The Radical Cation from Hexamethyl(Dewar Benzene): Derived from a Substitution Product of Hexamethylbenzene?

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Photolysis of thallium(III) trifluoroacetate and pentamethylbenzyl acetate or pentamethylbenzyl alcohol in neat trifluoroacetic acid at −11 °C produces a well-resolved 13 × 8-line EPR spectrum of what probably originates from pentamethylbenzyl trifluoroacetate radical cation; the same spectrum could be generated by similar treatment of hexamethyl(Dewar benzene).

It was recently shown[1] that a persistent 13-line EPR spectrum (a^{H} = 1.07 ± 0.01 mT) could be obtained from hexamethyl(Dewar benzene) (HMD) by the vacuum deposition of HMD or hexamethylprismane onto solid dioxygenyl hexafluoroantimonate at 77 K and warming the sample to room temperature. The spectrum was identical to that obtained from HMD in frozen matrices[2] and ascribed to the $^2B_2$ state of HMD$^{\cdot+}$.

In a different context,[3] we have tested various methods for the generation of radical cations from hexamethylbenzene (HMB) and derivatives thereof, among them pentamethylbenzyl acetate **1**. Fig. 1(*a*) shows the EPR spectrum obtained by UV irradiation of a solution of **1** (20 mmol dm^{-3}) and Tl^{III} trifluoroacetate (25 mmol dm^{-3}) in neat trifluoroacetic acid (TFA) at −11 °C. No EPR activity was seen after mixing, and the spectrum of Fig. 1(*a*) was obtained after 3 min of irradiation. Continued irradiation slowly decreased the intensity of the spectrum. When the light was shut off, the signal decayed within seconds. In [^{2}H]TFA, a spectrum of identical appearance and behaviour was obtained. The same spectrum, although of much lower intensity, was generated by irradiation of **1** with Hg^{II} trifluoroacetate[4] or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[5] in TFA at −11 °C. A less well resolved spectrum was obtained by irradiation of a dichloromethane–TFA (0.8 mol dm^{-3}) solution of **1** and Tl^{III} trifluoroacetate at −60 °C [Fig 1(*b*); this spectrum is remarkably similar to earlier published 13-line spectra originating from the oxidation of HMD].

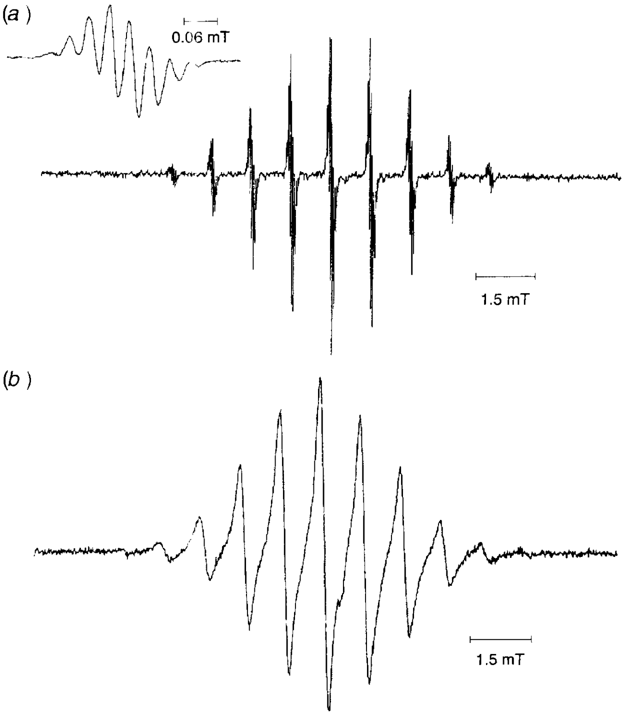

Fig. 1 (*a*) EPR spectrum of an irradiated solution of **1** and Tl^{III} trifluoroacetate in TFA at −11 °C. The insert shows the 8-line splitting of each major line. (*b*) EPR spectrum of an irradiated solution of **1** and Tl^{III} trifluoroacetate in dichloromethane–TFA (0.8 mol dm^{-3}) at −60 °C.

