

Reactions of Quinones with Aromatic Ethers. Part VI.¹ Triphenylenols from Mono- and Di-chlorobenzoquinones and Veratrole

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

Chlorobenzoquinone reacts with veratrole in aqueous 70% v/v sulphuric acid to give 2-chloro-6,7,10,11-tetramethoxytriphenylen-3-ol (II; X = R = H, Y = Cl) and arylated products. Mono- and di-chloro-(3,4-dimethoxyphenyl)benzoquinones behave in an analogous manner giving the corresponding triphenylenols and mono- and di-chlorotriphenylenequinones, *e.g.* (III; X = Y = Cl).

VERATROLE reacts with 2,5- and 2,6-dichlorobenzoquinone in the presence of acid to form the corresponding mono- and di-arylbenzoquinones together with the dibenzofurans which result from the cyclisation of these compounds.² This paper describes related reactions with certain mono- and di-chlorobenzoquinones which give rise, *inter alia*, to triphenylene derivatives.

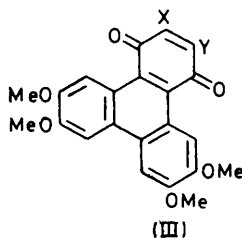
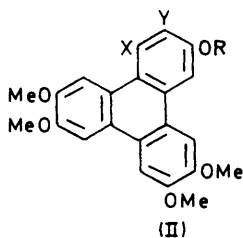
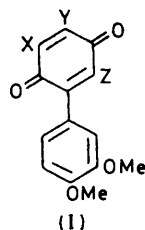
Chlorobenzoquinone and veratrole reacted together in aqueous 70% v/v sulphuric acid giving, after oxidation, a mixture of the expected monoarylchlorobenzoquinones (I; X = Cl, Y = Z = H), (I; Y = Cl, X = Z = H), and (I; Z = Cl, X = Y = H), and the diarylchlorobenzoquinones [I; X = Cl, Y = 3,4-(MeO)₂C₆H₃, Z =

mentation but giving a conspicuous M^{2+} ion. It shows n.m.r. signals corresponding to twelve methoxy-protons, one hydroxy-proton, and six apparently uncoupled aromatic protons, and we formulate it accordingly as the chlorotriphenylenol (II; X = R = H, Y = Cl). An alternative synthesis provides support for this structure. The desired starting material, the arylchlorobenzoquinone (I; X = Z = H, Y = Cl), could be separated from the isomeric compound (I; X = Cl, Y = Z = H) only with difficulty by t.l.c. and we were obliged to use a mixture of the two compounds. This reacted with veratrole in aqueous sulphuric acid to give, after oxidation, two of the three possible diarylquinones, namely [I; X = Cl, Y = 3,4-(MeO)₂C₆H₃, Z = H] and [I; X = 3,4-(MeO)₂C₆H₃, Y = Cl, Z = H]. The third isomer cyclised under these conditions to give the chlorotriphenylenequinone (III; X = Cl, Y = H), which showed spectral properties very similar to those of the corresponding dichloro-compound (III; X = Y = Cl).¹ The main product from the reaction was a mixture of triphenylenols which we acetylated and were then able to separate into the 1-chloro-acetate (II; X = Cl, Y = H, R = Ac) and the major component, the 2-chloro-acetate (II; X = H, Y = Cl, R = Ac). The structures of these products follow from their n.m.r. spectra. Hydrolysis of the last-mentioned compound gave the desired 2-chlorotriphenylen-3-ol.

The aryldichlorobenzoquinone (I; X = Y = Cl, Z = H)¹ reacted with veratrole in aqueous sulphuric acid in a similar manner to form the dichlorotriphenylenol (II; X = Y = Cl, R = H). In addition, arylation of the benzoquinone and subsequent cyclisation of the product gave the dichlorotriphenylenequinone (III; X = Y = Cl), while oxidation of some of the veratrole by the starting quinone produced 2,3,6,7,10,11-hexamethoxytriphenylene.³ On the other hand no reaction occurred

² O. C. Musgrave and C. J. Webster, *J.C.S. Perkin I*, 1974, 2260.

³ O. C. Musgrave and C. J. Webster, *J. Chem. Soc. (C)*, 1971, 1397.



H] and [I; X = 3,4-(MeO)₂C₆H₃, Y = Cl, Z = H] which we separated by t.l.c. A minor product was a colourless phenol, C₂₂H₁₉ClO₅, which exhibits u.v. absorption resembling closely that of 2,3,6,7,10,11-hexamethoxytriphenylene.³ In the mass spectrometer it behaves as a typical polycyclic compound, undergoing little frag-

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

between veratrole and 4,4'-dichloro-2',5'-dimethoxybiphenyl-2,5-quinone under these conditions.

