

### Cation Radicals.<sup>1</sup> Reactions of Cation Radicals from Substrates containing a *p*-Dimethylaminophenyl Group

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Cation radicals have been formed from a number of compounds possessing a *p*-dimethylaminophenyl group by reactions with tris-(*p*-bromophenyl)ammoniumyl salts. Reaction products are suggested to arise *via* carbon-carbon bond formation, and carbon-hydrogen and carbon-carbon bond scission of the cation radicals according to substrate, and the results complement and help clarify those from comparable studies made using anodic or metal oxidant techniques.

OXIDATION of organic substrates using tris-(*p*-bromophenyl)ammoniumyl perchlorate (1), and antimonate (2) apparently occurs *via* primary one-electron transfer processes.<sup>2</sup> These reagents offer a convenient means of generating cation radicals from suitably activated

organic substrates free from the complications (*e.g.* ligand transfer) normally encountered in comparable

<sup>1</sup> Previous paper in this series, P. Beresford, D. H. Iles, L. J. Kricka, and A. Ledwith, *J.C.S. Perkin I*, 1974, 276.

<sup>2</sup> A. Ledwith, *Accounts Chem. Res.*, 1972, 5, 133.

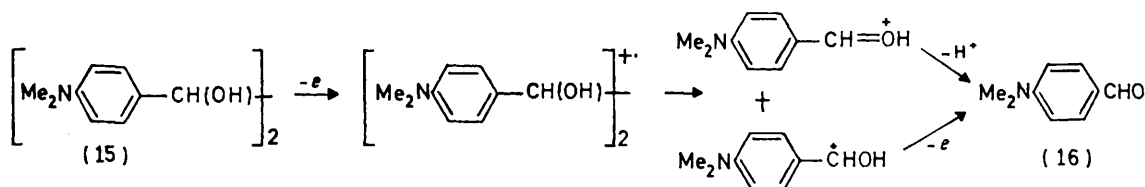




on the efficient coupling of *N*-vinylcarbazole by the ammonium salt (2).

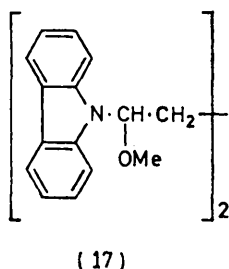
Oxidation of tris-(*p*-dimethylaminophenyl)methane (12) (Leucocystal Violet) by the ammonium salt (1) gave, in good yield, tris-(*p*-dimethylaminophenyl)methyl (Crystal Violet) perchlorate (14). The cation radical derived from (12) is unable to undergo a coupling reaction owing to the blocked *para* positions, *cf.* (9); instead it presumably either fragments to give a proton and the tris-(*p*-dimethylaminophenyl)methyl radical which is then oxidised by (1) to the highly stabilised Crystal Violet cation, or the cation radical (13) is oxidised directly to the Crystal Violet cation.

A further reaction pathway available to cation radical intermediates is illustrated by the reaction of 1,2-bis-(*p*-dimethylaminophenyl)ethane-1,2-diol (15) with (1), which affords *p*-dimethylaminobenzaldehyde (16), by a process involving carbon-carbon bond scission. Other examples of cation radical intermediates undergoing carbon-carbon bond scission are provided by the oxidation of *trans*-1,2-di(carbazol-9-yl)cyclobutane to



the open-chain dication [isolated as the methanolysis product (17)],<sup>17</sup> oxidation of bitropyl to the tropylium cation,<sup>4</sup> oxidative fragmentation of 2-phenylethanol to the benzyl radical,<sup>18</sup> and the more recently reported oxidative cleavage of 1,2-diarylethanes by ceric ammonium nitrate.<sup>19</sup>

In conclusion it may be stated that cation radicals derived by purely thermal processes from rather similar substrates may undergo carbon-carbon bond formation, and carbon-hydrogen and carbon-carbon bond scission,



depending on the substrate. The rather unambiguous one-electron oxidation mechanism associated with tris-(*p*-bromophenyl)ammonium salts affords an opportunity to supplement and clarify reaction possibilities for cation radicals more usually generated by metal oxidant or anodic processes.

<sup>17</sup> P. Beresford, M. C. Lambert, and A. Ledwith, *J. Chem. Soc. (C)*, 1970, 2508.

<sup>18</sup> A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *J.C.S. Perkin II*, 1973, 630.

## EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls. Visible absorption spectra were measured on a Unicam SP800 spectrophotometer. Alumina for chromatography was B.D.H. Brockmann grade I. Solvents were dried, prior to use, over molecular sieve type 4A (B.D.H.). Tris-(*p*-bromophenyl)ammonium hexachloroantimonate, m.p. 140–143° (decomp.) [lit.,<sup>20</sup> 141–142° (decomp.)] and tris-(*p*-bromophenyl)ammonium perchlorate, m.p. 129° (lit.,<sup>20</sup> 129°) were prepared as described previously.

