Approaches to Chiral Electrogenerated Bases.

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Electrogenerated radical-anions and dianions have been usefully employed[1] as electrogenerated bases (EGBs) and furthermore the kinetics of their reaction with acids are conveniently measured by electroanalytical methods. We here describe attempts at developing useful chiral EGBs, based on phenazine derivatives such as (**1**)- (**9**). The radical-anions of phenazine derivatives are known[2] to deprotonate carbon acids such as $RCH_2PPh_3^+$ at measurable rates.

The synthesis of the indicated phenazines and phenazinophanes is not trivial but good routes have been developed and, where appropriate, methods for resolution. The carbon acids used in this study include phosphonium salts and the epoxysulfone (**10**). In most cases the rates of reaction, in DMSO, between the phenazine radical-anions and the carbon acids were conveniently measured by a combination of cyclic voltammetry and digital simulation (DigiSim). The rates are affected by both electronic and steric factors and in one case [(**4**) + (**10**)] activation parameters (in DMF) were measured [$\Delta H^\# = 14$ kJ mol^{-1}, $\Delta S^\# = -162$ J mol^{-1} K^{-1}].

In an initial experiment, at the time of preparation of this abstract, preparative scale reduction of a chiral phenazine probase (**4**) in the presence of the sulfone (**10**) and an electrophilic trap (mesitoic anhydride) led to product (**11**) in good yield. Analysis of the product by chiral hplc indicated modest enantioselection between the enantiotopic protons H_a and H_b. We believe this to be the first demonstration, and proof of principle, of the possible usefulness of chiral EGBs. The probase is converted into the corresponding 5,10-dihydrophenazine but may be easily recovered by air oxidation. We expect soon to present examples with higher e.e.s.

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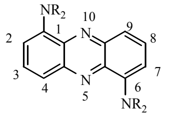
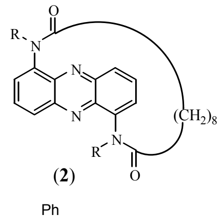
References: [**1**] J.H.P. Utley and M.F. Nielsen, Chapter 30 in *Organic Electrochemistry*, eds. H. Lund and O. Hammerich, Marcel Dekker, N.Y. 2001

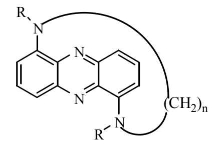
[**2**] A.-P. Bettencourt, A. M. Freitas, M. I. Montenegro, M. F. Nielsen and J.H.P. Utley, *J. Chem. Soc., Perkin Trans. 2,* 1998, 515.



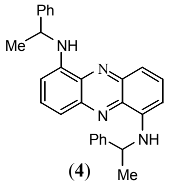
(**1**)



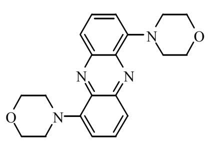
(**2**)



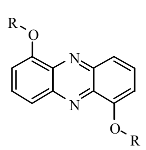
(**3**)



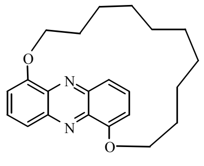
(**4**)



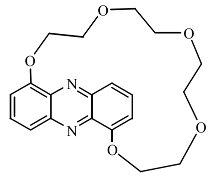
(**5**)



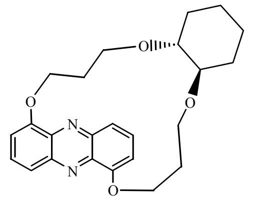
(**6**)



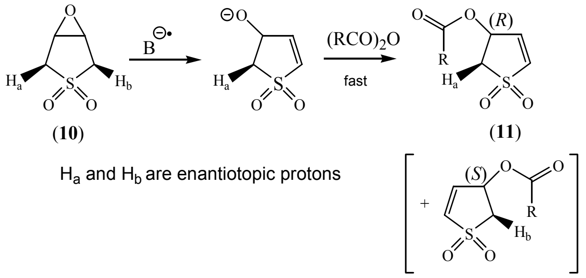
(**7**)



(**8**)



(**9**)



H_a and H_b are enantiotopic protons