The formation of, for example, the triphenylenol (II; X = R = H, Y = Cl) must involve electrophilic attack on veratrole by the carbonyl group of (I; X = Z = H, Y = Cl) adjacent to the aryl substituent, followed by dehydration and cyclisation. Although there are several examples of the addition of carbanions to the carbonyl groups of benzoquinones, related reactions involving aromatic nuclei have not been described previously.⁴ The structural features of the arylquinone (I) which appear to facilitate this reaction are (a) the absence of a bulky substituent Z, which permits the conjugation of the aryl group with the enone system of the quinone, and (b) the presence of the electron-withdrawing substituents X and Y. It is significant that the reactions² between veratrole and 2,5- or 2,6-dichlorobenzoquinone in aqueous sulphuric acid fail to give triphenylenols and that we were unable to obtain any recognisable products from a similar reaction between veratrole and 3,4-dimethoxyphenylbenzoquinone.

We prepared authentic specimens of the chloro-3,4-dimethoxyphenylbenzoquinones by treating chlorobenzoquinone with a buffered solution of 3,4-dimethoxybenzenediazonium chloride at 10°. The orientation of the substituents in the products follows from the structures of the compounds obtained from them by treatment⁵ with hydrochloric acid followed by iron(III) chloride. By this procedure, for example, the 2,6-disubstituted quinone (I; X = Cl, Y = Z = H) gave the known dichloro-quinones (I; X = Y = Cl, Z = H) and (I; X = Z = Cl, Y = H). In each case we also isolated the fully substituted trichloroarylquinone (I; X = Y = Z = Cl). As expected,¹ the most abundant fragment ion obtained from each of the new dimethoxyphenylbenzoquinones in the mass spectrometer is formed from the molecular ion by loss of a methoxyl radical.

EXPERIMENTAL

Details of the instruments and solvents used were given in Part V.¹ Mass spectral data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 21297 (12 pp., 1 microfiche).†

Reaction of Chlorobenzoquinone with Diazotised 3,4-Dimethoxyaniline.—A solution of the diazonium salt prepared from 3,4-dimethoxyaniline⁶ (3.83 g) in 3M-hydrochloric acid (32 ml) and sodium nitrite (1.73 g) in water (15 ml) at 0° was added to a vigorously stirred mixture of chlorobenzoquinone⁷ (3.6 g), anhydrous sodium acetate (7.7 g), and water (500 ml) at 10°. The mixture was stirred at 10° for 1 h and then at room temperature overnight. Extraction with ether gave a red solid (5 g), a portion (0.5 g) of which was separated by t.l.c. [benzene–light petroleum (4:1)] into (i) 2-chloro-3-(3,4-dimethoxyphenyl)benzoquinone,* which

crystallised from chloroform–ethanol as red needles (0.17 g), m.p. 200.5–201.5° (Found: M⁺, 278.0339. C₁₄H₁₁³⁵ClO₄ requires M, 278.0346), λ_{max.} (EtOH) 250 nm (log ε 4.29) and 451 nm (3.22), λ_{infl.} 278 (log ε 3.87) and 305 nm (3.20), ν_{max.} 1672 and 1658 cm⁻¹ (both quinone C=O), δ 3.89 and 3.94 (each 3H, s, ArOCH₃), and 6.80–7.00 (5H, m, ArH and quinone H), and (ii) a mixture (1:1) of 2-chloro-5- and 2-chloro-6-(3,4-dimethoxyphenyl)benzoquinone (0.17 g), m.p. 144–148°. The latter was separated (with considerable loss) by repeated t.l.c. with the same solvent mixture into 2-chloro-5-(3,4-dimethoxyphenyl)benzoquinone,* which crystallised from ethanol as violet needles (31 mg), m.p. 151–152° (Found: M⁺, 278.0344. C₁₄H₁₁³⁵ClO₄ requires M, 278.0346), λ_{max.} (EtOH) 253 (log ε 4.27) and 470 nm (3.46), λ_{infl.} 274 (log ε 4.09) and 310 nm (3.52), ν_{max.} 1657 cm⁻¹ (quinone C=O), δ 3.90 (6H, s, ArOCH₃), 6.94 (2H, s, quinone H), and 6.80–7.20 (3H, m, ArH), and 2-chloro-6-(3,4-dimethoxyphenyl)benzoquinone,* which crystallised from carbon disulphide as violet needles (31 mg), m.p. 157.5–158.5° (Found: M⁺, 278.0355. C₁₄H₁₁³⁵ClO₄ requires M, 278.0346), λ_{max.} (EtOH) 253.5 (log ε 4.28) and 466 nm (3.43), λ_{infl.} 273.5 (log ε 4.10) and 313 nm (3.36), ν_{max.} 1675 and 1642 cm⁻¹ (both quinone C=O), δ 3.93 (6H, s, ArOCH₃), 6.83 and 6.99 (each 1H, d, J 3 Hz, quinone H), and 7.00–7.20 (3H, m, ArH).

