

Reactions of Quinones with Aromatic Ethers. Part VII.¹ Triphenylene-1,4 : 5,8-diquinones from Reactions of Veratrole or 3,4-Dimethoxyphenylbenzoquinones with Benzoquinones

By Robert Buchan, Chemistry Department, Robert Gordon's Institute of Technology, Aberdeen AB1 1HG
Oliver C. Musgrave,* Chemistry Department, The University, Old Aberdeen AB9 2UE

Veratrole reacts with 1,4-benzoquinone in the presence of aluminium chloride to form 10,11-dimethoxytriphenylene-1,4:5,8-diquinone. Related products result when 2-chloro- and 2,3-dichloro-1,4-benzoquinone are used. 3,4-Dimethoxyphenyl-1,4-benzoquinone reacts in a similar manner with unsubstituted, 2-methyl-, 2-chloro-, and 2,3-dichloro-1,4-benzoquinone, and with itself. The structures of the diquinones follow from their spectroscopic properties and their conversion into the corresponding triphenylene-1,4,5,8-tetra-yl tetra-acetates by reductive acetylation.

POLY-METHOXY-TRIPHENYLENES^{1,2} and -triphenylene-monoquinones³ can be prepared by acid-catalysed reactions of benzoquinones with veratrole or substituted veratroles. This paper describes related reactions which result in dimethoxytriphenylenediquinones.

The reaction⁴ of 1,4-benzoquinone with an excess of veratrole and anhydrous aluminium chloride in carbon disulphide produces a red quinone, C₁₈H₆O₄(OMe)₂, which, for the reasons already given,⁵ we formulate as the triphenylenediquinone (I; A = B = C = D = H). The use of an excess of 1,4-benzoquinone resulted in a higher yield (10.9%, based on the weight of veratrole consumed) of the diquinone. The bisleucoacetate prepared from the diquinone shows u.v. absorption very similar to that² of 2,3,6,7,10,11-hexamethoxytriphenylene and n.m.r. signals which confirm that it is the tetra-acetoxytri-

phenylene (II; A = B = C = D = H). The singlets at δ 7.30 and 8.46 correspond to the aromatic protons at C-2, -3, -6, and -7, and at C-9 and -12, respectively, the latter protons being deshielded by the acetoxy-groups at C-1 and -8. The singlets at δ 4.05, 2.44, and 2.24 result from the methoxy-protons, the C-1 and -8 acetoxy-protons, and the C-4 and -5 acetoxy-protons, respectively. A model shows that the steric interaction of the C-4 and -5 acetoxy-groups forces them into conformations in which their methyl protons are weakly shielded by the aromatic rings. The use of other Friedel-Crafts catalysts such as titanium(IV) chloride, zirconium(IV) chloride, aqueous 70% v/v sulphuric acid, and polyphosphoric acid, resulted in little or none of the above-mentioned triphenylenediquinone. All the reactions now described

¹ R. Buchan and O. C. Musgrave, *J.C.S. Perkin I*, 1975, 568.

² Part VI, R. Buchan and O. C. Musgrave, *J.C.S. Perkin I*, 1975, 811.

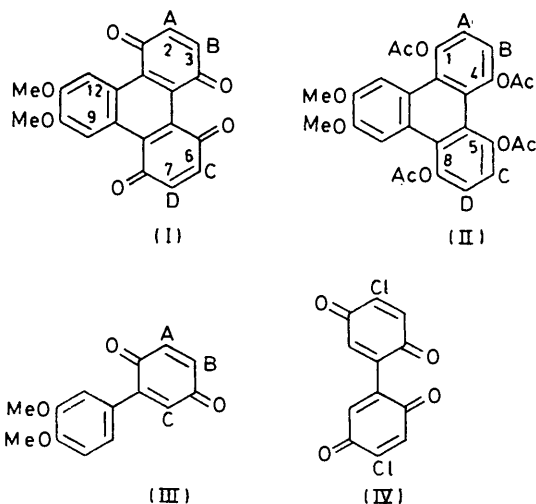
³ R. Pummerer, M. Dally, and S. Reissinger, *Ber.*, 1933, 66B, 792.

⁴ O. C. Musgrave and C. J. Webster, *J. Chem. Soc. (C)*, 1971, 1397.

⁵ B. W. Birrell, R. Buchan, and O. C. Musgrave, *Chem. Comm.*, 1969, 1341.

were therefore effected by using anhydrous aluminium chloride in carbon disulphide.

