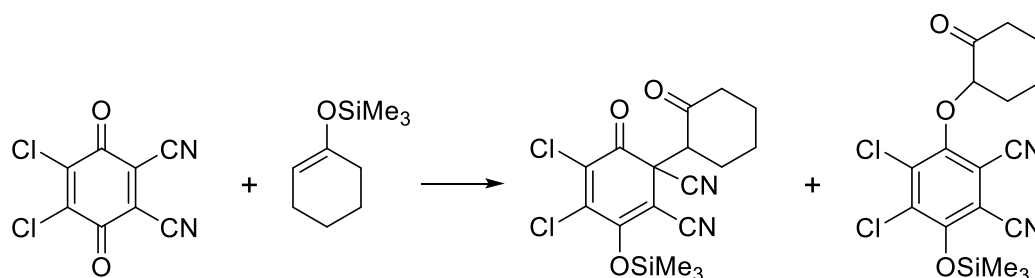


Polar and SET Reaction Pathways of Quinones

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2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) is one of the most important oxidizing reagents in organic chemistry. Its reactions with silylated enol ethers were reported to yield products arising from C- as well as from O-attack as illustrated in Scheme 1.¹ Though both products were suggested to be formed via a radical ion pair, the possibility of a nucleophilic attack of the silyl enol ether on DDQ to form the product of C-attack was explicitly mentioned as an alternative.¹



Scheme 1. Reaction of DDQ with 1-trimethylsilyloxycyclohexene^{1,2}

Bhattacharya's observation¹ prompted us to analyze the reactions of DDQ and other quinones with π -nucleophiles, amines, and hydride donors,²⁻⁴ using our linear free energy relationship (1),⁵ where electrophiles are characterized by one parameter (E) and nucleophiles are characterized by the solvent-dependent nucleophilicity parameter N and the susceptibility parameter s_N .

$$\lg k_{20^\circ\text{C}} = s_N(E + N) \quad (1)$$

By assigning electrophilicity parameters E to the different ring positions of a variety of quinones and correlation with the Gibbs free energies of SET processes, an ordering system for quinone reactivities has been established.²⁻⁴

1. Bhattacharya, A.; DiMichele, L. M.; Dolling, U.-H.; Grabowski, E. J. J.; Grenda, V. J. *J. Org. Chem.* **1989**, *54*, 6118–6120.
2. Guo, X.; Mayr, H.; *J. Am. Chem. Soc.* **2013**, *135*, 12377–12387.
3. Guo, X.; Mayr, H.; *J. Am. Chem. Soc.* **2014**, *136*, 11499–11512.
4. Guo, X.; Zipse, H.; Mayr, H.; *J. Am. Chem. Soc.* **2014**, *136*, 13863–13873.
5. (a) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H.; *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512. (b) Mayr, H.; Ofial, A. R.; *J. Phys. Org. Chem.* **2008**, *21*, 584–595.