Chlorination of the Chlorodimethoxyphenylbenzoquinones.—A mixture of 2-chloro-3-(3,4-dimethoxyphenyl)benzoquinone (0.10 g) and concentrated hydrochloric acid (10 ml) was boiled under reflux for 1.5 h, poured into water, and shaken with chloroform. The dried chloroform solution was shaken with iron(III) chloride (0.25 g), washed with 2M-hydrochloric acid and with water, and evaporated. The residual violet solid (0.12 g) was separated by t.l.c. [benzene–light petroleum (2:1)] into (i) starting material (2 mg), (ii) 2,3,5-trichloro-6-(3,4-dimethoxyphenyl)benzoquinone,* which crystallised from light petroleum (b.p. 60–80°) as violet needles (7 mg), m.p. 166–167.5° (Found: M⁺, 345.9573. C₁₄H₉³⁵Cl₃O₄ requires M, 345.9567), λ_{max.} (EtOH) 283 (log ε 4.27), 341 (3.25), and 495 nm (3.16), λ_{infl.} 265 nm (log ε 4.13), ν_{max.} 1685 cm⁻¹ (quinone C=O), δ 3.87 and 3.93 (each 3H, s, ArOCH₃), and 6.84–6.94 (3H, m, ArH), and (iii) 2,5-dichloro-3-(3,4-dimethoxyphenyl)benzoquinone, which crystallised from ethanol as red-violet needles (30 mg), m.p. 174–176° (lit.,² 177–178°), δ 3.88 and 3.93 (each 3H, s, ArOCH₃), 6.78–6.98 (3H, m, ArH), and 7.18 (1H, s, quinone H). Concentration of the mother liquors gave a violet solid (10 mg) which showed the i.r. absorption of a 1:1 mixture of 2,5- and 2,6-dichloro-3-(3,4-dimethoxyphenyl)benzoquinone.²

A similar reaction with 2-chloro-5-(3,4-dimethoxyphenyl)benzoquinone (50 mg) gave (i) starting material (12 mg), (ii) 2,3,5-trichloro-6-(3,4-dimethoxyphenyl)benzoquinone (5 mg), (iii) 2,3-dichloro-5-(3,4-dimethoxyphenyl)benzoquinone, which crystallised from ethanol as violet needles (15 mg), m.p. 203–204° (lit.,¹ 205–206°), and (iv) a violet solid which showed the i.r. absorption of a mixture of mainly 2,6-dichloro-3-(3,4-dimethoxyphenyl)benzoquinone¹ and a little of the 2,3-dichloro-5-isomer.

A similar reaction with 2-chloro-6-(3,4-dimethoxyphenyl)benzoquinone (54 mg) gave (i) starting material (4 mg), (ii) 2,3,5-trichloro-6-(3,4-dimethoxyphenyl)benzoquinone (9 mg), (iii) 2,3-dichloro-5-(3,4-dimethoxyphenyl)benzoquinone

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

⁴ J. M. Bruce in 'Rodd's Chemistry of Carbon Compounds,' ed. S. Coffey, Elsevier, Amsterdam, 2nd edn., 1974, vol. IIIB, pp. 94, 104.

⁵ J. F. Bagli and P. L'Écuyer, *Canad. J. Chem.*, 1961, **39**, 1037.

⁶ F. Pollecoff and R. Robinson, *J. Chem. Soc.*, 1918, **113**, 645.

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

(20 mg), and (iv) 2,5-dichloro-3-(3,4-dimethoxyphenyl)-benzoquinone (5 mg).

