Oxidation by a Cation Radical: Electron Transfer from 1,1-Bis-(*p*-dimethylaminophenyl)ethylene

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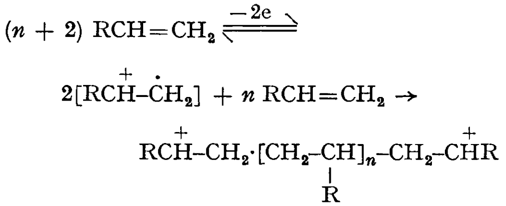
ONE-ELECTRON OXIDATION of neutral organic molecules gives rise to cation radicals. Although the e.s.r. and electronic absorption spectra of these intermediates have been extensively characterised,[1] there is little information relating to chemical reactivity.

Cation radicals have recently been proposed[2] as intermediates in the initiation of vinyl polymerisation and considerable interest arises from the possibility of a propagating dicationic derivative, following dimerisation of the radicals, *i.e.*



$$(n+2)\ \mathrm{RCH{=}CH_2} \xrightleftharpoons{-2e}$$

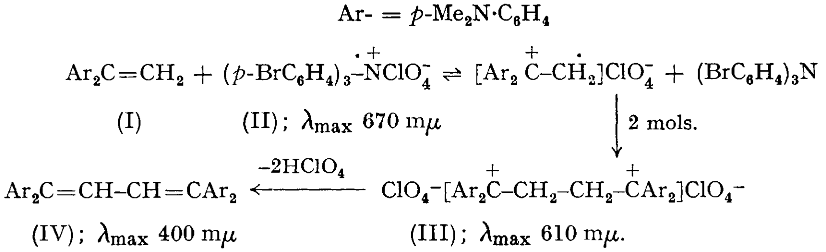
$$2[\mathrm{R}\overset{+}{\mathrm{C}}\mathrm{H}\text{–}\overset{\bullet}{\mathrm{C}}\mathrm{H_2}] + n\ \mathrm{RCH{=}CH_2} \rightarrow$$

$$\mathrm{R}\overset{+}{\mathrm{C}}\mathrm{H}\text{–}\mathrm{CH_2}\cdot[\mathrm{CH_2}\text{–}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}]_n\text{–}\mathrm{CH_2}\text{–}\overset{+}{\mathrm{C}}\mathrm{HR}$$

In order to establish whether dications can be formed following oxidation of olefinic molecules, we have studied the electron-transfer reactions of 1,1-bis-(*p*-dimethylaminophenyl)ethylene (I) using the cation radical, tri-(*p*-bromophenyl)aminium perchlorate (II)[3] as a simple one-electron oxidising agent. Olefins of this type do not polymerise beyond the dimer stage[4] and any cationic species formed would have a structure and stability similar to that of the well known diaryl methyl cationic dyes.[5]

On adding 50 ml. of a $7{\cdot}6 \times 10^{-2}$ M solution of (I) in ethanol to 25 ml. of a $16{\cdot}9 \times 10^{-2}$ M solution of (II) in methylene chloride, there was an immediate colour change and the resulting solution had $\lambda_{\max} = 610\ \mathrm{m}\mu$. At the same time, the e.s.r. spectrum of (II) completely disappeared, both observations being entirely consistent with the formation of a bis-(*p*-dimethylaminophenyl)methyl cationic dye (III).[5] After neutralisation with NaOH the mixture was worked up to give neutral tri-(*p*-bromophenyl)amine (85% recovery) and a light brown solid (IV), m.p. 185—187°, yield 75% based on (I).

