of Lewis-acids. The scope of the new formylation reaction covers those of the above mentioned reactions according to Gattermann, Gattermann-Koch and Vilsmeier-Haack.



The reactions proceed between  $-30$  to  $+20^\circ\text{C}$  with high regioselectivity. Typical solvents are the aromatic compound itself or chlorobenzene or 1,2-dichloroethane.

The formylation reagents 1-3 are known compounds, the orthoamide 4 can be prepared easily from 2 and sodium diformamide.

A further aldehyde synthesis, in which a mixture of formamide,  $\text{P}_4\text{O}_{10}$  and  $\text{AlCl}_3$  is used as formylating reagent, is just under investigation. In this way toluene and anisole have been transformed to the corresponding aldehydes.

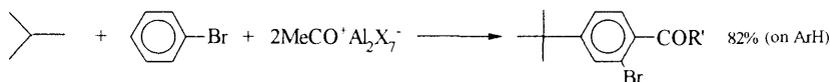
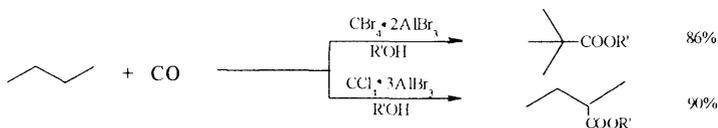
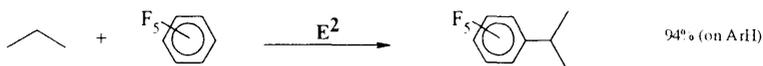
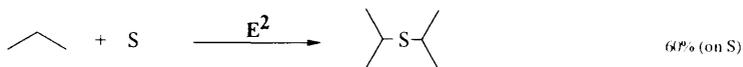
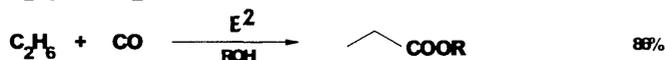
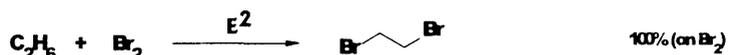
## NOVEL FUNCTIONALIZATION REACTIONS OF LOW ALKANES

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The involvement of the most available low alkanes in selective transformations is one of the fundamental problems of organic chemistry.

New functionalizations of C<sub>2</sub>-C<sub>4</sub> alkanes were performed by using two families of superelectrophiles (**E**), namely Friedel-Crafts type complexes RCOX•2AlX<sub>3</sub> (**E**<sup>1</sup>, R = Alk; X = Br, Cl), and complexes of polyhalomethanes combined with aluminum bromide (**E**<sup>2</sup>, CX<sub>4</sub>•nAlBr<sub>3</sub>, CHX<sub>3</sub>•nAlBr<sub>3</sub>; X = Br, Cl; n = 2 or 3). These reactions, as a rule, occur selectively to give alkane functionalized products in high yields under very mild conditions. Some examples of the elaborated reactions are presented below (yields are given with respect to **E** unless otherwise specified):

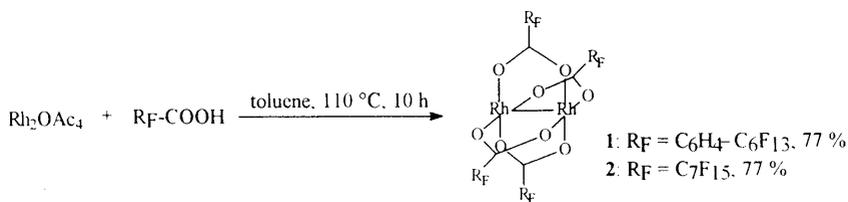


A FLUOROUS PHASE APPROACH TO RHODIUM-CATALYZED  
CARBENE TRANSFER REACTIONS

*Andreas Endres, Gerhard Maas*

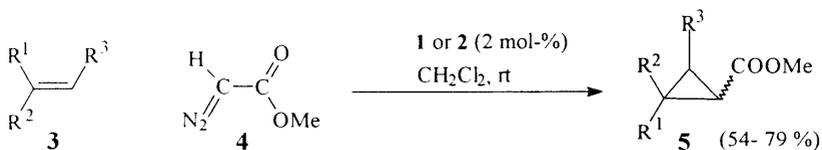
Abteilung Organische Chemie I, Universität Ulm, D-89069 Ulm, Germany

The fluorous phase concept can be applied to catalytic cyclopropanation of alkenes with diazoesters when rhodium(II) carboxylates with perfluoroalkyl chains are used as catalysts. To this end, the dinuclear rhodium(II) complexes  $\text{Rh}_2\text{L}_4$ ,  $\text{L} = \text{OOC}\text{C}_7\text{F}_{15}$  (**1**) and  $\text{OOC}\text{-C}_6\text{H}_4\text{-C}_6\text{F}_{13}$  (**2**) were prepared from  $\text{Rh}_2(\text{OAc})_4$  and 4-(perfluorohexyl)benzoic acid and commercially available perfluorooctanoic acid, respectively (Scheme 1). Complex **1** was obtained as a light-green powder, while **2** formed a dark-green waxy solid.



Scheme 1

Cyclopropanation of various alkenes **3** was achieved with methyl diazoacetate (**4**) in the presence of catalytic amounts of **1** or **2** (Scheme 2). The reactions were performed in a mixture of  $\text{CH}_2\text{Cl}_2$  and 10 equivalents of the alkene (based on diazoester) to suppress the formation of carbene dimers.



**3:** styrene,  $\alpha$ -methylstyrene, 1-hexene, 2-methyl-2-butene

Scheme 2

The catalysts could be extracted from the reaction mixture with perfluoro(methylcyclohexane) and reused at least four times without significant loss of activity.

Further applications of the fluorous phase concept to carbene transfer reactions will also be reported.

## NOVEL SILAHETEROCYCLES BY CARBENOID AND DIAZO REACTIONS

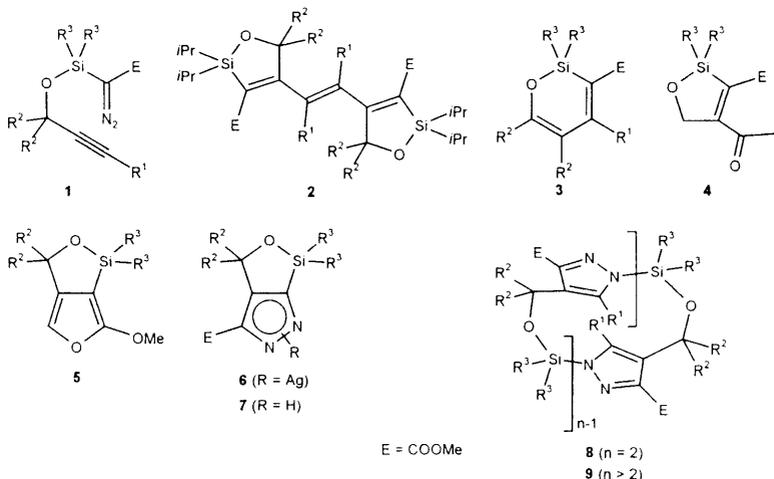
Volker Gettwert, Gerhard Maas

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For (alkynyloxy)silyl diazoacetates **1**, various intramolecular reactions involving the diazo (or latent carbene) function and the C,C triple bond have been achieved. Depending on reaction conditions and substituent pattern, silaheterocycles **2-7** can be prepared. Copper(I) triflate catalyzed decomposition of diazoacetates **1** leads to silaheterocycles **2**, **3**, and **4**. With copper(I) chloride as catalyst, the dediazonation of **1** leads to the bicyclic furan **5**.<sup>[1]</sup> Treatment of **1** with Ag<sub>2</sub>O does not decompose the diazo ester but rather leads to the silver pyrazolate **6**. Similarly, a thermally induced intramolecular 1,3-dipolar cycloaddition reaction generates pyrazole **7**.

A thermally induced inter-/intramolecular 1,3-dipolar cycloaddition sequence of **1** leads to [3.3](1,4)pyrazolophanes **8** and higher cyclooligomers thereof (**9**,  $n \geq 3$ ). In most cases, the cyclodimers **8** can be isolated by crystallization, while a complete separation of the mixture of the higher cyclooligomers **9** was not possible.



## References:

- [1] V. Gettwert, F. Krebs, G. Maas, *Eur. J. Org. Chem.* **1999**, 1213-1221.

## Nitration in Inert solvents.

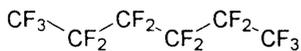
*Michael R. Crampton and L.M.Gibbons.*

*Department of Chemistry, Science Laboratories, University of Durham, South Road,  
DURHAM, DH1 3LE.*

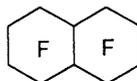
*e-mail: L.M.Gibbons@Durham.ac.uk.*

Traditional methods of nitration have several disadvantages including the environmental problem of disposal of the spent acid. A main aim of this work is to investigate alternative methods for nitration while minimising the amount of acid required.

