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BIQUINONES—III*

THE DIMERISATION OF 1,4-NAPHTHAQUINONES

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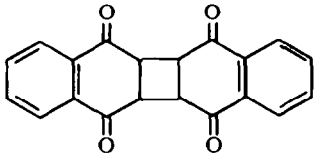
Abstract—2-Methyl-1,4-naphthaquinones, substituted at C-3 by alkyl, aralkyl, allyl, aryl or halogen groups, react in aqueous ethanolic NaOH to give dehydro-dimers, namely 1,2-bis(1,4-naphthaquinon-2-yl)ethanes. The reaction is analogous to the formation of bibenzyls from nitrotoluenes in basic media. In tBuOH containing tBuOK, 3-benzyl-2-methyl-1,4-naphthaquinone also undergoes oxidation at the benzyl carbon atom to give phthiocol and benzaldehyde, as well as dimer; allyl groups are cleaved similarly. A mechanism is proposed which also accounts for the final stage in the Dam–Karrer colour test for vitamin K.

2-Hydroxy-1,4-naphthaquinones are oxidised by persulphate to 2,2′-dihydroxy-3,3′-bi-1,4-naphthaquinonyls.

NAPHTHAQUINONES are known to dimerize in various ways according to the conditions and the structure of the monomer, but the information is scattered and there has been little systematic study of such reactions. For example 1,4-naphthaquinone forms the dimer I on irradiation[1] and II by warming in CH_3COOH containing pyridine.[2] On the other hand 2,3-dimethyl-1,4-naphthaquinone is converted into III[3] and 3-hydroxy-1,2-naphthaquinone into IV[4] in basic solution. Recent discoveries of naturally occurring binaphthaquinones[5] have encouraged further investigation of such reactions and we report here two methods for the oxidative dimerisation of 1,4-naphthaquinones which give simple dehydro-dimers.



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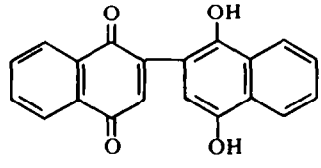

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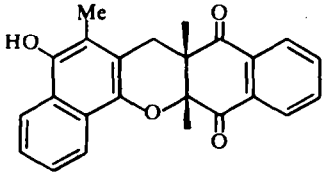

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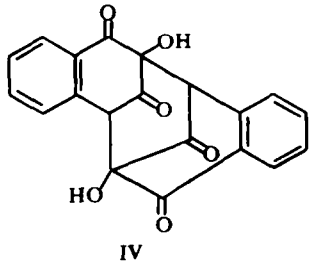

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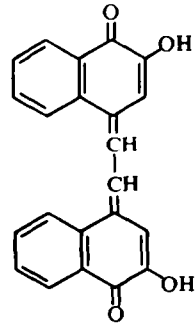
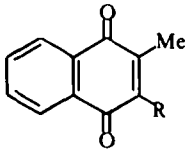


V

* Diquinones II, A. J. Shand and R. H. Thomson, *Tetrahedron* **19**, 1919 (1963).

Dimerisation of 2-methyl-1,4-naphthaquinones

Compounds of this type possess a reactive CH_3 group and tend to dimerise under alkaline conditions. This is illustrated by the conversion of 4-methyl-1,2-naphthaquinone into V[6] merely by keeping in EtOH containing $KHCO_3$ although the first observation was made by the Bergmanns[7] who treated 2,3-dimethyl-1,4-naphthaquinone with benzhydryl sodium and obtained *inter alia* two dimers, the binaphthaquinone VII (R = Me) and the compound later shown to be III.[3] We have confirmed the formation of VII (R = Me) but it is more conveniently obtained by using excess NaOMe in MeOH-EtOEt whereas III is best prepared by adding a few drops of methanolic KOH to the parent quinone in MeOH. Homologues of 2,3-dimethyl-1,4-naphthaquinone showed no tendency to form dimers of type III and all the other 2-methyl-1,4-naphthaquinones we examined gave only simple binaphthaquinones VII.