2,3-Dichloro-1,4-benzoquinone reacted with veratrole to give mainly the arylbenzoquinone (III; A = B = Cl, C = H) and only a low (0.5%) yield of the triphenylenediquinone (I; A = B = C = D = Cl). As expected,⁶



part of the veratrole was oxidised by the dichlorobenzoquinone with formation of 2,3,6,7,10,11-hexamethoxytriphenylene and a trace of 2,5,6,9,12,13-hexamethoxydibenzo[*fg,op*]naphthacene-1,10-quinone. Similar reactions between 2-chloro-1,4-benzoquinone and veratrole afforded the arylbenzoquinone (III; A = B = H, C = Cl), an inseparable mixture of the symmetrical 2,7- and 3,6-dichloro-diquinones (I; A = D = Cl, B = C = H) and (I; A = D = H, B = C = Cl), and a little of the unsymmetrical 2,6-dichloro-compound (I; A = C = Cl, B = D = H). The structure of the last-named compound follows from its n.m.r. spectrum, which shows signals at δ 7.06 and 7.22 corresponding to two quinonoid protons in different environments. We reductively acetylated the mixture of symmetrical dichloro-diquinones and obtained one of the resulting leucoacetates, the 3,6-dichloro-compound (II; A = D = H, B = C = Cl). The reductive acetylation of a crude mixture containing all three dichloroquinones gave a mixture of leucoacetates from which we were able to isolate the 2,6-dichloro-compound (II; A = C = Cl, B = D = H) as well as the 3,6-isomer. Attempted preparation of the 2,7-dichloro-diquinone (I; A = D = Cl, B = C = H) by the reaction of veratrole with the dichloro-diquinone (IV) was unsuccessful and gave only 2,3,6,7,10,11-hexamethoxytriphenylene.

The isolation of arylbenzoquinones from some of the above reactions suggested that such compounds, or, more probably, the corresponding quinols, are intermediates in the formation of the triphenylenediquinones. The preparation of the triphenylenediquinone (I; A = B = C = D = H) in improved yield (*ca.* 19%) by reactions between 1,4-benzoquinone and either the arylquinone (III; A = B = C = H) or the correspond-

ing quinol confirmed this. The former of these two reactions also yielded an inseparable mixture of the two isomeric aryltriphenylenediquinones [I; A = 3,4-(MeO)₂C₆H₃, B = C = D = H] and [I; B = 3,4-(MeO)₂C₆H₃, A = C = D = H], each formed by oxidative self-condensation of two molecules of the arylquinone. The structures of the components follow from the n.m.r. spectrum of the mixture, which shows signals corresponding to four methoxy-groups, two low-field aromatic protons, and six aromatic or quinonoid protons. The reaction of 2,3-dichloro-1,4-benzoquinone with the arylbenzoquinone (III; A = B = C = H) gave a similar mixture of the aryltriphenylenediquinones, together with the dichloro-diquinone (I; A = B = Cl, C = D = H) (4.5%). A much higher (44%) yield of the last-named compound resulted from the reaction between the arylchlorobenzoquinone (III; A = B = Cl, C = H) and benzoquinone. The lower yield is associated with the use of the dichlorobenzoquinone having the higher oxidation potential, namely 2,3-dichlorobenzoquinone. Presumably this oxidises the quinols which are necessary intermediates in the reaction of the two quinones and by so doing largely prevents the formation of the triphenylene system. The corresponding monochlorobenzoquinones behaved in a generally similar manner. 2-Chloro-1,4-benzoquinone reacted with the arylbenzoquinone (III; A = B = C = H) to give the expected mixture of the two aryltriphenylenediquinones and an inseparable mixture of the two chlorotriphenylenediquinones (I; A = Cl, B = C = D = H) and (I; B = Cl, A = C = D = H). Under similar conditions the arylchlorobenzoquinone (III; B = Cl, A = C = H) reacted with 1,4-benzoquinone more efficiently to form the chlorotriphenylenediquinone (I; B = Cl, A = C = D = H) as the sole product. Lastly, 2-methyl-1,4-benzoquinone reacted with the arylbenzoquinone (III; A = B = C = H) to give a mixture of the two methyltriphenylenediquinones (I; A = Me, B = C = D = H) and (I; B = Me, A = C = D = H) from which we isolated a small amount of the latter.

