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The Nitration of Some 4-Alkylphenols; Acid-Catalysed Rearrangements of Some Polysubstituted 4-Alkyl-4-hydroxycyclohexa-2,5-dienones

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Abstract

The nitrations of 4-methyl (6a) and 4-ethyl (9a) tetrabromo phenols, and 4-methyl (6b) and 4-ethyl (9b) 2,3,5-tribromo-6-nitrophenols are described. The acid-catalysed rearrangements of 4-alkyl-4-hydroxycyclohexa-2,5-dienones (7a,b) and (8a,b) in concentrated sulfuric acid are described, and the effects of the nature of the C 4-alkyl group and C 6-substituent (Br or NO_2) on the observed reactions are discussed.

Introduction

The nitration of 2-chloro-4-methyl-6-nitrophenol (1a) reported initially by Zincke *et al.*[1,2] has been shown recently[3] to yield the 5-chloro-2-methyl-3-nitro-1,4-benzoquinone (2a) (see Scheme 1). Similarly the nitrations of the bromo phenol (1b)[1,4] and dibromo nitro phenol (3)[4] have been shown to give the substituted 1,4-benzoquinones (2b) and (4) respectively.[3] The formation of the substituted 1,4-benzoquinones (2) and (4) was envisaged as occurring as shown in Scheme 1. In this reaction scheme the product-determining rearrangement step is the selective methyl group migration, promoted by the strongly electron-withdrawing nitro group. In the absence of a 2-nitro group, e.g. for substrates such as the bromo phenols (5a,b), nitration of the substituted 4-methylphenols did not yield products of methyl migration.[3]

For the nitrations referred to above, one or both of the C 3 and C 5 ring positions in the substrate are unsubstituted. Because of our interest in *ipso* aromatic substitution reactions, we have examined the nitration of the fully substituted 4-methylphenols (6a,b). In the light of earlier reports[5,6] of the differences in behaviour of the 4-alkyl-4-hydroxycyclohexa-2,5-dienones (7a) and (8a) on treatment with concentrated sulfuric acid, we extended the present study to include the nitrations of the 4-ethylphenols (9a,b). We now report the results of this nitration study, and the rearrangements in concentrated sulfuric acid of the 4-alkyl-4-hydroxycyclohexa-2,5-dienones (7a,b) and (8a,b).

[1] Zincke, T., *J. Prakt. Chem.*, 1901, **63**, 183.
[2] Zincke, T., Schneider, W., and Emmerich, W., *Justus Liebigs Ann. Chem.*, 1903, **328**, 268.
[3] Gray, M. J., Hartshorn, M. P., Penfold, B. R., and Vaughan, J., *Aust. J. Chem.*, 1984, **37**, 55.
[4] Zincke, T., and Emmerich, W., *Justus Liebigs Ann. Chem.*, 1905, **341**, 309.
[5] Zincke, T., and Buff, M., *Justus Liebigs Ann. Chem.*, 1905, **341**, 318.
[6] Zincke, T., and Reinbach, H., *Justus Liebigs Ann. Chem.*, 1905, **341**, 355.

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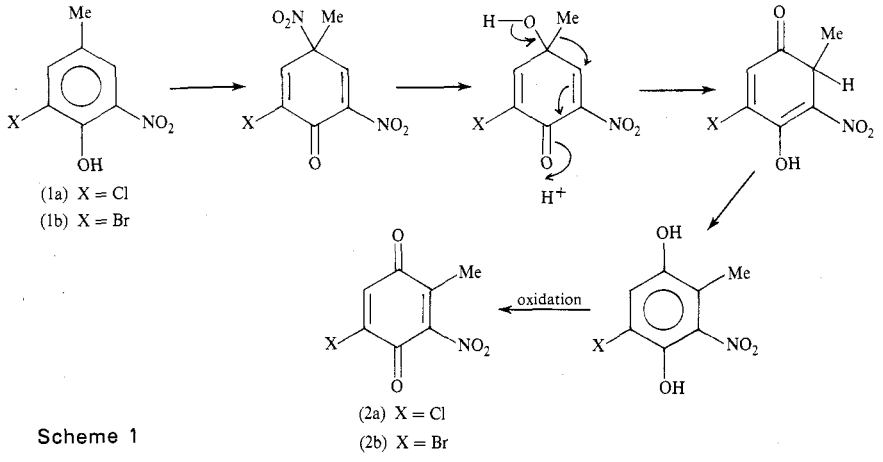
Discussion

(a) Nitration of the 4-Methylphenols (6a,b)

Reaction of the tetrabromo phenol (6a) with fuming nitric acid at 50° gave a mixture of the 4-nitrato dienone (10a) and the 4-hydroxy dienone (7a),[5] which were separated by chromatography. Under these reaction conditions the 4-hydroxy dienone (7a) is converted partly into the 4-nitrato dienone (10a) (control expt). The 4-nitrato dienone (10a) was identified by means of its spectroscopic data.

Nitration of the tribromo nitro phenol (6b) under similar conditions to the above also gave a mixture of the corresponding 4-nitrato dienone (10b) and the 4-hydroxy dienone (7b). Partial conversion of the 4-hydroxy dienone (7b) into the 4-nitrato dienone (10b) was again effected by treatment with fuming nitric acid. Reaction of the tribromo nitro phenol (6b) with fuming nitric acid in acetic acid gave the unstable 4,6-dinitro dienone (11), which on warming in acetic acid solution yielded the 4-hydroxy dienone (7b). The spectroscopic data for these compounds were in accord with the structures assigned to them.



