## 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

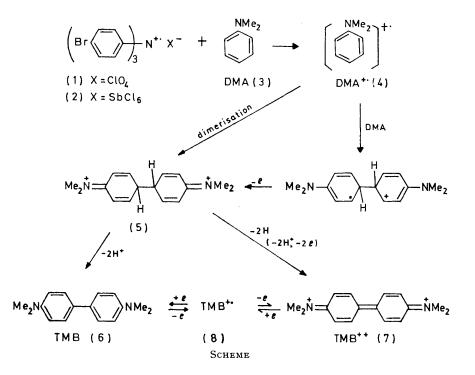
organic substrates free from the complications (e.g ligand transfer) normally encountered in comparable

Previous paper in this series, P. Beresford, D. H. Iles, L. J. Kricka, and A. Ledwith, J.C.S. Perkin I, 1974, 276.
A. Ledwith, Accounts Chem. Res., 1972, 5, 133.

reactions of metal oxidants. Previously we have reported the oxidation, by the ammonium salts (1) and (2), of methoxylated bibenzyls,<sup>3</sup> substituted cycloheptatrienes,<sup>4</sup> carbazoles, iminobibenzyls, and iminostilbenes.1

In an attempt to define the reaction characteristics of cation radicals derived from substrates containing the p-dimethylaminophenyl group, we have investigated oxidations of the derivatives (3), (9), (12), and (15) with the ammoniumyl salts (1) and (2). The tetramethylbenzidine in dichloromethane, when the same series of absorptions was obtained. If DMA is not freshly distilled a green colour is obtained upon oxidation instead of the usual yellow colour, and this is due to a spurious absorption at 610 nm which, coupled with the intense band at 472 nm, gives the oxidised mixture a green colour. Other workers have reported similar green colours during oxidations of DMA.<sup>5-8</sup>

Dropwise addition of a solution of DMA in dichloromethane to the ammoniumyl salt (2) in the same solvent



dimethylaminophenyl group was chosen because of its low oxidation potential, and because the introduction of groups having lone-pair electrons into extended conjugated systems greatly increases the thermal stability of resulting cation radicals.

The reaction between NN-dimethylaniline (DMA) (3) and tris-(p-bromophenyl)ammoniumyl hexachloroantimonate (2) was investigated spectrophotometrically. By suitable choice of reagent concentrations this reaction could be stopped at either the NNN'N'-tetramethylbenzidine cation radical  $[TMB^{+}, (8)]$  or the tetramethylbenzidine quinonoidal dication [TMB<sup>++</sup>, (7)] stage.

Addition of a solution of the ammonium salt (2) in dichloromethane to a solution of DMA in dichloromethane gave rise to a new series of absorptions in the visible region at 436, 458, and 472 nm, due to the tetramethylbenzidine cation radical (TMB<sup>+</sup>) (8). Confirmation of this assignment was obtained by the addition of a solution of the oxidant to a solution of

L. J. Kricka and A. Ledwith, J.C.S. Perkin I, 1973, 294.
P. Beresford and A. Ledwith, Chem. Comm., 1970, 15.

<sup>5</sup> J. E. Dubois, P. C. Lacaze, and A. Arande, Compt. rend., 1965, **260**, 3383.

gave rise to a new absorption at 485 nm assigned to the tetramethylbenzidine quinonoidal dication (TMB<sup>++</sup>).<sup>7</sup> If the reaction is halted at this stage, the absorption at 485 nm slowly decreases in intensity whilst new absorptions appear in the region 430-480 nm owing to TMB<sup>+</sup>, the thermodynamically favoured product. Similarly further addition of DMA causes a slow decrease in the intensity of the TMB<sup>++</sup> absorption, whilst absorptions in the region 430-480 nm increase in intensity. Eventually the solution became vellow and an orange precipitate of NNN'N'-tetramethylbenzidinium diperchlorate formed, leaving a mother liquor free from absorption at 485 nm (TMB<sup>++</sup>) and exhibiting new absorptions at 436, 458, and 472 nm due to the tetramethylbenzidine cation radical.

The proposed mechanism for the reaction between DMA and an ammoniumyl salt outlined in the Scheme is similar to those suggested earlier by other workers

<sup>6</sup> R. N. Adams and T. Mitzoguchi, J. Amer. Chem. Soc., 1962, 84, 2058, 2061, and 2065.
<sup>7</sup> F. T. Naylor and B. C. Saunders, J. Chem. Soc., 1950.

