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DIQUINONES II
THE FORMATION OF DIBENZOFURAN DERIVATIVES BY REARRANGEMENT OF DIQUINONES

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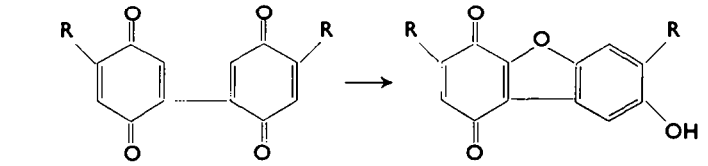
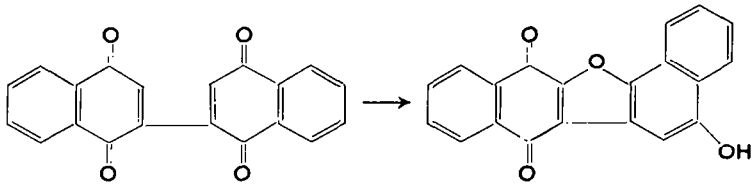
Abstract—Several diquinones (I, III, V) undergo photochemical and/or thermal rearrangement to dibenzofuranquinones (II, IV, VI). Structure IV has been established by synthesis and unambiguous structures have been assigned to several of its isomers.

It is shown that the hydroxyquinone II, and related compounds, undergo fission of the furan ring when dissolved in alkaline solution, the blue colour produced arising from the anion of the resultant *o*-hydroxyphenylquinone. It is suggested that the mechanism of ring opening is analogous to the alkyl-oxygen fission of esters.

Two well known rearrangements† of diquinones are those of Erdtman[1] I → II (R = OMe) and of Pummerer *et al.*[2] (III → IV). A characteristic feature of the rearrangement products, which are red, is the formation of blue or green colours in alkaline



I II



III IV

solution, a property not obviously in accord with structures II and IV. In view of this it seemed desirable to establish these structures by unambiguous synthesis as the original evidence was confined to analyses and the formation of derivatives. Since this work was completed, however, the structure of the quinone IV has been confirmed[4] by spectroscopic examination of its derivatives and by the formation of the parent dinaphthofuran on fusion with zinc dust. In this paper we report two syntheses of IV, the preparation of several isomers which also give blue or green colours in alkaline solution, and further examples of the molecular rearrangement. The origin of the blue colours is also discussed.

* Publication delayed at Authors' request.

† The rearrangement of diquinizaryl[3] was the first of this type but this is a more complex example which includes an oxidation step.

[1] H. G. H. Erdtman, *Proc. Roy. Soc.* A **143**, 223 (1934).

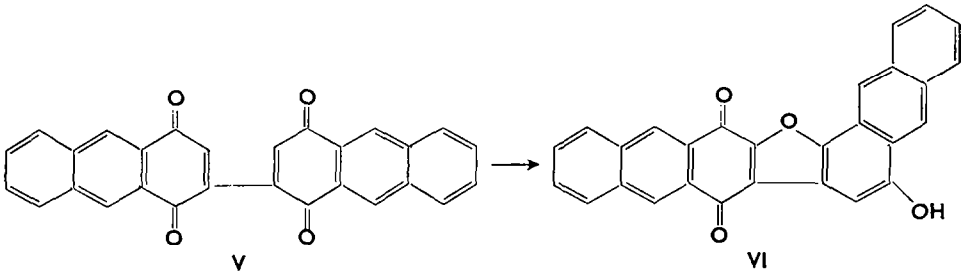
[2] R. Pummerer, A. Pfaff, G. Riegelbauer and E. Rosenhauer, *Ber. Dtsch. Chem. Ges*, **72**, 1623 (1939).

[3] R. E. Schmidt, B. Stein and C. Bamberger, *Ber. Dtsch. Chem. Ges.* **63**, 300 (1930).

[4] D. Schulte-Frohlinde and V. Werner, *Chem. Ber.* **94**, 2726 (1961).

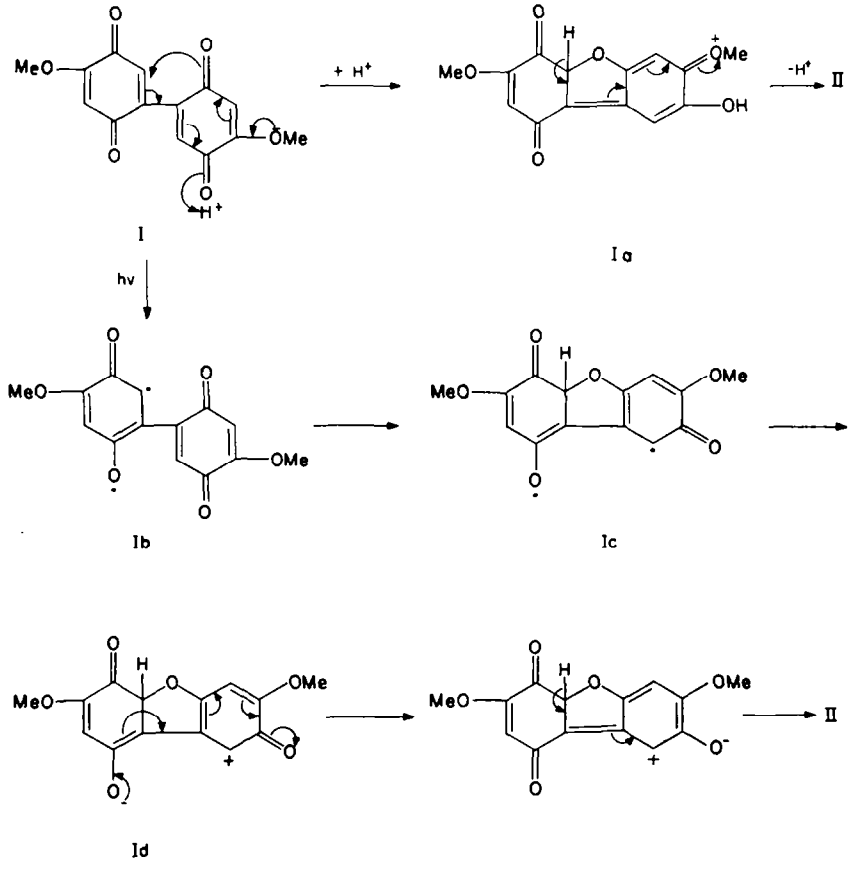
Diquinone rearrangements

The rearrangements I → II (R = OMe) and III → IV were effected thermally.[1,2] Similarly the diphenyldiquinone I (R = Ph) can be converted with II (R = Ph) by heating in α-bromonaphthaline, and the di-anthraquinone V yields the di-anthrafurandione VI. Both II (R = Ph) and VI give green colours in alkaline solution.



V VI

Erdtman[1] found that the I → II (R = OMe) rearrangement could be effected at lower temperatures in the presence of acids but we find that this change is most easily accomplished by u.v. irradiation at room temperature. The photochemical transformation of III into IV and I into II (R = Me) (in this case thermal rearrangement gives a very poor yield) was also effected smoothly but the diphenyldiquinone I (R = Ph) and the



I Ia Ib Ic Id

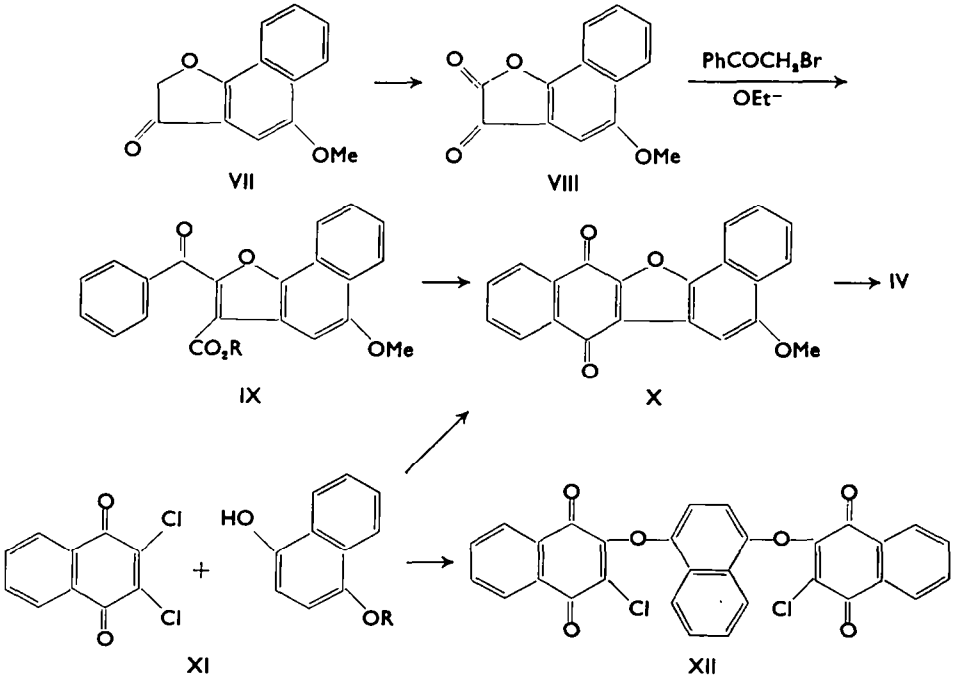
dianthraquinone V are stable to light. The halogenodiquinones I (R = Cl and Br) are stable to both heat and light.

The acid-catalysed rearrangement no doubt proceeds via Ia as indicated on the preceding page (this is essentially Erdtman's[1] interpretation). The photochemical (and possibly the thermal) transformation can be envisaged, following Zimmerman and Schuster,[5] as an initial $n \rightarrow \pi^*$ transition leading to Ib, formation of the oxygen bridge Ic, electron transfer ("demotion") and subsequent rearrangement of the zwitterionic species Id.