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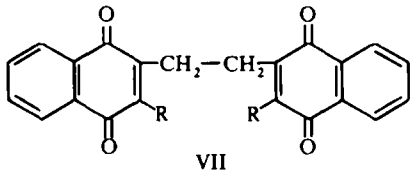

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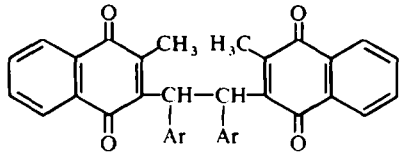


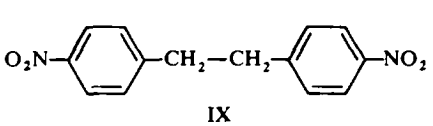
VIII

Treatment of the 2-methyl-1,4-naphthaquinones VI (R = alkyl, aryl, aralkyl, dimethylallyl, halogen, chloromethyl and methoxymethyl) with *aq* NaOH in cold EtOH gave the dimers VII, usually in 50–60% yield. Other reaction products were not usually pursued but in some cases (e.g. VI; R = $CHMe_2$) phthiocol (VI; R = OH) could be detected by TLC (see below). A series of colour changes was normally observed and in most cases the reaction was complete in *ca.* 15 min. by which time the rather insoluble dimer had separated from the solution. Certain dimers (VII; R = Et, CH_2Ph, $CHPh_2$ and Cl) are already known, being made previously either by reaction of the appropriate chloromethylquinone with Ag powder[8] or by base-catalysed decomposition of an 2-alkyl(or aralkyl)-1,4-naphthaquinone–doazomethane adduct.[9,10] The dibenzyl analogue VII (R = CH_2Ph) has now been synthesised from 3-benzyl-2-chloromethyl-1,4-naphthaquinone and its isomer (VIII; Ar = Ph) likewise from 3-α-chlorobenzyl-2-methyl-1,4-naphthaquinone, by reaction with Ag. The biquinone VII (R = Cl) was also obtained by chlorination of VII (R = H) which was prepared by oxidation of 1,2-di-β-naphthylethane with chromic acid. The structures of other new dimers were established by analysis and MW determinations, and spectroscopic comparison with their monomers.

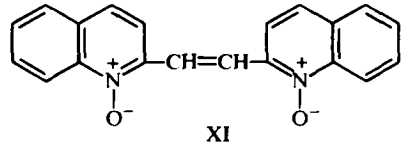
In halogenoquinones nucleophilic replacement of halogen is normally a facile process and we were surprised to find, in earlier work,[11] that the reaction of 3-chloro-2-methyl-1,4-naphthaquinone VI (R = Cl) with NaOMe (1 mol) in MeOH gave a product still containing chlorine; the use of 2 mol of base, however, gave a chlorine-

free compound. Analysis and spectroscopic data now show that the first compound is the biquinone VII (R = Cl) and the second is the dimethoxy analogue VII (R = OMe) which must arise by nucleophilic replacement of chlorine *after* oxidative dimerisation as we were unable to convert VI (R = OMe) into VII (R = OMe). In weakly basic solution there was no significant reaction whereas in strong base hydrolysis occurred to form phthiocol VI (R = OH). Similarly VI (R = Cl), with NaOEt in EtOH, gave VII (R = Cl and OEt), and the compounds VII (R = Br, OMe and OEt) were obtained in the same manner from VI (R = Br). Hydrolysis of VII (R = OMe and OEt) gave "biphthiocol" VII (R = OH) and this too was obtained by oxidative dimerisation of VI (R = Cl) in aqueous ethanolic NaOH. It was of interest to see how the chloromethyl derivative (VI; R = CH_2Cl) would behave under similar conditions. In fact, with NaOMe normal nucleophilic displacement afforded the methoxymethyl analogue VI (R = CH_2OMe) and with excess base this gave the dimer VII (R = CH_2OMe).