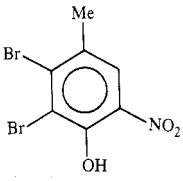
Scheme 1

(b) Nitration of the 4-Ethylphenols (9a,b)

Reaction of the tetrabromo ethyl phenol (9a) with fuming nitric acid at 50° gave a mixture of the 4-nitrato dienone (12a), the 4-hydroxy dienone (8a)[6] and the nitro phenol (9b), which were separated by chromatography. The mode of formation of the nitro phenol (9b) (yield *c.* 5%) is uncertain, but the nitrato dienone (12a) is formed from the hydroxy dienone (8a) under the reaction conditions (control expt). Nitration of the 4-ethylphenol (9a) with fuming nitric acid in acetic acid gave the 4-nitro dienone (13a), which was converted into the known[6] 4-hydroxy dienone (8a) on warming in acetic acid solution.

Nitration of the tribromo nitro phenol (9b) with fuming nitric acid at 50° also gave a mixture of the corresponding 4-nitrato dienone (12b) and the 4-hydroxy dienone (8b). Reaction of the 4-hydroxy dienone (8b) under similar conditions resulted in its partial conversion into the 4-nitrato dienone (12b) and the rearranged 2,3-dibromo-5-ethyl-6-nitro-1,4-benzoquinone (14a); the latter material was identical with that formed (below) on reaction of the 4-hydroxy dienone (8b) in concentrated

sulfuric acid. Nitration of the tribromo nitro phenol (9b) with fuming nitric acid in acetic acid gave the 4,6-dinitrodienone (13b); on warming in acetic acid solution the 4,6-dinitro dienone (13b) yielded the corresponding 4-hydroxy dienone (8b).



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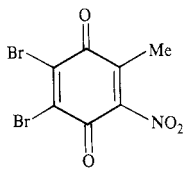

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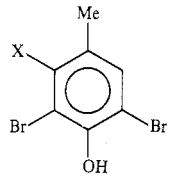
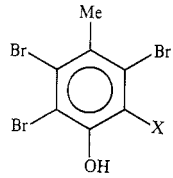


(5a) X = H
(5b) X = Br



(6a) X = Br
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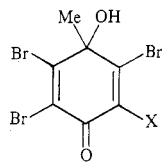
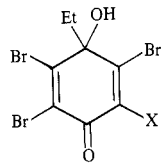
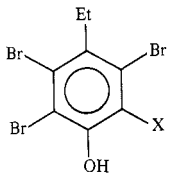


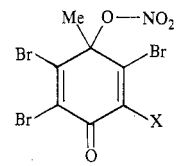
(7a) X = Br
(7b) X = NO_2



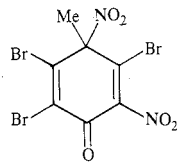
(8a) X = Br
(8b) X = NO_2



(9a) X = Br
(9b) X = NO_2



(10a) X = Br
(10b) X = NO_2



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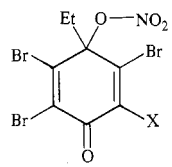
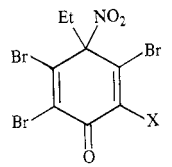
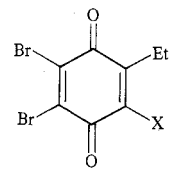


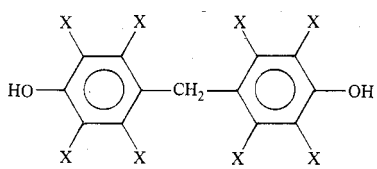
(12a) X = Br
(12b) X = NO_2



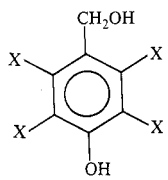
(13a) X = Br
(13b) X = NO_2



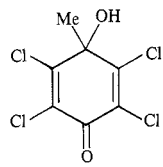
(14a) X = NO_2
(14b) X = Br



(15a) X = Br
(15b) X = Cl



(16a) X = Br
(16b) X = Cl

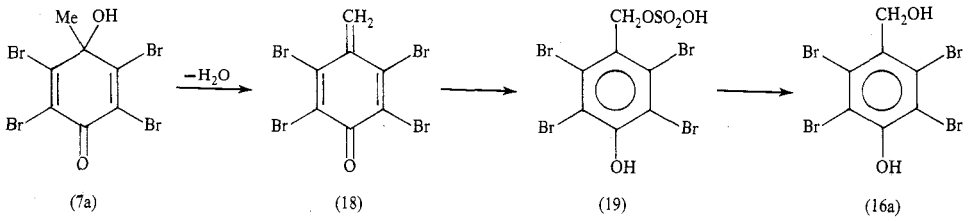


(17)

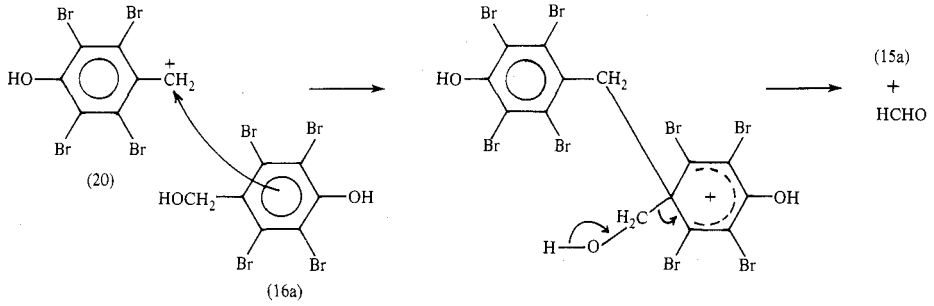
(c) Reaction Pathways in Nitrations of 4-Methylphenols (6a,b) and of 4-Ethylphenols (9a,b) with Fuming Nitric Acid at 50°

