Electrochemical Behaviour of Diazirines

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The electrochemical reductions of 3-aryl-3-chlorodiazirines and 3-n-butyl-3-phenyldiazirine have been studied by cyclic voltammetry and controlled potential electrolysis in acetonitrile.

Diazirines, RR′CN_2, are stable compounds and differ markedly in chemical behaviour from their linear isomers, the diazoalkanes.[1] Since their discovery in 1960, very few reports have appeared describing the electrochemical characteristics of diazirines and related diaziridines, RR′CN_2H_2.[2–4] In this report we describe the first account of the electrochemical behaviour of 3-aryl-3-chlorodiazirines and 3-n-butyl-3-phenyldiazirine. In both protic and aprotic media, the 3-aryl-3-chlorodiazirines undergo an irreversible, one-electron reduction to yield the corresponding arylnitriles. In contrast, 3-n-butyl-3-phenyldiazirine is reduced, in the presence of a proton source, to the corresponding diaziridine.

The cyclic voltammogram of $PhClCN_2$ at a vitreous carbon electrode in acetonitrile is shown in Figure 1 [curve (a)]. The cathodic peak potential (*E*p) was -1.87 V relative to an $Ag/AgNO_3$ (0.1 M in MeCN) reference electrode. The diffusion controlled, totally irreversible reduction characteristics were observed at all available scan rates (<1 V s^{-1}). This behaviour was also exhibited by (p-$MeOC_6H_4$)$ClCN_2$ but the peak potential had shifted *cathodically* to -2.05 V. This shift of *ca.* -0.19 V reflects the influence of the electron donating *para*-methoxy group relative to hydrogen.

The 3,3-pentamethylenediazirine, studied by Lund,[2] was also examined in MeCN. Cyclic voltammetry between 0 and -2.7 V failed to find a reduction wave in agreement with the earlier report[2] of this diazirine which described its reduction only in protic media.

Controlled potential electrolysis of $PhClCN_2$ and (p-$MeOC_6H_4$)$ClCN_2$ at a large vitreous carbon electrode in MeCN at 10 °C produced the corresponding arylnitriles, X-C_6H_4CN (X=H or p-MeO) in *ca.* 80—90% yield. The nitriles were characterized by melting point and n.m.r., i.r., and mass spectra. Coulometry confirmed that one electron had been transferred per molecule. The addition of 0.1% acid to the electrolyte gave results consistent with those from cyclic voltammetry experiments.

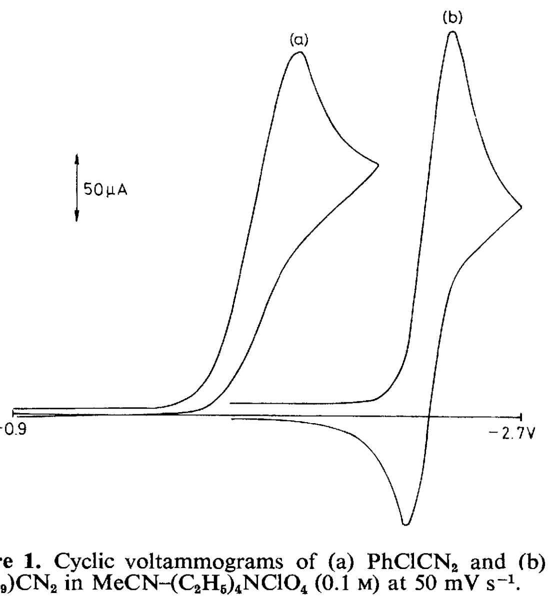

Figure 1. Cyclic voltammograms of (a) $PhClCN_2$ and (b) Ph(C_4H_9)CN_2 in MeCN–$(C_2H_5)_4NClO_4$ (0.1 M) at 50 mV s^{-1}.

The 3-n-butyl-3-phenyldiazirine, by contrast, demonstrated different reduction characteristics [Figure 1, curve (b)]. At slow scan rates a small anodic peak was observed on the reverse scan; however, the system approached reversibility ($ip_a/ip_c \rightarrow 1$) as the scan rate was increased and the temperature lowered. Such behaviour is typical of a chemical step following the electron transfer reaction.[5] Malachesky's R value[6] was found to be 4.38, a value somewhat below the theoretical value of $4.96n^{\frac{1}{2}}$ (n = number of electrons transferred per molecule) but, nonetheless, a value which indicated a single electron was involved. The reduced species was, therefore, assumed to be the radical monoanion of the parent diazirine. Based on the assumption that the radical anion underwent a pseudo first-order reaction, the rate constant and half life were 8×10^{-2} s^{-1} and 9 ± 1 s respectively at 16 °C, as determined by the methods of Schwarz and Shain[7] and Nicholson and Shain.[5] The slow rate of reaction explained why the voltammograms approached reversibility and a catalytic wave was not observed.

The difference in cathodic peak potentials between $PhClCN_2$ and $Ph(C_4H_9)CN_2$ was approximately -0.6 V. This difference reflected not only the difference in inductive effects between the chloro and n-butyl groups but also the difference in stabilities of the reduced species. For the chlorodiazirine, the reduction step was irreversible since the electron transfer reaction was accompanied by loss of Cl^-, a good leaving group, to produce stable benzonitrile. The n-butyl compound underwent a reversible reduction to yield a reactive mono-anion since the n-butyl group was a poor leaving group.

The behaviour of $Ph(C_4H_9)CN_2$ changed when a proton source was added to the electrolyte. When the electrolyte contained 0.1% acetic acid, the voltammogram displayed a totally irreversible reduction at all scan rates and the peak potential shifted anodically by approximately 0.1 V. I.r. data have suggested that the product of the electrolysis of the n-butyl diazirine in the presence of acetic acid at 10 °C is the diaziridine, $Ph(C_4H_9)CN_2H_2$. This assignment was confirmed by oxidizing the diaziridine to diazirine with $AgNO_3$ in methanol, and observing the disappearance of the –NH bands and the appearance of the N=N band.

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