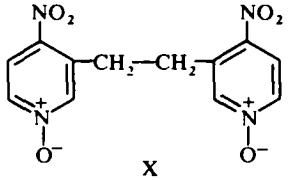
Although these dimerisations are new, analogous reactions are known in which oxidative coupling takes place at an activated CH_3 or methylene group in a basic medium. Examples are the formation of IX[12] and X[13] from *p*-nitrotoluene and 3-methyl-4-nitropyridine-1-oxide, respectively, and, under more vigorous conditions conversion of 2-methylquinoline-1-oxide and 2-methylanthraquinone into the



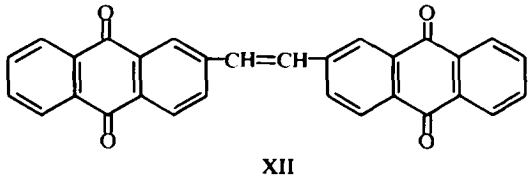
IX



XI



X



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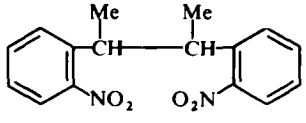
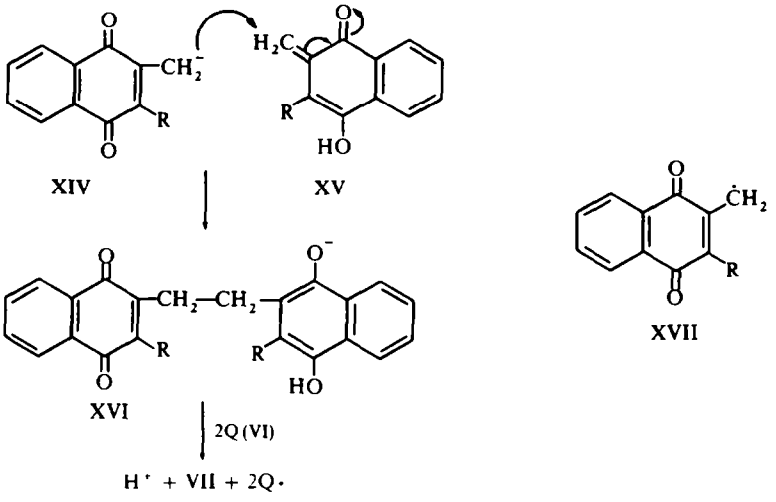


XIII

respective stilbenes, XI[14] and XII.[15] There is little doubt that in all these examples the reaction is initiated by formation of a carbanion $ArCH_2^-$ or QCH_2^- (XIV) which accounts for the preferred dimerisation of the dialkylnaphthaquinones on the CH_3 groups (primary carbanion). This is consistent with the failure of 2,3-methyl-1,4-naphthaquinone to form a dimer under the usual conditions although similar dimerisations on a secondary carbon atom have been reported, e.g. XIII[16] is the main product of the reaction of *o*-nitroethylbenzene with KOEt in ethyl oxalate. (The use of strong base is considered later.)

The formation of VII (R = Me) by base-catalysed decomposition of the 2-methyl-1,4-naphthaquinone–diazomethane adduct has been examined in detail by Dean[9, 17] and his colleagues but while it was firmly established that VII (R = Me) was formed by way of the carbanion (XIV) the precise mechanism was difficult to determine. The route most favoured proceeds by Michael addition of XIV to XV (derived from and in equilibrium with XIV) to form XVI which is subsequently oxidised by air and/or the parent quinone to the final product. In the dimerisations VI → VII the final oxidation is effected mainly by the starting quinone since in parallel experiments with VI (R = CH_2Ph) yields of 45% and 63% were obtained under nitrogen* and air, respectively. In the former case a red residue (quinhydrone?) gave starting material (24%) on oxidation with AgO. These dimerisations are clearly very similar to the



formation of the bibenzyl IX from *p*-nitrotoluene in basic solution which has been studied at length by Russell and his coworkers.[18] A mechanism similar to the above has been proposed (alternatively, XVI might be derived from a XIV–VI charge transfer complex) the function of oxygen being merely to regenerate the starting material from its radical-anion. However a radical mechanism cannot be completely

$$\text{XIV} \xrightarrow[\text{or } O_2]{\text{VI}} \text{XVII} \longrightarrow \text{VII}$$