Nitration of the four polysubstituted phenols (6a,b) and (9a,b) would be expected to yield the corresponding 4-nitrocyclohexa-2,5-dienones. It appears that, under the reaction conditions, the 4-nitro dienone rearranges to give the 4-nitrito dienone, which on hydrolysis yields the corresponding 4-hydroxy dienone. It is conceivable that the 4-nitrato dienones might be formed by oxidation of 4-nitrito dienones; however, it is clear that the 4-nitrato dienones can be formed by esterification of the 4-hydroxy dienones. Only in the reaction of 4-hydroxy dienone (8b) with fuming nitric acid

was a rearrangement product, 2,3-dibromo-5-ethyl-6-nitro-1,4-benzoquinone (14a), isolated, and then only in low yield. As this was clearly a product of acid-catalysed rearrangement of the 4-hydroxy dienone (8b), we examined the rearrangements of the 4-hydroxy dienones (7a,b) and (8a,b) in concentrated sulfuric acid.



Scheme 2



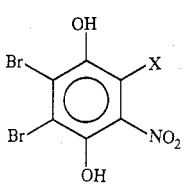
Scheme 3

(d) Rearrangement of 4-Hydroxy Dienone (7a) in Concentrated Sulfuric Acid

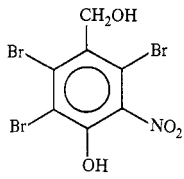
Zincke and Buff[5] reported that reaction of the 4-hydroxy dienone (7a) with warm concentrated sulfuric acid gave the diphenylmethane derivative (15a) with the release of formaldehyde. In the present work, reaction of the hydroxy dienone (7a) with concentrated sulfuric acid at 20° for 14 h, followed by quenching with ice-water, gave a high yield (*c.* 94%) of 2,3,5,6-tetrabromo-4-hydroxybenzenemethanol (16a). The structure of this product was assigned on the basis of its spectroscopic data and elemental analysis. In particular, the ^{1}H n.m.r signal at δ 5·12 and the ^{13}C n.m.r signal at δ 68·7 pointed to the presence of the benzenemethanol structural feature [for benzenemethanol: ^{1}H n.m.r. ($CDCl_3$) δ 4·70, CH_2;[7] ^{13}C n.m.r. ($CDCl_3$) δ 64·7, CH_2 [8]]; for diphenylmethane the CH_2 resonance appears at δ 42·1.[9] The benzenemethanol derivative (16a) melted with decomposition at a temperature (175–180°) below that quoted earlier[10] for (16a) [m.p. 200° (dec.)]; however, the sample resolidified and melted with decomposition at a temperature (270°) just below that quoted[5] [m.p. 280–281° (dec.)] for the purified diphenylmethane derivative (15a). It should be noted that Zincke and Böttcher[11] reported that the benzenemethanol derivative (16a) is converted into the diphenylmethane derivative (15a) on heating at 200° for 30 min.

[7] 'Aldrich Library of N.M.R. Spectra' 1974, **5**, 1.
[8] Bose, A. K., and Srinivasan, P. R., *Tetrahedron*, 1975, **31**, 3025.
[9] Proulx, T. W., and Smith, W. B., *J. Magn. Reson.*, 1976, **23**, 477.
[10] Eistert, B., Fink, H., and Müller, A., *Chem. Ber.*, 1962, **92**, 2403.
[11] Zincke, T., and Böttcher, K., *Justus Liebigs Ann. Chem.*, 1905, **343**, 100.

Zincke and Hunke[12] reported that, under the reaction conditions employed earlier,[5] i.e. *warming* with concentrated sulfuric acid, both the tetrachlorobenzenemethanol derivative (16b) and the tetrachloro hydroxy dienone (17) were converted into the diphenylmethane derivative (15b). It appears, therefore, that in the present reaction of the tetrabromo hydroxy dienone (7a) with concentrated sulfuric acid at 20° the intermediate benzenemethanol derivative (16a) has been isolated. The probable mode of formation of this compound (16a) is given in Scheme 2. Acid-catalysed dehydration of the hydroxy dienone (7a) would give the quinone methide (18); addition of sulfuric acid to the quinone methide (18), followed by hydrolysis (on workup) of the hydrogen sulfate (19), would yield the benzenemethanol derivative (16a). The formation of the diphenylmethane derivative (15a) from this intermediate (16a) clearly involves *ipso* attack by the benzylic cation (20) on the benzenemethanol derivative (16a), with subsequent loss of formaldehyde from the *ipso* Wheland intermediate (Scheme 3).



(21a) X = Me
(21b) X = Et



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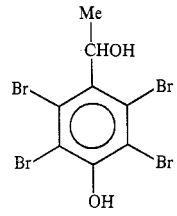

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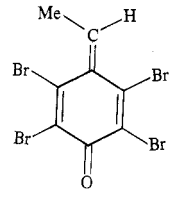

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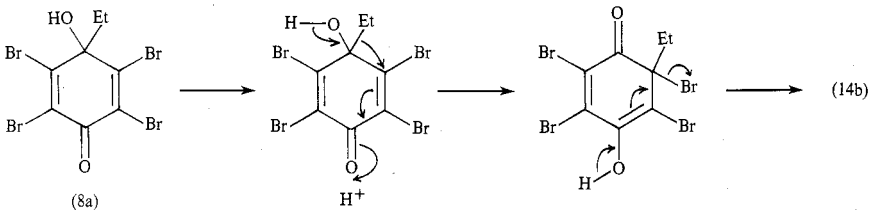

(8a)

Scheme 4

(e) Rearrangement of the 4-Hydroxy Nitro Dienone (7b) in Concentrated Sulfuric Acid

Brief treatment of the 4-hydroxy nitro dienone (7b) resulted in partial conversion of the material into two incompletely characterized compounds tentatively assigned the hydroquinone (21a) and benzenemethanol (22) structures on the basis of their spectroscopic data (see Experimental section).