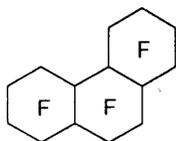
Perfluorocompounds have been used as 'bulking agents' to partially replace the acid solvent. 1, Perfluorohexane (PP1), 2, perfluorodecalin (PP6), 3, perfluoroperhydrophenanthrene (PP11), and 4, perfluoromethylcyclohexane (PP2), 5, perfluoroether (HT135), have been studied. They are chemically inert and may be reused without the need for purification. (A major advantage of the perfluoroether is that it is cheaper than the perfluorocarbons.)



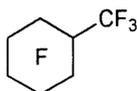
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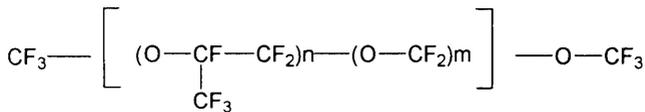
(2)



(3)



(4)



(5)

Nitrations of aromatic species have been successfully studied in these solvents using nitric acid, nitric plus sulfuric acids, or dinitrogen pentoxide. Results of both synthetic and kinetic experiments have been obtained. The kinetic results relate to homogeneous nitrations by dinitrogen pentoxide of substrates including 4-chloroanisole, 4-bromophenetole and various chlorophenols.

ON THE DIRECTING EFFECT OF REMOTE AMIDE GROUPS IN THE OXIDATIVE  
CYCLIZATION OF ALKENES AND PALLADIUM(0)

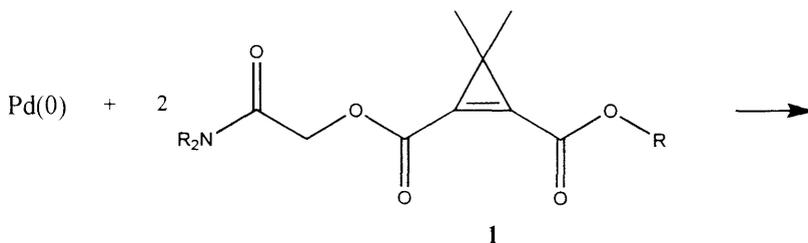
*Andreas Rivas Nass and A. Stephen K. Hashmi*

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In the course of our efforts to prepare catalysts that base on palladacycles,<sup>[1]</sup> we have recently developed a stereoselective synthesis of C<sub>2</sub>-symmetrical palladacycloalkane-derivatives.<sup>[2]</sup> In this synthesis not a facial selection but a regio selection in the step of the oxidative cyclization forming the metallacyclopentane ring from Pd(0) and two olefins is responsible for the observed diastereoselectivity of the process (*d.r.* = 94 : 6 or better).

In efforts to understand the basis of this regio selection, we considered an remote ester group to direct Pd to one specific end of the olefinic double bond by coordination. If this type of 1,4-induction would be valid, the effects should be more pronounced with the corresponding amide.

As test systems we prepared the cyclopropenes **1**. The results of the oxidative cyclization, which possibly could form up to three constitutional isomers, will be reported and their implications on the mechanism of the 1,4-induction will be discussed.



*References:*

- [1] A. S. K. Hashmi, F. Naumann, R. Probst, J. W. Bats, *Angew. Chem.* **1997**, *109*, 127-130.  
[2] A. S. K. Hashmi, F. Naumann, M. Bolte, *Organometallics* **1998**, *17*, 2385-2387.

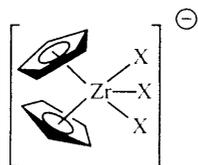
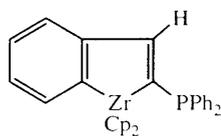
## Cycloaddition Reactions involving Zirconocene (IV) Complexes, Species Isolobal to Organic Carbenium Ions

Victorio Cadierno<sup>a</sup>, Maria Zablocka<sup>b</sup>, Alain Igar<sup>a</sup>,  
Jean-Pierre Majoral<sup>a</sup>, Aleksandra Skowronska<sup>b</sup>

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*b) Centre of Molecular and Macromolecular Studies of Lodz, Polish Academy of Sciences,  
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Examination of the known chemistry of anionic metallocene chemistry of complexes of type **I** shows that these five-coordinated compounds are postulated as intermediates in a number of stoichiometric and catalytic reactions. Only very few of these metal species have been spectroscopically and structurally characterized. Most of these compounds exhibit electrostatic anion-cation pairing resulting in dimer, trimer, oligomer, or polymeric structures. We report the preparation and structural characterization of stable zwitterionic monomeric species through [2 + 3] cycloaddition reactions involving various acetylenic systems, aldehydes or heterocumulenes and the 2-phosphino-1-zircona-indene **II** or through [1 + 3] cycloaddition reactions involving various azides and the complex **II**.

**I****II**

## Zirconium Reagents as tools in Phosphaorganic Chemistry

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Jean-Pierre Majoral<sup>b</sup>, Aleksandra Skowronska<sup>a</sup>

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Stenkiewicza 112 90-362 Lodz - Poland*

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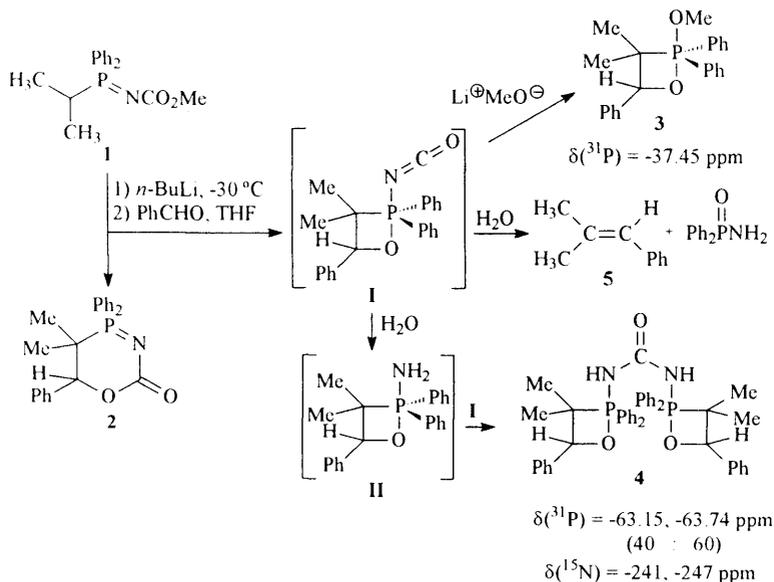
Reductive elimination reactions are among the most valuable processes to form carbon-carbon bonds in organic synthesis. Readily available metallacycles incorporating group 4 elements are useful tools for ring formation through a carbon-carbon coupling. We report a powerful one pot synthesis of unprecedented bi- or tricyclic  $\beta$ -phosphino-imines from  $\alpha$ -phosphino cyclic organozirconocenes and isocyanides through a process involving three successive and controlled steps : a regioselective Zr-C isocyanide insertion reaction followed by a carbon-carbon coupling reaction to form a neutral  $\eta^1$ -imine zirconocene complex and subsequent reductive elimination of zirconocene fragment  $[\text{Cp}_2\text{Zr}]$ . The synthesis of  $\beta$ -amino indenophosphines is also reported as well as the use of all these new molecules as ligands.

OLEFINATION REACTIONS THROUGH PHOSPHAZENES.  
INSIGHT INTO THE REACTION MECHANISM

*Emma Peralta Pérez, Carmen M. Andújar Sánchez, Isidro Pérez Álvarez and  
Fernando López Ortiz*

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Lithiated *P*-diphenyl(alkyl)(*N*-methoxycarbonyl)phosphazenes have been found to afford olefins quantitatively in their reaction with aldehydes and ketones.<sup>[1]</sup> The diphenylphosphoramidate side-product formed is easily eliminated. The *Z* isomer is obtained preferentially, although the stereoselectivity of the process is relatively low (75 : 25). We present here the identification and full characterization by multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, and <sup>31</sup>P) of the oxaphosphetanes **3** and **4** formed when *P*-diphenyl(1-methylethyl)(*N*-methoxycarbonyl)phosphazene and benzaldehyde are used as starting materials. Based on the structure of these intermediates a mechanism is proposed for the synthesis of tri- and tetra-substituted alkenes mediated through phosphazenes.



*References*

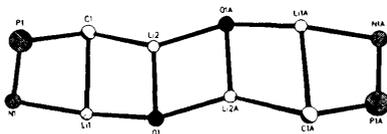
- [1] E. Peralta-Pérez, F. López-Ortiz, manuscript in preparation.

STRUCTURAL STUDY AND SYNTHETIC APPLICATIONS OF LITHIATED  
PHOSPHAZENES COMPLEXED WITH STERICALLY HINDERED LITHIUM PHENOLATES.

