

Phenoxide Ions as Nucleophiles in $S_{RN}1$ Aromatic Nucleophilic Substitution

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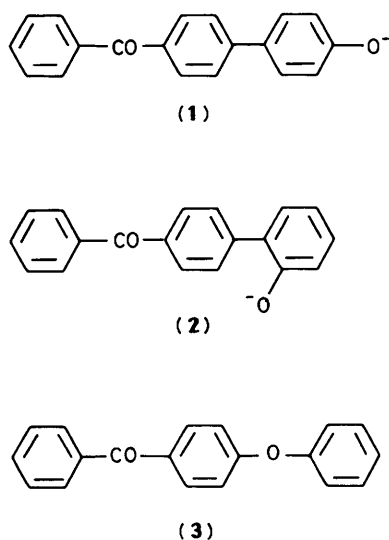
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Phenoxide ions react with 4-bromobenzophenone under electrochemical catalysis in liquid NH_3 and Me_2SO , yielding *ortho* and *para* carbon coupling products, contrary to the belief that they are unreactive in $S_{RN}1$ aromatic nucleophilic substitution.

Nucleophilic aromatic substitution catalysed by electron injection (electrochemical, photochemical, solvated electrons, redox reagents), *i.e.*, reactions occurring by an $S_{RN}1$ mechanism¹, have been shown to occur with a large variety of nucleophiles and leaving groups.^{2–8} It is noteworthy however that phenoxide ions do not appear to react. Although halogenobenzenes have been reported⁹ to react with phenox-

ide ions in aqueous *t*-butyl alcohol upon treatment with sodium amalgam yielding diphenyl ether, these results could not be reproduced by other workers.¹⁰ Other attempts to make phenoxide ions react have also been unsuccessful.¹¹ We have found that phenoxide ions do undergo $S_{RN}1$ reactions, although reacting as a C- rather than an O-nucleophile.

In liquid NH_3 , the cyclic voltammetric waves (Figure 1) of



4-bromobenzophenone, *i.e.*, the first two-electron irreversible wave (A) corresponding to: $\text{ArX} + e^- \rightleftharpoons \text{ArX}^{\cdot-}$, $\text{ArX}^{\cdot-} \rightarrow \text{Ar}^{\cdot} + \text{X}^-$, $\text{Ar}^{\cdot} + \text{ArX}^{\cdot-} \rightarrow \text{Ar}^- + \text{ArX}$, $\text{Ar}^- + \text{H}^+ \rightarrow \text{ArH}$ and a second one-electron reversible wave (B) corresponding to: $\text{ArH} + e^- \rightleftharpoons \text{ArH}^{\cdot-}$, decrease upon addition of phenoxide ions at the expense of a new, more negative, one-electron reversible wave (C) located at a potential identical to that obtained with the *ortho* and *para*-carbon coupling products, (1) and (2) [$E_p = -1.27$ V vs. (Ag/Ag⁺ 0.01 M)], and clearly different from that of the oxygen coupling ether (3) [$E_p = -1.30$ V vs. (Ag/Ag⁺ 0.01 M)].

Preparative scale electrolysis carried out at the reduction potential of 4-bromobenzophenone confirmed the results and permitted a more precise identification of the reaction products: a mixture of benzophenone (40%) and coupling products (60%). As shown by vapour phase chromatography (*v.p.c.*), high pressure liquid chromatography (*h.p.l.c.*), mass spectrometry, and ¹³C n.m.r. spectroscopy the coupling products were found to contain not the ether oxygen-coupling product but a mixture of the *ortho* (2/3) and *para* (1/3) phenols, the carbon coupling products. The consumption of electricity (0.8 Faraday per mole of consumed 4-bromobenzophenone) corresponded exclusively to the formation of benzophenone according to a two-electron per molecule stoichiometry, showing that the formation of the coupling product consumed no electricity, *i.e.*, arose from an electro-catalytic process.

Similar results were obtained in Me₂SO. A marked reduction in the magnitude of the 4-bromobenzophenone waves was obtained upon addition of sodium or tetramethylammonium phenoxide with concomitant appearance of the coupling product wave. On a preparative scale, 50% of coupling product was obtained, again consisting of a 2 : 1 mixture of the *ortho* and *para* carbon coupling products.