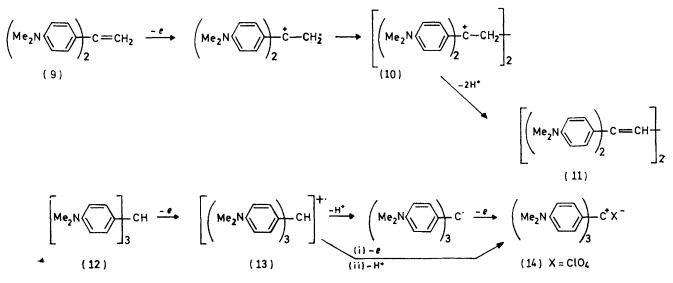
3519.

<sup>&</sup>lt;sup>8</sup> J. W. Eastman, G. Engelsma, and M. Calvin, J. Amer. Chem. Soc., 1962, 84, 1339.

following chemical 8,9 or electrochemical studies.10 Reactions employing an excess of oxidant indicated that TMB<sup>++</sup> forms prior to the complete oxidation of DMA to TMB<sup>++</sup>, suggesting that, in this case, TMB<sup>++</sup> does not arise via oxidation of TMB<sup>+.</sup> but instead arises directly via oxidation of the essentially colourless intermediate (5).\* The latter may be produced either by dimerisation of the DMA cation radical (DMA<sup>+</sup>) or by a radical-parent process.<sup>11</sup> Spectral studies failed to detect DMA<sup>+</sup> owing to its very short life-time.

quinonoidal dication formed in the reaction between DMA and an ammoniumyl salt appears not to arise via direct oxidation of TMB or its radical cation, a result which is not apparent from related studies using more complex oxidants.

Similar results were obtained in oxidations employing tris-(p-bromophenyl)ammoniumyl perchlorate (I) with the additional observation that on standing the reaction mixtures showed loss of absorption at 472 nm and formation of the characteristic Crystal Violet absorption



Although the foregoing results suggest that an equilibrium process may exist involving TMB, its radical cation, and dication (e.g.,  $TMB \stackrel{-r}{\longleftarrow} TMB^{+} \stackrel{-r}{\longleftarrow}$ TMB<sup>++</sup>), this may be discounted since addition of a small quantity of TMB to a reaction mixture containing DMA, the ammoniumyl salt (1), and  $TMB^{++}$  caused the immediate disappearance of TMB<sup>++</sup> with formation of TMB<sup>++</sup>. Thus in the oxidation of DMA by an ammoniumyl salt no TMB can be present in equilibrium with TMB<sup>++</sup>, otherwise the latter would rapidly convert into TMB.+. Also the reaction of excess TMB with the ammoniumyl salt (1) was characterised by the initial formation of TMB+, and an absorption due to TMB<sup>++</sup> did not appear until all the TMB had been oxidised to its cation radical as anticipated from the relative oxidation potentials of the three species, viz.  $TMB < DMA < TMB^{+}$ . Thus in agreement with our proposed mechanistic scheme, the tetramethylbenzidine

\* Overall this corresponds to the apparent disproportionation  $2 \times (5) \longrightarrow TMB^{++} + 2DMA$ .

V. Sterba, Z. Sagner, and M. Matra, Coll. Czech. Chem. Comm., 1965, 30, 2475.

<sup>10</sup> N. L. Weinberg and T. B. Reddy, J. Amer. Chem. Soc., 1968,
90, 91; V. Dvorak, I. Nemec, and J. Zyka, Microchem. J., 1967,
12, 99, 324, and 350.
<sup>11</sup> S. C. Creason, J. Wheeler, and R. F. Nelson, J. Org. Chem.,

 <sup>10</sup> S. C. Iclason, J. Wheeler, and R. F. Velson, J. Og. Ch.
<sup>10</sup> E. M. Kosower, Progr. Phys. Org. Chem., 1965, 3, 81.
<sup>13</sup> H. C. Volger, Rec. Trav. chim., 1967, 86, 677; C. E.
Bawn, F. A. Bell, and A. Ledwith, Chem. Comm., 1968, 599. E. H. at 585 nm. This result suggests that oxidation of DMA to Crystal Violet by quinones and related oxidants<sup>12</sup> may involve reaction between the tetramethylbenzidine cation radical and DMA.

