

Cation Radicals: Reaction of Methoxylated Benzil and Bibenzyl Derivatives with Tris-(*p*-bromophenyl)ammoniumyl Hexachloroantimonate

By L. J. Kricka and A. Ledwith,* Donnan Laboratories, University of Liverpool, Liverpool L69 3BX

Oxidation of 3,3',4,4'-tetramethoxybibenzyl (IIIc) by tris-(*p*-bromophenyl)ammoniumyl hexachloroantimonate (I) yielded 2,3,6,7-tetramethoxyphenanthrene as a major product. Isomeric tetramethoxybibenzyls and the corresponding benzils were largely unreactive. The reactions are thought to occur *via* initial formation of cation radicals and the results are compared with the fragmentation behaviour of molecular ions produced in mass spectrometry and by anodic oxidation.

TRIS-(*p*-BROMOPHENYL)AMMONIUMYL † HEXACHLOROANTIMONATE(I) has been shown to be a useful oxidising agent for a variety of organic substrates, *e.g.* vinylcarbazoles,

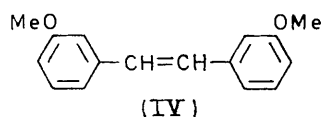
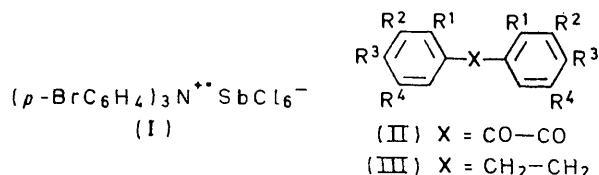
† Previously we have preferred the term aminium for this radical cation (see ref. 1).

NN-dimethylaniline derivatives, 1,1-diarylethylenes, and substituted cycloheptatrienes.¹ The apparently uncomplicated single electron transfer involved in these

¹ A. Ledwith, *Accounts Chem. Res.*, 1972, **5**, 133.

processes offer scope for generation, in thermally equilibrated phases, of cation radicals equivalent to molecular ions observed in mass spectrometry, and observation of any fragmentation behaviour. With this in mind we have studied the reactions of the ammonium salt (I) with a series of di- and tetra-methoxy-benzils and -bibenzyls. Methoxy-derivatives were chosen because the introduction of substituents having lone electron pairs into an extended conjugated system greatly increases the ease of oxidation and thermal stability of resulting cation radicals. The benzils (IIa—f) were synthesised by benzoin condensations² of the appropriate aldehydes and oxidation of the benzoin with Fehling's solution. Reduction of the benzils (IIa—e) with zinc amalgam gave the bibenzyls (IIIa—e) in moderate yields. An exception was 3,3'-dimethoxybenzil (IIf), which upon reduction gave the corresponding stilbene (IV). All attempts to reduce the stilbene with di-imide, generated *in situ* from hydrazine and sodamide, were unsuccessful.

The benzils (IIa and c) proved inert towards one-electron oxidation by the ammonium salt; it had been



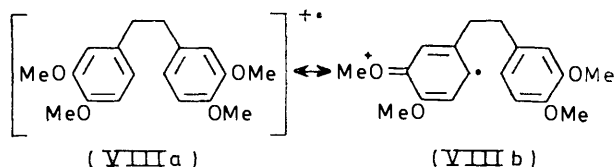
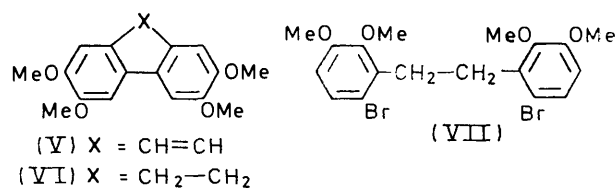
a; R¹ = R² = OMe, R³ = R⁴ = H d; R² = R⁴ = OMe, R¹ = R³ = H
b; R¹ = R⁴ = OMe, R² = R³ = H e; R³ = OMe, R¹ = R² = R⁴ = H
c; R² = R³ = OMe, R¹ = R⁴ = H f; R² = OMe, R¹ = R³ = R⁴ = H

anticipated that successive one-electron oxidation and intramolecular coupling would give rise to phenanthrene-9,10-dione derivatives. In contrast, 3,3',4,4'-tetramethoxybibenzyl (IIIc) reacted with 4 equiv. of the ammonium salt to give 2,3,6,7-tetramethoxyphenanthrene, *via* a green-coloured cation radical species. A minor product isolated was tentatively identified, on the basis of its mass spectrum and an accurate mass measurement of the molecular ion, as a chlorinated dimer of the bibenzyl. The reaction was found to be dependent upon solvent basicity; no reaction occurred in dichloromethane, but dichloromethane-acetonitrile (1:1 v/v) was a successful solvent system.