(f) Rearrangement of 2,3,5,6-Tetrabromo-4-ethyl-4-hydroxycyclohexa-2,5-dienone (8a) in Concentrated Sulfuric Acid

Reaction of the 4-hydroxy dienone (8a) with cold concentrated sulfuric acid for 17 h gave a mixture from which the substituted 1,4-benzoquinones (14b)[6] and tetrabromo-4-ethylphenol (9a) were isolated. We have no information which points to the mode of formation of the tetrabromo-4-ethylphenol (9a), but the substituted 1,4-benzoquinone (14b) is probably formed by the acid-catalysed rearrangement outlined in Scheme 4.

[12] Zincke, T., and Hunke, L., *Justus Liebigs Ann. Chem.*, 1906, **349**, 97.

It is of interest to note that neither the 1-phenylethanol derivative (23), nor products derived therefrom, appear among the reaction products. In comparison with the reaction of the 4-hydroxy 4-methyl dienone (7a) [section (*d*) above] two factors probably lead to the differences observed in the reaction of the 4-ethyl 4-hydroxy dienone (8a). On the one hand rearrangement, as in Scheme 4, would be promoted by the greater migratory aptitude of the ethyl group,[13] and on the other hand the formation of the quinone methide (24)—the intermediate in the formation of the 1-phenylethanol derivative (23)—would be suppressed by steric interactions between the alkyl group and the adjacent bromine atoms.

(g) Rearrangement of 2,3,5-Tribromo-4-ethyl-4-hydroxy-6-nitrocyclohexa-2,5-dienone (8b) in Concentrated Sulfuric Acid.

Reaction of the hydroxy nitro dienone (8b) with sulfuric acid at 20° for 17 h gave essentially a mixture of the substituted 1,4-benzoquinone (14a) and its hydroquinone (21b). These compounds were identified from their spectroscopic data and elemental analyses, and their structural relationship established by reduction of the 1,4-benzoquinone (14a) to give the hydroquinone (21b).

The acid-catalysed rearrangement of the hydroxy dienone (8b) is notable in leading to products of ethyl migration in high yield (*c.* 86%). In this substrate the relatively high migratory aptitude of the 4-ethyl group is reinforced by the presence of a 6-nitro substituent.

Experimental

For general experimental information refer to the earlier paper.[3]

Nitration of 2,3,5,6-Tetrabromo-4-methylphenol (6a)

The tetrabromo phenol (6a) (1·01 g) was added over 10 min to stirred fuming nitric acid (*d* 1·5; 4·5 ml) at *c.* 50°. The resulting solution was stirred at *c.* 50° for a further 20 min, cooled, water added, and the crude product (815 mg) isolated by filtration. Chromatography of this material on a Chromatotron silica gel plate gave the following compounds in order of elution.

2,3,5,6-Tetrabromo-4-methyl-4-nitratocyclohexa-2,5-dienone (10a) (380 mg; 33%), m.p. 153–153·5° (dec.) (Found: C, 17·6; H, 0·8; Br, 66·1; N, 2·8. $C_7H_3Br_4NO_4$ requires C, 17·4; H, 0·6; Br, 65·9; N, 2·9%). ν_{max} (Nujol) 1675, conjugated ketone; 1657, 1276, 824 cm^{-1}, ONO_2. ^1H n.m.r. ($CDCl_3$) δ 1·85, s, Me. ^{13}C n.m.r. (CD_3COCD_3) δ 26·6, CH_3; 87·5, C4; 129·0, C2,6; 146·4, C3,5; signal for C1 not observed. λ_{max} ($CHCl_3$) 276, 308 nm (ε 12900, 2900).

2,3,5,6-Tetrabromo-4-hydroxy-4-methylcyclohexa-2,5-dienone (7a) (430 mg; 41%), m.p. 209–212° (lit.[5] 205°). ν_{max} (Nujol) 3400, 3260, OH; 1675, 1668, 1572 cm^{-1}, conjugated ketone. ^1H n.m.r. ($CDCl_3$) δ 1·83, Me; 2·70, OH. ^{13}C n.m.r. (CD_3COCD_3) δ 27·7, CH_3; 75·8, C4; 123·5, C2,6; 152·7, C3,5; 167·3, C1. λ_{max} ($CHCl_3$) 272, 309 nm (ε 11600, 3200).

Reaction of 2,3,5,6-Tetrabromo-4-hydroxy-4-methylcyclohexa-2,5-dienone (7a) with Fuming Nitric Acid

The hydroxy dienone (7a) (200 mg) was added over 4 min to stirred fuming nitric acid (*d* 1·5; 1 ml) at 50°. The resulting solution was stirred at 50° for a further 7 min, cooled, water added, and the crude product (173 mg) isolated by filtration. Separation on a Chromatotron silica gel plate gave the 4-nitrato dienone (10a) (65 mg) and the 4-hydroxy dienone (7a) (100 mg).