Synthesis of brazanquinones

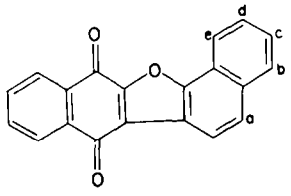
The dinaphthofurandione IV has been synthesised by Chatterjea's procedure.[6] The keto-lactone VIII, obtained in three steps from the methoxybenzocoumaranone VII, was condensed with ω-bromoacetophenone in the presence of sodium ethoxide to give the keto-ester IX (R = Et) which was cyclised, via the acid chloride, to the dinaphthofurandione X. Demethylation with pyridine hydrochloride gave a product identical with that obtained by rearrangement of 2,2'-dinaphthyl-1,4:1',4'-diquinone III. The methyl ether of IV (i.e. X) was also obtained in one step by condensation of 2,3-dichloro-1,4-naphthaquinone with 4-methoxy-1-naphthol (XI; R = Me) in boiling pyridine.

This last reaction is a general procedure for the preparation of brazanquinones and by this means eleven isomeric α (XIII)- and γ (XIV)-brazanquinones, with hydroxyl groups at positions *a* to *f*, have been obtained by condensing 2,3-dichloro-1-4-naphthaquinone with the appropriate dihydroxynaphthalenes or their monomethyl

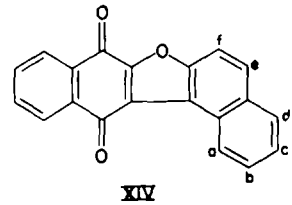


[5] H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.* **83**, 4486 (1961).
[6] J. N. Chatterjea, *J. Indian Chem. Soc.* **31**, 101 (1954).

ethers. Several of these hydroxybrazanquinones are already known;[7–11] new ones are recorded in the experimental section. The synthesis fails with 1,4-dihydroxynaphthalene XI (R = H), the product being a yellow, highly insoluble compound which contains chlorine but no hydroxyl group; it appears to be the diquinone XII. It was formerly assumed by Buu-Hoï[7,12,13] that this reaction with 2,3-dichloro-1,4-naphthaquinone was characteristic of β-naphthols only, although he found subsequently[14]



XIII



XIV

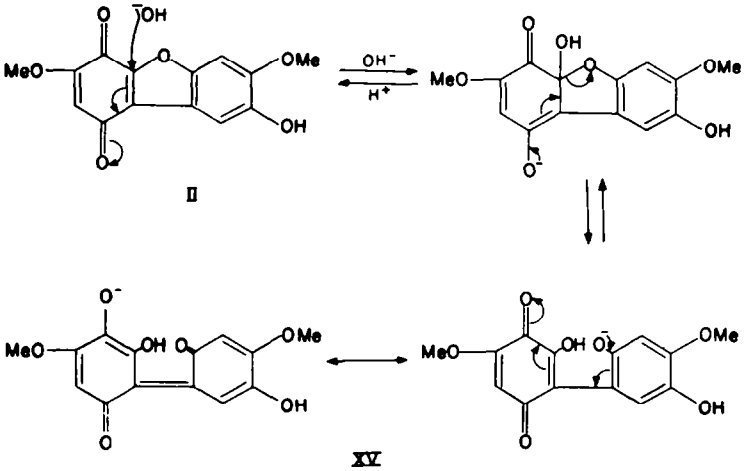
that α-naphthols condensed equally well as Fieser and Brown[15] had already demonstrated. In fact α-hydroxyl groups are usually more reactive than β since both 1,6-and 1,7-dihydroxynaphthalenes react exclusively at the α-position to give the corresponding α-brazanquinones XIII. (1,3-Dihydroxynaphthalene appears to be an exception.) These structures were established by synthesis of the respective methyl ethers by interaction of 2,3-dichloro-1,4-naphthaquinone with 6- and 7-methoxy-1-naphthol.

Partial methylation of 1,6-dihydroxynaphthalene gives a monomethyl ether which Buu-Hoi[7] assumed to be 5-methoxy-2-naphthol since it readily gave a brazanquinone by reaction with 2,3-dichloro-1,4-naphthaquinone. Although the assumption was invalid the structure of the methoxynaphthol is correct and the derived brazanquinone is therefore XIV (d = OMe; $a = b = c = e = f$ = H). However the product of demethylation, XIV (d = OH; $a = b = c = e = f$ = H) is *not* the same as that obtained by direct condensation of 2,3-dichloro-1,4-naphthaquinone with 1,6-dihydroxynaphthalene, i.e. XIII (c = OH; $a = b = d = e$ = H),as was stated.[7] 8-Methoxy-2-naphthol, required for the preparation of XIV (a = OMe; $b = c = d = e = f$ = H) was obtained by partial methylation of 1,7-dihydroxynaphthalene and by an unambiguous synthesis starting from 7-nitro-1-tetralone (see Experimental).

A characteristic feature of the quinone II, and related compounds, is the formation of blue colours in alkaline solution. The reason for this is not immediately obvious; the anion of II is not likely to be blue since the phenolic group is situated *meta* to the carbon-carbon bond linking the two carbocyclic rings and is therefore not in conjugation with the quinone system. Furthermore the blue colour (λ_{max} 644 mμ) is not a consequence of some redox reaction since it appears when II is dissolved in alkali under nitrogen, the original quinone being recovered on acidification.

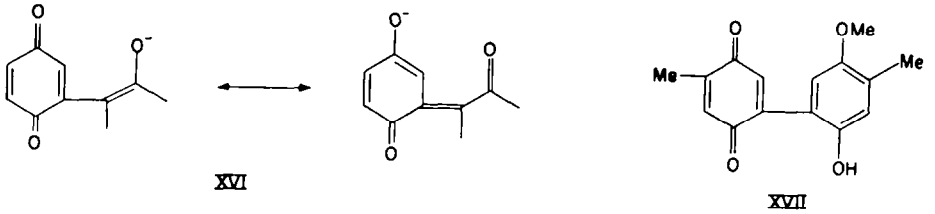
[7] Ng. Ph. Buu-Hoï, *J. Chem. Soc.* 2871 (1951).
[8] Ng. Ph. Buu-Hoï, *J. Chem. Soc.* 491 (1952).
[9] Ng. Ph. Buu-Hoï, *J. Org. Chem.* **20**, 1191 (1955).
[10] Ng. Ph. Buu-Hoï and D. Lavit, *J. Org. Chem.* **21**, 21 (1956).
[11] R. V. Acharya, B. D. Tilak and M. R. Venkiteswaran, *J. Sci. Ind. Res. India* **16 B**, 554 (1957).
[12] Ng. Ph. Buu-Hoï, *J. Org. Chem.* **16**, 185 (1951).
[13] Ng. Ph. Buu-Hoï, *J. Chem. Soc.* 489 (1952).
[14] Ng. Ph. Buu-Hoï and P. Demerseman, *J. Chem. Soc.* 4699 (1952).
[15] L. F. Fieser and R. H. Brown, *J. Amer. Chem. Soc.*, **71**, 3609 (1949).

The oxygen bridge in quinone II is part of a vinylogous ester structure which might undergo normal alkaline hydrolysis, as indicated, resulting in opening of the furan ring and formation of the mesomeric anion XV which, by analogy, should be

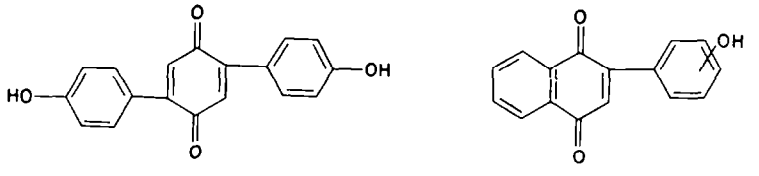


II XV

blue. It is well known that mesomeric anions of structure XVI are blue; this is the basis of the Craven, Kesting and Dam-Karrer colour tests,[16] and a close analogy with the present case is the phenolic quinone XVII[17] which gives a blue colour in alkaline solution. The same is true of the quinone XVIII[18] in which the phenolic groups are



XVI XVII



XVIII XIX

situated *para* to the internuclear links. As a further check we synthesised the three 2-(hydroxyphenyl)-1,4-naphthaquinones XIX; the *o*- and *p*- hydroxy isomers gave blue

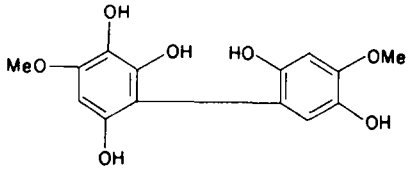
[16] R. Craven, *J. Chem. Soc.* 1605 (1931); W. Kesting, *Ber. Dtsch. Chem. Ges.* **62**, 1422 (1929); P. Karrer, *Helv. Chim. Acta* **22**, 1146 (1939); R. H. Thomson, *Naturally Occurring Quinones* p. 147. Butterworths, London (1957).

[17] Th. Posternak, W. Alcalay, R. Luzzatti and A. Tardent, *Helv. Chim. Acta* **31**, 525 (1948).

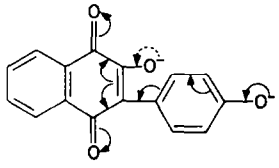
[18] R. Pummerer and E. Prell, *Ber. Dtsch. Chem. Ges.* **55**, 3105 (1922).

solutions in alkali (λ_{max} 563 and 572 mμ respectively) whereas the *m*-isomer which has a non-conjugated hydroxyl group (cf. II) formed a red solution (λ_{max} 485 mμ).

Since the quinone II is precipitated on acidification of its alkaline solution it is not possible to isolate the conjugate acid of XV, nor could we obtain derivatives by alkylation or acylation reactions in alkaline solution. However hydrogenation of II in alkaline solution over Raney nickel gave the diphenyl derivative XX which was isolated as its penta-acetate. This establishes that ring opening does occur when II is dissolved in alkaline solution.

