# Reactions of Quinones with Aromatic Ethers.  Part V.[1]  Triphenylene-1,4-quinones from 2,3-Diaryl-1,4-benzoquinones

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2,3-Diaryl-1,4-benzoquinones, prepared by the Meerwein arylation of other benzoquinones, undergo Scholl reactions on treatment with acids and oxidising agents with the formation of triphenylene-1,4-quinones.

FOR work associated with the synthesis of triphenylene-diquinones[2] we required 2,3-, 2,5-, and 2,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone.  The Meerwein arylation of chlorobenzoquinone has been shown[3] to give all three possible disubstituted products and we found that 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone reacted with diazotised 3,4-dimethoxyaniline in a similar manner in the presence of sodium acetate to give the desired 2,3-(7·1%), 2,5- (0·6%), and 2,6- (2·5%) diarylquinones.  The direct arylation of 1,4-benzoquinone itself gave the same products more conveniently and in similar yields.  The high proportion of the 2,3-isomer is noteworthy as related



(I)

(II)

(III)

(IV)

(V)

reactions have previously[4] been thought to give only 2,5-diarylquinones.  The n.m.r. spectrum indicated the orientation of the substituents in the 2,3-diarylquinone, the proximity of the aromatic rings leading to their shielding[5] each other's *meta*-methoxy-protons and aromatic protons.  We established the structures of the 2,5- and 2,6-isomers by chlorinating[3] them with hydrochloric acid followed by iron(III) chloride.  The 2,5-diarylquin-

one gave the known[6] 3,6-dichloro-derivative [I; X = Z = Cl, Y = 3,4-(MeO)$_2$C$_6$H$_3$] and the 2,6-diarylquinone gave the known[6] 3,5-dichloro-isomer [I; X = 3,4-(MeO)$_2$C$_6$H$_3$, Y = Z = Cl].  In each case we also isolated the corresponding monochloro-derivative.  The 2,3-diarylbenzoquinone [I; X = Y = H, Z = 3,4-(MeO)$_2$-C$_6$H$_3$] behaved in a different way when subjected to the chlorination procedure.  The product was an inseparable mixture which appeared from its spectral properties to be composed of derivatives of the triphenylene-1,4-quinone (II; X = H, Y = Z = MeO).  Such compounds have not been described previously and we have therefore investigated their formation further.
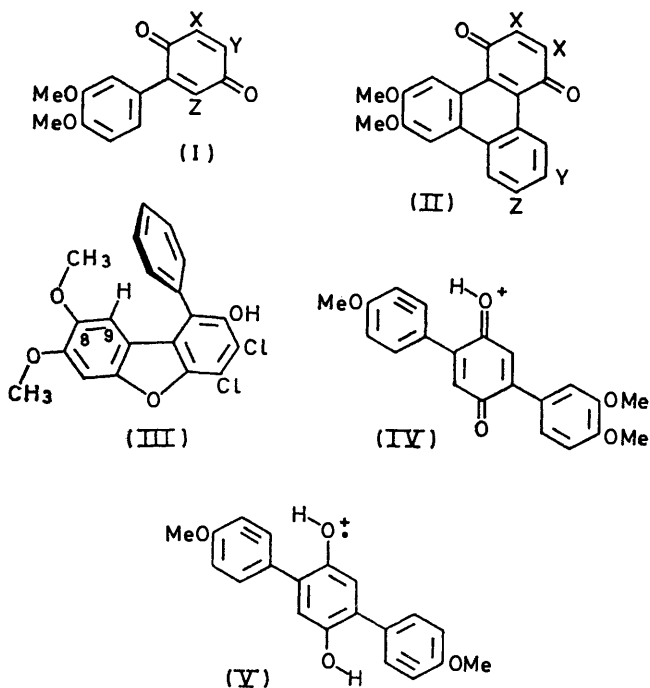
The conversion of a 2,3-diaryl-1,4-benzoquinone into a triphenylenequinone clearly involves an acid-catalysed Scholl reaction[7] between the two aryl nuclei and, in agreement with this, we found that anhydrous aluminium chloride in carbon disulphide effected the cyclisation of the quinone [I; X = Y = H, Z = 3,4-(MeO)$_2$C$_6$H$_3$] under mild conditions.  The product obtained by the iron(III) chloride oxidation of the resulting quinol was the triphenylenequinone (II; X = H, Y = Z = MeO).  The yield (32%) was improved when 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was added to the reacton mixture but an attempted cyclisation with aqueous 70% v/v sulphuric acid gave only a little of the compound.  The symmetrical structure of the triphenylenequinone follows from the simplicity of its n.m.r. spectrum, which shows singlets corresponding to twelve methoxy-protons (of two types), two quinonoid protons, and four aromatic protons, two of which (H-5 and H-12) are strongly deshielded by the adjacent carbonyl groups.[5]