2,3,5-Tribromo-4-methyl-4,6-dinitrocyclohexa-2,5-dienone (11)

Fuming nitric acid (*d* 1·5; 1·2 ml) was added rapidly to a stirred suspension of 2,3,5-tribromo-4-methyl-6-nitrophenol (6b) (1·2 g) in acetic acid (6 ml) at 20°, and the mixture was stirred for a further 20 min. The mixture was cooled and the deposited nitro dienone (11) (940 mg) isolated

[13] Pilkington, J. W., and Waring, A. J., *J. Chem. Soc., Perkin Trans. 2*, 1976, 1349.

by filtration; further nitro dienone (11) (110 mg) was obtained by addition of water to the filtrate. The nitro dienone (11) had m.p. 115–117° (dec.). ν_{max} (Nujol) 1679, conjugated ketone; 1574, 1545 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 2·33, Me. ^{13}C n.m.r. (CD_3COCD_3; −25°) δ 25·6, CH_3; 96·3, C4; 131·6, 132·4, C2,5; 141·5, C3; 166·5, C1; signal for C6 was not observed. λ_{max} ($CHCl_3$) 262, 306 nm (ε 10300, 3400).

2,3,5-Tribromo-4-hydroxy-4-methyl-6-nitrocyclohexa-2,5-dienone (7b)

The 4,6-dinitro dienone (11) (1·11 g) was suspended in acetic acid (5 ml), and the mixture heated at 45–55° for 30 min. Water was added to the resulting solution, which was then cooled. The crystalline material was isolated by filtration to give the *hydroxy nitro dienone* (7b) (700 mg), m.p. 157–159° (dec.) (Found: C, 20·6; H, 1·0; Br, 58·9; N, 3·4. $C_7H_4Br_3NO_4$ requires C, 20·7; H, 1·0; Br, 59·1; N, 3·5%). ν_{max} (Nujol) 3470, OH; 1669, 1570, conjugated ketone; 1540 cm^{-1} (NO_2). ^1H n.m.r. ($CDCl_3$) δ 1·87, Me; 3·08, OH. ^{13}C n.m.r. (CD_3COCD_3) δ 29·3, CH_3; 76·6, C4; 126·0, C2; 144·9, C5; 156·5, C3; 167·2, C1; signal for C6 was not observed. λ_{max} ($CHCl_3$) 261, 306 nm (ε 13800, 4000).

Nitration of 2,3,5-Tribromo-4-methyl-6-nitrophenol (6b)

The tribromo nitro phenol (6b) (900 mg) was added over 12 min to stirred fuming nitric acid (*d* 1·5; 4·1 ml) at 50°. The resulting solution was stirred at 50° for a further 5 min, cooled, water added, and the crystalline material isolated by filtration to give *2,3,5-tribromo-4-methyl-4-nitrato-6-nitrocyclohexa-2,5-dienone* (10b) (286 mg; 27%), m.p. 174–175° (dec.) (Found: C, 18·6; H, 1·2; Br, 53·4; N, 6·0. $C_7H_3Br_3N_2O_6$ requires C, 18·7; H, 0·7; Br, 53·2; N, 6·2%). ν_{max} (Nujol) 1688, conjugated ketone; 1661, 1278, 825, ONO_2; 1549 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1·92, Me. ^{13}C n.m.r. (CD_3COCD_3) δ 26·0, CH_3; 85·8, C4; 129·4, C2; 138·2, C5; 147·6, C3; 166·6, C1; signal for C6 was not observed. λ_{max} ($CHCl_3$) 263, 305 nm (ε 14300, 4550).

Addition of further water to the filtrate, above, gave the hydroxy nitro dienone (7b) (total 627 mg; 56%), identical with authentic material.

Reaction of 2,3,5-Tribromo-4-hydroxy-4-methyl-6-nitrocyclohexa-2,5-dienone (7b) with Fuming Nitric Acid

The hydroxy nitro dienone (7b) (473 mg) was added over 15 min to stirred fuming nitric acid (*d* 1·5; 2·2 ml) at 50°. The resulting solution was stirred at 50° for a further 5 min, cooled, and water added to give the 4-nitrato dienone (10b) (175 mg), identical with authentic material. Further addition of water to the filtrate gave the 4-hydroxy dienone (7b) (225 mg), identical with authentic material. Finally, further dilution of the filtrate, above, with water, and isolation by means of chloroform extraction gave a mixture (71 mg; *c.* 3 : 1) of the 4-nitrato dienone (10b) and the 4-hydroxy dienone (7b).

2,3,5,6-Tetrabromo-4-ethyl-4-nitrocyclohexa-2,5-dienone (13a)

Fuming nitric acid (*d* 1·5; 5 ml) was added over 1 min to a stirred suspension of 2,3,5,6-tetrabromo-4-ethylphenol (9a) (5 g) in acetic acid (40 ml) at 20°, and the resulting mixture stirred at 20° for 45 min. The mixture was cooled and the crystalline material isolated by filtration; addition of water to the filtrate gave a second crop of crystals of the *4-nitro dienone* (13a) (total 4·9 g), m.p. 91–92° (dec.) (Found: C, 20·0; H, 0·8; Br, 66·0; N, 2·7. $C_8H_5Br_4NO_3$ requires C, 19·9; H, 1·0; Br, 66·2; N, 2·9%). ν_{max} (Nujol) 1690, 1602, conjugated ketone; 1573, 1561 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 0·75, t, *J* 7·5 Hz, Me; 2·79, q, *J* 7·5 Hz, CH_2. ^{13}C n.m.r. (CD_3COCD_3; −25°) δ 7·3, CH_3; 32·6, CH_2; 101·4, C4; 132·6, C2,6; 140·0, C3,5; signal for C1 not observed. λ_{max} ($CHCl_3$) 274, *c.* 310 nm (ε 15000, 2800).