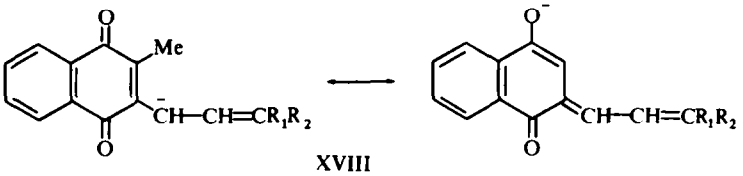
excluded although we could obtain no positive evidence in support (ESR spectra are swamped by signals from semiquinone radical-anions). Radical coupling was rejected by Russell on the basis that *p*-nitrobenzyl radicals would be scavenged by oxygen†

* The dimers IX and X can also be obtained from their monomers in the absence of air or added oxidising agent.[13, 18]

† Not necessarily true for XVII. The fact that phenylacetic acid can be oxidized by persulphate in the presence of air to give bibenzyl in substantial amount seems to demonstrate that benzyl radicals can couple in solution despite the presence of oxygen.[19]

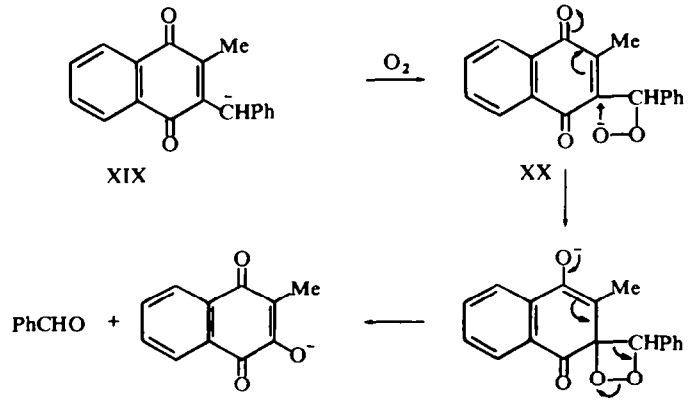
and the possibility that these radicals might be trapped in some way by a rapid reaction with *p*-nitrobenzyl anions was considered. A similar combination of XVII and XIV is a possible alternative route to VII by way of its radical-anion.

When 2-methyl-3-dimethylallyl-1,4-naphthaquinone VI ($R = CH_2CH{=}CMe_2$) is treated with base in the usual way the solution becomes blue and then changes to red, and on working-up phthiocol VI ($R = OH$) can be isolated as well as dimer. The formation of a blue or violet colour in base is characteristic of allylnaphthaquinones[20]



XVIII

and has been used as a test (Dam-Karrer reaction) for vitamins K. The colour, which was attributed[21] to the mesomeric anion XVIII, is also the basis[22] of the Kesting[23] and Craven[24] tests for quinones. However the colour is transient and changes to brownish red as the anion of phthiocol appears. To examine the bond cleavage further we studied the behaviour of the benzyl analogue VI ($R = CH_2Ph$) which is more convenient to handle than the allyl analogue. Under the usual conditions the benzyl compound VI ($R = CH_2Ph$) gives only a trace of phthiocol but more was obtained using an excess of strong base (tBuOK in tBuOH) which gave a deep blue solution changing to red. The best procedure is to shake the blue solution in oxygen until 1 mol is absorbed although the yield of phthiocol never exceeded 10% (the yields obtained from allylquinones are likewise poor[20]); benzaldehyde is also formed and the yield of dimer VII ($R = CH_2Ph$) is diminished. Under these conditions a secondary (benzylic) carbanion (XIX*) can be formed which, we suggest, reacts stepwise,[25] with oxygen to form a hydroperoxide anion (XX) leading, via a cyclic peroxide to cleavage of a C—C bond and the formation of phthiocol anion and benzaldehyde, as shown below. Alkyl naphthaquinones may be regarded as vinylogous ketones and