In order to assess the utility of this reaction we needed some related 2,3-diaryl-1,4-benzoquinones.  2,3-Dichloro-1,4-benzoquinone has only two adjacent positions available for further substitution and on treatment with diazotised 3,4-dimethoxyaniline gave the arylquinone (I; X = Y = Cl, Z = H).  Further arylation with the appropriate diazonium compounds afforded the 2,3-diarylquinones [I; X = Y = Cl, Z = 3,4-(MeO)$_2$C$_6$H$_3$], (I; X = Y = Cl, Z = 3-MeOC$_6$H$_4$), and (I; X = Y = Cl, Z = Ph).  Each of these underwent cyclisation and oxidation on treatment with aqueous 70% v/v sulphuric acid and chloranil, giving the triphenylenequinones (II; X = Cl, Y = Z = MeO) (88%), (II; X = Cl, Y = MeO, Z = H) (67%), and (II; X =

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[2] B. W. Birrell, R. Buchan, and O. C. Musgrave, *Chem. Comm.,* 1969, 1341.
[3] J. F. Bagli and P. L'Écuyer, *Canad. J. Chem.,* 1961, **39,** 1037.
[4] P. Brassard and P. L'Écuyer, *Canad. J. Chem.,* 1958, **36,** 709; M. Akagi and K. Hirose, *J. Pharm. Soc. Japan,* 1942, **62,** 191 (*Chem. Abs.,* 1951, **45,** 6169d).

[5] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, 2nd edn., ch. 2—2.
[6] O. C. Musgrave and C. J. Webster, *J.C.S. Perkin I,* 1974, 2260.
[7] O. C. Musgrave, *Chem. Rev.,* 1969, **69,** 499.

Cl, Y = Z = H) (10%), respectively. The diarylbenzo-quinone [I; X = Y = Cl, Z = 3,4-(MeO)$_2$C$_6$H$_3$] also underwent cyclisation on treatment with hydrochloric acid and, after treatment with iron(III) chloride, afforded the expected dichlorotriphenylenequinone (II; X = Cl, Y = Z = MeO) (32%). The relevant n.m.r. signals and the u.v. and visible absorption spectra of the products resemble closely those of the unchlorinated quinone (II; X = H, Y = Z = MeO). In the mass spectrometer the four triphenylenequinones undergo little fragmentation, the only abundant fragment ion in each case being formed by the loss of Me˙ and CO. The quinone (II; X = Cl, Y = Z = MeO) formed a leucoacetate which gives the expected n.m.r. signals and which shows u.v. absorption resembling closely that [8] of 2,3,6,7,10,11-hexamethoxy-triphenylene.

The major product obtained from the reaction of the benzoquinone (I; X = Y = Cl, Z = Ph) with aqueous sulphuric acid and chloranil is a colourless phenol, C$_{20}$H$_{14}$Cl$_2$O$_4$, which, by analogy with similar products [6] from other arylquinones, we formulate as the dibenzo-furan (III). Its u.v. absorption resembles that [6] of 1,3-dichloro-7,8-dimethoxydibenzofuran-2-ol, and its n.m.r. signals agree well with those [1] of related dibenzofurans. We attribute the unusually high values for the resonances of the C-8 methoxy-protons and the C-9 proton to the shielding effect of the phenyl group.[5] The relative diffi-culty of effecting a Scholl reaction with the unactivated phenyl group is no doubt the reason for the preferred formation of this compound.

Veratrole reacts with 2,5- and 2,6-dichlorobenzoquin-one in aqueous 70% v/v sulphuric acid to give the corresponding diarylquinones [6] and it appeared possible that 3,4,3′,4′-tetramethoxybiphenyl and 2,3-dichloro-1,4-benzoquinone might react together under similar condi-tions to provide an alternative route to the triphenylene-quinone (II; X = Cl, Y = Z = MeO). In fact the di-chloroquinone effected the oxidation of the biphenyl and the only product obtained was 2,5,6,9,12,13-hexameth-oxydibenzo[fg,op]naphthacene-1,8-quinone.[9]

The mass spectra of the 2,3-, 2,5-, and 2,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinones show differences which can be correlated with their structures. The 2,5-isomer, in which each carbonyl group is adjacent to an aryl group, readily loses one or two methoxyl radicals to form ions for which structures such as (IV) and (V), respectively, may be written. In contrast, the 2,6-iso-mer, which has only one carbonyl group adjacent to an aryl group, loses carbon monoxide followed by one methoxyl radical. Fragmentation of the 2,3-isomer is more complicated. This has a carbonyl group adjacent to each aryl group and, as expected, loses one or two meth-oxyl radicals. The proximity of the two aryl groups appears to be responsible for the second mode of frag-mentation in which the molecular ion loses a methyl

radical followed by a methoxyl radical or methanol. No appreciable cleavage of the quinone ring occurs in this case.

The 2,3-dichloro-5,6-diarylquinones (I; X = Y = Cl, Z = Ar) do not possess definite m.p.s but decompose on being heated. We associate this behaviour with the ease with which these compounds can cyclise. Some of the monoarylbenzoquinones prepared during this work showed variations in their solid-state properties depend-ing on how they had been purified.[10] For example, sublimed specimens of 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone exhibited i.r. absorption different from that of crystallised samples and the related 2-(2-chloro-4,5-dimethoxyphenyl)-1,4-benzoquinone crystallised from ethanol either as orange rhombohedra or as violet needles, depending largely on the rate of cooling of the solution.