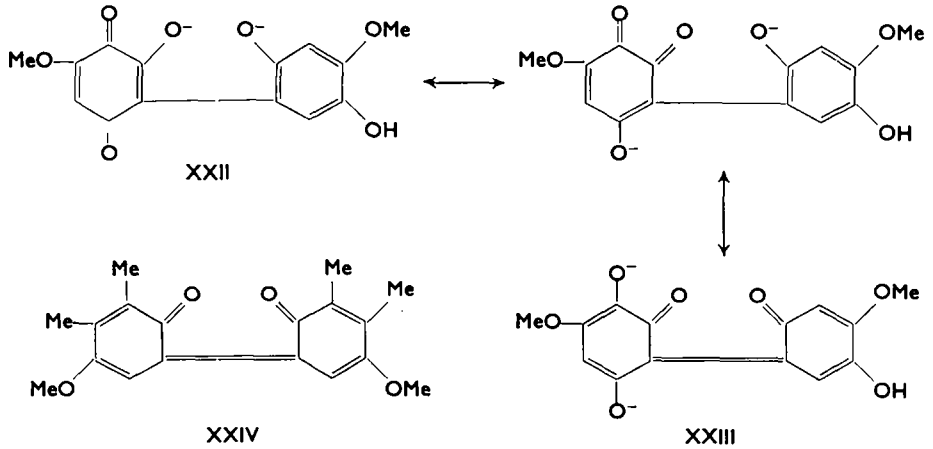


XX



XXI

In excess alkali the acidic quinone hydroxyl group in XV would also be ionised, and it is pertinent to compare the di-anion XXII* with the di-anion XXI of 2-hydroxy-3-(p-hydroxyphenyl)-1,4-naphthaquinone. (The *o*-hydroxy isomer would be a better model but this could not be obtained and the *p*-isomer was not very stable.) 2-Hydroxy-naphthaquinones are normally red in alkaline solution, the anion of 2-hydroxy-1,4-naphthaquinone showing λ_{max} 467 mμ, whilst hydroxybenzoquinones show red to violet colours, e.g., the anion of 2-hydroxy-3,6-dimethylbenzoquinone has λ_{max} 530 mμ. In excess alkali 2-hydroxy-3-(*p*-hydroxyphenyl)-1,4-naphthaquinone gives a violet solution showing maxima at 460 and 606 mμ, the former arising from the 2-hydroxyl anion. The di-anion of II however, shows no visible absorption attributable to the 2-hydroxy anion (Fig. 1), and the dominant contributions to the light absorption must come from XXIII, and related structures involving



the 4′-methoxyl group, in which the 2-hydroxyl anion is redundant. This view is supported by comparing XXIII with the blue *o*-diphenoquinone XXIV[19] which shows λ_{max} 375 and 624 mμ (in cyclohexane).

* and similar dianions from the dinaphthofuranquinones discussed on p. 1927.

[19] D. Schulte-Frohlinde and F. Erhart, *Angew. Chem. internat. Edit.* **1**, 112 (1962).

The evidence, so far, establishes the origin of the blue colour but does not validate the hydrolysis mechanism shown on p. 1923, which assumes that hydroxyl ion attacks a vinylogous ester system, the overall reaction being equivalent to acyl-oxygen fission. The hydrolysis is remarkably facile, proceeding rapidly in the cold in weak bases such as dilute ammonium hydroxide and sodium carbonate,* and it will be noted that

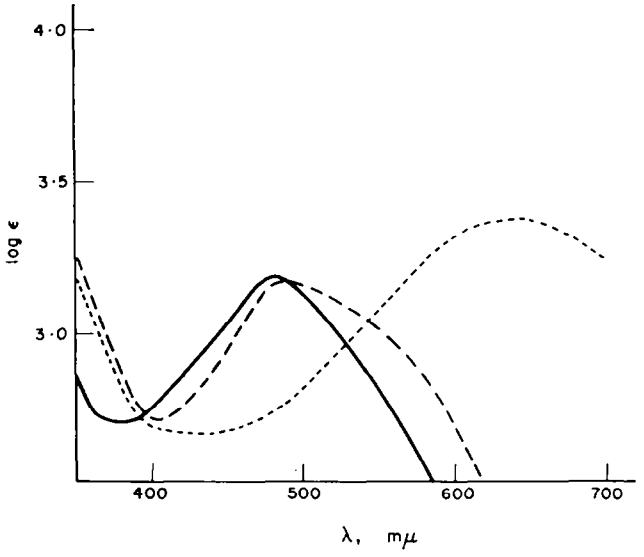


FIG. 1. Visible absorption of quinone II in (a) EtOH (——), (b) EtOH +1 equiv. NaOH (- - -), (c) EtOH + 2 equiv. NaOH (.....).

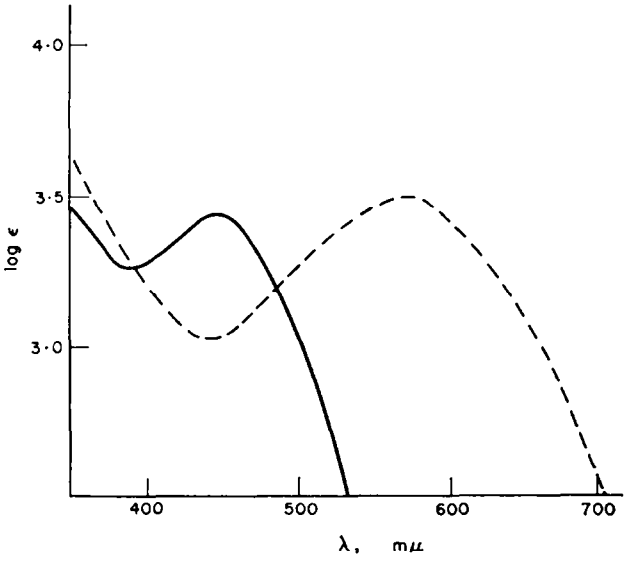
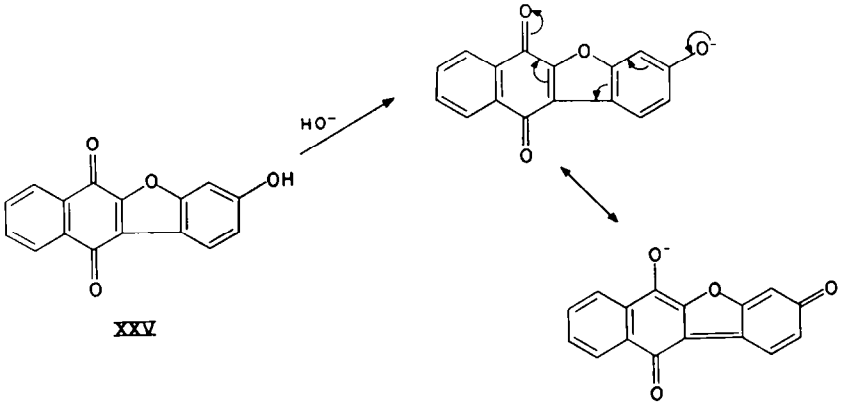


FIG. 2. Visible absorption of quinone XXV in (a) EtOH (——), (b) EtOH + 1 equiv. NaOH (- - -).

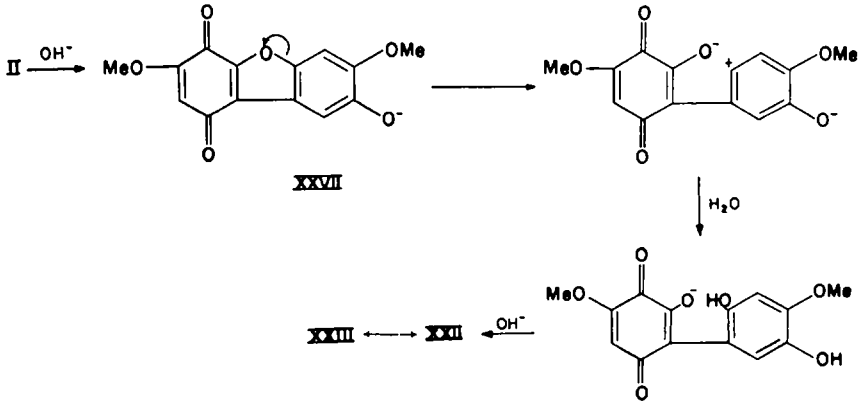
* On heating in aqueous sodium acetate a blue colour develops, changing to red on cooling.

there appears to be no attack on the other vinylogous ester system involving the quinone methoxyl group, since the starting material is recovered unchanged on acidification of the blue solution. Further evidence, which casts doubt on the hydrolysis mechanism assumed initially, was obtained when the behaviour of II in alkaline solution was compared with that of XXV, an easily accessible example of a dibenzofuranquinone containing a hydroxyl group conjugated with the quinone system. Like II it gives a blue colour in alkaline solution (λ_{max} 575 mμ, see Fig. 2). Spectrophotometric titration at 575 mμ showed that the long wave-length peak began to appear immediately alkali (NaOH) was added reaching maximum intensity on addition of one equivalent, so that in this case (XXV) the blue colour arises simply by ionisation of the hydroxyl group and formation of the mesomeric anion XXVI.



XXV XXVI

However spectrophotometric titration of II at 644 mμ reveals a different course of events. On addition of one equivalent of sodium hydroxide the solution remains red (see Fig. 1) and there is no absorption >600 mμ until further alkali is added, *two* equivalents being required to reach maximum intensity. This implies that ionisation of the hydroxyl group in II precedes the ring opening stage. That the formation of the anion XXVII is a *necessary requirement* for ring opening follows from the fact



XXVII XXIII XXII

that if the hydroxyl group is methylated, or if it is absent,* no blue colour appears even on boiling with 5 N sodium hydroxide. From these data and the stability of the vinylogous methyl ester system, noted previously, it is evident that the blue anion is not formed by the mechanism indicated on p. 1923 which leads us to suggest that the reaction proceeds, as shown on the preceding page, by a mechanism analogous to the alkyl-oxygen fission of esters. Although aryl-oxygen fission does not appear to have been observed before it would be favoured in this case by the weakly alkaline aqueous medium and assisted by the powerful +I effect of the negative charge on the phenolic oxygen atom. A kinetic study is obviously needed to establish this.