2,3,5,6-Tetrabromo-4-ethyl-4-hydroxycyclohexa-2,5-dienone (8a)

The 4-nitro dienone (13a) (4·4 g) was suspended in acetic acid (20 ml), and heated at 50–60° for 1 h. Addition of water to the reaction mixture, and cooling gave the 4-hydroxy dienone (8a) (total 3·45 g), m.p. 139–141° (lit.[6] 139–140°). ν_{max} (Nujol) 3460, OH; 1666 cm^{-1}; conjugated ketone. ^1H n.m.r. ($CDCl_3$) δ 0·61, t, *J* 7 Hz, 2·21, q, *J* 7 Hz, CH_2; 3·10, OH. ^{13}C n.m.r. (CD_3COCD_3) δ 7·6, CH_3; 35·6, CH_2; 82·3, C4; 126·9, C2,6; 153·8, C3,5; 170·0, C1. λ_{max} ($CHCl_3$) 272, 309 nm (ε 12400, 2400).

Nitration of 2,3,5,6-Tetrabromo-4-ethylphenol (9a)

The tetrabromo phenol (9a) (1 g) was added over 20 min to stirred fuming nitric acid (*d* 1·5; 4·5 ml) at 50°. The resulting solution was stirred at 50° for a further 5 min, excess water added, and the crude product (1·07 g) isolated by means of chloroform. Chromatography on a Chromatotron silica gel plate gave the following compounds in order of elution.

2,3,5,6-Tetrabromo-4-ethyl-4-nitratocyclohexa-2,5-dienone (12a) (195 mg; 17%), m.p. 118–119° (Found: C, 19·3; H, 1·1; Br, 64·2; N, 2·7. $C_8H_5Br_4NO_4$ requires C, 19·3; H, 1·0; Br, 64·1; N, 2·8%). ν_{max} (Nujol) 1683, conjugated ketone; 1652, 1273, 831 cm^{-1}, ONO_2. ^1H n.m.r. ($CDCl_3$) δ 0·70, t, *J* 7 Hz, Me; 2·16, q, *J* 7 Hz, CH_2. ^{13}C n.m.r. (CD_3COCD_3) δ 6·5, CH_3; 31·9, CH_2; 91·3, C4; 129·8, C2,6; 145·3, C3,5; 169·6, C1. λ_{max} ($CHCl_3$) 276, 305 nm (ε 16300, 3200).

2,3,5-Tribromo-4-ethyl-6-nitrophenol (9b) (48 mg; 5%), identical with authentic material.

2,3,5,6-Tetrabromo-4-ethyl-4-hydroxycyclohexa-2,5-dienone (8a) (651 mg; 63%), identical and authentic material.

Reaction of 2,3,5,6-Tetrabromo-4-ethyl-4-hydroxycyclohexa-2,5-dienone (8a) with Fuming Nitric Acid

The 4-hydroxy dienone (8a) (300 mg) was added over 10 min to stirred fuming nitric acid (*d* 1·5; 1·4 ml) at 50°. The resulting solution was stirred at 50° for a further 10 min, cooled, water added, and the crude product (270 mg) isolated by filtration. Chromatography of this mixture on a Chromatotron silica gel plate gave the following compounds.

2,3,5,6-Tetrabromo-4-ethyl-4-nitratocyclohexa-2,5-dienone (12a) (173 mg).

2,3,5,6-Tetrabromo-4-ethyl-4-hydroxycyclohexa-2,5-dienone (8a) (96 mg).

Both samples were identical with authentic material.

Reaction of 2,3,5,6-Tetrabromo-4-ethylphenol (9a) with Sodium Nitrite in Acetic Acid

Powdered sodium nitrite (2·36 g) was added over 30 min to a stirred suspension of the tetrabromo phenol (9a) (10 g) in acetic acid (100 ml) at 20°. The resulting solution was stirred at 20° for 2 h, excess water added, and the crude product isolated by means of dichloromethane. Chromatography on a silica gel column gave the following compounds.

(i) 2,3,5,6-Tetrabromo-4-ethylphenol (9a) (3·5 g).

(ii) 2,3,5-Tribromo-4-ethyl-6-nitrophenol (9b) (3·5 g), m.p. 127–128° (dec.) (lit.[6] 122–123°). ν_{max} (Nujol) 3410, OH; 1534 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1·17, t, *J* 7·5 Hz, Me; 3·15, q, *J* 7·5 Hz, CH_2; 6·65, OH. ^{13}C n.m.r. (CD_3COCD_3) δ 12·6, CH_3; 32·9, CH_2; 113·9, 117·4, C2,5; 129·4, C3; 137·8, C4; 146·2, C1; signal for C6 not observed.

(iii) 2,3,5,6-Tetrabromo-4-ethyl-4-hydroxycyclohexa-2,5-dienone (8a) (500 mg).

Compounds (i) and (iii) were identical with authentic samples.

2,3,5-Tribromo-4-ethyl-4,6-dinitrocyclohexa-2,5-dienone (13b)

Fuming nitric acid (*d* 1·5; 5 ml) was added over 2 min to a stirred suspension of 2,3,5-tribromo-4-ethyl-6-nitrophenol (9b) (5 g) in acetic acid (15 ml) at 20°, and the mixture was stirred at 20° for 45 min. The mixture was cooled, and the deposited 4,6-dinitro dienone (13b) (4·66 g) isolated by filtration; a further crop of this material was obtained by addition of water to the filtrate. The *4,6-dinitro dienone* (13b) (total 4·83 g) had m.p. 92–93° (dec.) (Found: C, 21·4; H, 0·9; Br, 53·0; N, 5·8. $C_8H_5Br_3N_2O_5$ requires C, 21·4; H, 1·1; Br, 53·4; N, 6·2%). ν_{max} (Nujol) 1692, 1642, conjugated ketone; 1575, 1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 0·83, t, *J* 7 Hz, Me; 2·82, q, *J* 7 Hz, CH_2. ^{13}C n.m.r. (CD_3COCD_3; −25°) δ 7·2, CH_3; 32·7, CH_2; 99·7, C4; 132·0, 132·9, C2,5; 140·9, C3; 151·7, C6; 166·4, C1. λ_{max} ($CHCl_3$) 263, 309 nm (ε 9100, 3000).