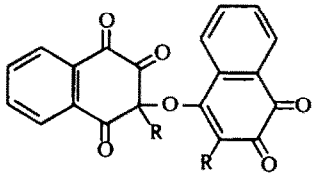
XIX XX

* The failure to detect the dimer VIII ($R = Ph$) which could arise from XIX may reasonably be attributed to steric difficulties as well as competitive reaction with oxygen.

this cleavage reaction is exactly parallel to the behaviour of ketones when autoxidised under alkaline conditions.[26] Under milder conditions (exposure to air in a test-tube) the reaction will occur less readily but there is little doubt that the Dam-Karrer anion (XVIII) undergoes oxidative cleavage in the same way. In contrast photolysis[27] of an allylnaphthaquinone generates the 3′-hydroperoxide followed by fission of the side chain at the 2′–3′ bond.

Dimerisation of 2-Hydroxy-1,4-naphthaquinones

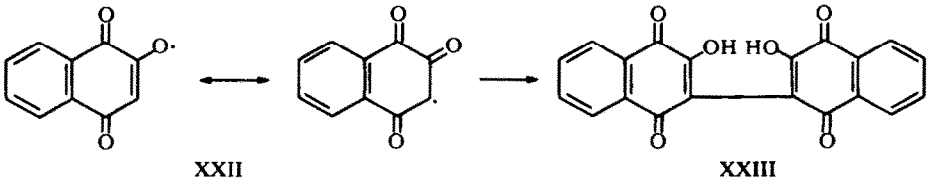
It was noted in 1893 that solutions of lawsone (2-hydroxy-1,4-naphthaquinone) deposited dimeric material on prolonged keeping, and later[28] it was shown that the reaction could be effected on a preparative scale by exposing a hot aqueous solution to UV irradiation. The structure of the product XXIII was established by the formation of three isomeric internal anhydrides, one of which gave a mono- and another a di-azine on reaction with *o*-phenylenediamine. It seemed to us that this dimerisation could be achieved using a suitable oxidising agent and, if 2-hydroxy-1,4-naphthaquinone is regarded as an enolised β-diketone, there is ample precedent in the literature for the oxidation of β-diketones to dehydro-dimers. Besides electrolysis.[29] the reagents used include $K_3Fe(CN)_6$,[30] $Pb(OAc)_4$,[31] PbO_2,[32] oxygen,[33] and 2,3-dichloro-5,6-dicyanobenzoquinone,[34] the products being carbon–carbon or carbon–oxygen dimers. An analogous carbon–oxygen dimer in the naphthaquinone series is "lapachol peroxide", obtained from lapachol by oxidation with PbO_2,[35] and regarded as XXI.[36] Probably all these dimers are formed by radical coupling



R = CH_2—CH=CMe_2

XXI

reactions and previous work with carboxylic acids[19, 37] suggests that persulphate oxidation of a 2-hydroxy-1,4-naphthaquinone would generate the mesomeric radical XXII capable of coupling at C-3 to form a carbon–carbon or carbon–oxygen dimer. In fact XXIII was obtained in this way from 2-hydroxy-1,4-naphthaquinone in *ca.* 60% yield and the carbon–oxygen dimer was not found. This was first observed by Baillie[38] in preliminary experiments and the reaction was subsequently used for the synthesis of the natural biquinone aurofusarin.[39]* We now find it to be general



XXII XXIII

* In this paper[39] reference 8 should refer to A. C. Baillie and not A. G. Wylie.

(see Table 1). The dimers are very similar spectroscopically to the monomers, as expected, but rather insoluble.