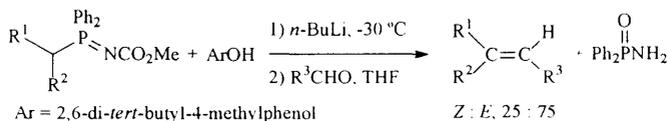
Ignacio Fernández<sup>#</sup>, Richard D. Price<sup>§</sup>, Emma Peralta Pérez<sup>#</sup>, Baudilio Tejerina,  
Matthew G. Davidson<sup>§</sup>, John. A. Cowart<sup>§</sup>, Andrés E. Goeta<sup>§</sup>, Judith A. K. Howard<sup>§</sup>, and  
Fernando López Ortiz<sup>#</sup>

Area de Química Orgánica, Universidad de Almería, 04120 Almería, Spain<sup>#</sup> and Department of  
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The role of lithium salts on the reactivity of phosphorus-stabilized anions and the mechanism of interaction of these carbanions with electrophiles remains a challenging problem.<sup>[1]</sup> We describe here the solid-state and solution structure of the complex obtained in the metallation of *P*-diphenyl(methyl)(*N*-phenyl)phosphazene in the presence of equimolar amounts of 2,6-di-*tert*-butyl-4-methylphenol in toluene. The X-ray structure is the first example of the formation of a mixed dimer giving rise to a ladder arrangement of the phosphazene and phenol linked by lithium cations. The NMR studies show that the solid-state structure is retained in toluene solution. At low temperature the symmetry is lost probably due to steric hindrance arising from the *tert*-Bu groups and some conformational equilibria are observed.



The complexation of metallated phosphazenes with phenolates produce a large decrease in their reactivity and stereoselectivity when they react with aldehydes. However, using *N*-methoxycarbonyl phosphazenes under the same reaction conditions an inversion of the stereoselectivity is observed, compared with the reaction carried out in the absence of phenolate. In this way, olefins enriched in the *E* isomer can be obtained.



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## SOLUTION AND SOLID-STATE STRUCTURES OF MODIFIED WITTIG-REAGENTS

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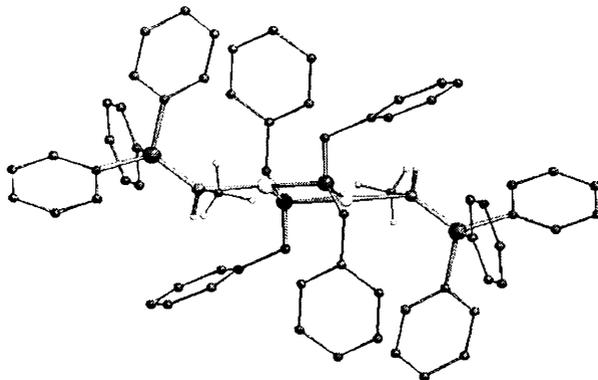


Fig. 1 A phosphonium ylide complexed-lithium amide

Recently we have been interested in the chemistry of s-block metals complexes of phosphonium ylides<sup>1</sup> and iminophosphoranes.<sup>2,3</sup> We have shown that phosphonium ylides can behave as neutral Lewis base donors to alkali metals and that stoichiometric 1:1 complexes can be isolated.

Herein we report the solid-state structures (Fig. 1) of several alkali metal complexes, together with a study of their solution-state dynamics. A study of the effect of lithium complexation on the stereochemical outcome of the Wittig reaction is also presented.

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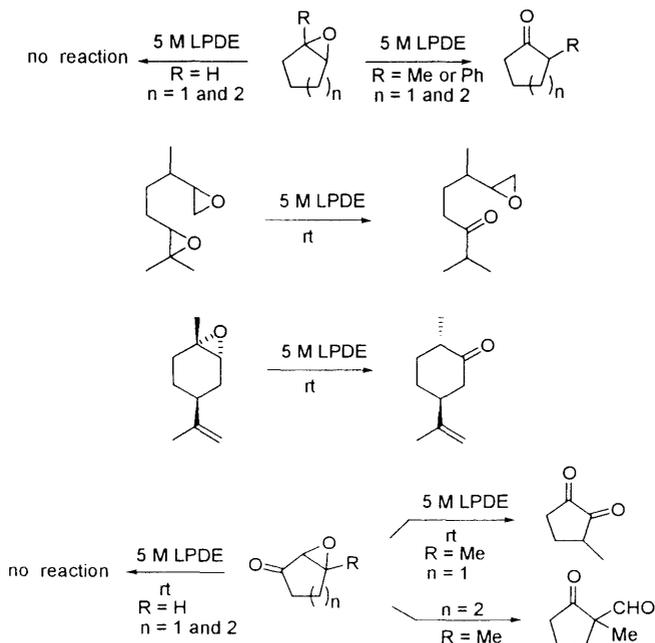
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# HIGHLY SELECTIVE CONVERSION OF EPOXIDES TO CARBONYL COMPOUNDS IN LITHIUM PERCHLORATE-DIETHYL ETHER MEDIUM

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Conversion of an epoxide to a carbonyl compound is a synthetically very useful reaction. However the lack of chemo-, regio- and stereoselectivities in the ring opening step can limit the use of this reaction in synthetic sequences. We find that epoxides from simple olefins and  $\alpha,\beta$ -unsaturated carbonyl compounds are not only activated in a highly selective manner depending upon the structure of the epoxide but also undergo rearrangement in a very selective manner when carried out in 5 M lithium perchlorate-diethyl ether (5 M LPDE) medium. The following examples illustrate the selectivities observed during the epoxide rearrangement. The mild Lewis acidity of lithium ion in 5 M LPDE is responsible for the observed selectivities.



## THE REACTIONS OF 4H-SELENOPYRANS WITH HALOGENS

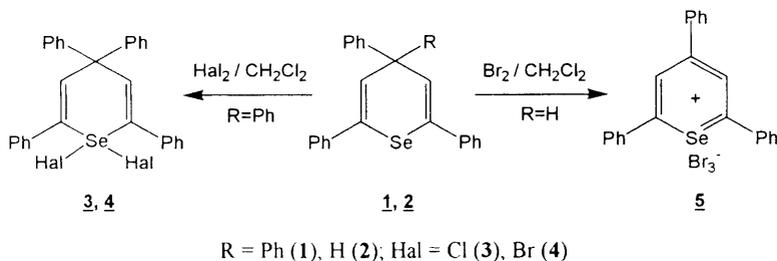
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It is known that 4H-thiopyrans react with halogens forming thiopyrylium salts or the halogen addition products to the double bonds of thiopyrylium ring<sup>[1]</sup> 1,1-Dihalogen derivatives have been isolated only for 4H-telluropyrans with sp<sup>2</sup>-carbon at C<sup>4</sup>-position.<sup>[2,3]</sup> 4,4-Diaryl-substituted 4H-pyrans and thiopyrans form the products of hydrogen substitution at C3-position<sup>[4,5]</sup> The aim of present work was the study on the reaction of arylsubstituted 4H-selenopyrans **1** and **2** with halogens.

It is established that 2,4,4,6-tetraphenyl-4H-selenopyran **1** reacts with chlorine and bromine in dichloromethane giving corresponding 1,1-dichloro- or 1,1-dibromoderivatives **3** and **4** with high yields (83 and 94%). The reaction is found to be reversible and it takes the excess amount of halogen for more complete conversion of the initial selenopyran **1**. 2,4,6-Triphenyl-4H-selenopyran **2** reacts with bromine forming 2,4,6-triphenylselenopyrylium tribromide **5** (yield 69%).



The results obtained show that 1,1-dihalogen derivatives of 4H-selenopyran **1** are more stable compared to halogen derivatives of 4H-thiopyran.

The mechanism of salt **5** formation is discussed.

## References:

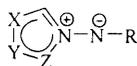
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## HYDROPEROXY-INDUCED RING ENLARGEMENT OF N-ACCEPTORFUNCTIONALIZED AZOLIUM-N-IMIDES

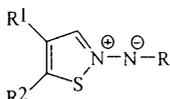
*Arne Kolberg<sup>1)</sup>, Lothar Hennig<sup>1)</sup>, Bärbel Schulze<sup>1)</sup>, L. L. Rodina<sup>2)</sup>*

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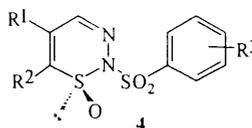
Azolium imides (AI) exhibit high reactivity and are widely used in the synthesis of heterocyclic ring systems.<sup>[1]</sup> One synthetic approach to AI **1** is the direct ring closure of hydrazones by means of condensation and oxidation. By this pathway were recently also prepared stable heteroaromatic isothiazolium N-imides **2** and **3** via ring closure of  $\beta$ -thiocyanatovinylaldehyde hydrazones.<sup>[2]</sup>



**1**  
X, Y, Z = N  
X or Z = S



**2**: R = R<sup>3</sup>-C<sub>6</sub>H<sub>4</sub>CO  
**3**: R = R<sup>3</sup>-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>  
R<sup>1</sup>, R<sup>2</sup> = CH<sub>3</sub>, CH<sub>3</sub>, (CH<sub>2</sub>)<sub>4</sub>



**4**

Isothiazole-2-imides **2,3**, which are N-acceptor substituted, are oxidized with hydrogen peroxide in acetic acid. The oxidation of N-benzoylimides **2** with hydrogen peroxide (30%) gave stable five-membered 3-hydroperoxysultams, respectively.

Surprisingly, stable 1,2,3-thiadiazine-1-oxides **4** are obtained by the oxidation of N-benzene-sulfonylimides **3** as hydroperoxy-induced ring enlargement products. The mechanism of the oxidation will be discussed.