2,3,5-Tribromo-4-ethyl-4-hydroxy-6-nitrocyclohexa-2,5-dienone (8b)

The 4,6-dinitro dienone (13b) (4·56 g) was suspended in acetic acid (20 ml), and heated at 50–60° for 1 h. Water was added to the resulting solution, and after cooling the product was isolated by filtration to give the *4-hydroxy 6-nitro dienone* (8b) (2·43 g), m.p. 140–142° (Found: C, 22·9; H, 1·4; Br, 56·9; N, 3·3. $C_8H_6Br_3NO_4$ requires C, 22·9; H, 1·4; Br, 57·1; N, 3·3%). ν_{max} (Nujol) 3540, OH; 1677, conjugated ketone; 1543 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ

0·71, t, *J* 7·5 Hz, Me; 2·27, q, *J* 7·5 Hz, CH_2; 3·13, OH. ^{13}C n.m.r. (CD_3COCD_3) δ 7·4, CH_3; 35·4, CH_2; 80·5, C4; 126·9, C2; 143·8, C5; 155·5, C3; 167·4, C1; signal for C6 not observed. λ_{max} ($CHCl_3$) 262, 307 nm (ε 14800, 4100).

Nitration of 2,3,5-Tribromo-4-ethyl-6-nitrophenol (9b)

The tribromo nitro phenol (9b) (1 g) was added over 15 min to stirred fuming nitric acid (*d* 1·5; 4·5 ml) at 50°. The resulting solution was stirred at 50° for a further 5 min, cooled, water added, and the crude product (1·1 g) isolated by means of chloroform. Chromatographic separation on a Chromatotron silica gel plate gave the following compounds in order of elution:

2,3,5-Tribromo-4-ethyl-4-nitrato-6-nitrocyclohexa-2,5-dienone (12b) (219 mg), m.p. 140–141° (Found: C, 20·9; H, 1·1; Br, 51·7; N, 5·9. $C_8H_5Br_3N_2O_6$ requires C, 20·7; H, 1·1; Br, 51·6; N, 6·0%). ν_{max} (Nujol) 1687, conjugated ketone; 1658, 1274, 830, ONO_2; 1550 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 0·80, t, *J* 7 Hz, Me; 2·22, q, *J* 7 Hz, CH_2. ^{13}C n.m.r. (CD_3COCD_3) δ 6·5, CH_3; 32·2, CH_2; 89·3, C4; 130·1, C2; 137·5, C5; 146·9, C3; 166·7, C1; signal for C6 not observed. λ_{max} ($CHCl_3$) 263·5, 308 nm (ε 16200, 4900).

2,3,5-Tribromo-4-ethyl-4-hydroxy-6-nitrocyclohexa-2,5-dienone (8b) (617 mg), identical with authentic material.

Reaction of 2,3,5-Tribromo-4-ethyl-4-hydroxy-6-nitrocyclohexa-2,5-dienone (8b) with Fuming Nitric Acid

The hydroxy nitro dienone (8b) (300 mg) was added over 15 min to stirred fuming nitric acid (*d* 1·5; 1·4 ml) at 50°. The resulting solution was stirred at 50° for a further 5 min, cooled, water added, and the deposited 4-nitrato dienone (12b) (147 mg) isolated by filtration. Addition of further water to the filtrate gave the 4-hydroxy dienone (8b) (105 mg). Extraction of this second filtrate with chloroform gave an extract (53 mg) which on chromatography on a Chromatotron silica gel plate gave 2,3-dibromo-5-ethyl-6-nitro-1,4-benzoquinone (14a) (5 mg) (see below) and 4-hydroxy dienone (8b) (23 mg). Compounds (8b), (12b) and (14a), above, were identical with authentic samples.

Reaction of 2,3,5,6-Tetrabromo-4-hydroxy-4-methylcyclohexa-2,5-dienone (7a) in Sulfuric Acid

Powdered hydroxy dienone (7a) (1 g) was added to stirred sulfuric acid (*d* 1·84; 8 ml) at 20°. The resulting mixture was stirred in the dark for 14 h, before being poured into ice-water. The solid which deposited was isolated by filtration and identified as *2,3,5,6-tetrabromo-4-hydroxybenzenemethanol* (16a) (942 mg), [m.p. 175–180° (dec.) {lit.[10] 200° (dec.)}; resolidified above 210°, m.p. 270° (dec.) {lit.[5] for compound (15a) 280–281° (dec.)}] (Found: C, 19·2; H, 0·8; Br, 72·5. $C_7H_4Br_4O_2$ requires C, 19·1; H, 0·9; Br, 72·7%). ν_{max} (Nujol) 3500 cm^{-1}, OH. ^1H n.m.r. (CD_3COCD_3) δ 5·12, CH_2. ^{13}C n.m.r. [CD_3COCD_3; $Cr(acac)_3$] δ 68·7, CH_2; 115·3, C3,5; 128·5, C2,6; 134·3, C1; 153·3, C4.