TABLE 1. VISIBLE ABSORPTION OF HYDROXYDINAPHTHOFURANQUINONES (XIII AND XIV)

Position of OH group in XIII	λ_{max} (mμ).		Position of OH in XIV	λ_{max} (mμ).	
	EtOH	EtOH + NaOH		EtOH	EtOH + NaOH
4″ (a)	481	590	3″ (f)	457*	423, 580*
5″ (b)	461	600	4″ (e)	485	590
6″ (c)	459	580	5″ (d)	475	592
7″ (d)	428	450	6″ (c)	470	580
8″ (e)	470	632	7″ (b)	461	580
			8″ (a)	475	585

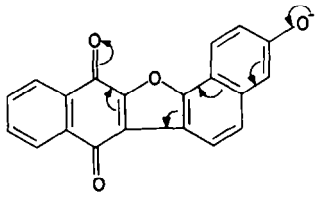
* In dioxan

All these considerations can be extended to the dinaphthofurandione series. With one exception, the eleven isomers XIII and XIV, having a hydroxyl group at the positions marked *a* to *f*, give blue† solutions in alkali (see Table 1), whereas if the hydroxyl groups are methylated (or absent) the reaction is negative. If the hydroxyl group is in conjugation with the quinone system, i.e. XIII (OH at *c* or *e*) and XIV (OH at *b*, *d* or *e*) spectrometric titration at the wavelength of maximum absorption in the 600 mμ region shows that maximum intensity is reached after the addition of *one* equivalent of sodium hydroxide. On the other hand, where the hydroxyl group is not conjugated with the quinone ring, i.e., XIII (OH at *a*, *b* or *d*) and XIV† (OH at *a*, *c* or *f*) no long-wave peak near 600 mμ is observed until more than one equivalent of sodium hydroxide has been added, maximum intensity being reached on addition of *two* equivalents. The situation closely parallels that found when comparing the behaviour of II and XXV. In the conjugated series the blue colours arise by simple ionisation to give mesomeric anions such as XXVIII and XXIX, but in the non-conjugated series ionisation of the phenolic group precedes the "blue stage", which presumably involves fission of the oxygen bridge. An inexplicable exception is the non-conjugated isomer XXX which gives a brown solution in alkali; the structure of XXX is firmly established.

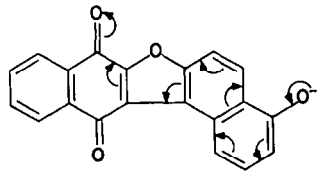
* The compounds tested were dibenzofuranquinone, the benzonaphthofuranquinone XXXI, the quinones XIII and XIV (*a* to *f* = H), and 5′-methoxyl-5″-methyl-(1″,2″-5,4)benzo-(2′,3′-2,3)-naphthofuran-1′,4′-dione.[20]

† The visible colour ranges from blue-violet to green, the long wave absorption bands being very broad; both the visible colour and the position of λ_{max} tend to alter with age. XIV (*f* = OH, *a* to *e* = H) is particularly insoluble and gives a yellowish-green colour in aqueous alkaline dioxan (see Table 1), but could not be satisfactorily titrated.

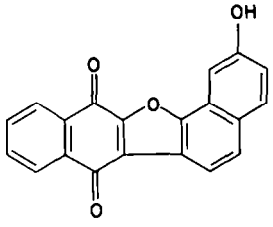
[20] E. Simonitsch, W. Eisenhuth, O. A. Stamm and H. Schmid, *Helv. Chim. Acta* **43**, 58 (1960).



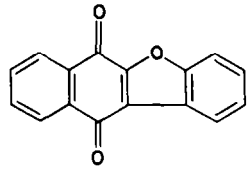
XXVIII



XXIX



XXX

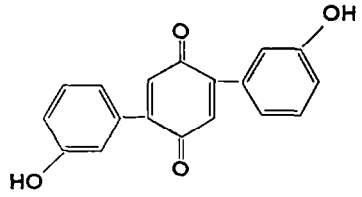


XXXI

The model compounds XIX were obtained by Diels–Alder addition of butadiene to the appropriate methoxyphenylbenzoquinone and subsequent oxidation and demethylation, and by Meerwein arylation of 2-chloro-1,4-naphthaquinone followed by dechlorination and demethylation. The *o*- and *p*-isomers of XIX were somewhat unstable. Direct demethylation of the *m*-methoxy compound XIX (*m*-MeO in place of OH) and of 2-hydroxy-3-(*p*-methoxyphenyl)-1,4-naphthaquinone failed and it was necessary in both cases to reduce to the quinol before effecting demethylation with boron tribromide. Demethylation of 2-hydroxy-3-(*o*-methoxyphenyl)-1,4-naphthaquinone gave, as expected, the benzonaphthofuranquinone XXXI.

Natural products.

Two naturally occurring quinones are of interest in connection with the foregoing discussion. Volucrisporin XXXII,[21] which contains two *m*-hydroxyphenyl groups, is said to dissolve readily in dilute sodium hydroxide giving a purple colour, which is

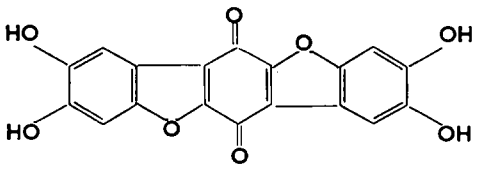


XXXII

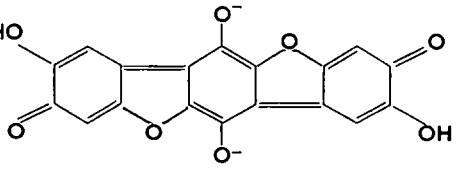
rather surprising (cf. XVIII and XIX). We found that the *initial* colour in alkali is a brownish-yellow (λ_{max} 315 and 365 mμ in EtOH) which changes to a pinkish-violet on shaking in air, the visible absorption increasing in extent and intensity with time. This suggests that a reaction is occurring (volucrisporin is not recoverable on acidification), probably hydroxylation of the quinone ring.

Thelephoric acid XXXIII[22] is an almost black solid showing λ_{max} 484 mμ in

[21] P. V. Divekar, G. Read, L. C. Vining and R. H. Haskins, *Canad. J. Chem.* **37**, 1970 (1959).
[22] J. Gripenberg, *Tetrahedron* **10**, 135 (1960).



XXXIII



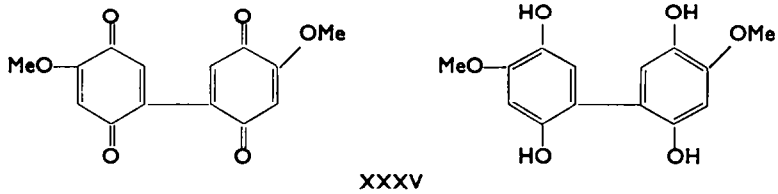
XXXIV

alcohol. On addition of sodium hydroxide the red solution becomes blue and absorbs strongly throughout the visible region showing a maximum at 740 mμ scarcely diminished in intensity at 1 μ. This may be attributed to poly-anions having the extended conjugated system of XXXIV.

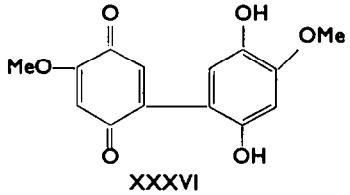
EXPERIMENTAL

Diquinones

4,4'-Dimethoxydiphenyl-2,5:2',5'-diquinone (I; R = OMe). This was obtained by chromic acid oxidation of its violet quinhydrone which can be formed by acid catalysed dimerization of methoxybenzoquinone in various ways.[1,25-26] The structure of the quinhydrone [violet-blue needles, m.p. 237–238° (lit[1,25,27] 230°, 238°, 269°] is still uncertain. It was also obtained (a) by mixing equimolecular amounts of the diquinone I (R = OMe) and its diquinol, (b) by boiling for 5 min in aqueous suspension with one mole of quinol. According to Erdtman[1] in treatment with acetic anhydride it affords the diquinone and the diquinol tetraacetate. None of these properties distinguish decisively between the "external" XXXV and the "internal" XXXVI quinhydrone structures; the formation of red-violet



XXXV



XXXVI

solutions in hot solvents favours the latter (or a tautomeric form) (see refs 1 and 27) but the brownish-yellow colour in alkaline solution does not.

4,4'-Dimethyldiphenyl-2,5:2',5'-diquinone (I; R = Me). The two-stage oxidation[17] of toluquinol dimethyl ether can be effected in one step. A solution of toluquinol dimethyl ether (2 g) in glacial acetic acid (25 ml) containing water (7 ml) and conc sulphuric acid (2 ml) was cooled to 0° and treated dropwise, with a solution of potassium dichromate (3 g) in water (12 ml). The yellow crystalline product which separated, crystallised from ethanol in golden needles, m.p. 168–169° (dec) (lit.[17,25] 162° 173°); yield 1·2 g (75)%.

[25] I. S. Ioffe and A. F. Sukhina, *J. Gen. Chem. U.S.S.R.* **23**, 1370 (1953).
[26] F. M. Dean, A. M. Osman and A. Robertson, *J. Chem. Soc.* 11 (1955).
[25] H. Davidge, A. G. Davies, J. Kenyon and R. F. Mason, *J. Chem. Soc.* 4569 (1958).
[26] C. D. Logan, R. M. Husband and C. B. Purves, *Canad. J. Chem.* **33**, 82 (1955).
[27] Th. Pasternak, W. Alcalay and R. Huguenin, *Helv. Chim. Acta* **39**, 1556 (1956).
[28] Fr. Fichter and H. Ris, *Helv. Chim. Acta* **7**, 803 (1924).

4,4′-Diphenyl-diphenyl-2,5:2′,5′-diquinone (I; R = Ph). (cf. Ref. 17) A mixture of 2,5-dimethoxydiphenyl (2 g), glacial acetic acid (15 ml), conc sulphuric acid (2 ml) and water (10 ml), was treated with a solution of 6 N-sodium dichromate (5 ml). The violet quinhydrone which formed, was collected and, without purification, added to a hot mixture of nitric acid (*d*, 1·42; 10 ml) and water (10 ml), heated at 80° for 5 min and poured into a large volume of ice-water. The precipitated diquinone crystallised from nitrobenzene in yellow needles, m.p. 304–306° (lit.[17] 304–309°); yield 1·1 g (64%).