*Reaction of NN-Dimethylaniline with Tris-(p-bromophenyl)ammonium Perchlorate.*—A suspension of tris-(*p*-bromophenyl)ammonium perchlorate (5.8 g) in dichloromethane (50 ml) was added to a solution of *NN*-dimethylaniline (0.6 g) in dichloromethane (50 ml). The mixture was allowed to stand for 3 h and the resulting orange-red precipitate filtered off. A second crop was obtained by addition of the mother liquor to cold ether (200 ml). The precipitates were combined, dissolved in acetonitrile-methanol (1:1 v/v), and then treated with a saturated solution of sodium hydroxide in ethanol. The brown solution was washed with water, dried (CaCl<sub>2</sub>), and evaporated to afford a brown residue which was recrystallised

from benzene-petroleum to give *NNN'N'*-tetramethylbenzidine (0.48 g, 80%), m.p. and mixed m.p. 194–194.5° (lit.,<sup>7</sup> 194°).

*Reaction of 1,1-Bis-(p-dimethylaminophenyl)ethylene with Tris-(p-bromophenyl)ammonium Hexachloroantimonate.*—A solution of 1,1-bis-(*p*-dimethylaminophenyl)ethylene (0.13 g) in ethanol (20 ml) was added to a solution of the ammonium salt (0.82 g) in dichloromethane (250 ml). After 3 h the mixture was evaporated to low bulk and shaken with aqueous sodium hydroxide. The organic material was extracted with ether, and the ether extracts were washed with water and dried (K<sub>2</sub>CO<sub>3</sub>). Evaporation afforded a brown solid which was extracted with cold ethanol (2 × 25 ml) to give a pale yellow solid, identified by i.r. spectroscopy as tris-(*p*-bromophenyl)amine (88% recovery). The combined ethanol extracts were evaporated and the residue recrystallised from methanol to give 1,1,4,4-tetrakis-(*p*-dimethylaminophenyl)buta-1,3-diene (0.11 g, 83%), m.p. 258–261° (decomp.) having i.r., n.m.r., and mass spectra identical with those of an authentic sample.<sup>4</sup>

Similar oxidations in dichloromethane and in methanol (heterogeneous conditions) also afforded the oxidative dimer (11).

*Reaction of Tris-(p-dimethylaminophenyl)methane with Tris-(p-bromophenyl)ammonium Perchlorate.*—A solution of tris-(*p*-dimethylaminophenyl)methane (0.097 g) in dichloromethane (20 ml) was added to a solution of the ammonium salt (0.334 g) in dichloromethane (100 ml).

<sup>19</sup> W. Trahanovsky and D. W. Brixins, *J. Amer. Chem. Soc.*, 1973, **95**, 6778.

<sup>20</sup> F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. (C)*, 1969, 2719.

After 0.5 h the mixture was washed with water, concentrated to half-bulk, and poured into ice-cold carbon tetrachloride (100 ml). Filtration afforded tris-(*p*-dimethylaminophenyl)methyl perchlorate (0.077 g, 63%) (Found: C, 64.3; H, 6.3; N, 8.5. Calc. for  $C_{25}H_{31}ClN_3O_4$ : C, 63.6; H, 6.4; N, 8.9%). The i.r., visible, and n.m.r. spectra of this material were identical with those of an authentic sample prepared by treating an aqueous solution of tris-(*p*-dimethylaminophenyl)methyl chloride with an aqueous solution of lithium perchlorate.

A similar oxidation employing tris-(*p*-bromophenyl)ammoniumyl hexachloroantimonate afforded tris-(*p*-dimethylaminophenyl)methyl hexachloroantimonate (71%).

*Reaction of 1,2-Bis-(p-dimethylaminophenyl)ethane-1,2-diol with Tris-(p-bromophenyl)ammoniumyl Hexachloroantimonate.*—A solution of 1,2-bis-(*p*-dimethylamino)phenylethane-1,2-diol (0.2 g) in acetonitrile (20 ml) was added to a solution of the ammoniumyl salt (1.1 g) in dichloromethane (450 ml), and the green mixture left to

stand for 1 h. The reaction mixture was then washed with aqueous sodium carbonate, water, and dried over molecular sieve (type 4A). Evaporation gave a brown solid which was extracted with ice-cold methanol to leave an insoluble material identified as tris-(*p*-bromophenyl)amine. The methanol extracts were evaporated and the residue chromatographed on a column of neutral alumina made up in petroleum. Elution with petroleum (b.p. 30–40°) afforded *p*-dimethylaminobenzaldehyde (0.17 g, 84%), m.p. 74° (lit.,<sup>21</sup> 74°), from *n*-hexane. The i.r. spectrum of this material was identical with that of an authentic sample.

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<sup>21</sup> R. Fields and H. B. F. Dixon, *Biochem. J.*, 1968, **108**, 883.