Recently Parker *et al.*³ have described the electrochemical oxidation of the bibenzyl (IIIc) to the phenanthrene (V). The reaction was shown to proceed *via* the dihydrophenanthrene (VI), although this intermediate was not isolated. Our attempts to prepare the dihydrophenanthrene (VI) by treating the bibenzyl (IIIc) with

* This product is identified as the 6,6'-dibromide by analogy with the reported bromination of 3,3',4,4'-tetramethoxybibenzyl (see ref. 4). However, the referees have pointed out that the spectral evidence does not exclude the identification of this product as the 4,4'-isomer.

2 equiv. of the ammonium salt gave only the fully aromatised product (V).



2,2',3,3'-Tetramethoxybibenzyl (IIIa) reacted with 4 equiv. of the ammonium salt to give a dark green mixture, indicative of the formation of a cation radical species. Work-up and chromatography gave starting material and, in low yield, a dibromo-compound identified* as 6,6'-dibromo-2,2',3,3'-tetramethoxybibenzyl (VII). Its i.r. spectrum showed a sharp absorption at 803 cm⁻¹ indicative of two adjacent aromatic hydrogen atoms, and the n.m.r. spectrum showed two doublets, centred at τ 2.92 and 3.40, having a coupling constant of 8 Hz, which is appropriate to *ortho*-coupled protons. This product was identical with material synthesised by bromination of the bibenzyl (IIIa) with bromine in acetic acid.

The remaining bibenzyls (IIIb and d—f) were all unchanged on treatment with the ammonium salt. *meta*-Dimethoxybenzene, *ortho*-dimethoxybenzene (veratrole), and 4-bromoveratrole were also unreactive. An exploratory reaction of 3,3'-dimethoxystilbene with the ammonium salt gave inconclusive results.

The mass spectra of the benzil and bibenzyl derivatives (Table) showed that there were no similarities between the behaviour of cation radicals generated in solution and equivalent but highly energised species formed in the gas phase by electron impact. For both classes of compound loss of two or four mass units from the molecular ion, *i.e.* intramolecular cyclisation leading to phenanthrene-9,10-dione and phenanthrene derivatives, respectively, does not occur to any measurable extent. The principal mode of fragmentation in the mass spectrometer, for both classes of compound, is one of symmetrical cleavage—this type of behaviour is not a feature of the solution chemistry of the cation radicals derived from benzil or bibenzyl derivatives.

The results of the reactions of the ammonium salt with the benzils (IIa and c) and with the bibenzyls (IIIa—c) do not fall into a clear pattern. The unreactive nature of the benzil derivatives may be attributed to the influence of the electron-withdrawing carbonyl group, which would increase both ionisation and oxidation potentials.

² W. S. Ide and J. S. Buck, *Org. Reactions*, 1948, **4**, 269.

³ A. Ronlan and V. D. Parker, *Chem. Comm.*, 1970, 1567.

⁴ H. Erdtman, *Annalen*, 1933, **505**, 195.

Mass spectra [m/e (%)] of di- and tetra-methoxybenzyls and -bibenzyls

(IIa)	330 (M^+ , 5), 271 (45), 222 (13), 195 (78), 194 (100), 193 (24), 179 (28), 165 (89), 135 (36), 91 (18), and 77 (26)
(IIb)	330 (M^+ , 6), 166 (10), 165 (100), 122 (5), and 107 (7)
(IIc)	330 (M^+ , 1), 166 (12), 165 (100), 137 (13), 122 (10), 107 (11), 94 (12), and 92 (14); m^* 114 (165 \rightarrow 137)
(IId)	330 (M^+ , 16), 166 (12) and 165 (100).
(IIe)	270 (M^+ , 20), 136 (63), 135 (100), 107 (32), and 92 (50); m^* 85 (135 \rightarrow 107) and 68 (270 \rightarrow 135)
(IIf)	270 (M^+ , 10), 136 (10), 135 (100), 107 (30), 92 (14), and 77 (17)
(IIIa)	302 (M^+ , 52), 303 ($M + 1$, 11), 300 (12), 152 (11), 151 (100), 136 (96), 121 (11), 106 (10), and 91 (39); m^* 122 (151 \rightarrow 136)
(IIIb)	302 (M^+ , 47), 303 (8), 152 (10), 151 (100), and 121 (37)
(IIIc)	302 (M^+ , 22), 152 (11), 151 (100), and 107 (5)
(IIId)	302 (M^+ , 10), 246 (52), 203 (100), 190 (48), 189 (26), 152 (95), 151 (82), 123 (26), 121 (21), 105 (21), 97 (26), and 95 (11)
(IIIe)	242 (M^+ , 82), 243 (14), 122 (66), 121 (100), 106 (7), 105 (14), 91 (18), 85 (93), and 83 (98); m^* 60.5 (242 \rightarrow 121) and 92.5 (121 \rightarrow 106)