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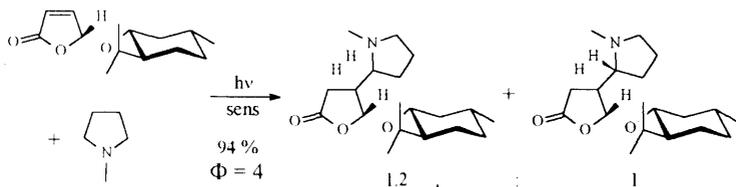
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## Efficient Radical Addition of Tertiary Amines to Electron Deficient Alkenes Initiated by a Photochemical Electron Transfer

Samuel Bertrand, Norbert Hoffmann, Jean-Pierre Pete

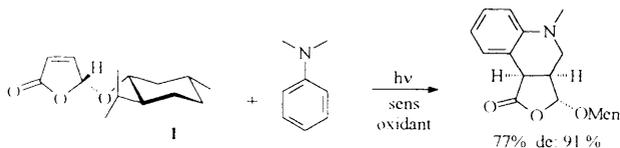
Université de Reims Champagne Ardenne, Laboratoire de Réactions Sélectives et Applications  
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We became interested in the radical addition of tertiary amines to alkenes because a lot of natural products and compounds with important biological activities should be available by this process. When initiating the radical chain reaction by a photochemical induced electron transfer using conventional sensitizers like benzophenone, we could isolate the desired products only with low yields as known for a long time.<sup>[1]</sup> However, applying electron donor substituted aromatic ketones (e.g. 4,4'-dimethoxybenzophenone) as sensitizer, the reaction became quite efficient as well as product yields and quantum yields are concerned (Scheme 1).<sup>[2]</sup>



**Scheme 1**

More interestingly, the new reaction conditions can be applied to radical tandem processes (Scheme 2). During the addition process of N,N-dialkylaniline derivatives to the furanone **1**, a rearomatization process takes place. In order to optimize the reaction, we have studied details of this mechanistical step by isotopic labeling of the N,N-dimethylaniline.



**Scheme 2**

### Literature

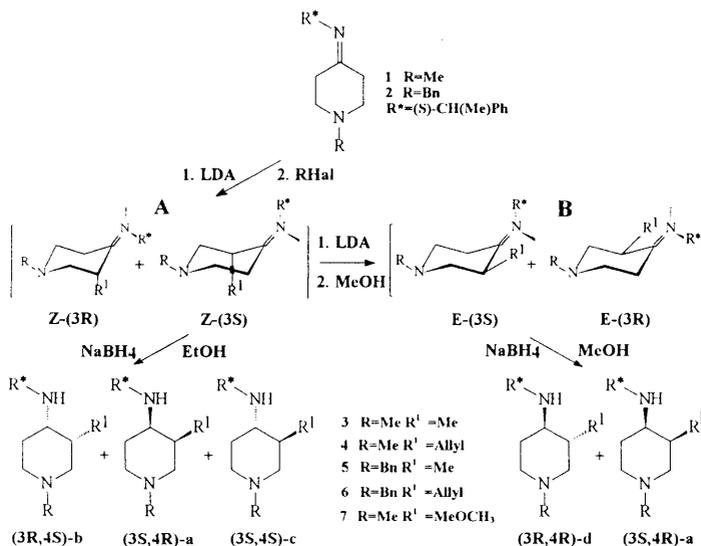
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CHIRAL CIS- AND TRANS-3-ALKYL-4-AMINOPIPERIDINES. A NOVEL EFFICIENT  
ASYMMETRIC SYNTHESIS AND STEREOCHEMISTRY

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4-Aminopiperidine derivatives have found many applications for producing biologically active and medicinal compounds, especially novel potent analgesics. The first efficient asymmetric synthesis of the optically pure trans-(3S,4S)-c and optically active cis-diastereomeric pair (3S,4R)-a, (3R,4S)-b of N-substituted 3-alkyl-4-aminopiperidines 3 a,b,c -7a,b,c is developed. The key step of this method is the sequence of two reactions as an one-pot process, namely: the alkylation of the conformationally fixed imine 1, 2 anions by alkyl halides and the reduction of prochiral C=N bond in the 3-alkylated imine [Z-(3S) and Z-(3R) intermediate (A) with NaBH<sub>4</sub>/C<sub>2</sub>H<sub>5</sub>OH. The cis-(3S,4R)-a and trans-(3R,4R)-d diastereomers with 90% and 96% diastereomeric purities respectively are obtained by the NaBH<sub>4</sub>/MeOH reduction of the E-(3S) and E-(3R) 3-alkylated imine [intermediate B], arisen at metalation of the intermediate A by LDA at -78° C. The stereochemistry of the asymmetric synthesis of optically active cis and trans isomers of the 3-alkyl-4-aminopiperidines is discussed.

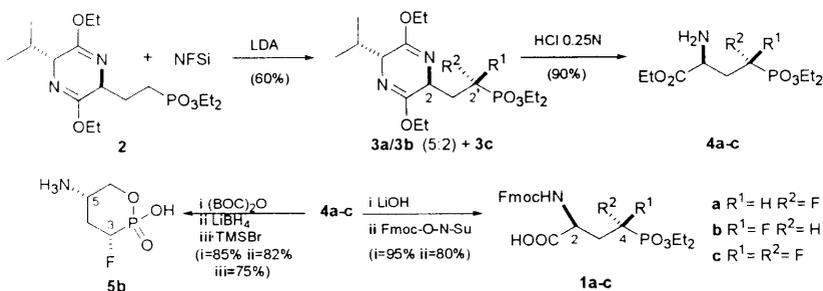


ASYMMETRIC SYNTHESIS OF  $\alpha$ -FLUORINATED PHOSPHONOSERINE SUITABLY PROTECTED FOR SOLID-PHASE PEPTIDE SYNTHESIS (SPPS)

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$\alpha$ -Fluorophosphonates have been recognized as particularly effective hydrolytically stable mimics for naturally occurring phosphates.<sup>[1]</sup> As part of a project directed toward the design of new bioactive phosphonates,<sup>[2]</sup> we report here the diastereoselective synthesis of ( $\alpha$ -fluoromethyl)phosphonates **1a-c** analogues of L-phosphoserine suitably protected for Fmoc-SPPS



In this way, slow addition of LDA to an equimolar solution of *N*-fluorobenzenesulfonimide (NFSi) and bislactim ether **2** at low temperature led to the selective formation of 2'-fluorinated compounds **3a-c**. After flash chromatography separation, mild acid hydrolysis of the bislactim ether provided the amino esters **4a-c** in excellent yield. Chemoselective hydrolysis of the carboxylic ester followed by *N*-Fmoc protection under standard conditions enabled the isolation of the fluorophosphono amino acids **1a-c**. Compound **4b** was converted into the cyclic derivative **5b**, in order to study the relative stereochemistry by NOEDS analysis. As **5b** resulted to be a crystalline solid amenable to X-ray structure determination, a 3,5-*cis* (2,4-*syn*) configuration was established for the minor monofluorinated compound **5b** (**1b**).

*Financial support from CYT (SAF 970184) and Xunta de Galicia (XUGA 10306098) is gratefully acknowledged. J. J. Guillín wishes to thank MEC for a FPU fellowship.*

References:

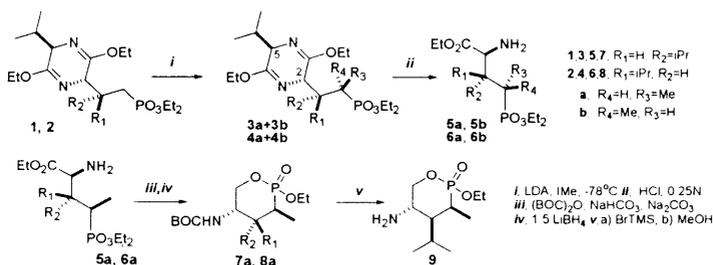
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SYNTHESIS OF 2-AMINO-3-ISOPROPYL-4-METHYLPHOSPHONOBUTANOIC ACID  
DERIVATIVES

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As part of a project directed to the design of new bioactive phosphonates,<sup>[1]</sup> in this communication we report the synthesis of 2-amino-3-isopropyl-4-methylphosphonobutanoic acid derivatives from the bislactim ethers **1** or **2**. In this way, the lithium salts derived from **1** or **2** reacted regio and stereoselectively with methyl iodide leading to epimeric mixtures of the corresponding 2'-methylated products **3a+3b** or **4a+4b** in a 3.5:1 or 5.5:1 ratio, respectively. The *anti/syn* selectivity in the 2'-substitution was determined by analysis of <sup>31</sup>P-NMR spectra of the crude reaction mixtures. Retention of configuration at C-2 and C-5 during the substitution process indicates the absence of interchange in metal position after deprotonation.