Reaction of 2,3,5-Tribromo-4-hydroxy-4-methyl-6-nitrocyclohexa-2,5-dienone (7b) in Sulfuric Acid

Powdered hydroxy nitro dienone (7b) (260 mg) was added to stirred sulfuric acid (*d* 1·84; 2 ml) at 20°. The resulting mixture was stirred at 20° in the dark for 25 min, poured onto ice-water, and the crude product isolated by extraction with chloroform. Chromatography on a Chromatotron silica gel plate gave the following compounds in order of elution.

2,3-Dibromo-5-methyl-6-nitro-1,4-hydroquinone (21a) (59 mg), m.p. 143–144° [Found: c.i. (isobutane) MH^+ 326. $C_7H_6Br_2NO_4^+$ requires 326; insufficient for elemental analysis]. ν_{max} (Nujol) 3500, OH; 1564 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 2·43, Me; 10·97, OH; 11·08, OH.

2,3,5-Tribromo-4-hydroxy-4-methyl-6-nitrocyclohexa-2,5-dienone (7b) (45 mg), identical with authentic material.

2,3,6-Tribromo-4-hydroxy-5-nitrobenzenemethanol (22) (46 mg), as an impure solid, m.p. 170–171° (dec.). ν_{max} (Nujol) 3410, OH; 1540 cm^{-1}, NO_2. ^1H n.m.r. (CD_3COCD_3) δ 5·08, CH_2.

Reaction of 2,3,5,6-Tetrabromo-4-ethyl-4-hydroxycyclohexa-2,5-dienone (8a) in Sulfuric Acid

Powdered tetrabromo hydroxy dienone (8a) (500 mg) was added to stirred sulfuric acid (*d* 1·84; 4 ml), stirring continued for 1 h at 20°, and the mixture allowed to stand at 20° for 17 h. The mixture was added to ice-water, and the crude product (436 mg) isolated by filtration.

Chromatographic separation on a silica gel Chromatotron plate gave the following compounds in order of elution.

2,3,6-Tribromo-5-ethyl-1,4-benzoquinone (14b) (222 mg), m.p. 117–118° (lit.[6] 118–120°). ν_{max} (Nujol) 1678, 1664, 1568 cm^{-1}, 1,4-benzoquinone. ^1H n.m.r. ($CDCl_3$) δ 1·13, t, *J* 7 Hz, Me; 2·77, q, *J* 7 Hz, CH_2. ^{13}C n.m.r. (CD_3COCD_3) δ 11·9, CH_3; 26·1, CH_2; 134·3, 138·1, 140·1, C 2,3,5; 151·0. C 6; 171·8, C 1; 175·6, C 4. λ_{max} ($CHCl_3$) 304·5 nm (ε 24000).

2,3,5,6-Tetrabromo-4-ethylphenol (9a) (129 mg), identical with an authentic sample.

Reaction of 2,3,5-Tribromo-4-ethyl-4-hydroxy-6-nitrocyclohexa-2,5-dienone (8b) in Sulfuric Acid

Powdered hydroxy nitro dienone (8b) (500 mg) was added to stirred sulfuric acid (*d* 1·84; 4 ml), stirred at 20° for 1 h, and stored at 20° for 16 h. The reaction mixture was added to ice-water, and the crude product (350 mg) isolated by filtration. Chromatographic separation on a Chromatotron silica gel plate gave the following compounds in order of elution.

2,3-Dibromo-5-ethyl-6-nitro-1,4-benzoquinone (14a) (208 mg), m.p. 103–104° (Found: C, 28·5; H, 1·6; Br, 46·9; N, 4·1. $C_8H_5Br_2NO_4$ requires C, 28·4; H, 1·5; Br, 47·2; N, 4·1%). ν_{max} (Nujol) 1679, carbonyl; 1534 cm^{-1}, NO_2. ^1H n.m.r. ($CDCl_3$) δ 1·19, t, *J* 8 Hz, Me; 2·55, q, *J* 8 Hz, CH_2. ^{13}C n.m.r. (CD_3COCD_3) δ 13·1, CH_3; 21·4, CH_2; 137·3, 141·2, C 2,3,5; 170·5, C 4; 177·0, C 1; signal for C 6 not observed. λ_{max} ($CHCl_3$) 287, 378 nm (ε 10400, 1100).

2,3-Dibromo-5-ethyl-6-nitro-1,4-hydroquinone (21b) (139 mg), m.p. 158–159° (Found: C, 28·4; H, 2·4; Br, 46·9; N, 4·0. $C_8H_7Br_2NO_4$ requires C, 28·2; H, 2·1; Br, 46·9; N, 4·1%). ν_{max} (Nujol) 3520, 3400, OH; 1530 cm^{-1}, NO_2. ^1H n.m.r ($CDCl_3$) δ 1·23, t, *J* 7 Hz, Me; 2·76, q, *J* 7 Hz, CH_2. ^{13}C n.m.r. (CD_3COCD_3) δ 13·9, CH_3; 21·2, CH_2; 113·8, C 2; 125·0, C 3; 140·6, 142·7, 147·3, C 1,4,5; signal for C 6 not observed.

Reduction of 2,3-Dibromo-5-ethyl-6-nitro-1,4-benzoquinone (14a)

A suspension of stannous chloride (200 mg) in water (5 ml) was added to the 1,4-benzoquinone (14a) (50 mg) in acetic acid (1 ml) at 5°, and the mixture slowly warmed to 20° over 1 h. Water was added to the mixture, and 2,3-dibromo-5-ethyl-6-nitro-1,4-hydroquinone (21b) (49 mg) isolated by filtration. This material was identical with an authentic sample.

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