The triphenylenediquinones are readily recognised by their characteristic u.v. and visible absorption maxima at *ca.* 395 and 475 nm and by the u.v. spectra of the corresponding leucoacetates, which show the fine structure typical of triphenylene derivatives. The more abundant fragment ions in the mass spectrum of each of the chlorotriphenylenediquinones result from the expulsion of carbon monoxide and a chlorine atom, or of a methoxyl radical,³ from the molecular ion. The alkyl- and aryl-triphenylenediquinones fragment initially by expelling carbon monoxide or a methoxyl radical, or, where appropriate, 3,4-dimethoxyphenylacetylene. Each of the triphenylenediquinones shows the expected n.m.r. signals for the methoxy and aryl protons, the latter being deshielded by the adjacent carbonyl groups. The following arguments permit the assignment of the quinonoid proton signals in most cases. The location of

⁶ O. C. Musgrave and C. J. Webster, *J.C.S. Perkin I*, 1974, 2260.

the chlorine atom at C-3 in the monochlorotriphenylenediquinone (I; B = Cl, A = C = D = H) follows from the structure of the arylchlorobenzoquinone (III; B = Cl, A = C = H) used in its synthesis. The singlet at δ 7.07 in the spectrum of the former therefore corresponds to the isolated proton at C-2, and the singlet at δ 7.28 shown by the mixture of monochlorotriphenylenediquinones (I; A = Cl, B = C = D = H) and (I; B = Cl, A = C = D = H) must originate from the isomer having an isolated proton at C-3. The observed quinonoid proton signals for the three related dichlorotriphenylenediquinones (I; A = C = Cl, B = D = H), (I; A = D = Cl, B = C = H), and (I; B = C = Cl, A = D = H) are in accord with these values. Now the chlorine atom in a 2-chloro-1,4-naphthoquinone deshields the adjacent quinonoid proton by *ca.* 0.25 p.p.m. and consequently the C-2 and C-7 protons and the C-3 and C-6 protons of the dechloro-compound, the triphenylenediquinone (I; A = B = C = D = H), should resonate at *ca.* δ 6.82 and 7.03, respectively; these values are in good agreement with those observed (at δ 6.87 and 7.06). The remaining quinonoid signals for the chlorotriphenylenediquinone (I; B = Cl, A = C = D = H) (at δ 6.89 and 7.05) and the corresponding signals for the methyl compound (I; B = Me, A = C = D = H) (at δ 6.87 and 7.03) can now be assigned to the protons at C-7 and C-6, respectively. Finally, since the methyl group in a 2-methyl-1,4-naphthoquinone shields the adjacent quinonoid proton by *ca.* 0.15 p.p.m. it follows that the isolated quinonoid protons in the methyltriphenylenediquinones (I; A = Me, B = C = D = H) and (I; B = Me, A = C = D = H) should resonate at *ca.* δ 6.91 and 6.72, respectively. The spectrum of the compound isolated shows a signal at δ 6.69 for the proton coupled to the methyl group indicating that this proton is attached to C-2, *i.e.* that the product is the 3-methyl isomer (I; B = Me, A = C = D = H). Similar arguments establish that the C-2 proton in a 3-chlorotriphenylene tetra-acetate such as (II; B = Cl, A = C = D = H) resonates at δ *ca.* 7.41 whereas the C-3 proton in the corresponding 2-chloro-compound resonates at δ *ca.* 7.54.

EXPERIMENTAL

Details of instruments and solvents used are given in Part V.³

Reaction of Veratrole with 1,4-Benzoquinone.—(a) *Excess of veratrole.* A solution of veratrole (13.8 g) in carbon disulphide (50 ml) was added dropwise to a stirred suspension of benzoquinone (16.2 g) and anhydrous aluminium chloride (26.6 g) in carbon disulphide (175 ml) and the mixture was stirred for 24 h. Ice (150 g) and 5M-hydrochloric acid (150 ml) were added and the mixture was stirred for 2 h and steam-distilled to remove carbon disulphide, veratrole (10 g), benzoquinone (1 g), and a mixture (9.7 g) of quinol and chloroquinol. The residual brown solid was extracted successively with cold acetone (100 ml), boiling acetone (30 ml), and boiling toluene (150 ml). Concentration of the toluene solution gave a red solid (0.1 g) which crystallised from toluene to give 10,11-dimethoxytriphenylene-1,4:5,8-diquinone as deep red rhombohedra, containing

toluene (0.5 mol) of crystallisation, m.p. (evacuated capillary) 230–240° (decomp.) (lit.,⁴ m.p. 290° with darkening at 245°), δ 2.35 (1.5 H, s, PhCH₃), 7.22 (2.5 H, C₆H₅Me), 4.08 (6 H, s, CH₃O), 6.87 and 7.06 (4 H, ABq, *J* 10 Hz, H-2 and H-7, H-3 and H-6), and 8.92 (2 H, s, H-9 and H-12). This lost toluene on being heated at 140° and 0.1 mmHg to give the pure quinone, m.p. 250–255° (decomp.) (Found: C, 68.8; H, 3.5; MeO, 19.9%; *M*⁺, 348.0634. C₂₀H₁₂O₆ requires C, 68.95; H, 3.45; 2 MeO, 17.8%; *M*, 348.0634), ν_{\max} 1 680 and 1 655 (quinone C=O), and 1 615 cm⁻¹ (quinone C=C), λ_{\max} 292.5 (log ϵ 4.09), 386 (3.93), and 467 nm (3.78), λ_{infl} 492 nm (3.70).