The other diquinones were made by published methods.

Rearrangements

8-Hydroxy-3,7-dimethoxybenzofuran-1,4-dione (II; R = OMe). A solution of 4,4′-dimethoxydiphenyl-2,5:2′,5′-diquinone (1 g) in dry methanol (500 ml) contained in a silica tube (with internal cooling) was irradiated with a 500-watt mercury lamp for 6 hr. The red solution was evaporated under red. press. and the residue crystallised from ethanol in deep red needles, m.p. and mixed m.p. 248–249°; yield 0·9 g (90%). The yield obtained by the thermal process[1] was 48%. The two products had identical I.R. spectra showing strong bands at 3300, 1680 and 1630 cm^{-1}. The compound gave a blue solution in aqueous sodium hydroxide, sodium carbonate and ammonia. The acetate separated from ethanol in bright red needles, m.p. 255° (lit.[1] 252–254°). (Found: C, 60·4; H, 3·9; OAc, 18·6. Calc. for $C_{16}H_{12}O_7$: C, 60·7; H, 3·8; OAc, 18·7%). The *methyl ether* was obtained by shaking the hydroxyquinone (0·5 g) in acetone (100 ml) with methyl iodide (2 ml) and silver oxide (1 g). The same amounts of methyl iodide and silver oxide were added after 1 hr and shaking continued a further 4 hr. The product obtained on working up crystallised from ethanol in red needles, m.p. 284–285°, (Found: C, 62·6; H, 4·2; OMe; 31·7. $C_{15}H_{12}O_6$ requires: C, 62·3; H, 4·2; OMe, 32·4%).

8-Hydroxy-3,7-dimethyldibenzofuran-1,4-dione (II; R = Me). 4,4′-Dimethyldiphenyl-2,5:2′,5′-diquinone (0·5 g) in dry methanol (250 ml) was irradiated as before with a 125-watt mercury lamp for 5 hr, the solution changing from yellow to red. After removal of the solvent the residue separated from toluene in bright red needles, m.p. 235–236° not depressed on admixture with the product of thermal rearrangement (lit.[1] m.p. 218–220°). Infrared spectra of the two samples were identical. Yield 0·42 g (84%). The yield obtained by the thermal method was only 5% and the product was difficult to purify. (Found: C, 69·5; H, 4·1. Calc. for $C_{14}H_{10}O_4$ C, 69·4; H, 4·1%). In aqueous sodium hydroxide and sodium carbonate the compound gave a blue solution which became rapidly violet, and then brown after a few minutes. The *acetate* formed light yellow needles (from ethanol), m.p. 188–189° (dec), (Found: C, 67·6; H, 4·3. $C_{16}H_{12}O_5$ requires: C, 67·6; H, 4·2%).

8-Hydroxy-3,7-diphenyldibenzofuran-1,4-dione (II; R = Ph). 4,4′-Diphenyldiphenyl-2,5:2′,5′-diquinone (100 mg) was rearranged by heating in α-bromonaphthalene (3 ml) for 5 min at 260–270°. The *dibenzofuranquinone* separated on cooling and was collected and washed successively with methanol, water and ether. It crystallised from benzene in glistening red needles, m.p. 300–302°; ν_{max} 3350, 1670 and 1645 cm^{-1} (nujol), yield 54 mg. (Found: C, 78·6; H, 3·7. $C_{24}H_{14}O_4$ requires: C, 78·7; H, 3·8%). In warm methanolic sodium hydroxide it gave a green solution which rapidly turned brown.

4″-Hydroxydinaphtho-(2′,3′-2,3)(1″,2″-5,4)-furan-1′,4′-dione (IV). A solution of 2,2′-dinaphthyl-1,4:1′,4′-diquinone[2] (200 mg) in dry benzene (750 ml) containing *o*-dichlorobenzene (5 ml) was irradiated for 24 hr in a cooled silica tube using a 1 kw mercury lamp. The red residue, obtained after removal of the solvent under red. press., crystallised from nitrobenzene in dark red needles, m.p. 375°, undepressed by the product of thermal rearrangement (lit.[2,4] >360°, 360°). Yield 150 mg (75%) (47% by thermal rearrangement). Schulte-Frohlinde and Werner[4] found that the dinaphthyldiquinone was stable to monochromatic radiation at 365 mμ in benzene solution and rearrangement could only be effected in hydroxylic solvents. We confirm that rearrangement takes place in methanol. The product IV gives a green solution in methanolic sodium hydroxide and a blue colouration with conc sulphuric acid. The acetate had m.p. 282–283° (lit.[4] m.p. 280–281°) (from ethanol). The *methyl ether* was obtained by refluxing the hydroxyquinone (500 mg) in acetone (100 ml) with dimethyl sulphate (2 ml) and anhydrous potassium carbonate (5 g) for 4 hr. It crystallised from ethanol in yellow needles, m.p. 355°, (Found: C, 77·2; H, 3·6. $C_{21}H_{12}O_4$ requires: C, 76·8; H, 3·7%), and gave a blue colouration in conc sulphuric acid.

4″-Hydroxydianthra-(2′,3′-2,3)(1″,2″-5,4)-furan-1,′4′-dione (VI). 2,2′-Dianthranyl-1,4:1′,4″-diquinone[29] (200 mg) in α-bromonaphthalene (2 ml) was refluxed for 10 min, the yellow solution changing

[29] Y. Lepage, *Bull. Soc. Chim. France*, 991 (19).

to red. The product which separated on cooling, was washed with methanol, water and ether, and crystallised from nitrobenzene in red plates, m.p. >350°; ν_{max} 3350, 1675 and 1635 cm^{-1} (nujol), yield 20 mg (10%). A sample was heated *in vacuo* at 150° for 24 hr before analysis but could not be completely freed from nitrobenzene (cf. IV[2]). (Found: C, 77·3; H, 3·6. $C_{28}H_{14}O_4 \cdot \frac{2}{3}C_6H_5NO_2$ requires: C, 77·4; H, 3·5%). The compound gives a green solution in aqueous sodium hydroxide and a violet colouration with conc sulphuric acid.

Synthesis of 4″*-hydroxydinaphtho*-(2′,3′-2,3)(1″,2″-5,4)-*furan*-1′,4′-*dione* (IV)

2-*Chloroacetyl*-1,4-*dimethoxynaphthalene*. A solution of 1,4-dimethoxynaphthalene (7·5 g) and chloroacetyl chloride (5·6 g) in dry toluene (60 ml) was stirred at 0° with gradual addition of anhydrous aluminium chloride (8·5 g) When the initial vigorous reaction had subsided the mixture was refluxed for 3 hr, cooled, and poured on to ice and hydrochloric acid. After 15 min the yellow precipitate was collected. It crystallised from ethanol in lemon-yellow needles m.p. 151°; yield 6·4 g (60%). Extraction of the filtrate with toluene yielded a dark oil which solidified. It crystallised from light petroleum (b.p. 40–60°) in buff needles, m.p. 55°, not depressed on admixture with an authentic sample of 4-methyl-ω-chloroacetophenone. When the Friedel-Crafts reaction was carried out in tetrachloroethane solution the naphthalene derivative was obtained in only 20% yield, in benzene the yield was 35%, and in carbon disulphide following the method of Spruit[30] only 5% was obtained.

5-*Methoxy*-6,7-*benzocoumaran*-3-*one* (VII). The above ketone (5 g) was refluxed in ethanol (30 ml) with anhydrous sodium acetate (6·25 g) for 10–15 min. Cooling and dilution with water afforded a precipitate which crystallised from methanol in cream-coloured needles, m.p. 144–145° (lit.[28] m.p. 143°); yield 3·6 g (90%). The coumaranone gives an intense olive-green fluorescence in alcohol or benzene solution.

2-*Hydroxyimino*-5-*methoxy*-6,7-*benzocoumaran*-3-*one*. A solution of the above coumaranone (2·7 g) in glacial acetic acid (5 ml) was stirred in an ice-bath and treated, dropwise, with an ice-cold solution of sodium nitrite (3 g) in water (4 ml). After a few hr more sodium nitrite (3 g) in water (4 ml) was added and the mixture then left overnight. The precipitate which formed, crystallised from glacial acetic acid in fine orange needles, m.p. 220° (dec); yield 2 g (64%). (Found: C, 64·3; H, 3·9; N, 5·7. $C_{13}H_9NO_4$ requires: C, 64·2; H, 3·7; N, 5·7%).

1-*Hydroxy*-4-*methoxy*-2-*naphthylglyoxylic acid*. The above oxime (2 g) was heated at 80° for 3 hr with conc hydrochloric acid (15 ml). The yellow solution was then cooled and diluted with water to precipitate the acid, which crystallised from benzene in pale yellow rosettes, m.p. 233–234° (dec); yield 1·9 g (94%). (Found: C, 63·6; H, 4·2. $C_{13}H_{10}O_5$ requires: C, 63·4; H, 4·1%).

5-*Methoxy*-6,7-*benzocoumaran*-2,3-*dione* (VIII). Cyclization of 1-hydroxy-4-methoxy-2-naphthylglyoxylic acid using Chatterjea's method[31] (i.e. heating for a short time with acetic anhydride) gave only the *acetate* which crystallised from benzene in yellow needles, m.p. 225°, (Found: C, 62·5; H, 4·0. $C_{15}H_{12}O_6$ requires: C, 62·5; H, 4·2%). The desired compound (VIII) was obtained by heating the glyoxylic acid (1·5 g) with phosphorus pentoxide (12·5 g) in boiling benzene (50 ml) for 4 hr. The tarry mixture was cooled and poured into ice-water, and the whole extracted with ether, which was washed with aqueous sodium carbonate, and dried (Na_2SO_4). After removal of the solvent the residual *ketolactone* crystallised from ethanol in pale yellow needles, m.p. 148°, yield 1·2 g (85%). (Found: C, 68·5; H, 3·8. $C_{13}H_8O_4$ requires: C, 68·4; H, 3·5%).