EXPERIMENTAL

U.v. absorption spectra were measured for solutions in chloroform, unless stated otherwise, with a Unicam SP 800 spectrophotometer; i.r. absorption spectra were obtained for Nujol mulls with a Unicam SP 200 or 200G spectro-photometer. N.m.r. spectra were recorded for solutions in [$^2$H]chloroform with Varian A60 (60 MHz) and HA-100 (100 MHz) spectrometers (tetramethylsilane as internal standard). Mass spectra were obtained with an A.E.I. MS9 instrument. Silica gel (Merck Kieselgel GF$_{254}$) was used for t.l.c. ' Light petroleum ' refers to the fraction of b.p. 40—60°.

2-(3,4-Dimethoxyphenyl)-1,4-benzoquinone.—This [11] crys-tallised from ethanol–acetone as red rhombohedra m.p. 133—134° (lit.,[11] 134—136°, 134—135°), $\lambda_{max.}$ (EtOH) 246·5 (log ε 4·30) and 445 nm (3·42), $\lambda_{infl.}$ 276 nm (log ε 3·84), $\nu_{max.}$ 1645 cm$^{-1}$ (quinone C=O), δ 3·91 (6H, s, ArOCH$_3$), 6·81 (3H, s, QH), and 6·95—7·25 (3H, m, ArH). After sublimation at 90° and 0·1 mmHg it had m.p. 135—136°, $\nu_{max.}$ 1655 cm$^{-1}$. The two specimens showed identical i.r. spectra in CS$_2$ solu-tion [$\nu_{max.}$ (CS$_2$) 1653 cm$^{-1}$].

Arylation of 1,4-Benzoquinone.—A solution of the di-azonium salt prepared from 3,4-dimethoxyaniline [13] (3·83 g) in 3M-hydrochloric acid (32 ml) and sodium nitrite (1·73 g) in water (15 ml) at 0° was added, together with a solution of anhydrous sodium acetate (7 g) in water (25 ml), to a vigor-ously stirred solution of 1,4-benzoquinone (2·7 g) in acetone (125 ml) at 10°. Stirring was continued for 2 h, water (100 ml) was added, and the mixture was concentrated (to 200 ml) under reduced pressure. Extraction with chloroform gave an oily solid which was chromatographed on a column of silica gel. Elution successively with benzene and ben-zene–chloroform (1 : 1) gave 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone (1·92 g), m.p. 133—134°, followed by a violet solid which was separated by t.l.c. [benzene–ethyl acetate (20 : 1)] into three bands. The first of these afforded 2,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone, which crystal-lised from chloroform–ethanol as orange needles (60 mg), m.p. 194—195° (Found: M$^{+\cdot}$, 380·1255. C$_{22}$H$_{20}$O$_6$ re-quires M, 380·1260), $\lambda_{max.}$ 255 (log ε 4·39), 288 (4·29), and 437 nm (3·79), $\lambda_{infl.}$ 364 nm (log ε 3·50), $\nu_{max.}$ 1648 cm$^{-1}$ (quinone C=O), δ 3·93 (12H, s, ArOCH$_3$), 6·90 (2H, s, QH), and 6·85—7·31 (6H, m, ArH), m/e 380 (100%, M$^{+\cdot}$), 349 [41%,

[8] O. C. Musgrave and C. J. Webster, J. Chem. Soc. (C), 1971, 1397.

[9] O. C. Musgrave and C. J. Webster, J. Chem. Soc. (C), 1971, 1393.

[10] Cf. R. Pummerer and H. Fiedler, Ber., 1927, 60, 1439.

[11] M. Akagi, J. Pharm. Soc. Japan, 1942, 62, 202 (Chem. Abs., 1951, 45, 2898e); P. Brassard and P. L'Écuyer, Canad. J. Chem., 1958, 36, 700.

[12] F. Pollecoff and R. Robinson, J. Chem. Soc., 1918, 113, 645.