Reaction of Veratrole with Chlorobenzoquinone.—A mixture of chlorobenzoquinone (2 g), veratrole (1.5 g), and aqueous 70% v/v sulphuric acid (30 ml) was shaken for 6 h, kept for 1 week, and diluted with water (250 ml). The resulting deep blue oily solid (2.5 g) was collected and separated into its components in two ways. One portion (0.15 g) was shaken with chloroform and iron(III) chloride (0.5 g) and the mixture was then washed with 2M-hydrochloric acid and with water. Evaporation of the chloroform afforded a red oily solid which was separated by repeated t.l.c. [benzene-ethyl acetate (20:1)] into 2-chloro-5-(3,4-dimethoxyphenyl)benzoquinone (5 mg), 2-chloro-6-(3,4-dimethoxyphenyl)benzoquinone (10 mg), 2-chloro-3-(3,4-dimethoxyphenyl)benzoquinone (5 mg), and a red solid (12 mg) which showed the i.r. absorption of a mixture of 3-chloro-2,5- and 2-chloro-3,5-bis-(3,4-dimethoxyphenyl)benzoquinone.¹ Another portion (0.5 g) was separated by column chromatography on silica gel. Elution with benzene-chloroform (5:1) gave veratrole (100 mg) and a mixture of the above-mentioned 2-chloro-(3,4-dimethoxyphenyl)benzoquinones (25 mg). Elution with benzene-chloroform (1:1) afforded a solid (170 mg) which was shaken with chloroform and *m*-sodium hydroxide solution. Acidification of the aqueous layer and extraction with chloroform yielded a solid (65 mg) which after repeated crystallisation from chloroform-ethanol afforded 2-chloro-6,7,10,11-tetramethoxytriphenylen-3-ol* (10 mg) as needles, m.p. 294–295° (Found: M^+ , 398.0922. $C_{22}H_{19}^{35}ClO_5$ requires M , 398.0921), λ_{max} 269 (log ϵ 4.84), 278 (4.97), 308 (4.36), 346.5 (3.50), and 365 nm (3.19), λ_{inf} 262 (log ϵ 4.66), 314 (4.33), 321 (4.24), and 331 nm (3.90), ν_{max} 3440 cm^{-1} (phenolic OH), δ [(CD₃)₂SO] 4.03 (12H, s, ArOCH₃), 7.80, 8.08, and 8.66 (each 1H, s, ArH), 7.94 (3H, s, ArH), and 10.29br (1H, s, ArOH).

Reaction of Veratrole with a Mixture of 2-Chloro-5- and 2-Chloro-6-(3,4-dimethoxyphenyl)benzoquinone.—A 1:1 mixture of the chlorobenzoquinones (see above) (0.28 g) was shaken with a mixture of veratrole (0.15 g) and aqueous 70% v/v sulphuric acid (60 ml) for 3 h, kept for 3 days, and diluted with water (250 ml). A portion (0.15 g) of the resulting grey solid (0.3 g) was shaken with chloroform (100 ml) and iron(III) chloride (0.5 g) and the chloroform layer was washed successively with 2M-hydrochloric acid, water, and 2M-sodium hydroxide. Acidification of the aqueous alkaline solution and extraction with chloroform gave a mixture of 1- and 2-chloro-6,7,10,11-tetramethoxytriphenylen-3-ol (45 mg) which could not be separated by t.l.c. or crystallisation (see below). Evaporation of the chloroform layer gave a red solid which was separated by t.l.c. [benzene-ethyl acetate (9:1)] into starting material (20 mg), a mixture of 3-chloro-2,5- and 2-chloro-3,5-bis-(3,4-dimethoxyphenyl)benzoquinone (8 mg), and a violet solid. A solution of the last-mentioned solid in chloroform was shaken with alkaline aqueous sodium dithionite and the aqueous layer was acidified and shaken with chloroform. The dried chloroform layer was then shaken with iron(III) chloride, washed with 2M-hydrochloric acid and with water, and evaporated. Purification of the resulting solid by t.l.c. [benzene-ethyl acetate (4:1)] followed by crystallisation from chloroform-ethanol gave 2-chloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone* as violet rhombohedra (2 mg), m.p. 302–305° (Found: M^+ , 412.0714. $C_{22}H_{17}^{35}ClO_6$ requires M , 412.0714), λ_{max} 274 (log ϵ 4.84), 351 (3.57), and 520 nm

(3.80), λ_{inf} 298 (log ϵ 4.41), 315 (4.00), and 328 nm (3.72), ν_{max} 1650 cm^{-1} (quinone C=O), δ 4.09 and 4.13 (each 6H, s, ArOCH₃), 7.08 (1H, s, quinone H), 7.69 (2H, s, H-8 and -9), and 8.92 (2H, s, H-5 and -12).

