Photolytic Generation of Free-radical Anions

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PREVIOUSLY,[1] it has been shown that radical anions of benzophenone and nitro-substituted aromatics may be produced by photolytic reduction in which alkoxide ions function as reducing agents. It has now been shown that lithium salts of free-radical anions in general may conveniently be prepared by photolysis (in an inert atmosphere) of the corresponding hydrocarbon in the presence of phenyl-lithium.

In a typical example a reaction vessel was charged with 20 ml. of diethyl ether, 3 ml. of 0·5 M-phenyl-lithium solution[2] and 0·1 g of anthracene. A small amount of the solution was transferred to a side-arm of quartz and immersed into a constant-temperature bath (20°) where it was irradiated at a distance of *ca.* 5 cm. from an immersed high-pressure lamp.[3] The intensely coloured solution was diluted by vacuum distillation from the main solution in the reaction vessel and the electron spin resonance spectrum measured.[4]

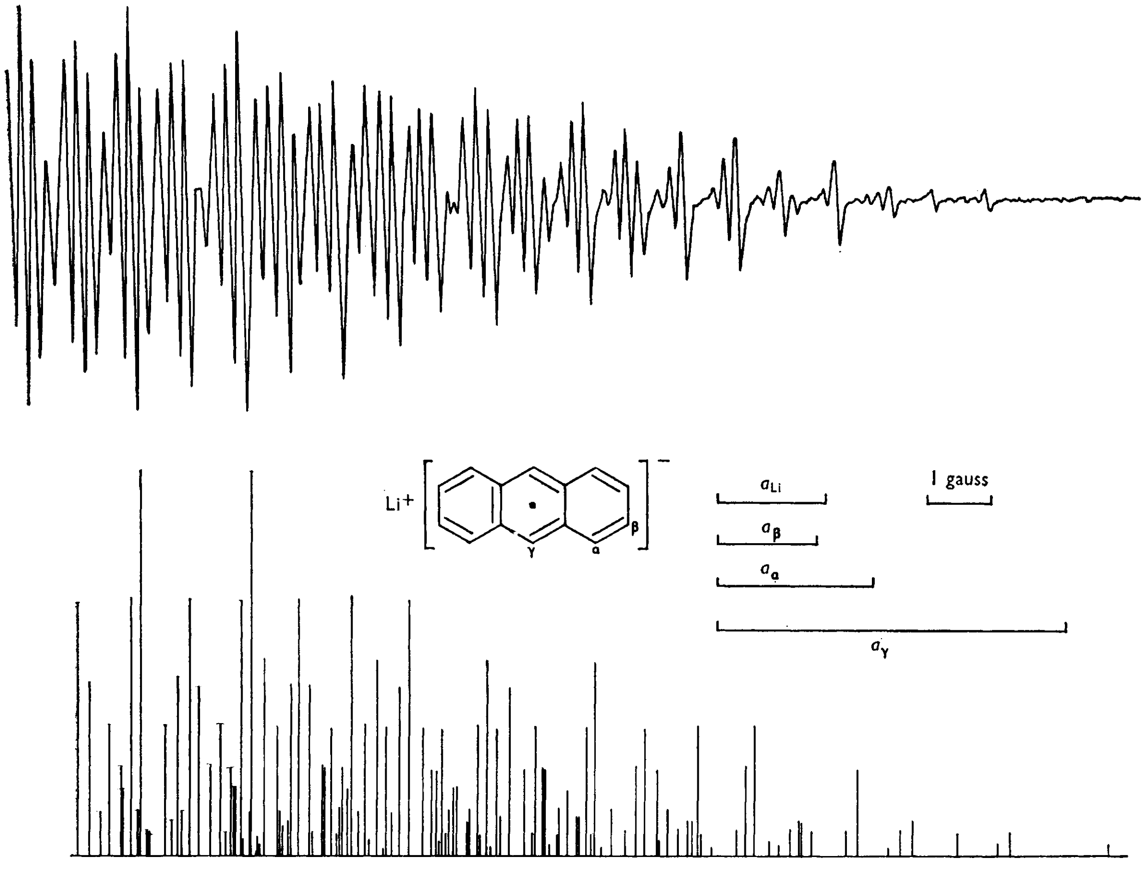

FIGURE. *Electron spin resonance spectrum of lithium anthracene radical-anion in diethyl ether.*

The method is general and has been applied to the following hydrocarbons: biphenyl, triphenylene, naphthalene, phenanthrene, chrysene, pyrene, anthracene, perylene, pentacene, and acenaphthene.