(b) *Excess of benzoquinone.* A similar reaction of veratrole (6.9 g) with benzoquinone (37.8 g) and anhydrous aluminium chloride (33.4 g) in carbon disulphide (400 ml) gave the triphenylenediquinone (0.55 g), quinol (20 g), and unchanged veratrole (4.7 g) and benzoquinone (8 g).

Reductive Acetylation of 10,11-Dimethoxytriphenylene-1,4:5,8-diquinone.—A mixture of the diquinone (105 mg), acetic anhydride (5 ml), zinc dust (210 mg), and triethylamine (0.2 ml) was boiled under reflux for 45 min and poured into hot water. Extraction with chloroform yielded a solid (100 mg) which crystallised from toluene and then from chloroform-ethanol to give 10,11-dimethoxytriphenylene-1,4,5,8-tetra-yl tetra-acetate as needles, m.p. 247–249° (Found: C, 64.3; H, 4.3; MeO, 12.2; AcO, 46.2%; *M*⁺, 520.1369. C₂₈H₂₄O₁₆ requires C, 64.6; H, 4.65; 2 MeO, 11.9; 4 AcO, 45.4%; *M*, 520.1370), ν_{\max} (KCl) 1 748 cm⁻¹ (aryl acetate C=O), λ_{\max} 279 (log ϵ 4.77) and 372 nm (3.33), λ_{infl} 275 (log ϵ 4.75), 315 (4.07), 328 (4.00), and 352 nm (3.45), λ_{\max} (EtOH) 219 (log ϵ 4.40), 276 (4.86), and 368 nm (3.42), λ_{infl} 311 (log ϵ 4.15), 325 (4.07), and 348 nm (3.59), δ 2.24 (6 H, s, CH₃CO₂ at C-4 and C-5), 2.44 (6 H, s, CH₃CO₂ at C-1 and C-8), 4.05 (6 H, s, CH₃O), 7.30 (4 H, s, H-2, H-3, H-6, and H-7), and 8.46 (2 H, s, H-9 and H-12).

Reaction of Veratrole with 2,3-Dichloro-1,4-benzoquinone.—Anhydrous aluminium chloride (3.5 g) was added slowly to a stirred solution of 2,3-dichloro-1,4-benzoquinone⁷ (2.5 g) and veratrole (2.0 g) in carbon disulphide (100 ml). The mixture was stirred for 24 h, treated with ice (50 g) and m-sulphuric acid (20 ml), and distilled with steam to remove carbon disulphide and unchanged veratrole (1.2 g). The residual solid A (2.4 g) was collected; extraction of the aqueous filtrate with ether afforded a mixture (0.7 g) of 2,3-dichloro-1,4-benzoquinone and 2,3-dichloroquinol. The solid A was washed with ethanol (200 ml) and extracted with cold benzene (250 ml) to remove 2,3-dichloro-5-(3,4-dimethoxyphenyl)benzoquinone which crystallised from chloroform-ethanol as violet needles (430 mg), m.p. 204–205.5° (lit.,³ 205–206°). A solution of part (100 mg) of the residual pale purple solid (230 mg) in benzene-chloroform (17 ml) was filtered through a column of silica gel which was washed with benzene followed by benzene-chloroform (1 : 4). Evaporation of the benzene solution afforded a solid which crystallised from ethanol to give 2,3,6,7-tetrachloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone as red crystals (3 mg), m.p. 326° (decomp.) (Found: *M*⁺, 483.9080. C₃₀H₈³⁵Cl₄O₆ requires *M*, 483.9075), ν_{\max} (KBr) 1 690 and 1 678 (quinone C=O), and 1 600 cm⁻¹ (quinone C=C), λ_{\max} 321 (log ϵ 3.99), 418 (3.76), and 488 nm (3.71), λ_{infl} 278 (log ϵ 4.30) and 298 nm (4.15), δ 4.12 (6 H, s, CH₃O) and 9.02 (2 H, s, H-9 and H-12). Evaporation of the benzene-chloroform solution yielded a solid which crystallised from chloroform-

⁷ J. B. Conant and L. F. Fieser, *J. Amer. Chem. Soc.*, 1923, **45**, 2194.

ethanol to give 2,3,6,7,10,11-hexamethoxytriphenylene (80 mg), m.p. 315—317° (lit.,² 317.5—318.5°). Extraction of the blue band which remained at the top of the column with boiling chloroform afforded 2,5,6,9,12,13-hexamethoxydibenzo[*fg,op*]naphthacene-1,10-quinone² as a deep blue solid (<1 mg), identical (u.v.) with an authentic specimen.

