Lead Tetra-acetate–Boron Trifluoride: A Powerful One-electron Oxidizing System

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BORON trifluoride has been used to catalyze the oxidation, by lead tetra-acetate, of ketones,[1] cyclic olefins,[2] and phenols.[3] We now report that certain benzenoid compounds undergo one-electron oxidation to give cation-radicals when treated with lead tetra-acetate in methylene chloride in the presence of boron trifluoride–ether complex. We have observed the electron spin resonance spectra of these radicals by mixing the reactants at −78°, transferring the solution to the cavity of the spectrometer, and allowing it to warm up to room temperature. The spectra are mostly well resolved, and those which are not are often improved by using degassed solutions.

For example, *p*-dimethoxybenzene gives a spectrum, similar to that previously obtained by

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[1] H. B. Henbest, D. N. Jones, and G. P. Slater, *J. Chem. Soc.*, 1961, 4472.

[2] M. Finkelstein, *Chem. Ber.*, 1957, **90**, 2097.

[3] E. Hecker and R. Lattrell, *Annalen*, 1963, **662**, 48.

controlled-potential oxidation,[4] which analyses for $a(CH_3)$, 3·30 ± 0·03; a(aromatic-H), 1·56 ± 0·03 gauss. 4,4′-Dimethoxybiphenyl gives the same spectrum with lead tetra-acetate in the presence of boron trifluoride as with aluminium trichloride in nitromethane (we have confirmed the previous report that there is strong e.s.r. absorption in the latter conditions[5] and, by using degassed solutions, have obtained a spectrum containing 21 lines).

The radical observed may be one derived from a product rather than from the reactant: *e.g.*, anisole gives the same spectrum as 4,4′-dimethoxybiphenyl, and the latter compound is a product of the reaction of anisole. Comparison of the spectrum obtained from 2,4,6-trideuteroanisole with that from anisole then enables the following assignments to be made for the splittings in the radical-cation from 4,4′-dimethoxybiphenyl: $a(CH_3) = a(2\text{-H})$, 1·73 ± 0·08; a(3-H), 0·87 ± 0·04 gauss ($g = 2{\cdot}0031$). Similarly, *NN*-dimethylaniline and *NNN′N′*-tetramethylbenzidine give the same spectrum, identical with that of the cation-radical of the latter which has previously been generated by anodic oxidation.[6]

Triphenylamine reacts even in the absence of boron trifluoride, although only a very weak spectrum of three lines (1 : 1 : 1) is obtained; in the presence of boron trifluoride the signal becomes intense and splits into 45 equally spaced lines (a, 1·05 ± 0·06 gauss; $g = 2{\cdot}0028$)* which becomes a 1 : 1 : 1 triplet (a_N, 8·55 ± 0·2 gauss) when the *ortho-* and *para*-positions are deuterated. When excess of triphenylamine is used, the spectrum obtained is the same as that derived from the oxidation of *NNN′N′*-tetraphenylbenzidine and is ascribed to the corresponding cation-radical ($a_N[2]$, 4·3 gauss). We conclude that the dimeric cation-radical is derived from reaction between the monomeric cation-radical and triphenylamine.

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* This spectrum is similar to that reported for the radical-cation formed by treating triphenylamine with iodine; it was not at that time clear whether the superhyperfine splitting was due to interaction of the unpaired electron with a neutral iodine molecule or nuclear protons.[7]

[4] A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Amer. Chem. Soc.*, 1964, **86**, 4124.
[5] H. M. Buck, W. Bloemhoff, and L. J. Oosterhoff, *Tetrahedron Letters*, 1960, No. **9**, **5**.
[6] Z. Galus and R. N. Adams, *J. Chem. Phys.*, 1962, **36**, 2814.
[7] D. N. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, 1963, **85**, 2557.