Mild acid hydrolysis of the mixture of bislactim ethers **3a+3b** or **4a+4b** gave rise to the amino esters mixtures **5a+5b** or **6a+6b** that could be separated by chromatography. As previously reported for similar cases,<sup>[2]</sup> conversion of the major amino esters **5a** or **6a** into cyclic derivatives **7a** or **8a** and **9** allowed the determination of the stereochemical course of the methylation. Fortunately, *N*-Boc derivative **7a** was a crystalline solid amenable to X-ray structure determination. On the other hand, deprotection of **8a** provided oxaphosphorinane **9**, suitable for its analysis by NOE Difference Spectroscopy. Thus, X-ray analysis and NOEDS confirmed the 2,2'-*anti* configuration for major compounds **3a** and **4a** obtained by the electrophilic methylation of bislactim ethers **1** and **2**.

Financial support from CICYT (SAF 970184) and Xunta de Galicia (XUGA 10306098) is gratefully acknowledged. Aniana Diaz thanks U.D.C. for a doctoral fellowship.

*References:*

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## SYNTHESIS OF ACTIVE MIFEPRISTONE DERIVATES

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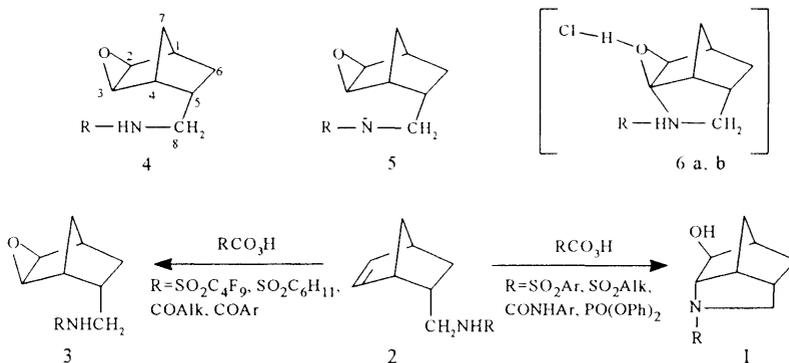
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The aim of this study was the synthesis of active mifepristone derivatives bearing a spacer at position 6 of the steroid scaffold. These compounds should be used to target anticancer drugs to tumour cells expressing high levels of steroid receptors. Since a direct derivatisation of mifepristone at this position was impossible, the steroid moiety itself had to be synthesised from suitable precursors. Accordingly, *2-hydroxymethylene-6-methoxytetralone* (**2**) was generated in the first step of the synthesis, containing "the modification of ring C", by formylation of *6-methoxytetralone* (**1**), which contributes ring B and C to the steroid scaffold. (**2**) was then reacted with hydroxylamine to give *6-methoxy-3,4-dihydronaphthal[2,1d]isoxazole* (**3**). After the opening of the heterocyclic five-membered ring and, without isolation of *2-cyano-6-methoxytetralone* (**3**), *2-cyano-2-methyl-6-methoxytetralone* (**4**) was obtained by methylation. The key step in the second part of the synthesis ("construction of ring D") was the reaction of (**4**) with diethylsuccinate via a Stobbe condensation to *3-keto-7-methoxy-3a-methyl-3,3a,4,5-tetrahydro-2H-cyclopentaen[a]naphthaline-1-carboxylic acid ethylester* (**5**). Reduction, saponification and decarboxylation of (**5**) yielded *7-methoxy-3a-methyl-3,3a,4,5-tetrahydro-2H-cyclopentaen[a]naphthaline-3-ol* (**8**), which was further reduced to *7-methoxy-3a-methyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthaline-3-ol* (**9**) with molecular hydrogen. The first step of the third part of the synthesis ("modification of ring B") was the introduction of a functional group via chloromethylation of (**9**) (Blanc-reaction). After hydrolysis *8-hydroxymethyl-7-methoxy-3a-methyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthaline-3-ol* (**10**) was obtained, which enables a physiologically stable ether linkage via the hydroxymethyl-group. This yielded exclusively the desired product (**10**) and substitution at position 6 of (**9**) was never observed. The following Birch-reduction and the final oxalacid hydrolysis enabled the isolation of *8-hydroxymethyl-7-methoxy-3a-methyl-2,3,3a,4,5,6,9,9b-octahydro-1H-cyclopenta[a]naphthaline-3-ol* (**12**), constituting the last step of the third part of the synthesis. The fourth part of the synthesis will include the construction of the ring A of the steroid scaffold, and the fifth part will include the substitution at position 11 $\beta$  and 17 $\alpha$  of the steroid scaffold to produce the completed functionalised mifepristone derivative.

## EXPERIMENTAL AND THEORETICAL INVESTIGATION OF AZABRENDANE SYSTEMS FORMATION

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Azabrendanes (1) formation is a result of intramolecular cyclization that occurs during epoxidation of aminomethylnorbornene derivatives bearing endo-oriented substituents (2). Analgesic, antiphlogistic and antidiuretic activities have been discovered for compound (1) ( $\text{R}=\text{SO}_2\text{C}_6\text{H}_4\text{NO}_2\text{-p}$ ).

It has been established that sulfonamides derived from norbornene turn into azabrendanes under the influence of epoxidizing agents excepting the compounds that contain electron-seeking perfluorosulfonyl group  $\text{SO}_2\text{C}_4\text{F}_9$  and cyclohexylsulfonyl group. The latter turn into epoxides (3) under influence of peroxy acids. During the epoxidation of aryl ureas ( $\text{R}=\text{CONHAr}$ ), we came across with formation of corresponding azabrendanes. However, no cases of intramolecular cyclization have been observed in similar reactions of numerous group of carboxamides ( $\text{R}=\text{COAlk}$ ,  $\text{COAr}$ ). Epoxides that are not caused to heterocyclization in reaction conditions appeared to be the products of this process. The structures of oxidation products (2, 3) have been confirmed using NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectroscopy including two-dimensional spectra. In some cases X-ray diffraction analysis data have been used.

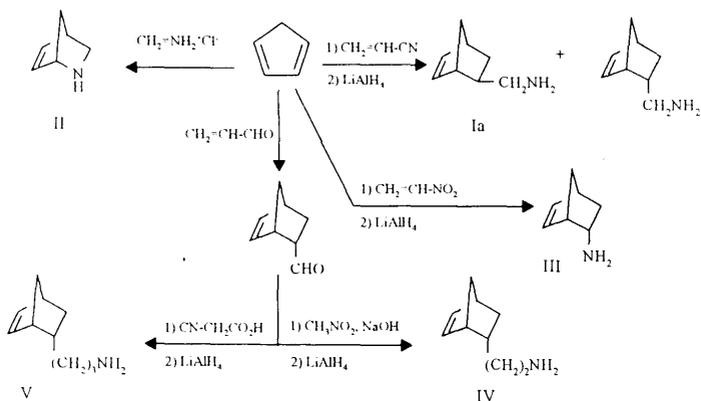
To clear up factors that influence upon chemical behavior of various epoxy norbornanes in this reaction, potential energy surface for heterocyclization of neutral molecule, proper anion and for cyclization with acid activation of epoxide oxygen atom in gaseous phase and with regard of solvent influence (model 4, 5, 6a, b, respectively) has been studied. Results of quantum chemical calculations using (6b) model (PM3 method) have shown the best correspondence to experimental data. For molecules of epoxides undergoing cyclization, the following values of activation enthalpies have been obtained (kilojoule per mole):  $\text{R}=\text{SO}_2\text{CH}_3$ , 93.64;  $\text{SO}_2\text{C}_6\text{H}_5$ , 118.70;  $\text{CONHC}_6\text{H}_5$ , 130.21;  $\text{CH}_2\text{C}_6\text{H}_5$ , 35.90;  $\text{PO}(\text{OC}_6\text{H}_5)_2$ , 107.36. At the same time, the similar values that are calculated for carboxamides exceed 133 kJ/mole. This level corresponds with real situation and therefore confirms the reasonableness of model chosen.

## BIOLOGICALLY ACTIVE DERIVATIVES OF AMINES WITH THE CARCASS FRAME

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In the recent years we have shown that some derivatives of stereoisomeric amines (**Ia**, **Ib**) possess valuable neurotropic properties. For extension of compounds range as well as for investigation of influence of the distance between amino group and bicyclic frame on biological activity, we synthesized a series of amines (**II-V**) with the various distance of amino-group from a carcass.



On the base of amines (**II-V**) in mild conditions new derivatives (sulfonamides, amides, ureas, thioureas, etc.) have been obtained. The structures of the compounds have been confirmed using IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Interesting data of biological tests have been obtained. Under study of the neurotropic activity of compounds, the sulfonamidic derivatives have been examined more significantly. It has been found that sulfonamides derived from amine (**II**) have higher tranquilizer activity. Analgesic and anticonvulsive effects are more characteristic for sulfonamides derived from amine (**Ib**). For amines (**Ia**, **b**) the data about influence of substituent character at the amino-group (sulfonamide, carboxamide or urea) on biological activity have been obtained too.