Reaction of Veratrole with 2-Chloro-1,4-benzoquinone.—(a) A similar reaction using anhydrous aluminium chloride (3.5 g), 2-chloro-1,4-benzoquinone (4.0 g), veratrole (0.69 g), and carbon disulphide (200 ml) gave a product, steam-distillation of which removed carbon disulphide, unchanged veratrole (0.25 g), and a mixture (2 g) of chloroquinol and unchanged chlorobenzoquinone. The residual solid was washed with ethanol (50 ml) and extracted with chloroform. Evaporation of the chloroform solution gave a red solid (100 mg) which was separated by repeated t.l.c. [benzene-ethyl acetate (10 : 1), and benzene], into (i) a mixture (*ca.* 1 : 4) of 2,7- and 3,6-dichloro-10,11-dimethoxytriphenylene-1,4 : 5,8-diquinone which crystallised from chloroform-ethanol as red crystals (20 mg) (Found: M^+ , 415.9861. Calc. for $C_{20}H_{10}^{35}Cl_2O_8$: M , 415.9854, λ_{max} , 297 (log ϵ 4.23), 400 (3.88), and 475 nm (3.76), λ_{inf} , 277 (log ϵ 4.34) and 490 nm (3.73), ν_{max} (KBr) 1 690, 1 680, and 1 650 (all quinone C=O), and 1 618 cm^{-1} (quinone C=C), δ 4.09 (6 H, s, CH_3O), 7.10 (1.6 H, s, H-2 and H-7), 7.29 (0.4 H, s, H-3 and H-6), and 8.91 (2 H, s, H-9 and H-12), and (ii) 2,6-dichloro-10,11-dimethoxytriphenylene-1,4 : 5,8-diquinone which crystallised from chloroform-ethanol as red crystals (5 mg), m.p. 202—205° (decomp.) (Found: M^+ 415.9853. $C_{20}H_{10}^{35}Cl_2O_8$ requires M , 415.9854, λ_{max} 402 (log ϵ 3.84) and 478 nm (3.76), λ_{inf} , 277 (log ϵ 4.32), 296 (4.17), and 497 nm (3.71), ν_{max} (KCl) 1 675 and 1 660 (both quinone C=O), and 1 620 cm^{-1} (quinone C=C), δ 4.08 (6 H, s, CH_3O), 7.06 (1 H, s, H-7), 7.22 (1 H, s, H-3), and 8.92 (2 H, s, H-9 and H-12). The mixture of the 2,7- and 3,6-dichloro-diquinones was reductively acetylated as described above for the unchlorinated diquinone. Crystallisation of the mixture of leucotetra-acetates from chloroform-ethanol gave 3,6-dichloro-10,11-dimethoxytriphenylene-1,4,5,8-tetra-yl tetra-acetate as needles, m.p. 216.5—217.5° (Found: C, 56.9; H, 3.7%; M^+ , 588.0591. $C_{28}H_{22}Cl_2O_{10}$ requires C, 57.05; H, 3.75%. $C_{28}H_{22}^{35}Cl_2O_{10}$ requires M , 588.0590, λ_{max} , 284 (log ϵ 4.85), 364 (3.52), and 381 nm (3.49), λ_{inf} , 277 (log ϵ 4.77), 307 (4.17), 318 (4.13), and 332 nm (4.05), ν_{max} , 1 760 cm^{-1} (aryl acetate C=O), δ 2.31 (6 H, s, CH_3CO_2 at C-4 and C-5), 2.43 (6 H, s, CH_3CO_2 at C-1 and C-8), 4.02 (6 H, s, CH_3O), 7.43 (2 H, s, H-2 and H-7), and 8.33 (2 H, s, H-9 and H-12).