The i.r. spectrum of (IV) was similar to that of (I) but lacked the $\rangle\mathrm{C{=}CH_2}$ out of plane deformation mode at 895 cm^{-1}, while several peaks between 1100 $\mathrm{cm.}^{-1}$ and 1220 $\mathrm{cm.}^{-1}$ had changed in intensity. The n.m.r. analysis showed only two unresolved multiplets centred at 7·0 ($-\mathrm{NMe_2}$) and 3·0 τ (aromatic and $=\mathrm{CH}-$) with relative intensities of 4 : 3 and the mass spectrum showed a highest *m/e* peak at 530. Compound (IV) must therefore be the butadiene formed by oxidative coupling of the original olefin. Final proof of structure was obtained by an independent oxidative coupling of (I) using palladous acetate in acetic acid.[6]



$$\text{Ar-} = p\text{-}Me_2N{\cdot}C_6H_4$$

$$\underset{\text{(I)}}{Ar_2C{=}CH_2} + \underset{\text{(II); }\lambda_{\max}\text{ 670 m}\mu}{(p\text{-}BrC_6H_4)_3\text{-}\overset{\cdot+}{N}ClO_4^-} \rightleftharpoons [Ar_2\,\overset{+}{C}\text{-}\overset{\cdot}{C}H_2]ClO_4^- + (BrC_6H_4)_3N \;\Big\downarrow \text{2 mols.}$$

$$\underset{\text{(IV); }\lambda_{\max}\text{ 400 m}\mu}{Ar_2C{=}CH\text{-}CH{=}CAr_2} \xleftarrow{-2HClO_4} \underset{\text{(III); }\lambda_{\max}\text{ 610 m}\mu.}{ClO_4^-[Ar_2\overset{+}{C}\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{C}Ar_2]ClO_4^-}$$

The formation of (III) and (IV) by dimerisation of the initially formed cation radical $[Ar_2\,\overset{+}{C}\text{-}\overset{\cdot}{C}H_2]$ would be analogous to the well known dimerisations of related anion radical derivatives.[7]

However, it is equally likely that (III) results from a reaction between $[Ar_2\overset{+}{C}{=}\overset{\cdot}{C}H_2]$ and neutral olefin (I) giving a second cation radical $[Ar_2\overset{+}{C}\text{-}CH_2\text{-}\overset{\cdot}{C}H_2\text{-}CAr_2]$ which would be immediately oxidised by the aminium salt (II).

These experiments provide ample support for earlier suggestions[2,8] concerning the formation of dications from polymerisable olefins and also demonstrate that comparatively stable cation radicals can be extremely useful one-electron oxidising agents.

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[1] E. T. Seo, R. F. Nelson, J. F. Fritsch, D. W. Leedy, and R. N. Adams, *J. Amer. Chem. Soc.*, 1966, **88**, 3498; L. S. Singer and I. C. Lewis, *J. Chem. Phys.*, 1965, **43**, 2712; F. Gerson and J. Heinzer, *Helv. Chim. Acta*, 1967, **50**, 1852.

[2] C. E. H. Bawn, C. Fitzsimmons, and A. Ledwith, *Proc. Chem. Soc.*, 1964, 391; A. Ledwith and M. Sambhi, *Chem. Comm.*, 1965, 64; N. Tokura, T. Nagai, and Y. Sonoyama, *Tetrahedron Letters*, 1965, 1145; L. P. Ellinger, *Polymer*, 1964, **5**, 559; 1965, **6**, 549; S. Tazuke, T. Bu Tjoa, and S. Okamura, *J. Polymer Sci., Part A*1, *Polymer Chem.*, 1967, **5**, 1911; H. Scott, G. A. Miller, and M. Labes, *Tetrahedron Letters*, 1963, **17**, 1073; J. Pac and P. H. Plesch, *Polymer*, 1967, **8**, 237.

[3] R. I. Walter, *J. Amer. Chem. Soc.*, 1955, **77**, 5999.

[4] A. G. Evans and E. D. Owen, *J. Chem. Soc.*, 1959, 4123, and earlier papers.

[5] C. C. Barker and G. Hallas, *J. Chem. Soc.*, 1961, 1395.

[6] H. C. Volger, *Rec. Trav. chim.*, 1967, **86**, 677.

[7] A. G. Evans and J. C. Evans, *Trans. Faraday Soc.*, 1965, **61**, 1202.

[8] A. Ledwith, *J. Applied Chem.*, 1967, **17**, 344; A. Ledwith, *Trans. New York Acad. Sci.*, 1968, in the press.