

Design of Superbasic Organophosphorus Compounds

Borislav Kovačević,^a Danijela Barić,^a Julius Kögel,^b
and J. Sundermeyer^b

^aRudjer Boskovic Institute, Bijenička 54, 10000 Zagreb, CROATIA
boris@irb.hr

^bPhilipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, GERMANY

Phosphazene bases are extremely strong uncharged bases, built on a unit where a nitrogen basic center is double bonded to pentavalent phosphorus. One of the most basic representatives, *t*Bu-P₄, with an acetonitrile *pK_a* of the conjugate acid of 42.7, was synthesized and characterized by R. Schwesinger.¹ On the other side, Alder discovered the phenomenon of proton sponges in 1968, noticing the unexpectedly high basicity of 1,8-bis(dimethylamino) naphthalene (DMAN).² Such strong nonionic organic bases possess two basic nitrogen centers able to act as a chelate ligand for a proton which commonly is ligated in an asymmetric hydrogen bond N–H•••N. In this work we show that Schwesinger's phosphazene base concept and Alder's concept of proton chelation can be combined in a design of highly basic nonionic superbases. Some of them are synthesized and their basicities are theoretically rationalized.^{3,4} Moreover, newly designed substituents that enable a construction of proton sponges with acetonitrile basicity several orders of magnitude more basic than *t*Bu-P₄ are proposed. Finally, some organophosphorus compound where intramolecular hydrogen bonds play a crucial role in their superbasic properties will be presented too.⁵

1. R. Schwesinger, et al., *Liebigs Ann.* **1996**, 1055.
2. P. S. Bowman, W. R. S. Steele, D. R. Winterman, R. W. Alder *Chem. Commun.* **1968**, 723.
3. J. F. Kögel, B. Oelkers, B. Kovačević, J. Sundermeyer *J. Am. Chem. Soc.* **2013**, 135, 17768.
4. J. F. Kögel, X. Xie; E. Baal, D. Gesevičius, B. Oelkers, B. Kovačević, J. Sundermeyer *Chemistry - A European Journal* **2014**, 20, 7670.
5. D. Barić, I. Dragičević, B. Kovačević *Journal of Organic Chemistry* **2013**, 78, 4075.