Zweig *et al.*⁵ have found the half-wave oxidation potentials ($E_{1/2}$) of a series of methoxylated benzenes to lie within the range 0.81—1.49 V * which is within the useful range of the ammonium salt ($E_{1/2}$ 1.05 V *). However, only 3,3',4,4'-tetramethoxybibenzyl has been successfully cyclised with the ammonium salt. The radical cation derived from this molecule is activated towards intramolecular coupling at the 6- and 6'-positions by the methoxy-group at positions 3 and 3' [*cf.* (VIIIa and b)]. The lack of reactivity of the remaining bibenzyls must be ascribed either to the lack of suitably positioned activating groups, or to steric effects. Thus 3,3',5,5'-tetramethoxybibenzyl fails to cyclise despite the activating influence of the 3- and 3'-methoxy-groups, because of unfavourable steric interactions between the substituents at positions 5 and 5' in the transition state. Similarly 2,2',5,5'-tetramethoxybibenzyl does not cyclise owing to steric interaction between the 5- and 5'-substituents.

The anomalous behaviour of 2,2',3,3'-tetramethoxybibenzyl, especially the unexpected formation of the dibromo-compound (VII), is the subject of continuing investigations, but may be taken as further indication¹ of the unpredictability of electron transfer reactions of organic cation radicals.

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls. ¹H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were measured by the Physico-Chemical

* Standard calomel reference electrode.

⁵ A. Zweig, W. G. Hodson, and W. H. Jura, *J. Amer. Chem. Soc.*, 1964, **86**, 4124.

⁶ F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. (C)*, 1969, 2719.

⁷ A. Schonberg and W. Malchow, *Ber.*, 1922, **55B**, 3746.

⁸ M. Boesler, *Ber.*, 1881, **14**, 327.

⁹ J. L. Hartwell and S. R. L. Kornberg, *J. Amer. Chem. Soc.*, 1945, **67**, 1606.

¹⁰ N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *J. Amer. Chem. Soc.*, 1949, **71**, 2997.

Measurements Unit at Harwell. G.l.c. analyses were performed on a column (1.6 m) containing silicone oil (May and Baker) as stationary phase at 180°. 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° (decomp.) [lit.,⁶ 141—142° (decomp.)], was obtained as reported.⁶

3,3'-Dimethoxybenzil (26%), m.p. 80—82° (lit.,⁷ 83°) was prepared by oxidation of 3,3'-dimethoxybenzoin with warm Fehling's solution.⁴ The intermediate benzoin, prepared by refluxing *m*-methoxybenzaldehyde with potassium cyanide in aqueous ethanol, was not isolated.

A similar procedure afforded the following benzils: 4,4'-dimethoxybenzil (34%), m.p. 132—133° (lit.,⁸ 133°); 2,2',5,5'-tetramethoxybenzil (56%), m.p. 154—155° (lit.,⁹ 154—155°); 2,2',3,3'-tetramethoxybenzil (42%), m.p. 142—143° (lit.,¹⁰ 143—144°) (from ethanol) (Found: C, 71.4; H, 7.2. Calc. for C₁₈H₂₂O₄: C, 71.5; H, 7.3%; ν_{\max} 1665 (C=O), 1590, 1495, 1260br (C-O), 1185, 1085, 1070, 1000, 945, 830, 800, 765, and 745 cm⁻¹, τ 2.25—2.95 (6H, m, ArH), 6.18 (6H, s, OMe), and 6.42 (6H, s, OMe); 3,3',4,4'-tetramethoxybenzil (70%), m.p. 223—224° (lit.,⁴ 223°); and 3,3',5,5'-tetramethoxybenzil (23%), m.p. 165—166° (lit.,¹¹ 165—166°).