$(M - \text{MeO})^+]$, 321 [12%, $(349 - \text{CO})^+]$, 318 [47%, $(349 - \text{MeO})^{+\cdot}]$, and 162 {31%, $[3,4-(\text{MeO})_2\text{C}_6\text{H}_3\text{C}\equiv\text{CH}]^{+\cdot}\}$, $m^*$ 320·5 (380 $\longrightarrow$ 349) and 289·7 (349 $\longrightarrow$ 318). The product from the second band crystallised from ethanol to give 2,6-*bis*-(3,4-*dimethoxyphenyl*)-1,4-*benzoquinone* as violet needles (0·25 g), m.p. 168—169·5° (Found: $M^{+\cdot}$, 380·1263. $\text{C}_{22}\text{H}_{20}\text{O}_6$ requires $M$, 380·1260), $\lambda_{\text{max.}}$ 280·5 (log ε 4·26) and 460 nm (3·72), $\lambda_{\text{infl.}}$ 360 nm (log ε 3·34); $\nu_{\text{max.}}$ 1660sh and 1647 cm⁻¹ (quinone C=O), $\nu_{\text{max.}}$ (2% CHCl₃) 1665 and 1647 cm⁻¹, δ 3·92 (12H, s, ArOC$H_3$), 6·85 (2H, s, QH), and 6·88—7·28 (6H, m, ArH), $m/e$ 380 (100%, $M^{+\cdot}$), 352 [9%, $(M - \text{CO})^+]$, 337 [11%, $(352 - \text{Me})^+]$, 321 [13%, $(352 - \text{MeO})^+]$, and 162 {26%, $[3,4-(\text{MeO})_2\text{C}_6\text{H}_3\text{C}\equiv\text{CH}]^{+\cdot}\}$, $m^*$ 326·0 (380 $\longrightarrow$ 352) and 322·6 (352 $\longrightarrow$ 337). The third band afforded 2,3-*bis*-(3,4-*dimethoxyphenyl*)-1,4-*benzoquinone*, which crystallised from chloroform–ethanol as clusters of deep red rhombohedra (0·60 g), m.p. 199—200·5° (Found: $M^{+\cdot}$, 380·1263. $\text{C}_{22}\text{H}_{20}\text{O}_6$ requires $M$, 380·1260), $\lambda_{\text{max.}}$ 283 (log ε 4·01) and 480 nm (3·38), $\nu_{\text{max.}}$ 1660 and 1651 cm⁻¹ (both quinone C=O), δ 3·61 and 3·84 (each 6H, s, 3- and 4-OMe), 6·90 (2H, s, QH), and 6·51—6·72 (6H, m, ArH); $m/e$ 380 (100%, $M^{+\cdot}$), 365 [7%, $(M - \text{Me})^+]$, 349 [7%, $(M - \text{MeO})^+]$, 334 [7%, $(365 - \text{MeO})^{+\cdot}]$, 333 [11%, $(365 - \text{MeOH})^+]$, and 318 [19%, $(349 - \text{MeO})^{+\cdot}]$, $m^*$ 350·5 (380 $\longrightarrow$ 365), 320·5 (380 $\longrightarrow$ 349), 303·8 (365 $\longrightarrow$ 333), and 289·7 (349 $\longrightarrow$ 318).

*Arylation of 2-(3,4-Dimethoxyphenyl)-1,4-benzoquinone.*— The reaction of the buffered diazonium solution prepared from 3,4-dimethoxyaniline (0·7 g) with 2-(3,4-dimethoxyphenyl)-1,4-benzoquinone (0·73 g) in acetone (100 ml) and water (100 ml) at −5°, as described above for benzoquinone, gave the unchanged arylbenzoquinone (0·17 g), and 2,5-(10 mg), 2,6- (40 mg), and 2,3-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (0·11 g).

A similar reaction with acetic acid (25 ml) as solvent instead of aqueous acetone afforded the unchanged arylbenzoquinone (0·20 g), and 2,6- (60 mg) and 2,3-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (80 mg).

*2,3-Dichloro-5-(3,4-dimethoxyphenyl)-1,4-benzoquinone.*— The reaction of the buffered diazonium solution prepared from 3,4-dimethoxyaniline (1·2 g) with 2,3-dichloro-1,4-benzoquinone [13] (0·55 g) in acetone (70 ml) at 0° as described above for benzoquinone gave the *arylbenzoquinone*, which crystallised from chloroform–ethanol as violet needles (0·31 g), m.p. 205—206° (Found: C, 53·5; H, 3·3; Cl, 22·7; MeO, 20·5. $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{O}_4$ requires C, 53·7; H, 3·2; Cl, 22·65; 2MeO, 19·85%). $\lambda_{\text{max.}}$ 260 (log ε 4·22), 278 (4·14), 337 (3·56), and 508 nm (3·46), $\nu_{\text{max.}}$ 1675 and 1652 cm⁻¹ (both quinone C=O), δ 3·90 and 3·92 (both 3H, s, ArOC$H_3$) and 6·80—7·10 (4H, m, ArH and quinone H).

*2-(2-Chloro-4,5-dimethoxyphenyl)-1,4-benzoquinone.*— The reaction of the buffered diazonium solution prepared from 2-chloro-4,5-dimethoxyaniline [8] (0·38 g) with 1,4-benzoquinone (0·25 g) in water at 10°, as described above, gave the *chloroquinone* (0·28 g), which crystallised from ethanol, on being cooled slowly, as orange rhombohedra, m.p. 130—130·5° (Found: C, 60·4; H, 4·0; Cl, 12·6; MeO, 22·6. $\text{C}_{14}\text{H}_{11}\text{ClO}_4$ requires C, 60·35; H, 4·0; Cl, 12·75; 2MeO, 22·25%. Found: $M^{+\cdot}$, 278·0349. $\text{C}_{14}\text{H}_{11}{}^{35}\text{ClO}_4$ requires $M$, 278·0346), $\lambda_{\text{max.}}$ (EtOH) 244 (log ε 4·39), 283 (3·81), and 427 nm (3·04), $\lambda_{\text{infl.}}$ 324 (log ε 3·04) and 345 nm (2·98), $\nu_{\text{max.}}$ 1660 cm⁻¹ (quinone C=O), δ 3·85 and 3·90 (each 3H, s, ArOC$H_3$) and 6·69—6·93 (5H, m, ArH and quinone H). Crystallisation of the compound from ethanol with rapid cooling and agitation gave violet needles, $\nu_{\text{max.}}$ 1658 cm⁻¹,