(b) Another, similar, preparation afforded 2-chloro-3-(3,4-dimethoxyphenyl)-1,4-benzoquinone (17 mg), m.p. 200.5—201.5° (lit.,¹ 200.5—201.5°), and a mixture of 2,6-, 2,7-, and 3,6-dichloro-10,11-dimethoxytriphenylene-1,4 : 5,8-diquinone as a red solid (90 mg) which was converted, as described above, into a mixture of the corresponding leucotetra-acetates. This was separated by t.l.c. [benzene-chloroform (1 : 4)] into 3,6-dichloro-10,11-dimethoxytriphenylene-1,4,5,8-tetra-yl tetra-acetate (30 mg), m.p. 216—217°, and a mixture of the corresponding 2,6- and 2,7-dichloro- compounds which, after repeated crystallisation from toluene and chloroform-ethanol, gave 2,6-dichloro-10,11-dimethoxytriphenylene-1,4,5,8-tetra-yl tetra-acetate as needles (20 mg), m.p. 227—229° (Found: M^+ , 588.0591. $C_{28}H_{22}^{35}Cl_2O_{10}$ requires M , 588.0590, λ_{max} , 288 (log ϵ 4.86) and 381 nm (3.38), λ_{inf} , 278 (log ϵ 4.77), 320 (4.14), 335 (4.04), and 360 nm (3.49), ν_{max} (KCl) 1 770 cm^{-1} (aryl acetate C=O), δ 2.17 and 2.38 (each 3 H, s, CH_3CO_2 at C-4 and C-5), 2.45

(6 H, s, CH_3CO_2 at C-1 and C-8), 4.02 (6 H, s, CH_3O), 7.39 and 7.54 (each 1 H, s, H-7 and H-3 respectively), and 8.31 and 8.43 (each 1 H, s, H-9 and H-12). The 2,7-dichloro-compound could not be obtained pure.

Reaction of Veratrole with 4,4'-Dichlorobiphenyl-2,5:2',5'-diquinone.—A solution of veratrole (0.7 g) in carbon disulphide (50 ml) was added dropwise to a stirred suspension of the dichloro-diquinone⁸ (2.83 g) and anhydrous aluminium chloride (4.0 g) in carbon disulphide (100 ml). The mixture was stirred for 24 h, then treated with ice (30 g) and m-sulphuric acid (30 ml), and the organic layer was evaporated under reduced pressure to remove carbon disulphide and unchanged veratrole (0.25 g). The resulting solid was collected and washed with acetone to remove a mixture (0.58 g) of the unchanged dichloro-diquinone and the corresponding bisquinol. The residual solid was extracted with chloroform (100 ml) and the extract was concentrated and filtered through a column of silical gel which was washed with benzene followed by benzene-chloroform (1 : 4). Evaporation of the benzene-chloroform solution yielded a solid which crystallised from chloroform-ethanol to give 2,3,6,7,10,11-hexamethoxytriphenylene (250 mg), m.p. 315°.

Reaction of 2-(3,4-Dimethoxyphenyl)-1,4-benzoquinone with 1,4-Benzoquinone.—A solution of 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone³ (0.122 g) in carbon disulphide (100 ml) was added dropwise to a stirred mixture of 1,4-benzoquinone (0.54 g), anhydrous aluminium chloride (1.0 g), and carbon disulphide (50 ml). The mixture was stirred for 24 h, then treated with ice (20 g) and m-sulphuric acid (20 ml), and the organic layer was evaporated under reduced pressure to remove solvent and unchanged 1,4-benzoquinone. The aqueous layer was decanted and the residual red oil was separated by t.l.c. (benzene) into unchanged 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone (20 mg), 10,11-dimethoxytriphenylene-1,4 : 5,8-diquinone (28 mg), and a brown solid (21 mg) which was dissolved in chloroform and filtered through a column of alumina. Evaporation of the eluate and crystallisation of the residue from chloroform-ethanol gave a mixture of 2- and 3-(3,4-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4 : 5,8-diquinone as red crystals (15 mg), m.p. 210—215° (decomp.) (Found: M^+ , 484.1160. Calc. for $C_{28}H_{20}O_8$: M , 484.1158, λ_{max} , 298 (log ϵ 4.34), 383 (3.99), and 470 nm (3.98), λ_{inf} , 290 (log ϵ 4.32) and 490 nm (3.92), ν_{max} , 1 680, 1 660, and 1 645 (all quinone C=O) and 1 600 cm^{-1} (quinone C=C), δ 3.97 and 4.00 (each 3 H, s, CH_3O at C-3' and C-4'), 4.07 and 4.09 (each 3 H, s, CH_3O at C-10 and C-11), 6.87—7.38 (6 H, m, ArH and quinone H), and 8.97 and 9.05 (each 1 H, s, H-9 and H-12). The components of the mixture could not be separated by repeated t.l.c.

A similar reaction using 1,4-benzoquinone (1.08 g) and 2-(3,4-dimethoxyphenyl)quinol [0.246 g, prepared by reducing 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone with aqueous sodium dithionite] gave only 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone (90 mg) and 10,11-dimethoxytriphenylene-1,4 : 5,8-diquinone (40 mg).