4,4'-Dimethoxybibenzyl (59%), m.p. 126—127° (lit.,¹² 127—128°), was prepared by reduction of the corresponding benzil with concentrated hydrochloric acid-glacial acetic acid and amalgamated zinc,¹³ as described.⁴

Similarly prepared were the following bibenzyls: 2,2',5,5'-tetramethoxybibenzyl (13%), m.p. 64—66° (lit.,¹⁴ 64—66°); 2,2',3,3'-tetramethoxybibenzyl (68%), m.p. 87—88° (lit.,¹⁵ 88—89°); 3,3',4,4'-tetramethoxybibenzyl (45%), m.p. 109—110° (lit.,⁴ 109—110°); and 3,3',5,5'-tetramethoxybibenzyl (30%), m.p. 99—100° (lit.,¹⁶ 98—99°).

Reduction of 3,3'-dimethoxybenzil as previously described gave 3,3'-dimethoxystilbene (28%), m.p. 96—98° (lit.,¹⁷ 99°), and not the desired bibenzyl. An attempt to reduce the stilbene with di-imide, generated *in situ* from hydrazine and sodamide,¹⁸ was also unsuccessful.

6,6'-Dibromo-2,2',3,3'-tetramethoxybibenzyl (VII).—A mixture of bibenzyl (IIIa) (1.08 g) and bromine (0.3 g) in glacial acetic acid was stirred at room temperature for 4 h. The precipitate was filtered off and recrystallised from glacial acetic acid-benzene (5:1 v/v) to afford 6,6'-dibromo-2,2',3,3'-tetramethoxybibenzyl (0.7 g, 43%), m.p. 175—177° (Found: M^+ , 457.9717; C, 46.8; H, 4.5; Br, 34.5. Calc. for C₁₈H₂₀Br₂O₄: M , 457.9728; C, 47.0; H, 4.4; Br, 34.7%), ν_{\max} 1595, 1590, 1300, 1278, 1225, 1018, 1065, 1020, 840, 805, and 750 (C-Br) cm⁻¹, τ 2.92 and 3.40 (2H, d, J 8 Hz, ArH), 6.18 and 6.20 (6H, s, OMe), and 6.98 (4H, s, ArCH₂), m/e 462/460/458 (M^+ , 14/21/15%), 381 ($M - Br$, 12), 379 ($M - Br$, 14), 302 (14), 301 (50), 300 ($M - 2Br$, 100), 270

¹¹ D. W. Cameron and E. M. Hildyard, *J. Chem. Soc. (C)*, 1968, 166.

¹² R. C. Elderfield and V. B. Meyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1883.

¹³ A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 3rd edn.

¹⁴ J. Green, D. McHale, S. Marcinkiewicz, P. Mamalis, and P. R. Watt, *J. Chem. Soc.*, 1959, 3362.

¹⁵ H. S. Mason, *J. Amer. Chem. Soc.*, 1945, **67**, 1538.

¹⁶ M. Yamato, *Yakugaku Zasshi*, 1959, **79**, 1069.

¹⁷ J. W. Cornforth and Sir Robert Robinson, *J. Chem. Soc.*, 1942, 684.

¹⁸ T. Kaufmann, C. Kosel, and W. Schoeneck, *Chem. Ber.*, 1963, **96**, 999.

(11), 231 (28), 229 (28), 216 (36), 214 (36), 151 (54), 136 (36), and 91 (25), m^* 195—197 (462, 460, and 458 \rightarrow 300), 242 (300 \rightarrow 270), 202 (231 \rightarrow 216), and 200 (229 \rightarrow 214).

Reaction of 2,2',3,3'-Tetramethoxybenzil (IIa) with Tris-(p-bromophenyl)ammoniumyl Hexachloroantimonate (Typical Procedure).—A mixture of the benzil (IIa) (1.0 g), the ammoniumyl salt (5.0 g, 2 equiv.), and potassium carbonate (2.0 g) in dichloromethane-acetonitrile (1 : 1 v/v; 200 ml) was stirred at room temperature under nitrogen overnight, during which time the deep blue solution developed a dark green colouration and was then decolourised. The mixture was poured into water, the aqueous phase was extracted with ether, and the combined extracts were dried (MgSO_4). Evaporation afforded an oil which was repeatedly triturated with ice-cold methanol; the resulting solid crystallised from methanol to afford tris-(p-bromophenyl)amine (1.3 g), m.p. 142—144° (lit.,¹⁹ 144.5—146°). Evaporation of the methanolic extracts gave an oil which was dissolved in chloroform-benzene (2 : 1 v/v; 15 ml) and chromatographed on a column of neutral alumina (ca. 200 g) made up in petroleum (b.p. 60—80°). Elution with petroleum-benzene (9 : 1 v/v; 2 l) gave tris-(p-bromophenyl)amine (0.6 g). Further elution, with benzene-ether (7 : 3 v/v; 2 l and 1 : 1 v/v; 4 l), afforded starting material (0.9 g, 90% recovery).