Some of the advantages of the method are: (1) Unlimited choice of inert solvents.[5] (2) The ready adjustment of concentration by the time of photolysis. (3) The removal of trace amounts of moisture and oxygen by the organolithium reagent.[6] (4) No induction period as in the conventional type of preparation of alkali-metal salts of radical anions.

Usually the electron spin resonance spectra of lithium or alkali-metal salts of radical anions of aromatic hydrocarbons are measured in tetrahydrofuran or dimethoxyethane.[7] We have now found that some of the above-mentioned salts in diethyl ether show unusually high hyperfine splitting constants due to lithium (^{7}Li, $I = 3/2$). This is presumably caused by the increased intimacy of ion pairing. The spectrum[4] of lithium anthracene radical-anion is shown in the Figure together with the spectrum calculated on basis of the following hyperfine splitting constants: $a_\gamma = 5{\cdot}53$; $a_\alpha = 2{\cdot}45$; $a_\beta = 1{\cdot}58$; $a_{\mathrm{Li}} = 1{\cdot}70$ gauss.

Several of the other hydrocarbons give similar hyperfine splitting by lithium in ether.

We had previously, in agreement with a recent communication,[8] noticed that biphenyl (in addition to benzene) is formed on photolysis of phenyl-lithium on a preparative scale. However, we find the reaction extremely sensitive to reaction conditions.

The reaction for the production of the lithium salts of free-radical anions is in our opinion a photosensitized one-electron transfer from the "anion of the organolithium reagent" to the hydrocarbon. It is very much dependent upon the following equilibria.[9]

$$\text{Arene} + \text{Li} \rightleftharpoons \text{Li}^+ (\text{Arene})^-$$

$$2\,\text{Li}^+ (\text{Arene})^- \rightleftharpoons \text{Arene} + \text{Li}_2 (\text{Arene})^{2-}$$

In the case of biphenyl as photosensitizer–electron acceptor, the first equilibrium lies far to the left.[10] In contrast, for anthracene the equilibrium favours the radical anion; or, in the presence of an excess of lithium, the dilithio-compounds. In agreement with this proposal we have found that the free-radical anion of anthracene is formed spontaneously, but slowly, in the dark from phenyl-lithium and anthracene. Under ultraviolet irradiation the reaction is accelerated (under our experimental conditions) by at least a factor of 10^5. In the absence of anthracene (or biphenyl) as photosensitizer, phenyl-lithium slowly yields finely dispersed lithium. An e.s.r. spectrum of anthracene radical-anion can be observed on addition of anthracene to such dispersions.

An alternate route involves the intermediacy of lithium or the biphenyl radical-anion which readily transfers an electron to a hydrocarbon of higher electron affinity. Studies of the mechanism are in progress.

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[1] P. B. Ayscough and F. P. Sargent, *Proc. Chem. Soc.*, 1964, 94, and G. A. Russell and E. J. Geels, *Tetrahedron Letters*, 1963, 1333.

[2] The phenyl-lithium was prepared from bromobenzene and lithium in diethyl ether, freshly distilled from benzophenone ketyl. All operations were performed in an inert atmosphere.

[3] A high pressure Hanau-lamp, PL 313 (70 w) was used.

[4] We wish to express our thanks to Drs. G. and S. Olivé-Henrici for performing these measurements.

[5] We have used pure and mixed hydrocarbon and ether type solvents.

[6] Phenyl-lithium is known to react with oxygen to give mainly biphenyl, hence it was necessary to take extensive precautions to ensure the absence of this side reaction, E. Müller and T. Toepel, *Ber.*, 1939, **72**, 273.

[7] A. Carrington, *Quart. Rev.*, 1963, **17**, 67, and A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 1959, 947.

[8] E. E. van Tamelen, J. L. Brauman, and L. E. Ellis, *J. Amer. Chem. Soc.*, 1965, **87**, 4964.

[9] For other one-electron transfer processes see: G. A. Russell, E. G. Jantzen, and E. T. Strom, *J. Amer. Chem. Soc.*, 1964, **86**, 1807.

[10] N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Amer. Chem. Soc.*, 1936, **58**, 2442.