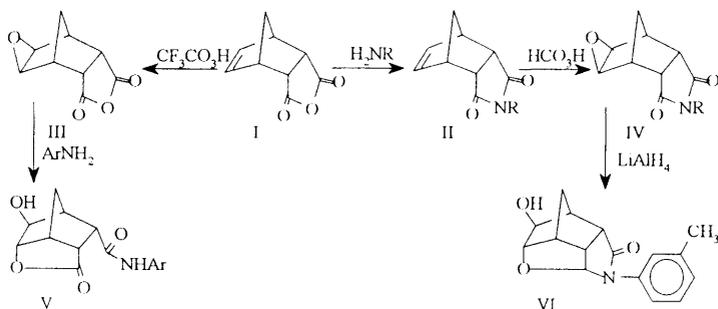
HETEROCYCLIZATION OF EPOXY DERIVATIVES OF NORBORN-2-ENE-ENDO-5, 6-DICARBOXYLIC ACID ANHYDRIDE AND IMIDES

*Lilia I. Kasyan, Oxana V. Krishchik, Andrey O. Kasyan\**

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The cases of heterocyclization of unsaturated dicarboxylic acids derived from norbornene in reactions with electrophilic reagents are widely known. In contrast to oxygen-containing cyclization products, the nitrogen-containing polycyclic systems are not studied enough and presumably can be biologically active substances.



The aim of this work is the obtaining of new groups of nitrogen- and oxygen-containing substances with use of epoxy derivatives of endic anhydride (**I**) and aromatic imides of norbornene series (**II**).

The epoxidation of alkenes by strong peracids results in epoxides (**III**, **IV**) with a quantitative yield. Amines and lithium aluminium hydride have been selected as nucleophilic reagents resulting into chemoselective reacting of electrophilic centers of the substituent. The reactions were concluded by intramolecular rear attack of intermediate on electrophilic centers of oxiranes.

The experiments on reduction of epoxides **IV** have shown that the structure of reaction product depends on properties of the substituent at nitrogen atom, solvent properties and reaction temperature. Aryl substituent prevents with full reduction of an imide fragment. The reduction of epoxide (**IV**,  $\text{R}=\text{C}_6\text{H}_5\text{CH}_3\text{-m}$ ) has resulted in formation of new polycyclic system with two heteroatoms — substituted 6-aza-4-oxatetracyclo[5.2.1.1.3.5]undecane (**VI**). The structures of the substances are confirmed on basis of IR spectra, NMR  $^1\text{H}$  and  $^2\text{D}$  spectra analysis; for substance **VI**, X-ray crystal analysis data have been obtained.

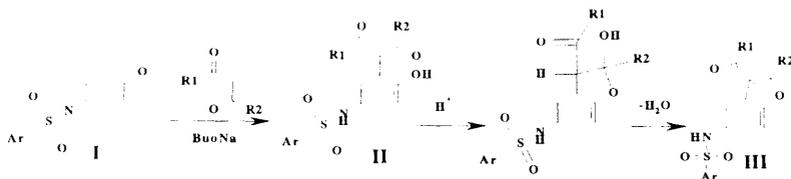
FEATURES OF INTERACTION OF N-ARYLSULFONYL - 1,4 -  
BENZOQUINONEMONOIMIDES WITH A BENZOYLACETONE.

*Natalya V. Velichko . Aleksandr N. Vasylenko.*

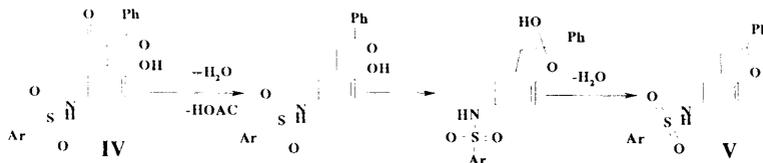
“Stan” Ltd. 343922 Przevalsky St. 3, Kramatorsk, Donetsk reg., Ukraine.

Tel (380 0626) 415265 – e-mail: stan@kuv.ins.dn.ua

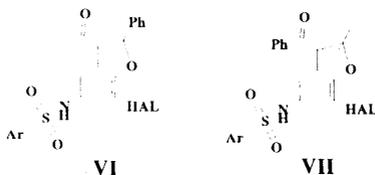
Interactions of N - arylsulfonyl - 1,4-benzoquinonemonoimides (**I**) with 1,3 diketones and 1,3 ketoesters is not limited typical for this class of compounds to 1,4 addition to system of the conjugated quinones connections. The adducts (**II**) in acid environment undergo further intramolecular cyclisation, forming derivative benzofuran (**III**).



While studying of interaction of (**I**) with a benzoylacetone a major product has unexpectedly appeared to be compound (**V**) i.e. as it was expected acetic group mainly attaches a proton, but at a stage of attack of a OH - group, water appears to be competitive and there is diketone splitting and subsequent product cyclisation. It is necessary to add, that attempt to get product (**V**) by interaction (**I**) with an acetophenone, was unsuccessful.



To change speeds ratios of hydrolysis and intramolecular attack of a hydroxyle of an amidophenol ring is possible by introduction of a halogen in ortho - position to OH- group. During treatment with HCl an adduct 2 - chloro(bromo) - N-arylsulfonyl - 1,4 - benzoquinonemonoimides with a benzoylacetone is resulting products are (**VI**) and (**VII**).



## A NEW SYNTHESIS OF

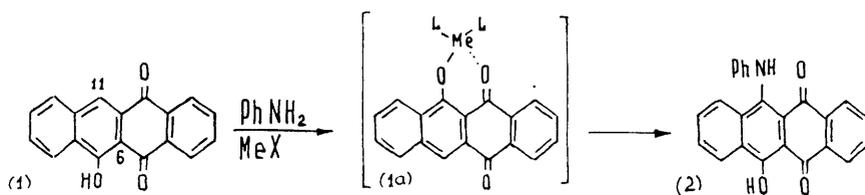
6-HYDROXY-11-PHENYLAMINO-5,12-NAPHTHACENEQUINONE FROM  
6-HYDROXY-5,12-NAPHTHACENEQUINONE PROMOTED BY METAL IONS

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The reaction of 6-hydroxy-5,12-naphthacenequinone (1) (HNO) with aniline in the presence of some metal ions and atmospheric oxygen leads to 6-hydroxy-11-phenylamino-5,12-naphthacenequinone (2). The activity of metal ions decreased in following order:  $\text{CuClIIO} > \text{MnClIIO} > \text{CoClIIO} > \text{CrClIIO} > \text{NiClIIO} > \text{CeClIIO}$ .



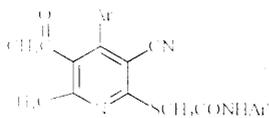
The effects of mole ratio and complex anions of copper(II) salts, the kind of the solvent, atmosphere on the 11-phenylamination of the HNO were studied. A possible mechanism involving the formation of a metal complex (1a), in which the HNO coordinates with the metal ion, followed by the nucleophilic attack of amine at the 11 position and the oxidative abstraction of the hydride anion by atmospheric oxygen is proposed.

**SYNTHESIS OF SOME NEW THIENOPYRIDINES,  
PYRIDOTHIENOPYRIMIDINES AND PYRIDOTHIENOTRIAZINES  
WITH ANTICIPATED BIOLOGICAL ACTIVITY**

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Assiut 71516, Egypt

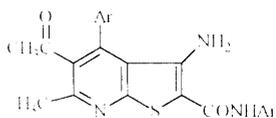
The versatile applications of thienopyridines<sup>1</sup>, pyridothienopyrimidines<sup>2</sup> and pyridothienotriazines<sup>3</sup> promoted us to synthesis other new derivatives with expected biological and medicinal importance. Thus, the reaction of 5-acetyl-4-aryl-3-cyano-6-methylpyridine-2(1H)-thiones (**1a-c**) with N-arylchloroacetamides gave the corresponding N-(aryl)-carbamoylmethylthio-derivatives **2a-i**. The latter compounds underwent intramolecular Thorpe-Ziegler cyclization to give the promising thieno [2,3-b]pyridine derivatives **3a-i** upon treatment with sodium ethoxide in boiling ethanol. The compounds **3a-i** were subjected to some reactions to produce several new pyrido [3',2':4,5]thieno[3,2-d]pyrimidines **4-6a-i** and pyrido[3',2':4,5]thieno[3,2-d][1,2,3]triazines **7a-i**.



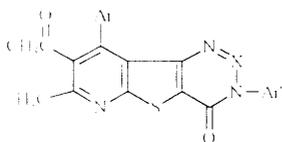
**2a-i**

Ar = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, OMe, C<sub>6</sub>H<sub>4</sub>-Cl(p)

Ar' = Ph, C<sub>6</sub>H<sub>4</sub>, Me(p), C<sub>6</sub>H<sub>4</sub>-Cl(p)

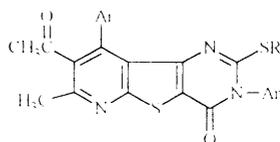


**3a-i**



**4a-i, R = CH<sub>3</sub>**

**7a-i, R = N**



**5a-i, R = H**

**6a-i, R = CH<sub>3</sub>**

1. G. Wagner; H. Vieweg; J. Prantz; S. Leistner; Pharmazie, **48** (3), 185 (1993).
2. G.D. Madding; M.D. Thompson; J. Heterocyclic Chem., **24**, 581 (1987).
3. G. Wagner; S. Leistner; H. Vieweg; V. Krassel and J. Prantz; Pharmazie, **48** (7), 514 (1993).