1,1-Bis-(p-dimethylaminophenyl)ethylene (9) also undergoes oxidative coupling upon treatment with either tris-(p-bromophenyl)ammoniumyl hexachloroantimonate or perchlorate; but since the position para to the dimethylamino-group is blocked, coupling occurs at the  $\beta$ -olefinic carbon atom to afford the dicationic species (10). The latter was characterised spectroscopically  $[(10), (ClO_4^-)_2, \lambda_{max.} 610; (10), (SbCl_6^-)_2, \lambda_{max.} 624 \text{ nm}]$ and could be isolated as the air-sensitive bis-hexachloroantimonate or di-perchlorate salt, which when treated with base gave the oxidatively coupled product 1,1,4,4-tetrakis-(p-dimethylaminophenyl)buta-1,3-diene (11). This material was identical with an authentic sample prepared by oxidation of (9) with palladium(II) acetate in acetic acid.<sup>13</sup> Oxidative coupling of olefins may be achieved in a variety of ways <sup>14, 15</sup> and is relevant to the generation of propagating species in polymerisation processes. In this context we have previously reported <sup>16</sup>

<sup>14</sup> H. Weingarten and J. S. Wager, Tetrahedron Letters, 1969, 3267; J. Org. Chem., 1970, 35, 1750; F. Effenberger and O. Gerlach, Tetrahedron Letters, 1970, 1669.

<sup>&</sup>lt;sup>15</sup> H. Schäfer and E. Steckham, Angew. Chem., 1969, **81**, 532; J. M. Fritsch and W. Weingarten, J. Amer. Chem. Soc., 1968, **90**, 793; B. Belleau and Y. K. Au-Young, Canad. J. Chem., 1969, 47, 2117.

<sup>&</sup>lt;sup>16</sup> A. Ledwith and D. C. Sherrington, Macromol. Synth., 1972, 4, 183.

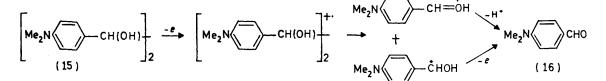
on the efficient coupling of N-vinylcarbazole by the ammoniumvl salt (2).

Oxidation of tris-(p-dimethylaminophenyl)methane (12) (Leucocrystal Violet) by the ammoniumyl salt (1) gave, in good yield, tris-(p-dimethylaminophenyl)methyl (Crystal Volet) 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-vl)cyclobutane to EXPERIMENTAL

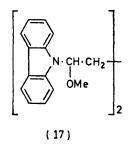
I.r. spectra were recorded for Nujol mulls. Visible absorption spectra were measured on a Unicam SP800 spectrophotometer. Alumina for chromatography was B.D.H. Brockmann grade I. Solvents were dried, prior to use, over molecular sieve type 4A (B.D.H.). Tris-(p-bromophenyl)ammoniumyl hexachloroantimonate.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

Reaction of NN-Dimethylaniline with Tris-(p-bromophenyl)ammoniumyl Perchlorate.-A suspension of tris-(p-bromophenyl)ammoniumvl 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 acetonitrilemethanol (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



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.19

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) ammoniumyl salts affords an opportunity to supplement and clarify reaction possibilities for cation radicals more usually generated by metal oxidant or anodic processes.

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

Reaction of 1,1-Bis-(p-dimethylaminophenyl)ethylene with Tris-(p-bromophenyl)ammoniumyl Hexachloroantimonate.-A solution of 1,1-bis-(p-dimethylaminophenyl)ethylene (0.13 g) in ethanol (20 ml) was added to a solution of the ammoniumyl 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  $(K_2CO_3)$ . Evaporation afforded a brown solid which was extracted with cold ethanol (2  $\times$  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.4

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)ammoniumyl Perchlorate.-- A solution of tris-(p-dimethylaminophenyl)methane (0.097 g) in dichloromethane (20 ml) was added to a solution of the ammoniumyl salt (0.334 g) in dichloromethane (100 ml).

<sup>&</sup>lt;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.

<sup>&</sup>lt;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.

<sup>(</sup>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<sub>28</sub>H<sub>31</sub>ClN<sub>3</sub>O<sub>4</sub>: 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 hexachloroantimomate afforded tris-(p-dimethylaminophenyl)methyl hexachloroantimonate (71%).

Reaction of 1,2-Bis-(p-dimethylaminophenyl)ethane-1,2diol with Tris-(p-bromophenyl)ammoniumyl Hexachloroantimonate.—A solution of 1,2-bis-(p-dimethylaminophenyl)ethane-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.