It can thus be concluded that phenoxide ions act as efficient nucleophiles in S_{RN}1 reactions, not deserving the reputation for unreactivity that they have acquired in this respect. Work is currently in progress to extend the scope of the reaction to other aryl halides. This should be an attainable goal since it has been achieved with a number of other nucleophiles in electrochemically catalysed S_{RN}1 aromatic nucleophilic sub-

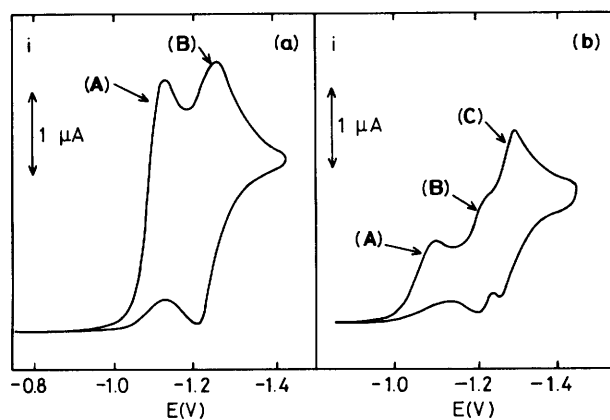


Figure 1. Cyclic voltammetry of 4-bromobenzophenone (1.7 mM) in liquid NH₃ + 0.1 M KBr at -40 °C on a hanging mercury drop in the (a) absence and (b) presence of phenoxide ions (22 mM). Sweep rate: 0.2 V s⁻¹.

stitutions.^{3,5,7,8} A more complete kinetic analysis of the reaction mechanism, including the role of proton transfer, is being undertaken. In our view, there are two main points of interest in the reaction described above. One is mechanistic in nature: the reaction of phenoxide ions with aryl radicals allows one to relate two apparently different types of reaction: S_{RN}1 aromatic nucleophilic substitution and homolytic aromatic substitution. The other pertains to synthesis: if it appears possible to generalise the reaction to other substrates and to optimise the yields using redox catalysis,¹² as seems likely, the reaction would appear an interesting route to valuable chemicals, namely electron-donor-acceptor substituted biaryls.

Received, 13th July 1987; Com. 997

References

- 1 J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, 1970, **92**, 7465.
- 2 J. F. Bunnett, *Acc. Chem. Res.*, 1978, **11**, 413.
- 3 J. M. Savéant, *Acc. Chem. Res.*, 1980, **13**, 323.
- 4 R. A. Rossi, *Acc. Chem. Res.*, 1982, **15**, 164; R. A. Rossi and R. H. Rossi, 'Aromatic Nucleophilic Substitution by the S_{RN}1 Mechanism,' ACS Monograph 178, The American Chemical Society, Washington, D.C., 1983.
- 5 C. Amatore, J. Pinson, J. M. Savéant, and A. Thiébaud, *J. Am. Chem. Soc.*, 1981, **103**, 6930.
- 6 D. Lexa and J. M. Savéant, *J. Am. Chem. Soc.*, 1982, **104**, 3503; A. B. Penenory, A. B. Pierini, and R. A. Rossi, *J. Org. Chem.*, 1984, **49**, 3834.
- 7 C. Amatore, C. Combella, S. Robvielle, J. M. Savéant, and A. Thiébaud, *J. Am. Chem. Soc.*, 1986, **108**, 4754.
- 8 C. Amatore, M. Gareil, M. A. Oturan, J. Pinson, J. M. Savéant, and A. Thiébaud, *J. Org. Chem.*, 1986, **51**, 3757.
- 9 S. Rajan and P. Sridaran, *Tetrahedron Lett.*, 1977, 2177.
- 10 R. A. Rossi and A. B. Pierini, *J. Org. Chem.*, 1980, **45**, 2914.
- 11 R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, 1973, **38**, 3020; F. Ciminale, G. Bruno, L. Testaferri, and M. Tiecco, *ibid.*, 1978, **43**, 4509; M. F. Semmelhack and T. Bargar, *J. Am. Chem. Soc.*, 1980, **102**, 7765.
- 12 C. Amatore, M. A. Oturan, J. Pinson, J. M. Saveant, and A. Thiébaud, *J. Am. Chem. Soc.*, 1984, **106**, 6318; J. E. Swatz and T. T. Stentzel, *ibid.*, 2520.