NEW FUSED PYRAZINES. SYNTHESIS OF PYRIDO[3',2':4,5]THIENO[2,3-E]  
PYRROLO[1,2-A] PYRAZINE DERIVATIVES

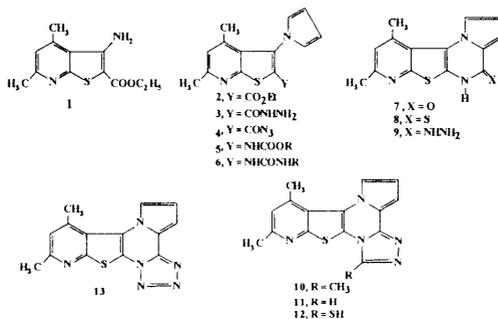
*A.M. Kamal El-Dean, A. A. Geies and H. S. El-Kashef*

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In continuation of our program in the synthesis of heterocyclic compounds including thienopyridine moiety<sup>(1,2)</sup> herein we report the synthesis of some thienopyridine fused with other heterocyclic systems.

Ethyl 4,6-dimethyl-3-(pyrrol-yl)thieno[2,3-b]pyridine-2-carboxylate **1** which obtained by the interaction of the thienopyridine aminoester **1** with 2,5-dimethoxy tetrahydrofuran, was converted into the corresponding carbohydrazide **3** by its treatment with hydrazine hydrate. Upon treatment **3** with nitrous acid gave carboazide **4**. Carboazide **4** underwent Curtius rearrangement into, carbamates **5**, ureas **6** or into pyridothienopyrrolopyrazine **7** upon heating with alcohols, amines or in inert solvent. pyridothienopyrrolopyrazine **7** was converted into corresponding thione derivative **8** using P<sub>2</sub>S<sub>5</sub>/pyridine, which was reacted with hydrazine hydrate to produce hydrazino derivative **9**. Compound **9** was reacted with different reagents such as acetic acid, triethyl orthoformate, CS<sub>2</sub>/pyridine and nitrous acid to give compounds **10-13** respectively.



*References:*

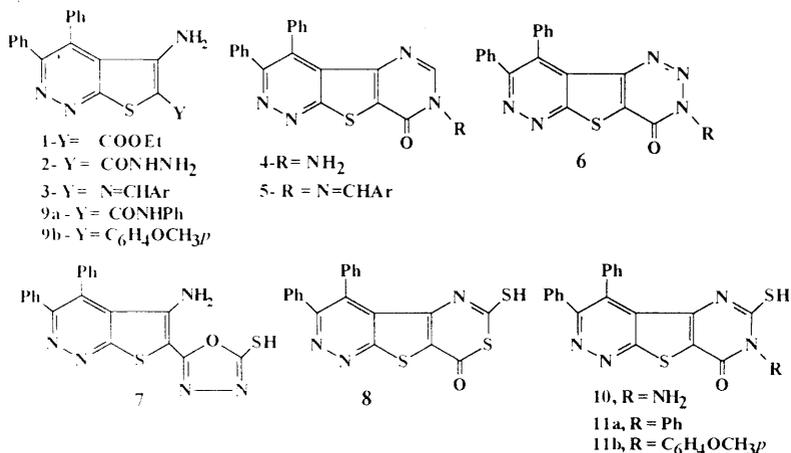
- [1] E. A. Bakhite, A. A. Geies, A. M. Kamal El-Dean and H. S. El-Kashef; *Phosphorus, Sulfur and Silicon* 1994, 104, 143.  
 [2] Adel M. Kamal El-Dean; *J. Chem. Research(M)* 1996, 1401.

## SYNTHESIS OF PYRIDAZOTHIENOTHIAZINES AND PYRIMIDOTHIENOPYRIDAZINES

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In continuation of our work in the synthesis of pyridazines and due to their biological activity here in we report the synthesis of some fused pyridazines. 2-Amino-4,5-diphenylthieno[2,3-c]pyridazine-3-carbohydrazide **2**, which was synthesized via hydrazinolysis of corresponding carboxylate compound **1**, reacted with aromatic aldehydes to produce the corresponding aryldiene carbohydrazones **3**. Both compounds **2** and **3** was reacted with triethyl orthoformate, to produce the corresponding pyrimidothienopyridazines **4**, and **5** pyridazothienotriazines **6** were prepared by reacting compounds **3** with nitrous acid. When carbohydrazide **2** allowed to react with CS<sub>2</sub> in pyridine gave the corresponding oxadiazolyl derivative **7**, while carbohydrazones **3** under the same conditions gave pyridazothienothiazines **8**. Thiazino compound **8** was reacted with hydrazine hydrate to produce pyrimidothienopyridazine **10**, also was reacted with aromatic amines to give compounds **11a,b**, which were obtained by another route by reacting carboxamide derivatives **9a,b** with CS<sub>2</sub> in pyridine.



### References

1- A. M. Kamal El-Dean, Sh. M. Radwan, Pharmazie, 53, 839 (1998).

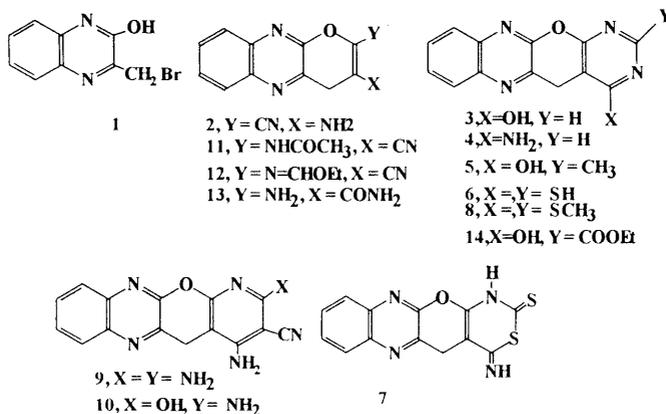
SYNTHESIS OF NEW PYRANOQUINOXALINES AND PYRIMIDO(PYRIDIO)  
PYRANOQUINOXALINES

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Due to biological activities of quinoxalines and in continuation of our work in the synthesis of heterocyclic systems including quinoxaline moiety<sup>[1-2]</sup> herein we report synthesis of pyranoquinoxalines and pyrimidopyranoquinoxalines. 3-bromomethyl quinoxalin-2(1H)one reacts with malononitrile in presence of a basic catalyst to afford pyrano[2,3-b] quinoxaline **2**. The reaction of **2** with reagents such as formic acid/ formamide, formamide acetyl chloride, carbon disulfide, acetic anhydride and orthophosphoric acid gave the fused heterocyclic systems pyrimido-[4',5':6,5]pyrano[2,3-b]quinoxalines **3-6**, **8**, **14**, while the reaction of **2** with malono-nitrile and ethyl cyanoacetate afford pyridino[2',3':6,5]pyrano[2,3-b]quinoxaline derivatives **9,10**. Also, compound **1** reacted with sodium cyanide, thiourea to gave the quinoxaline derivatives **15-18**.



*References:*

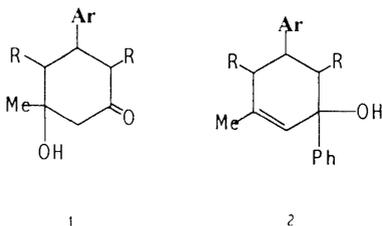
- [1] A. A. Geies, A. M. K. EL-Dean, O. S. Moustafa, *Monatshefte für Chemie*, **127**: 1263(1996).  
 [2] O. S. Moustafa, E. A Bakhite, M. Z. A Badr, *Afinidad*, **476**: 285(1998).

**THE USE OF THE GRIGNARD REAGENTS IN THE SYNTHESIS OF NEW  
CYCLOHEXENE DERIVATIVES OF POTENTIAL BIOLOGICAL  
ACTIVITY**

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Egypt.*

The reactivity of 3-aryl-2,4-dicarboxanilides-5-hydroxy-5-methylcyclohexanones **1** towards arylmagnesium halides was investigated to give the cyclohexanol derivative **2**. The formation of the Grignard products involved one molecule of  $\text{ArMgBr}$  and addition to the cyclic ketone followed by elimination of one molecule of water affording **2**.



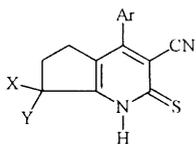
$\text{R} = \text{CONHAr}$

SYNTHESIS AND REACTIONS OF NEW CYCLOPENTA[E]THIENO[2,3-B] PYRIDINES  
AND RELATED HETEROCYCLIC SYSTEMS

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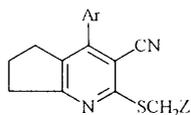
Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

The reaction of arylidencyanothioacetamide (**1a-c**) with cyclopentanone was reinvestigated and proved to give a mixture of 4-aryl-3-cyanocyclopenta[b]pyridine-2(1H)-thione (**2a-c**) and the corresponding 7-arylidene derivative **3a-c**. Compounds **2a-c** were reacted with chloroacetonitrile, ethyl chloroacetate, chloroacetamide and/or chloro-N-arylacetamides to give the promising S-substituted-methylthiopyridines **4a-l**. The latter compounds underwent intramolecular Thorpe-Ziegler cyclization to furnish the expected cyclopenta[e]thieno[2,3-b]pyridines **5a-l** upon treatment with sodium ethoxide in boiling ethanol. The compounds **5a-l** were employed as versatile synthons for condensed heterocyclic systems of the types **6,7** and **8**.