which changed into the orange form at 120°. The i.r. spectra of Nujol mulls of the two specimens were different.

*2,3-Dichloro-5,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone.*—The reaction of the buffered diazonium solution prepared from 3,4-dimethoxyaniline (0·30 g) with 2,3-dichloro-5-(3,4-dimethoxyphenyl)-1,4-benzoquinone (0·30 g) in acetone (250 ml) at 10°, as described above for benzoquinone, gave a mixture which was separated by crystallisation from chloroform–ethanol and t.l.c. [benzene–ethyl acetate (10 : 1)] into the unchanged arylbenzoquinone (0·21 g) and a violet solid (50 mg) which by sublimation at 120° and 0·1 mmHg gave the *diarylbenzoquinone* (Found: $M^{+\cdot}$, 448·0484. $\text{C}_{22}\text{H}_{18}{}^{35}\text{Cl}_2\text{O}_6$ requires $M$, 448·0480), $\lambda_{\text{max.}}$ (EtOH) 253 (log ε 4·29), 326 (3·58), and 466 nm (3·28), $\lambda_{\text{infl.}}$ 273 nm (log ε 4·21), $\nu_{\text{max.}}$ 1670 cm⁻¹ (quinone C=O); δ 3·62 and 3·84 (each 6H, s, 3- and 4-OMe), and 6·50—6·80 (6H, m, ArH), $m/e$ 448 (100%, $M^{+\cdot}$), 401 [8%, $(M - \text{CH}_3 - \text{CH}_3\text{OH})^+]$, 386 [8%, $(M - \text{MeO} - \text{MeO})^{+\cdot}]$, and 382 [9%, $(M - \text{Cl} - \text{MeO})^{+\cdot}]$. The product, a violet solid, did not have a definite m.p. T.l.c. [benzene–ethyl acetate (10 : 1) and benzene–light petroleum (9 : 1)] showed it to be homogeneous.

*2,3-Dichloro-5-(3,4-dimethoxyphenyl)-6-(3-methoxyphenyl)-1,4-benzoquinone.*—The reaction of the buffered diazonium solution prepared from 3-methoxyaniline (0·25 g) with 2,3-dichloro-5-(3,4-dimethoxyphenyl)-1,4-benzoquinone (0·10 g) in acetone (150 ml) at 12°, as described above for benzoquinone, gave a mixture which was separated by t.l.c. (benzene) into the unchanged arylbenzoquinone (65 mg) and the *diarylbenzoquinone* (14 mg) (Found: $M^{+\cdot}$, 418·0374. $\text{C}_{21}\text{H}_{16}{}^{35}\text{Cl}_2\text{O}_5$ requires $M$, 418·0375), $\lambda_{\text{max.}}$ 264 (log ε 4·27), 332 (3·67), and 517 nm (3·30), $\lambda_{\text{infl.}}$ 275 nm (log ε 4·22), $\nu_{\text{max.}}$ 1673 (quinone C=O), δ 3·58, 3·66, and 3·84 (each 3H, s, ArOC$H_3$), and 6·42—7·32 (7H, m, ArH), $m/e$ 418 (100%, $M^{+\cdot}$), 371 [11%, $(M - \text{Me} - \text{MeOH})^+]$, 352 [10%, $(M - \text{MeO} - \text{Cl})^{+\cdot}]$, and 340 [9%, $(M - \text{Me} - \text{Cl} - \text{CO})^{+\cdot}]$. The product, a violet solid, did not have a definite m.p. T.l.c. [benzene–ethyl acetate (10 : 1) and benzene–light petroleum (9 : 1)] showed it to be homogeneous.