Reaction of 3,3',4,4'-Tetramethoxybibenzyl (IIIc) with the Ammoniumyl Salt.—The bibenzyl (IIIc) (1.0 g) was treated with the salt (5.5 g, 2 equiv.) according to the general method described. The crude product obtained after work-up was dissolved in benzene-chloroform (2 : 1 v/v; 20 ml) and chromatographed on a column of neutral alumina (ca. 200 g) made up in petroleum (b.p. 60—80°). Elution with petroleum afforded a small quantity of tris-(p-bromophenyl)amine. Benzene-petroleum (9 : 1 v/v; 2 l) and benzene (2 l) eluted 2,3,6,7-tetramethoxyphenanthrene (V) (0.45 g, 46%), m.p. 179—180° (lit.,²⁰ 180—181°) (from benzene).* Elution with benzene-ether (7 : 3 v/v; 1 l and 1 : 1 v/v; 2 l) gave yellow crystals, m.p. 265—266°, tentatively identified as a monochlorinated dimer of the bibenzyl (IIIc) (Found:

* We thank Dr. V. D. Parker for supplying us with i.r. and n.m.r. spectra of this material.

M^+ 628.1854; C, 67.0; H, 6.0; Cl, 4.3. Calc. for $\text{C}_{36}\text{H}_{33}\text{ClO}_8$: M , 628.1865; C, 68.7; H, 5.3; Cl, 5.6%), ν_{max} 1620, 1515, 1250br, 1125, 1040, 845, 830, and 790 cm^{-1} , τ 2.1—3.4 (9H, m, ArH), 5.86, 5.90, 5.93, and 6.01 (24H, all singlets, ArOMe), and 6.1—6.6 (8H, m, ArCH₂), m/e 630/628 (M^+ , 36/100%) 631/629 ($M + 1$, 14/42), and 613 ($M - \text{Me}$, 3).

A similar reaction employing 4 equiv. of the ammoniumyl salt gave, after work-up and chromatography, the phenanthrene (V) (0.3 g, 30%).

Reaction of the Ammoniumyl Salt with 2,2'-3,3'-Tetramethoxybibenzyl (IIIa).—The bibenzyl (IIIa) (1.0 g) and the salt (10.0 g) were treated as described previously. G.l.c. analysis of the crude product indicated the presence of starting material, identified by comparison of retention times and co-injection with authentic material. The crude product was chromatographed on a column of neutral alumina (200 g) made up in petroleum (b.p. 60—80°). Elution with petroleum (2 l) and petroleum-benzene (9 : 1 v/v; 2 l) afforded tris-(p-bromophenyl)amine (0.5 g), m.p. 142—144° (lit.,¹⁹ 144.5—146°). Benzene-ether (9 : 1 v/v; 2 l and 8 : 2 v/v; 2 l) eluted a crystalline material. This was dissolved in hot petroleum-benzene (1 : 9 v/v) and filtered free of insoluble material (200 mg). Evaporation gave an oil which crystallised from ethanol to afford starting material (IIIa) (0.7 g, 70% recovery), m.p. 83—85°, i.r., n.m.r., and mass spectra identical with those of an authentic sample.

The petroleum-benzene-insoluble material crystallised from glacial acetic acid-benzene (5 : 1 v/v) to afford 6,6'-dibromo-2,2',3,3'-tetramethoxybibenzyl, m.p. and mixed m.p. 175—177°.

We thank the S.R.C. for a research assistantship to (L. J. K.) and for mass spectrometric determinations *via* the P.C.M.U. service at Harwell.

[2/2069 Received, 1st September, 1972]

¹⁹ T. N. Baker, W. P. Doherty, W. S. Kelley, W. Newmeyer, J. E. Rogers, R. E. Spalding, and R. I. Walter, *J. Org. Chem.*, 1965, **30**, 3714.

²⁰ V. D. Parker, personal communication.