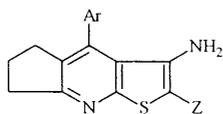
**2a-c**; X= Y= H

**3a-c**; XY= PhCH=

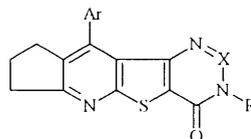


**4a-l**

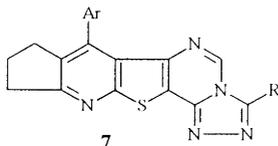
Z= CN, CO<sub>2</sub>Et, CONH<sub>2</sub>, CONHAr'



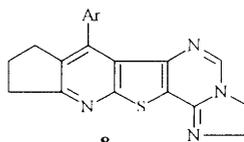
**5a-l**



**6**, X= CH, N



**7**



**8**

## BENZOQUINOLINES II. SYNTHESIS OF SOME NEW BENZO[h]PYRIMIDO[4',5':4,5]THIENO[2,3-b]QUINOLINE DERIVATIVES AND RELATED FUSED HEXACYCLIC SYSTEMS

Etify Abdel-Ghafar Bakhite

Chemistry Department, Faculty of Science, Assiut University,

Assiut 71516, Egypt

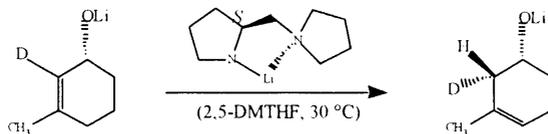
Reaction of 8-amino-7-(2-furyl)-5,6-dihydrobenzo[h]thieno[2,3-b]quinoline-9-carbonitrile (**3a**) with phenyl isothiocyanate, triethyl orthoformate, ethylenediamine and/or sodium azide afforded benzo[h]thieno[2,3-b]quinolines **4**, **7**, **20** and **25** respectively. Cyclization of thiourea derivative **4** furnished thioxopyrimidine derivative **5**. The dithioxopyrimidine **6** was prepared by reaction of **3a** with carbon sulfide. On treatment of **7** with hydrazine hydrate, 10-amino-7-(2-furyl)-11-imino-5,6,10,11-tetrahydrobenzo[h]pyrimido[4',5':4,5]thieno[2,3-b]quinoline (**8**) was obtained. Compounds **8**, **20** and **25** were used as key intermediates in the synthesis of the fused hexacyclic compounds **11-14**, **21-24** and **26-28** respectively. 8-Amino-7-(2-furyl)-5,6-dihydrobenzo[h]thieno[2,3-b]quinoline-9-carboxamide (**3b**) was reacted with some reagents namely, triethyl orthoformate, benzaldehyde, carbon disulfide, phenyl isothiocyanate, and/or acetic anhydride to give the corresponding benzo[h]pyrimido[4',5':4,5]thieno[2,3-b]quinolines **29**, **30**, **31**, **32** and **34**. Compound **29** underwent some sequence reactions to give **37-42**. Some of the prepared compounds were tested *in vitro* for their antibacterial and antifungal activities.

MECHANISTIC STUDIES OF SOLVENT INDUCED STEREOSPECIFIC ISOMERIZATION OF  
AN ALLYLIC ALCOHOL TO A HOMOALLYLIC ALCOHOL CATALYZED BY A CHIRAL  
LITHIUM AMIDE

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The isomerization of the lithium alkoxide of 3-methyl-2-cyclohexene-1-ol to the lithium alkoxide of 3-methyl-3-cyclohexene-1-ol is induced on changing the solvent from tetrahydrofuran to *e.g.* *cis*-2,5-dimethyltetrahydrofuran. The solvent induced isomerization has been shown to be 100 % stereospecific and close to 100 % intramolecular by deuterium labelling experiments.<sup>[1]</sup>



Further investigations of the details of the mechanism are being performed to answer the following questions: Does the proton transfer take place suprafacially or antarafacially? Is the rearrangement selective with respect to any one of the two protons in the 4-position of **1**? Is the abstracted proton delivered back to the carbon *syn* or *anti* to the oxygen on the ring? Results obtained so far will be presented.

*References:*

- [1] Arvidsson, P. I., Hansson, M., Khan, A. Z-Q., Ahlberg, P. *Can. J. Chem.* **1998**, 76, 795-799

## NMR STUDIES OF CHIRAL LITHIUM AMIDOCUPRATES

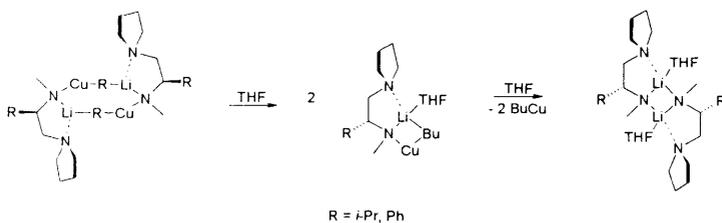
*Johan Eriksson, Per I. Arvidsson and Öyvind Davidsson*

Organic Chemistry, Department of Chemistry,  
 Göteborg University, SE-412 96 Göteborg, Sweden  
 eken@oc.chalmers.se

Since their discovery, the Gilman reagents have had a wide application in synthetic organic chemistry. This usefulness gave chemists a quest, finding a way to make the 1,4-addition to enones enantioselective. Two of the numerous chiral ligands that have been found is shown below.



We have examined the behaviour of these two chiral lithium amidocuprates in different solvent (diethyl ether, tetrahydrofuran (THF) and tetrahydrothiophene (THT)) using multinuclear NMR. We have shown that the complex is a dimer in etheral solution that disintegrate via a copper containing monomer to a copper free lithium amide dimer when THF is added (Scheme 1). Furthermore the study show that one of the Li atoms is much more prone to coordinate THF.



Scheme 1

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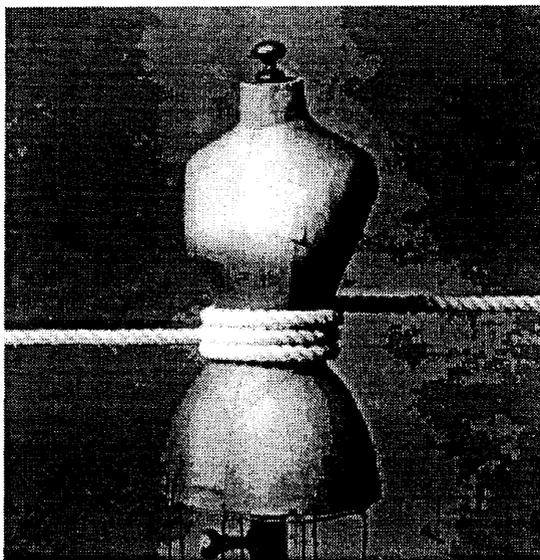
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► Vielleicht haben Sie sich ja längst in die schönen Augen der E-Klasse verguckt. Aber übersehen Sie deshalb nicht Ihre inneren Werte: Ihre Großzügigkeit im Kopf- und Beinraum zum Beispiel oder die Anschmiegsamkeit der körpergerechten Sitze. Ihre Window- und Fond-Sidebags werden Sie hoffentlich niemals sehen, die öffnen

sich nur bei einem Seitenaufprall zu Ihrem Schutz. Fahren Sie die E-Klasse doch mal Probe. Arrangieren Sie mit uns ein Rendezvous.



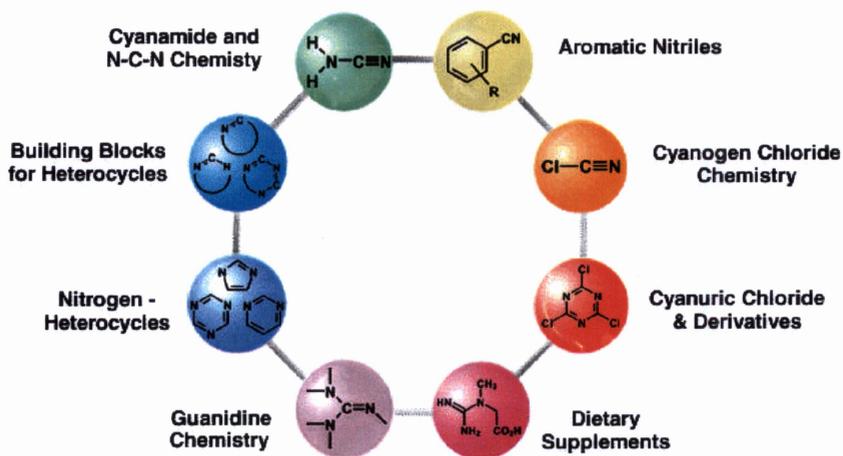
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