*2,3-Dichloro-5-(3,4-dimethoxyphenyl)-6-phenyl-1,4-benzoquinone.*—The reaction of the buffered diazonium solution prepared from aniline (0·37 g) with 2,3-dichloro-5-(3,4-dimethoxyphenyl)-1,4-benzoquinone (0·10 g) in acetone (150 ml) at 8°, as described above for benzoquinone, gave a red solid which, after purification by t.l.c. (benzene) afforded the *diarylquinone* as a violet solid (30 mg) (Found: $M^{+\cdot}$, 388·0267. $\text{C}_{20}\text{H}_{14}{}^{35}\text{Cl}_2\text{O}_4$ requires $M$, 388·0269), $\lambda_{\text{max.}}$ 262 (log ε 4·27), 331 (3·73), and 522 nm (3·25), $\lambda_{\text{infl.}}$ 257 (log ε 4·25), and 287 nm (3·95), $\nu_{\text{max.}}$ 1668 (quinone C=O), δ 3·56 and 3·85 (both 3H, s, 3- and 4-OMe), and 6·45—7·35 (8H, m, ArH), $m/e$ 388 (100%, $M^{+\cdot}$), 322 [34%, $(M - \text{MeO} - \text{Cl})^{+\cdot}]$, and 310 [15%, $(M - \text{Me} - \text{CO} - \text{Cl})^{+\cdot}]$. The product did not have a definite m.p. T.l.c. [benzene–ethyl acetate (10 : 1) and benzene–light petroleum (9 : 1)] showed it to be homogeneous.

*Chlorination of the Bis-(3,4-dimethoxyphenyl)-1,4-benzoquinones.*—A mixture of 2,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (43 mg) and concentrated hydrochloric acid (20 ml) was boiled under reflux for 1·5 h, poured into water (150 ml), 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, dried, and evaporated. The resulting red solid was separated by preparative t.l.c. [benzene–ethyl acetate (20 : 1)] into start-

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

ing material (10 mg), 2,5-dichloro-3,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (2 mg), m.p. 300—301° (lit.,[6] 306·5—307·5°), and 3-*chloro-2,5-bis-(3,4-dimethoxyphenyl)*-1,4-*benzoquinone* (15 mg), red needles or orange plates (from chloroform–ethanol), m.p. 208—209·5° (Found: $M^{+\cdot}$, 414·0866. $C_{22}H_{19}{}^{35}ClO_6$ requires $M$, 414·0870), $\lambda_{max.}$ 260 (log ε 4·37), 284 (4·28), and 464 nm (3·70), $\nu_{max.}$ 1665 and 1643 cm⁻¹ (both quinone C=O), δ 3·90 (3H, s, ArOC$H_3$), 3·95 (9H, s, ArOC$H_3$), and 6·92—7·17 (7H, m, ArH and quinone H); $m/e$ 416 [77%, $(M + 2H)^{+\cdot}$], 414 (100%, $M^{+\cdot}$), 383 [19%, $(M - MeO)^+$], 379 [12%, $(M - Cl)^+$], 352 [50%, (383 − MeO)$^{+\cdot}$], 348 [95%, (383 − Cl)$^{+\cdot}$], and 189 {22%, [3,4-(MeO)$_2C_6H_3C{\equiv}CCO]^+$}, $m^*$ 354·3 (414 ⟶ 383), 323·4 (383 ⟶ 352), 319·6 (379 ⟶ 348), and 316·2 (383 ⟶ 348).

A similar reaction with 2,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (70 mg) gave starting material (6 mg), 2,6-dichloro-3,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (6 mg) as violet needles (from chloroform–ethanol), m.p. 212—213·5° (lit.,[6] 211—213°), and 2-*chloro-3,5-bis-(3,4-dimethoxyphenyl)*-1,4-*benzoquinone* (43 mg) as violet needles (from chloroform–ethanol), m.p. 174·5—177° (Found: $M^{+\cdot}$, 414·0869. $C_{22}H_{19}{}^{35}ClO_6$ requires $M$, 414·0870), $\lambda_{max.}$ 257 (log ε 4·40), 280 (4·30), 320 (3·50), and 490 nm (3·66), $\nu_{max.}$ 1657 cm⁻¹ (quinone C=O), δ 3·90 and 3·93 (both 6H, s, ArOC$H_3$) and 6·80—7·18 (7H, m, ArH and quinone H), $m/e$ 414 (100%, $M^{+\cdot}$), 383 [6%, $(M - MeO)^+$], 379 [7%, $(M - Cl)^+$], 355 [25%, (383 − CO)$^+$], 351 [7%, (379 − CO)$^+$], and 189 {12%, [3,4-(MeO)$_2C_6H_3C{\equiv}CCO]^+$}, $m^*$ 354·3 (414 ⟶ 383), 346·9 (414 ⟶ 379), and 329·1 (383 ⟶ 355).

A similar reaction with 3-chloro-2,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (35 mg) gave 2,6-dichloro-3,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (5 mg) and starting material (20 mg).