1- and 2-Chloro-6,7,10,11-tetramethoxytriphenylen-3-yl Acetate.—The mixture of 1- and 2-chloro-6,7,10,11-tetramethoxytriphenylen-3-ol (45 mg) from the previous experiment was boiled under reflux for 45 min with acetic anhydride (15 ml) containing concentrated sulphuric acid (0.2 ml), and then poured into water. Extraction with chloroform gave a solid which was separated by t.l.c. [benzene-ethyl acetate (5:1)] into the 2-chloro-acetate,* which crystallised from chloroform-ethanol as needles (32 mg), m.p. 256.5–258° (Found: M^+ , 440.1026. $C_{24}H_{21}^{35}ClO_6$ requires M , 440.1027), λ_{max} 269 (log ϵ 4.75), 278 (4.91), 304.5 (4.32), 346 (3.43), and 364 nm (2.98), λ_{inf} 260 (log ϵ 4.56), 313 (4.25), and 329 nm (3.77), ν_{max} 1758 cm^{-1} (aryl acetate C=O), δ 2.46 (3H, s, CH₃CO₂Ar), 3.92 and 3.94 (each 3H, s, ArOCH₃), 4.03 (6H, s, ArOCH₃), 7.06 (2H, s, ArH), and 7.20, 7.30, 7.66, and 8.02 (each 1H, s, ArH), and the 1-chloro-acetate,* which crystallised from chloroform-ethanol as needles (4 mg), m.p. 159–163° (Found: M^+ , 440.1013. $C_{24}H_{21}^{35}ClO_6$ requires M , 440.1027), λ_{max} 281 (log ϵ 4.95), 350 (3.59), and 369 nm (3.38), λ_{inf} 264 (log ϵ 4.63), 273 (4.81), 303 (4.44), 314 (4.33), and 333 nm (3.80), ν_{max} 1750 cm^{-1} (aryl acetate C=O), δ 2.40 (3H, s, CH₃CO₂Ar), 4.07 and 4.09 (each 3H, s, ArOCH₃), 4.12 (6H, s, ArOCH₃), 7.47 and 8.09 (2H, dd, J_m 2 Hz, H-2 and -4), 7.72br (3H, s, H-5, -8, and -9), and 9.09 (1H, s, H-12).

Alkaline hydrolysis of the 2-chloro-acetate gave 2-chloro-6,7,10,11-tetramethoxytriphenylen-3-ol, identical with the specimen described above.

Reaction of Veratrole with 2,3-Dichloro-5-(3,4-dimethoxyphenyl)benzoquinone.—A mixture of veratrole (80 mg), the dichloro-quinone¹ (50 mg), and aqueous 70% v/v sulphuric acid (20 ml) was shaken vigorously for 1 h, and kept for 3 days. After being diluted with water (60 ml) the mixture was extracted with chloroform and the dried chloroform layer was shaken with iron(III) chloride (0.25 g) and then washed with 2M-hydrochloric acid and with water. Evaporation of the chloroform gave a solid which was separated by t.l.c. [benzene-ethyl acetate (4:1)] followed by benzene-acetone (7:1) into starting material (30 mg), 2,3,6,7,10,11-hexamethoxytriphenylene (3 mg), and a violet solid. The last-mentioned was shaken with chloroform (30 ml) and *m*-sodium hydroxide. The chloroform layer on evaporation afforded 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone¹ (4 mg). Acidification of the alkaline aqueous solution and extraction with chloroform gave 1,2-dichloro-6,7,10,11-tetramethoxytriphenylen-3-ol,* which crystallised from chloroform-ethanol as needles (5 mg), m.p. 264–265.5° (Found: M^+ , 432.0548. $C_{22}H_{16}^{35}Cl_2O_5$ requires M , 432.0531), λ_{max} 282.5 (log ϵ 4.92), 309 (4.38), and 374 nm (3.09), λ_{inf} 263 (log ϵ 4.52), 274 (4.75), 314 (4.37), and 352 nm (3.39), λ_{max} (EtOH) 249.5 (log ϵ 4.35), 280.5 (4.88), 308 (4.30), and 370 nm (3.11), λ_{inf} 264 (log ϵ 4.53), 273 (4.74), 316 (4.26), and 350 nm (3.33), ν_{max} 3430 cm^{-1} (phenolic OH), δ 4.07 and 4.09 (each 3H, s, ArOCH₃), 4.12 (6H, s, ArOCH₃), 8.05 and 8.94 (each 1H, s, H-4 and -12), and 7.76 (3H, s, ArH).

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

[4/2252 Received, 1st November, 1974]