2-*Benzoyl*-4′-*methoxynaphtho*-(1′,2′-4,5)*furan*-3-*carboxylic acid* (IX; R = H). (a) ω-Bromoacetophenone (1 g) was added to a stirred solution of the ketolactone (VIII; 1.14 g) and sodium ethoxide (from 165 mg sodium) in cold ethanol (10 ml). After boiling under reflux for 1 hr the solution was filtered and concentrated to small volume. The ester which separated was hydrolysed, without purification, by boiling with 10% methanolic sodium hydroxide (20 ml) for 1 hr. The alcohol was distilled off under red. press. and the alkaline solution acidified and extracted with ether. The residue obtained after evaporation of the dried extract crystallised from nitrobenzene in pale yellow needles, m.p. 153–155°, yield 0·73 g (41%). (Found: C, 73·1; H, 3·4. $C_{21}H_{14}O_5$ requires: C, 72·8; H, 4·0%).

4″-*Methoxydinaphtho*-(2′,3′-2,3)(1″,2″-5,4)-*furan*-1′,4′-*dione* (X). The above acid (500 mg) was stirred overnight with thionyl chloride (7 ml) at room temp. After removal of excess reagent the crude acid chloride was dissolved in nitrobenzene (10 ml) and anhydrous aluminium chloride (2 g) added gradually, at 10°. After stirring for 20 hr at room temp the mixture was poured into ice and

[30] C. J. P. Spruit, *Rec. Trav. Chim.* **67**, 285 (1948).

[31] J. N. Chatterjea, *J. Indian. Chem. Soc.* **31**, 194 (1954).

hydrochloric acid, and the solvent removed in steam. The product was collected on cooling and stirred with 5% aqueous sodium hydroxide (5 ml) to remove starting material (100 mg). The *quinone* crystallised from ethanol (charcoal) in yellow needles, m.p. 354–355°; yield 210 mg (42%). (Found: C, 76·8; H, 3·7. $C_{21}H_{12}O_4$ requires: 76·8; H, 3·7%).

(b) 2,3-Dichloro-1,4-naphthaquinone (1·3 g) and 4-methoxy-1-naphthol (1 g) were refluxed in pyridine (10 ml) for 18 hr, and then left overnight at 0°. The orange crystalline product was collected, washed successively with water, alcohol and ether, and recrystallised from nitrobenzene forming yellow needles, m.p. 355°; yield 0·87 g (47%). The compound was identified with that obtained in (a) and with the methyl ether of the rearrangement product (IV) by mixed m.p. determination and comparison of I.R. spectra.

4″-Hydroxydinaphtho-(2′,3′-2,3)(1″,2″-5,4)-furan-1′,4′-dione (IV). The preceding methyl ether (150 mg) was refluxed in pyridine hydrochloride (5 g) for 30 min, cooled and diluted with water. The red gelatinous precipitate separated from nitrobenzene in dark red needles, m.p. 375°, not depressed on admixture with the product obtained by rearrangement of 2,2′-dinaphthyl-1,4-1′,4′-diquinone. The two samples had identical I.R. spectra and colour reactions.

Naphthols

6-Methoxy-1-naphthol. 6-Methoxy-1-tetralone (500 mg) was heated with sulphur (90 mg) at 240–250° until evolution of hydrogen sulphide had ceased. The mixture was then distilled at 170–172° (bath)/10 mm. giving a colourless oil which solidified on storage at −5°. It crystallised from light petroleum (b.p. 60–80°) in plates, m.p. 84·5–85° (lit.[32,33] 79–80°, 85°); yield 110 mg (22%).

7-Methoxy-1-naphthol. This was obtained from 7-methoxy-1-tetralone in the same way. It distilled from the reaction mixture at 145–148° (bath)/0·01 mm giving a solid which crystallised from 50% aqueous ethanol in needles, m.p. 103–105 (lit.[32,34] m.p. 104·5–105°, 122–124°); yield 27%.

8-Methoxy-2-naphthol. (a) 7-Nitro-1-tetralone (0·96 g) was refluxed with N-bromosuccinimide (0·9) g in carbon tetrachloride (30 ml) containing a trace of benzoyl peroxide for 2 hr. More solvent (30 ml) was then added, the succinimide was filtered off and the solvent evaporated *in vacuo*. The residual light brown oil was dissolved in glacial acetic acid (10 ml) containing anhydrous sodium acetate, refluxed for 30 min and then diluted with water. The precipated *7-nitro-1-naphthol* crystallised from aqueous ethanol in fine orange needles, m.p. 209°; yield 0·7 g (73%). (Found: C, 63·3; H, 3·9. $C_{10}H_7NO_3$ requires: C, 63·45; H, 3·75%). It gave an orange-red solution in aqueous sodium hydroxide and a *methyl ether* (dimethyl sulphate–potassium carbonate–acetone) which separated from aqueous alcohol in yellow needles, m.p. 110°. (Found: C, 64·8; H, 4·5; N, 6·9. $C_{11}H_9NO_3$ requires: C, 65·0; H, 4·45; N, 6·8%). A suspension of 7-nitro-1-methoxynaphthalene (1·86 g) in ethyl acetate (60 ml) was hydrogenated over Adams' catalyst (0·1 g) until 3 moles of hydrogen were absorbed. After removal of catalyst and solvent the residual oily amine was dissolved in a mixture of water (16·5 ml) and conc sulphuric acid (1·25 ml) and warmed on a water-bath for 5–10 min. The suspension was cooled to 0°, sodium nitrite (0·7 g) in water (4·4 ml) added together with crushed ice (10 g), and the whole shaken vigorously for 10 min and then filtered. The orange filtrate was then added to a boiling solution of copper sulphate (2·75 g) in water (70 ml). The resulting dark red tarry solution was cooled in ice, extracted with ether and the extract shaken with 2 N NaOH. The alkaline solution was acidified and the product taken into ether, dried and evaporated. The residual violet oil distilled at 195–204° (bath)/0·3 mm as a pale yellow liquid which solidified in the refrigerator. Crystallisation from n-hexane gave *8-methoxy-2-naphthol* as plates, m.p. 71°; yield 0·65 g (40%). (Found: C, 75·8; H, 5·9. $C_{11}H_{10}O_2$ requires: C, 75·85; H, 5·8%). The *benzoate* had m.p. 92° (from aqueous ethanol). (Found: C, 77·8; H, 5·3. $C_{17}H_{14}O_3$ requires: C, 77·7; H, 5·1%). Acetylation of the crude amine (above) gave *7-acetamido-1-methoxynaphthalene*, m.p. 152° (from light petroleum b.p. 100–120°). (Found: C, 72·6; H, 6·2; N, 6·6. $C_{13}H_{13}O_2N$ requires: C, 72·55; H, 6·1; N, 6·5%).

(b) To a suspension of 1,7-dihydroxynaphthalene (3·2 g) and dimethyl sulphate (2·25 ml) in water (20 ml) at 5°, potassium hydroxide (1·2 g) was added in small portions with vigorous shaking. After 5 min more alkali (1 g) was added and the mixture was extracted with ether to remove any

[32] A. P. Lurie, G. H. Brown, J. R. Thistle and A. Weissberger, *J. Amer. Chem. Soc.* **83**, 5015 (1961).
[33] R. J. W. Byrde, D. F. Downing and D. Woodcock, *Biochem. J.* **72**, 344 (1959).
[34] A. Angeletti, *Gazz Chim. Ital.* **59**, 851 (1929).

dimethoxynaphthalene. The alkaline solution was then acidified with dil. hydrochloric acid and heated at 50° for 30 min. On cooling, the oil which separated was taken up in ether and dried (Na_2SO_4). Distillation at 134–137° (bath)/0·01 mm afforded a pale yellow viscous oil, which gradually solidified (0·6 g). Fractional crystallisation from light petroleum (b.p. 50–60°) yielded 8-methoxy-2-naphthol as needles, m.p. 68–69°, undepressed on admixture with the product obtained in (a).

Formation of brazanquinones from 2,3-*dichloro*-1,4-*naphthaquinone*

The general procedure followed that described above for X.

8″-*Hydroxydinaphtho*-(2′,3′-2,3)(1″,2″-5,4)-*furan*-1′,4′-*dione*. Obtained from 1,8-dihydroxynaphthalene; reaction time 7 hr. The product, after washing with methanol and ether, was extracted with boiling water to remove the betaine[35,36] and crystallised from nitrobenzene in blood-red needles, m.p. 290°; (57%). (Found: C, 76·4; H, 3·3. $C_{20}H_{10}O_4$ requires: C, 76·4; H, 3·2%). It gave a deep blue solution in methanolic sodium hydroxide and a blue solution in conc hydrochloric acid. The *acetate* formed golden yellow needles, m.p. 281° (from ethanol). (Found: C, 74·0; H, 3·5. $C_{22}H_{12}O_6$ requires: C, 74·2; H, 3·4%).

7″-*Hydroxydinaphtho*-(2′,3′-2,3)(1″,2″-5,4)-*furan*-1′,4′-*dione* was obtained from 1,7-dihydroxynaphthalene.[11] It gave a brown solution in methanolic sodium hydroxide and a blue solution in conc sulphuric acid. The *acetate* formed golden-yellow needles, m.p. 292–293° (dec) (from ethanol), (Found: C, 74·5; H, 3·2. $C_{22}H_{12}O_5$ requires: C, 74·2; H, 3·4%); λ_{max} 261 and 420 mμ (log ε 4·48 and 3·40), cf. dinaphtho-(2′,3′:2,3)(1″,2″:5,4)-furan-1′,4′-dione λ_{max} 257 and 422 mμ (log ε 4·14 and 3·52). The *methyl ether* (dimethyl sulphate–potassium carbonate–acetone) crystallised from ethanol in lemon-yellow needles, m.p. 257–258° (lit.[11] m.p. 255°). The identical compound (mixed m.p., I.R. spectra) was obtained by condensing 2,3-dichloro-1,4-naphthaquinone with 7-methoxy-1-naphthol; reaction time 4 hr. Demethylation of this product with pyridine hydrochloride gave the hydroxyquinone, m.p. and mixed m.p. 301–302°.