*Cyclisation of* 2,3-*Bis-(3,4-dimethoxyphenyl)*-1,4-*benzoquinone.*—(a) *With aluminium chloride.* A mixture of the benzoquinone (75 mg), anhydrous aluminium chloride (0·5 g) and carbon disulphide (100 ml) was stirred at room temperature for 3 days and then added to a mixture of ice (30 g) and M-sulphuric acid (10 ml). The carbon disulphide was evaporated off under reduced pressure and the aqueous mixture was shaken with chloroform. Anhydrous iron(III) chloride (0·20 g) was added to the dried chloroform layer, which was then washed with 2M-hydrochloric acid and evaporated. The residual solid was separated by t.l.c. [benzene–ethyl acetate (4 : 1)] into starting material (18 mg) and 6,7,10,11-*tetramethoxytriphenylene*-1,4-*quinone*, which crystallised from chloroform–ethanol as violet needles (24 mg, 32%), m.p. 289—291° (Found: $M^{+\cdot}$, 378·1091. $C_{22}H_{18}O_6$ requires $M$, 378·1103), $\lambda_{max.}$ 271 (log ε 4·76), 326 (3·63), 346 (3·49), and 494 nm (3·76), $\lambda_{infl.}$ 296 (log ε 4·24), 301·5 (4·18), and 312 nm (3·92), $\nu_{max.}$ 1645 cm⁻¹ (quinone C=O), δ 4·08 and 4·11 (each 6H, s, ArOC$H_3$), 6·82 (2H, s, H-2 and H-3), 7·58 (2H, s, H-8 and H-9), and 8·98 (2H, s, H-5 and H-12), $m/e$ 378 (100%, $M^{+\cdot}$), 335 [24%, $(M - CH_3 - CO)^+$], and 189 (10%, $M^{2+}$).

The addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0·15 g) to the reaction mixture gave a higher (50%) yield of the triphenylenequinone.

(b) *With aqueous sulphuric acid.* A mixture of the benzoquinone (100 mg) and aqueous 70% v/v sulphuric acid (15 ml) was shaken for 2 h, kept for 3 days at room temperature, and poured into water (60 ml). Treatment as in (a) gave starting material (21 mg) and the triphenylenequinone (3 mg).

2,3-*Dichloro*-6,7,10,11-*tetramethoxytriphenylene*-1,4-*quin-*

*one.*—(a) A mixture of 2,3-dichloro-5,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (40 mg), chloranil (100 mg), and aqueous 70% v/v sulphuric acid (40 ml) was shaken for 24 h and diluted with water (100 ml). Extraction with chloroform gave a violet solid which was separated by t.l.c. [benzene–ethyl acetate (10 : 1)] into chloranil and the *triphenylenequinone*, which crystallised from chloroform–ethanol as violet needles (35 mg), m.p. 310—313° (Found: $M^{+\cdot}$, 446·0338. $C_{22}H_{16}{}^{35}Cl_2O_6$ requires $M$, 446·0324), $\lambda_{max.}$ 276 (log ε 4·83), 355 (3·61), and 532 nm (3·80), $\lambda_{infl.}$ 300 (log ε 4·39), 316 (4·07), and 328 nm (3·84), $\nu_{max.}$ 1658 cm⁻¹ (quinone C=O), δ 4·08 and 4·13 (each 6H, s, ArOC$H_3$), 7·62 (2H, s, H-8 and H-9), and 8·78 (2H, s, H-5 and-12), $m/e$ 446 (100%, $M^{+\cdot}$), 403 [27%, $(M - CH_3 - CO)^+$], and 223 (7%, $M^{2+}$).

(b) A mixture of the diarylbenzoquinone (25 mg) and concentrated hydrochloric acid (25 ml) was boiled under reflux with stirring for 3 h, poured into water (100 ml), and extracted with chloroform. The dried chloroform layer was shaken with anhydrous iron(III) chloride (0·25 g), washed with 2M-hydrochloric acid and with water, dried, and evaporated. Purification of the resulting solid by t.l.c. [benzene–ethyl acetate (9 : 1)] gave the triphenylenequinone (8 mg).

2,3-*Dichloro*-6,7,10,11-*tetramethoxytriphenylene*-1,4-*diyl Diacetate.*—A mixture of 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (27 mg), acetic anhydride (10 ml), zinc dust (0·20 g), and triethylamine (0·2 ml) was heated under reflux for 1 h and poured into hot water (50 ml). Extraction with chloroform gave the *leucoacetate*, which crystallised from chloroform–ethanol as needles (28 mg), m.p. 231·5—233° (Found: $M^{+\cdot}$, 534·0642. $C_{26}H_{22}{}^{35}Cl^{37}ClO_8$ requires $M$, 534·0662), $\lambda_{max.}$ 287 (log ε 4·93), 361 (3·53), and 379 nm (3·48), $\lambda_{infl.}$ 258 (log ε 4·42), 269 (4·59), 277 (4·73), 304 (4·54), and 339 nm (3·66), $\nu_{max.}$ 1765 and 1755 cm⁻¹ (acetate C=O), δ 2·47 (6H, s, C$H_3CO_2$Ar), 4·04 and 4·08 (both 6H, s, ArOC$H_3$), and 7·70 and 8·46 (both 2H, s, H-8 and H-9, H-5 and H-12), $m/e$ 532 (20%, $M^{+\cdot}$), 490 [19%, $(M - CH_2CO)^{+\cdot}$], and 448 [100%, $(M - 2CH_2CO)^{+\cdot}$].