Reaction of 2,3-Dichloro-1,4-benzoquinone with 2-(3,4-Dimethoxyphenyl)-1,4-benzoquinone.—A similar reaction of 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone (244 mg) with 2,3-dichloro-1,4-benzoquinone (885 mg) and anhydrous aluminium chloride (2.0 g) in carbon disulphide (160 ml) gave 2,3-dichloroquinol (380 mg), unchanged 2,3-dichlorobenzoquinone (350 mg), and a red-brown solid which was

⁸ T. Posternak, W. Alcalay, R. Luzzati, and A. Tardent, *Helv. Chim. Acta*, 1948, **31**, 525.

separated by repeated t.l.c. [benzene-ethyl acetate (10 : 3) followed by benzene] into unchanged 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone (150 mg), a mixture of 2- and 3-(3,4-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (10 mg), and 2,3-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone which crystallised from chloroform-ethanol as red crystals (7 mg), m.p. 286–290° (decomp.) (Found: M^+ , 415.9852. $C_{20}H_{10}^{35}Cl_2O_6$ requires M , 415.9854), λ_{max} 323 (log ϵ 3.77), 398 (3.84), and 480 nm (3.75), λ_{inf} 293 nm (log ϵ 4.16), ν_{max} (KBr) 1 685 and 1 670 (quinone C=O) and 1 598 cm^{-1} (quinone C=C). Reductive acetylation of the dichloro-diquinone as described for the unchlorinated compound gave 2,3-dichloro-10,11-dimethoxytriphenylene-1,4,5,8-tetra-*l* tetra-acetate as needles, m.p. 251–253° (Found: M^+ , 588.0586. $C_{28}H_{22}^{35}Cl_2O_{10}$ requires M , 588.0590), λ_{max} 287 (log ϵ 4.80) and 379 nm (3.38), λ_{inf} 264 (log ϵ 4.55), 279 (4.75), 321 (4.10), 334 (4.04), and 358 nm (3.53), ν_{max} (KCl) 1 775 cm^{-1} (aryl acetate C=O), δ 2.16, 2.40, 2.40, and 2.50 (each 3 H, s, CH_3CO_2), 4.02 (6 H, s, CH_3O), 7.34br (2 H, s, H-6 and H-7), and 8.33 and 8.43 (each 1 H, s, H-9 and H-12).

Reaction of 2,3-Dichloro-5-(3,4-dimethoxyphenyl)-1,4-benzoquinone with 1,4-Benzoquinone.—A similar reaction of 1,4-benzoquinone (540 mg) with the dichloro-quinone (105 mg) and anhydrous aluminium chloride (1.0 g) in carbon disulphide (200 ml) gave a solid which was separated by t.l.c. (benzene) into unchanged dichloro-quinone (15 mg) and 2,3-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (53 mg).

Reaction of 2-(3,4-Dimethoxyphenyl)-1,4-benzoquinone with 2-Chloro-1,4-benzoquinone.—A similar reaction of the chloroquinone (855 mg) with the dimethoxyphenylquinone (244 mg) and anhydrous aluminium chloride (2.0 g) in carbon disulphide (140 ml) gave unchanged chlorobenzoquinone (400 mg), chloroquinol (400 mg), and an oily solid which was separated by t.l.c. [benzene-ethyl acetate (10 : 3)] into unchanged dimethoxyphenylquinone (88 mg), a mixture of 2- and 3-(3,4-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (20 mg), and an inseparable mixture (ca. 1 : 3) of 2- and 3-chloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone which separated from chloroform-ethanol as red crystals (24 mg), m.p. 235–240° (decomp.) (Found: M^+ , 382.0246. Calc. for $C_{20}H_{11}^{35}ClO_6$: M , 382.0244), λ_{max} 396 (log ϵ 3.80) and 475 nm (3.71), λ_{inf} 293 (log ϵ 4.09) and 490 nm (3.68), ν_{max} (KCl) 1 680 and 1 660 (both quinone C=O) and 1 615 cm^{-1} (quinone C=C), δ 4.08 (6 H, s, CH_3O), 6.89 and 7.05 (2 H, ABq, J 10 Hz, H-7 and H-6, respectively), 7.07 (0.75 H, s, H-2), 7.28 (0.25 H, s, H-3), and 8.90 and 8.95 (each 1 H, s, H-9 and H-12).

Reductive acetylation of the mixture of chloro-diquinones, as described for the unchlorinated compound, gave an inseparable mixture of 2- and 3-chloro-10,11-dimethoxytriphenylene-1,4,5,8-tetra-*l* tetra-acetate which crystallised from chloroform-ethanol as needles, m.p. 256–260° (Found: M^+ , 554.0976. Calc. for $C_{28}H_{23}^{35}ClO_{10}$: M , 554.0979), λ_{max} 282 (log ϵ 4.86) and 375 nm (3.36), λ_{inf} 276

(log ϵ 4.82), 317 (4.13), 330 (4.06), and 354 nm (3.52), ν_{max} 1 760 cm^{-1} (aryl acetate C=O).