The spectrum of Fig. 1(*a*) consists of 13 groups of lines [a = 1.03 mT (12 H); 2,3,5,6-Me$_4$], each split into eight lines [a^{H} = 0.078 mT (2 H) CH$_2$, a^{H} = 0.039 mT (3 H) 4-Me, or the reverse assignment] consistent with the structure of **1**$^{\cdot+}$ or a related structure of the general formula $Me_5C_6CH_2OX$ where X may be H or, most likely, CF_3CO. NMR spectral studies of **1** in [^{2}H]TFA showed that the acetyl group was rapidly split off, presumably resulting in the formation of the alcohol and/or trifluoroacetate. In keeping with this assumption, pentamethylbenzyl alcohol, upon photolysis with Tl^{III} trifluoroacetate in neat TFA (or [^{2}H]TFA) at −11 °C, gave a spectrum almost identical to that of Fig. 1 [a^{H} = 1.02 (12 H), a^{H} = 0.086 (2 H), a^{H} = 0.043 (3 H) mT].

Treatment of HMD with excess Tl^{III} trifluoroacetate in neat TFA gave a yellow solution which displayed a strong signal of the hexamethylbenzene radical cation (a^{H} = 0.65 mT, at least 15 visible lines)[4] which decayed with a half-life of *ca.* 14 min at 22 °C and *ca.* 2 h at −11 °C, the slow rate of disappearance being due to the intrinsic slowness of the reaction between HMD and Tl^{III}. The HMB$^{\cdot+}$ signal was allowed to decay at room temperature, and then the solution was irradiated with UV light at −11 °C. The same spectrum as in Fig. 1(*a*) then appeared, as shown in Fig. 2 [a^{H} = 1.04 (12 H), a^{H} = 0.080 (2 H), a^{H} = 0.040 (3 H) mT]. The weaker singlet lines with a spacing of 0.65 mT correspond to the EPR spectrum of HMB$^{\cdot+}$.

Thus we have demonstrated that HMD, upon oxidation by Tl^{III}, is converted into HMB$^{\cdot+}$, as observed for other HMD–electron acceptor pairs.[6] TFA then reacts with HMB$^{\cdot+}$ to give pentamethylbenzyl trifluoroacetate, a reaction known to occur upon anodic,[7] Tl^{III}[8] or Hg^{II}–$h\nu$[4] oxidation of HMB in trifluoroacetic acid. Finally, photolysis of the pentamethylbenzyl trifluoroacetate formed with a good electron acceptor, such as Tl^{III}, gives rise to a photostationary concentration of its radical cation (Fig. 2). The same radical cation is generated by photolysis of Tl^{III} and pentamethylbenzyl acetate or penta-

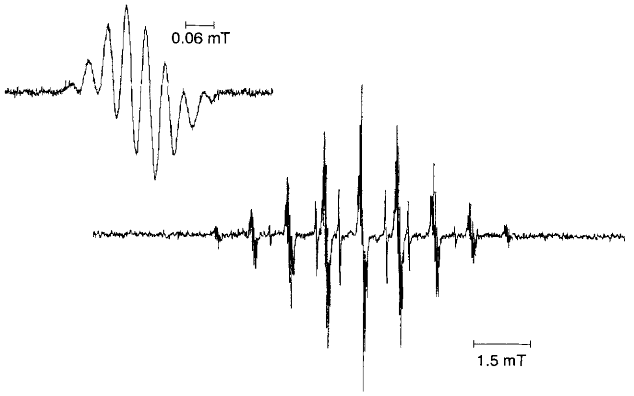

Fig. 2 EPR spectrum of an irradiated solution of HMD (10 mmol dm^{-3}) and Tl^{III} trifluoroacetate (50 mmol dm^{-3}) in TFA at −11 °C, recorded after the initial strong signal of HMB$^{\cdot+}$ had been allowed to decay at room temperature. The insert shows the 8-line splitting of each major line.

methylbenzyl alcohol in TFA. We suggest that structures of type $\mathbf{1}^{\cdot +}$, *i.e.* HMB substituted by an oxygen functionality, are the ones observed in previous observations of radical cations from the oxidation of HMD.[9]

Received, 27th October 1994; Com. 4/06571I

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