2,3-*Dichloro*-6,7,11-*trimethoxytriphenylene*-1,4-*quinone.*— A mixture of 2,3-dichloro-5-(3,4-dimethoxyphenyl)-6-(3-methoxyphenyl)-1,4-benzoquinone (12 mg), chloranil (25 mg), and aqueous 70% v/v sulphuric acid (20 ml) was shaken for 2 h, kept overnight, and diluted with water (100 ml). Extraction with chloroform gave a violet solid which was separated by t.l.c. [benzene–ethyl acetate (5 : 1)] into chloranil and the *triphenylenequinone*, which crystallised from chloroform–ethanol as violet needles (8 mg), m.p. 270—272° (Found: $M^{+\cdot}$, 416·0221. $C_{21}H_{14}{}^{35}Cl_2O_5$ requires $M$, 416·0218), $\lambda_{max.}$ 273 (log ε 4·81) and 536 nm (3·60), $\lambda_{infl.}$ 268 (log ε 4·75), 292 (4·38), 303 (4·25), 320 (3·93), and 354 nm (3·44), $\nu_{max.}$ 1660 cm⁻¹ (quinone C=O), δ 3·98, 4·04, and 4·10 (each 3H, s, ArOC$H_3$), 7·63 (1H, s, H-8), 8·60 (1H, s, H-5), and 7·20—8·68 (3H, m, H-9, H-10, and H-12), $m/e$ 416 (100%, $M^{+\cdot}$), 373 [21%, $(M - Me - CO)^+$], and 208 (10%, $M^{2+}$).

*Cyclisation of* 2,3-*Dichloro-5-(3,4-dimethoxyphenyl)-6-phenyl*-1,4-*benzoquinone.*—A mixture of the quinone (20 mg), chloranil (40 mg), and aqueous 70% v/v sulphuric acid (20 ml) was shaken for 4 h, kept overnight, and diluted with water (60 ml). Extraction with chloroform gave a red solid which was separated by t.l.c. (benzene) into (a) chloranil, (b) 2,3-*dichloro*-6,7-*dimethoxytriphenylene*-1,4-*quinone*, which crystallised from chloroform–ethanol as red needles (2 mg), m.p. 247·5—249·5° (Found: $M^{+\cdot}$, 386·0101. $C_{20}H_{12}{}^{35}Cl_2O_4$ requires $M$, 386·0113), $\lambda_{max.}$ 268 (log ε 4·75) and

514 nm (3·64), $\lambda_{infl.}$ 264 (4·72), 290 (4·30), 310 (4·06), 321 (3·92), and 350 nm (3·32), $\nu_{max.}$ 1662 cm$^{-1}$ (quinone C=O), $\delta$ 4·12 and 4·16 (each 3H, s, ArOC$H_3$), 7·99 (1H, s, H-8), 8·88 (1H, s, H-5), and 7·68—9·27 (4H, m, H-9, H-10, H-11, and H-12), $m/e$ 386 (100%, $M^{+\cdot}$), 343 [15%, $(M - CH_3 - CO)^+$], and 193 (8%, $M^{2+}$), and (c) 3,4-*dichloro*-7,8-*dimethoxy*-1-*phenyl-dibenzofuran*-2-*ol*, which crystallised from chloroform–ethanol as needles (15 mg), m.p. 173·5—174·5° (Found: $M^{+\cdot}$, 388·0271. $C_{20}H_{14}{}^{35}Cl_2O_4$ requires $M$, 388·0269), $\lambda_{max.}$ (EtOH) 250 (log $\varepsilon$ 4·23) and 319 nm (4·35), $\lambda_{infl.}$ 223 (log $\varepsilon$ 4·46) and 263·5 nm (4·13), $\nu_{max.}$ 3535 cm$^{-1}$ (phenolic OH), $\delta$ 3·56 and 3·92 (both 3H, s, 8- and 7-OMe), 5·46 (1H, s, ArO$H$), 6·36 (1H, s, H-9), 7·10 (1H, s, H-6), and 7·34—7·55 (5H, m, $C_6H_5$Ar), $m/e$ 388 (100%, $M^{+\cdot}$), 373 [8%, $(M -$ Me)$^+$], 341 [8%, (373 − MeOH)$^+$], 329 [9%, $(M -$ MeO −

CO)$^+$], and 310 [23%, (373 − COCl)$^{+\cdot}$], $m^*$ 358·6 (388 $\longrightarrow$ 373), 311·8 (373 $\longrightarrow$ 341), and 257·7 (373 $\longrightarrow$ 310).

*Reaction of 2,3-Dichloro-1,4-benzoquinone with 3,3′,4,4′-Tetramethoxybiphenyl.*—A mixture of the benzoquinone (0·5 g), the biphenyl (0·13 g), and aqueous 70% v/v sulphuric acid (15 ml) was shaken for 3 h, kept at room temperature for 4 days, and shaken with water (100 ml). Extraction of the resulting solid with chloroform removed starting materials and 2,3-dichloroquinol and afforded 2,5,6,9,12,13-hexamethoxydibenzo[*fg,op*]naphthacene-1,8-quinone [9] (90 mg) as an insoluble blue residue.