6″-*Hydroxydinaphtho*-(2′,3′-2,3)(1″,2″-5,4)-*furan*-1′4′-*dione*. Prepared from 1,6-dihydroxynaphthalene; blood-red needles (from nitrobenzene), m.p. 325–326° (lit.[7] 303–304°). It gave a blue solution in methanolic sodium hydroxide and in conc sulphuric acid. The *acetate* crystallised from glacial acetic acid in golden-yellow needles, m.p. 258°. (Found: C, 73·7; H, 3·3. $C_{22}H_{12}O_5$ requires: C, 73·9; H, 3·4%). The *methyl ether* separated from the same solvent as orange-red needles, m.p. 259–260°. (Found: C, 76·8; H, 3·7. $C_{22}H_{12}O_4$ requires: C, 76·8; H, 3·7%). The same compound (identified by mixed m.p. and I.R. spectra) was obtained by condensing 6-methoxy-1-naphthol with 2,3-dichloro-1,4-naphthaquinone; reaction time 3 hr.

5″-*Hydroxydinaphtho*-(2′,3′-2,3)(1″,2″-5,4)-*furan*-1′,4′-*dione*[9] forms an *acetate*, yellow needles, m.p. 285° (from glacial acetic acid). (Found: C, 74·0; H, 3·5. $C_{22}H_{12}O_5$ requires: C, 74·2; H, 3·4%). Methylation with dimethyl sulphate in the usual way gave the methyl ether, m.p. 305° identical with the product obtained by condensing 2,3-dichloro-1,4-naphthaquinone with 5-methoxy-1-naphthol.[9]

8″-*Hydroxydinaphtho*-(2′,3′-2,3)(1″,2″-4,5)-*furan*-1′,4′-dione. Condensation of 8-methoxy-2-naphthol with the dichloronaphthaquinone in the usual way (4 hr reflux) gave a red-black product which was dissolved in hot nitrobenzene. The material (m.p. >360°) which separated on cooling was filtered off, and the filtrate diluted with methanol and left overnight at 0°. The crystalline precipitate was collected, extracted with boiling water, and recrystallised from ethanol in red needles, m.p. 298–299°. (Found: C, 76·9; H, 3·8. $C_{22}H_{12}O_4$ requires: C, 76·8; H, 3·7%). The *methoxyquinone* gave a deep blue colouration with conc sulphuric acid. Demethylation was effected by heating with pyridine hydrochloride at 150–160° for 45 min. The 8″-*hydroxydinaphthofurandione* crystallised from nitrobenzene in red plates, m.p. 355–357°. (Found: C, 76·4; H, 3·3. $C_{20}H_{10}O_4$ requires: C, 76·4; H, 3·2%). The quinone gave a violet solution in aqueous sodium hydroxide and a blue colouration with conc sulphuric acid.

5″-*Hydroxydinaphtho*-(2′,3′-2,3)(1″,2″-4,5)-*furan*-1′,4′-*dione*. This was obtained from 5-methoxy-2-naphthol which gave the methyl ether, m.p. 270–271° (lit.[7] 261–262°), followed by demethylation with pyridine hydrochloride. It forms blood-red needles (from benzene), m.p. 304–306° (lit.[7] 303–304°) and is *not* the same as the product[7] (m.p. 325–326°) obtained by condensing 2,3-dichloro-1,4-naphthaquinone with 1,6-dihydroxynaphthalene. It gave a blue solution in aqueous sodium hydroxide and a violet colouration in concentrated sulphuric acid.

[35] F. Ullmann and M. Ettisch, *Ber. Dtsch. Chem. Ges.* **54**, 259 (1921).
[36] B. Eistert, *Ber. Dtsch. Chem. Ges.* **80**, 47 (1947).

4″-Hydroxydinaphtho-(2′,3′-2,3)(1″,2″-4,5)-furan-1′,4′-dione. 2,3-Dichloro-1,4-naphthaquinone (22·7 mg) and 1,3-dihydroxynaphthalene (160 mg) were added to a solution of sodium ethoxide (from 500 mg sodium) in ethanol (20 ml) at 5°. The mixture was refluxed for 4 hr the colour changing from yellow to deep red and finally to green. The solution was concentrated to 5 ml and acidified with dil. hydrochloric acid. The resulting precipitate was crystallised from nitrobenzene in red needles, m.p. 322–324°; yield 140 mg (45%). (Found: C, 76·4; H, 3·3. $C_{20}H_{10}O_4$ requires: C, 76·4; H, 3·2%). The quinone gave a blue solution in aqueous sodium hydroxide and a violet colouration with conc sulphuric acid. The structure is deduced from the absorption spectrum of the acetate and has not been rigorously established. The reaction failed when pyridine was used in place of sodium ethoxide–ethanol. The hydroxyquinone formed an *acetate*, yellow needles from benzene, m.p. 277–278° (dec) (Found: C, 74·4; H, 3·2. $C_{22}H_{12}O_5$ requires C, 74·2; H, 3·4%); λ_{max} 282 and 435 mμ (log ε 4·16 and 3·58), cf. dinaphtho-(2′,3′-2,3)(1″,2″-4,5)-*furan*-1′,4′-dione λ_{max} 285 and 440 mμ (log ε 4·15 and 3·53) and dinaphtho-(2′,3′-2,3)(1″,2″-5,4)-furan-1′,4′-dione λ_{max} 257 and 422 mμ (log ε 4·14 and 3.52).

5″-Hydroxybenzo-(1″,2″-5,4)naphtho-(2′,3′-2,3)furan-1,4-dione (XXV)

Preparation of this compound in pyridine[36] gave only red amorphous material showing no hydroxyl absorption in its I.R. spectrum. The following procedure was satisfactory: 2,3-dichloro-1,4-naphthaquinone (2·27 g) and resorcinol (1·1 g) were added to a solution of sodium ethoxide (from 0·23 g sodium) in dry ethanol (30 ml) at 5° and the solution refluxed for 3 hr, the colour changing from yellow to red to blue. The product was isolated by concentration to 5 ml, acidification with dil. hydrochloric acid and crystallisation of the precipitate from benzene. It formed red plates m.p. 310° (lit.[37] m.p. 305°) and gave an acetate, m.p. 290–291° (lit.[37] m.p. 289°).

Reactions of 8-hydroxy-3,7-dimethoxydibenzofuran-1,4-dione (II) *in alkaline solution*

(a) The deep blue solution of II (500 mg) in 2 N NaOH (20 ml) was left for 20 min and then acidified with dil. hydrochloric acid. The dark red colloidal precipitate which separated was well washed, dried, and crystallised from nitrobenzene in red plates, m.p. 248° alone and mixed with starting material. The acetate had m.p. and mixed m.p. 255°. The same result was obtained when the experiment was repeated under nitrogen.

(b) A solution of II (500 mg) in methanol (10 ml) and 2 N NaOH (10 ml) was hydrogenated over Raney nickel until 1 mole was absorbed (ca. 4 hr). All subsequent operations were conducted in an atmosphere of nitrogen. After removal of the catalyst, the pale yellow solution was acidified to pH 5 and transferred to a desiccator containing potassium hydroxide pellets and conc sulphuric acid. The desiccator was slowly evacuated and set aside until evaporation was complete (2–3 days). The residue (250 mg) was then stirred with acetic anhydride (1 ml) containing conc sulphuric acid (0·1 ml) until dissolution was complete, left overnight, and poured into ice-water. The resulting pale yellow oil gradually solidified. Crystallisation from glacial acetic acid (charcoal) afforded colourless needles, m.p. 196–197° (85 mg), not depressed on admixture with an authentic specimen of 2,3,6,3′,6′-pentaacetoxy-4,4′-dimethoxydiphenyl.[27] I.R. spectra were identical.

2-(p-*Methoxyphenyl*)-5,8-*dihydro*-1,4-*naphthaquinone*

A solution of *p*-methoxyphenyl-1,4-benzoquinone[38] (2·14 g) and butadiene (1·2 g) in glacial acetic acid (30 ml) was sealed and left at room temp for 48 hr. Excess butadiene was removed by gentle warming, more acetic acid (20 ml) was added, and the mixture was refluxed for 2 hr. After cooling to 60°, a solution of sodium nitrite (4 g) in water (10 ml) was added dropwise, with swirling, followed by dilution with water. The resulting orange precipitate crystallised from ethanol in golden yellow needles, m.p. 129–130°; yield 2·5 g (94%). (Found: C, 76·4; H, 5·3. $C_{17}H_{14}O_3$ requires: C, 76·7; H, 5·3%).

2-(p-*Methoxyphenyl*)-1,4-*naphthaquinone*

(a) The above dihydronaphthaquinone (2 g) in glacial acetic acid (20 ml) was heated to 50° and treated with a hot (65°) solution of sodium dichromate (2·5 g) in water (5 ml) containing conc sulphuric

[37] C. Liebermann, *Ber. Dtsch. Chem. Ges.* **32**, 924 (1899).
[38] P. Bassard and P. l'Ecuyer, *Canad. J. Chem.* **36**, 700 (1958).

acid (0·2 ml). The mixture was stirred at 55–60° for 15 min, poured into ice water and the precipitated *quinone* crystallised from ethanol in orange needles, m.p. 123–124°; yield 1·7 g (86%) (lit.[39] m.p. 122–123°).

(b) A solution of 2-chloro-1,4-naphthaquinone (0·72 g) and sodium acetate trihydrate (1·14 g) in glacial acetic acid (15 ml) was cooled to 5° and treated with an ice-cold solution of diazotised *p*-anisidine (from 0·46 g amine). Nitrogen was evolved immediately and a yellow precipitate separated. After stirring for 30 min the crude chloro-anisylquinone (0·5 g, m.p. 139°) was collected and boiled under reflux for 30 min with a mixture of conc hydrochloric acid (5 ml), acetic acid (5 ml) and stannous chloride (2 g),[40] cooled and treated with a solution of chromium trioxide (2 g) in water (10 ml). After cooling in ice, the precipitated methoxyphenylnaphthaquinone was collected and crystallised from ethanol. It formed orange needles, m.p. 123–124°, identical with the product obtained in (a) yield 0·23 g.