Reaction of 2-Chloro-5-(3,4-dimethoxyphenyl)-1,4-benzoquinone with 1,4-Benzoquinone.—A similar reaction of 1,4-benzoquinone (550 mg) with the chloro-quinone¹ (100 mg) and anhydrous aluminium chloride (1.0 g) in carbon disulphide (180 ml) gave a solid which was separated by t.l.c. [benzene-light petroleum (9 : 1)] into unchanged chloroquinone (10 mg) and 3-chloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone which separated from chloroform-ethanol as red crystals (75 mg), m.p. 267–270° (decomp.) (Found: M^+ , 382.0246. $C_{20}H_{11}^{35}ClO_6$ requires M , 382.0244), λ_{max} 396 (log ϵ 3.90) and 474 nm (3.78), λ_{inf} 293 (log ϵ 4.18) and 494 nm (3.73), ν_{max} 1 685 and 1 662 (quinone C=O), and 1 620 cm^{-1} (quinone C=C), δ 4.08 (6 H, s, CH_3O), 6.89 and 7.05 (2 H, ABq, J 10 Hz, H-7 and H-6, respectively), 7.07 (1 H, s, H-2), and 8.97 and 9.02 (each 1 H, s, H-9 and H-12). Reductive acetylation of the latter as described above gave 3-chloro-10,11-dimethoxytriphenylene-1,4,5,8-tetra-*l* tetra-acetate which crystallised from chloroform-ethanol as needles, m.p. 268.5–270.5° (Found: M^+ , 554.0978. $C_{28}H_{23}^{35}ClO_{10}$ requires M , 554.0979), λ_{max} 282 (log ϵ 4.80) and 375 nm (3.38), λ_{inf} 276 (log ϵ 4.77), 316 (4.09), 330 (4.03), and 354 nm (3.49), ν_{max} 1 762 cm^{-1} (aryl acetate C=O), δ 2.16 and 2.38 (each 3 H, s, CH_3CO_2 at C-4 and C-5), 2.43 and 2.45 (each 3 H, s, CH_3CO_2 at C-1 and C-8), 4.02 (6 H, s, CH_3O), 7.23 and 7.38 (2 H, ABq, J 6 Hz, H-6 and H-7), 7.41 (1 H, s, H-2), and 8.36 and 8.43 (each 1 H, s, H-9 and H-12).

Reaction of 2-(3,4-Dimethoxyphenyl)-1,4-benzoquinone with 2-Methyl-1,4-benzoquinone.—A similar reaction of the methylbenzoquinone (3.0 g) with the dimethoxyphenylbenzoquinone (0.4 g) and anhydrous aluminium chloride (3.0 g) in carbon disulphide (200 ml) gave 2-methylquinol (0.2 g), 2-(2,5-dihydroxy-4-methylphenyl)-5-methyl-1,4-benzoquinone⁹ (0.2 g), and an oil which was separated by t.l.c. [benzene-ethyl acetate (10 : 3)] into unchanged dimethoxyphenylbenzoquinone (70 mg), a mixture (1 : 1) of 10,11-dimethoxy-2- and -3-methyltriphenylene-1,4 : 5,8-diquinone (54 mg). The last-named, on being subjected to further t.l.c. (benzene), gave 10,11-dimethoxy-3-methyltriphenylene-1,4:5,8-diquinone which separated from chloroform-ethanol as red crystals (6 mg), m.p. 238–242° (decomp.) (Found: M^+ , 362.0781. $C_{21}H_{14}O_6$ requires M , 362.0790), λ_{max} 292 (log ϵ 4.03), 385 (3.78), and 466 nm (3.64), λ_{inf} 490 nm (log ϵ 3.54), ν_{max} 1 680, 1 658, and 1 638 (quinone C=O), and 1 615 cm^{-1} (quinone C=C), δ 2.23 (3 H, d, J 2 Hz, $CH_3 \cdot CH=$), 4.08 (6 H, s, CH_3O), 6.69 (1 H, q, J 2 Hz, $CH_3 \cdot CH=$), 6.87 and 7.03 (2 H, ABq, J 10 Hz, H-7 and H-6, respectively), and 8.96 and 9.01 (each 1 H, s, H-9 and H-12).

We thank the Physico-chemical Measurements Unit, Aldermaston, for the mass spectra.

[5/944 Received, 19th May, 1975]

⁹ T. Posternak, W. Alcalay, and R. Huguenin, *Helv. Chim. Acta*, 1956, 39, 1556.