2-(p-*Hydroxyphenyl*)-1,4-*naphthaquinone*

2-(*p*-Methoxyphenyl)-1,4-naphthaquinone (1 g) in glacial acetic acid (5 ml) was boiled under reflux for 15 min with hydrobromic acid (5 ml, 48% w/w), and then poured into ice-water. The brown precipitate obtained was extracted (Soxhlet) with light petroleum (b.p. 60–80°) giving, after removal of the solvent, a yellow residue which crystallised from methanol in yellow micro needles, m.p. 76°; ν_{max} 3490 and 1654 cm^{-1}, yield 0·45 g (47%). (Found: C, 76·8; H, 3·7. $C_{16}H_{10}O_3$ requires; C, 76·8; H, 4·0%). The quinone gave a blue solution in dil. sodium hydroxide, sodium carbonate and ammonia solutions and a violet colouration in conc sulphuric acid. After exposure to air for several hours it turned brown and could not be recrystallised. Methylation of the hydroxyphenylquinone with methyl iodide and silver oxide in acetone gave the original 2-(*p*-methoxyphenyl)-1,4-naphthaquinone.

2-(o-*Methoxyphenyl*)-5,8-*dihydro*-1,4-*naphthaquinone*

This was obtained from *o*-methoxyphenyl-1,4-benzoquinone[38] by the method used for the *p*-isomer. The *dihydronaphthaquinone* crystallised from methanol in fine orange-red needles, m.p. 104–105°; yield 84%. (Found: C, 76·4; H, 5·3. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%).

2-(o-*Methoxyphenyl*)-1,4-*naphthaquinone*

This was obtained by oxidation of the dihydro derivative (above) and from 2-chloro-1,4-naphthaquinone as for the *p*-isomer; orange needles from ethanol, m.p. 99–100° (dec). (Found: C, 77·5; H, 4·8. $C_{17}H_{12}O_3$ requires: C, 77·3; H, 4·5%).

2-(o-*Hydroxyphenyl*)-1,4-*naphthaquinone* was derived from the methoxyphenyl compound by treatment with hydrogen bromide as before. The initial red precipitate, obtained on dilution of the reaction mixture crystallised from aqueous methanol in orange needles, m.p. 77–78° (dec); yield 56%. The quinone decomposed in air after 2–3 hr and satisfactory analyses could not be obtained. It showed absorption peaks at 3410 and 1649 cm^{-1}, gave blue solutions (which turned yellow in 15–20 min) in aqueous sodium hydroxide and sodium carbonate, and yielded the original 2-(*o*-methoxyphenyl)-1,4-naphthaquinone on methylation with methyl iodide–silver oxide–acetone.

m-*Methoxyphenyl*-1,4-*benzoquinone*

m-Anisidine (2 g) was diazotized in the usual way and added, with stirring, to a suspension of benzoquinone (2·5 g) in water (300 ml) containing sodium acetate trihydrate (6 g). Nitrogen was evolved immediately and stirring was continued until the evolution ceased (4 hr). The crude product was collected and extracted (Soxhlet) with light petroleum (b.p. 80–90°). Evaporation of the solvent left an oil, which solidified. It crystallised from methanol in yellow needles, m.p. 112°; yield 2·48 g, (50%). (Found C, 72·8; H, 4·6. $C_{13}H_{10}O_3$ requires; C, 72·9; H, 4·7%).

2-(m-*Methoxyphenyl*)-1,4-*naphthaquinone*

(a) Diels-Alder addition of butadiene and *m*-methoxyphenylbenzoquinone was effected as before. The cooled reaction mixture was added, with stirring, to a solution of sodium dichromate (4 g) and conc sulphuric acid (2 ml) in water (20 ml). A dark brown oil separated which solidified on scratching.

[39] A. N. Grinev, A. P. Klyagina and A. P. Terent'ev, *Zhur. Obshchei Khim.* **29**, 2773 (1959).
[40] D. B. Bruce and R. H. Thomson, *J. Chem. Soc.* 1428 (1954).

It was extracted (Soxhlet) with light petroleum (b.p. 60–80°) from which it crystallised in yellow prisms, m.p. 98–99° (dec); yield 1·8 g, (73%). (Found: C, 77·5; H, 4·6. $C_{17}H_{12}O_3$ requires: C, 77·3; H 4·5%).

(b) From 2-chloro-1,4-naphthaquinone and diazotised *m*-anisidine as for the other isomers, followed by dechlorination and re-oxidation; yield 19%.

2-(m-*Hydroxyphenyl*)-1,4-*naphthaquinone*

2-(*m*-Methoxyphenyl)-1,4-naphthaquinone (0·5 g), stannous chloride (2 g), conc hydrochloric acid (5 ml) and glacial acetic acid (5 ml) were refluxed for 30 min, cooled, diluted with water (10 ml) and extracted with ether. The extract was washed with aqueous sodium bicarbonate, dried (Na_2SO_4) and evaporated. The residual quinol (0·4 g) was dissolved in dry benzene (50 ml) and a solution of boron tribromide (0·1 ml) in benzene (10 ml) added dropwise. The dark red solution was boiled under reflux for 1 hr, cooled, and treated with water (2 ml). When the vigorous reaction had ceased the mixture was poured into cold water (50 ml) and thoroughly extracted with ether. The extract was shaken with N NaOH (3 × 50 ml) and the aqueous phase acidified with conc hydrochloric acid. The pale yellow precipitate (0·32 g) was dried and added to a suspension of chloranil (0·31 g) in benzene (30 ml) and refluxed for 4 hr. The orange solution was cooled, filtered, taken to dryness under red. press., and the residual *quinone* crystallised from ethanol in yellow needles, m.p. 92–93°, ν_{max} 3400, 1670 and 1650 cm^{-1}; yield 0·2 g (42%). (Found: C, 76·8; H, 3·7. $C_{16}H_{10}O_3$ requires: C, 76·8; H, 4·0%). The compound gave a red solution in aqueous sodium hydroxide and sodium carbonate, and formed 2-(*m*-methoxyphenyl)-1,4-naphthaquinone when treated with methyl iodide–silver oxide–acetone. Direct demethylation of the latter using boron tribromide, hydrogen bromide and hydrogen iodide was unsuccessful.

1,2,4-*Trihydroxy*-3-(p-*methoxyphenyl*)*naphthalene*

2-Hydroxy-3-(*p*-methoxyphenyl)-1,4-naphthaquinone[41] (1 g) was reduced by heating under reflux with stannous chloride (5 g), conc hydrochloric acid (10 ml) and water (90 ml), for 30 min. The hot solution was treated with charcoal, filtered, and cooled rapidly in ice. The precipitated *quinol* separated from ethanol in plates, m.p. 124°; yield 0·7 g, (70%). (Found: C, 71·9; H, 4·8. $C_{17}H_{14}O_4$ requires: C, 72·3; H, 4·9%).

2-*Hydroxy*-3-(p-*hydroxyphenyl*)-1,4-*naphthaquinone*

The above quinol (0·5 g) in benzene (30 ml) was treated at 5° with a solution of boron tribromide (0·3 ml) in the same solvent (10 ml). The mixture was refluxed for 3 hr, cooled, diluted with water (50 ml), and extracted with ether. The extract was shaken with 2 N NaOH (2 × 25 ml), and the aqueous phase acidified, re-extracted with ether, and dried (Na_2SO_4). Evaporation afforded a cream-coloured residue (0·25 g) which was taken up in benzene (50 ml) to which chloranil (0·23 g) was added. The mixture was refluxed for 1½ hr, cooled, filtered, and taken to dryness. The residue crystallised from benzene–light petroleum (b.p. 60–80°) (2:1) in yellow micro needles, m.p. 149–150°; yield 0·2 g (42%). (Found: C, 71·2; H, 3·8. $C_{16}H_{10}O_4$ requires: C, 72·2; H, 3·8%). A satisfactory carbon analysis could not be obtained. In aqueous sodium hydroxide and sodium carbonate the compound gave an immediate red solution which rapidly turned violet.

2-*Hydroxy*-3-(o-*methoxyphenyl*)-1,4-*naphthaquinone*

To a vigorously stirred solution of 2-hydroxy-1,4-naphthaquinone (2 g) in 5% aqueous potassium hydroxide (100 ml) at 45–50° an ice-cold solution of diazotised *o*-anisidine (1·6 g) was added during 15 min. The mixture was stirred a further 15–20 min at this temperature, carefully acidified to pH 6 with dil. acetic acid and the red precipitate (hydroxyazoquinone) removed. The filtrate was further acidified with dil. hydrochloric acid and extracted with ether. The extract was dried and evaporated leaving a gum which gradually solidified. It crystallised from ethanol in red needles, m.p. 147–148°; yield 2·7 g (84%). (Found: C, 72·8; H, 4·0. $C_{17}H_{12}O_4$ requires: C, 72·8; H, 4·2%).

Benzo-(1″,2″-5,4)-*naphtho*-(2′,3′-2,3)*furan*-1′,4′-*dione*

A mixture of 2-hydroxy-3-(*o*-methoxyphenyl)-1,4-naphthaquinone (2 g), hydrobromic acid (10 ml) and glacial acetic acid (10 ml) was boiled under reflux for 2 hr, cooled and poured into water (50 ml).

[41] O. Neunhoeffer and J. Weise, *Ber. Dtsch. Chem. Ges.* **71**, 2703 (1938).

The brown precipitate obtained was sublimed *in vacuo* and then crystallised from ethanol in pale yellow needles, m.p. 243°; yield 0·14 g (8%). It did not depress the m.p. of an authentic sample of XXXI.[4]

Titrations. The hydroxyquinones (in ethanol) were titrated at the appropriate wavelength with 0·1 N NaOH, using a micrometer syringe burette, in a titration cell fitted to a Unicam S.P. 500 spectrometer.

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