TABLE 1. DIMERISATION OF 2-HYDROXY-1,4-NAPHTHAQUINONES BY PERSULPHATE OXIDATION

1,4-Naphthaquinone	3,3'-Bi-1,4-naphthaquinonyl	Yield (%)	Physical form	m.p.	Mol. Wt. Found	Mol. Wt. Required
2-Hydroxy	2,2'-Dihydroxy	61	yellow needles	280–281°	346·0486	346·0477
2-Hydroxy-5-methoxy	2,2'-Dihydroxy-5,5'-dimethoxy	75	orange plates	subl. 225°	406·0693	406·0688
2-Hydroxy-6-methoxy	2,2'-Dihydroxy-6,6'-dimethoxy	48	orange-yellow needles	257–259°	406·0689	406·0688
2-Hydroxy-7-methoxy	2,2'-Dihydroxy-7,7-dimethoxy	44	yellow needles	262–264°	406·0681	406·0688
6-Bromo-2-hydroxy	6,6'-Dibromo-2,2'-dihydroxy	82	yellow crystals	279–281°	501·8687	501·8689

EXPERIMENTAL

2-Benzyl-1,4-naphthaquinone. To a solution of 2-benzyl-1-naphthol (10 g) in CH_3COOH (350 ml) was added, with stirring, a soln of CrO_3 (25·6 g) in H_2O (35 ml) and CH_3COOH (130 ml), keeping the temperature between 20° and 30°. After 72 hr the mixture was diluted with H_2O (1·5 l) and left overnight. The ppt was crystallized from MeOH in needles, m.p. 82°, yield 37%. (Found: C, 82·1; H, 5·1. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·8%). The *leuco-acetate* crystallised from dilute acetic acid in plates, m.p. 105°. (Found: C, 75·3; H, 5·5. $C_{21}H_{18}O_4$ requires C, 75·7; H, 5·4%).

2-Benzyl-3-chloromethyl-1,4-naphthaquinone. HCl gas was passed into a mixture of 2-benzyl-1,4-naphthaquinone (3 g), CH_3COOH (3 ml) and aq HCHO (30%, 10 ml), for 30 min. The soln became reddish-brown. It was kept overnight, poured into H_2O and the resulting ppt was crystallised from EtOH in yellow plates, m.p. 106°, yield 61%. (Found: C, 72·7; H, 4·5; Cl, 11·9. $C_{18}H_{13}ClO_2$ requires C, 72·8; H, 4·4; Cl, 12·0%), τ (CF_3CO_2D) 5·80 (s, 2H, Q—CH_2Ph), 5·36 (s, 2H, Q—CH_2Cl) + ArH signals.

3-(α-4-Dichlorobenzyl)-2-methyl-1,4-naphthaquinone. A cooled mixture of 2-methyl-1,4-naphthaquinone (5 g) and *p*-chlorobenzaldehyde (5 g) in CH_3COOH (50 ml) was treated with HCl for 30 min and set aside overnight. The product obtained on dilution with H_2O, crystallised from EtOAc as yellow plates, m.p. 114–115°, yield 38%. (Found: C, 65·3; H, 3·6; Cl, 20·9. $C_{18}H_{12}Cl_2O_2$ requires C, 65·2; H, 3·6; Cl, 21·4%), τ (CF_3CO_2D) 7·79 (s, 3H, Q—CH_3), 3·22 (s, 1H, Q—CH(Cl)Ar) + ArH signals.

3-(4-Chlorobenzyl)-2-methyl-1,4-naphthaquinone. The above dichloroquinone (1 g) in CH_3COOH (40 ml) containing anhydrous NaOAc (1 g) was hydrogenated in the presence of 5% palladised $BaSO_4$ (0·2 g). After absorption of 2 mols of H_2, the suspension was filtered, and then oxidised by warming for 15 min on a water-bath with a soln of CrO_3 (0·5 g) in H_2O (40 ml). Dilution with H_2O precipitated a yellow solid, the bulk of which crystallised from EtOAc in yellow plates, m.p. 133–134°, yield 80%. (Found: C, 72·7; H, 4·8; Cl, 11·6. $C_{18}H_{13}ClO_2$ requires C, 72·8; H, 4·4; Cl, 12·0%); ν_{max} (KBr) 1662, 1598 cm^{-1}, τ (CF_3CO_2D) 7·69 (s, 3H, Q—CH_3), 5·91 (s, 2H, Q—CH_2Ar) + ArH signals. The less-soluble material (15 mg) crystallised from C_6H_6 as yellow prisms, m.p. 250° (ν_{max} 1660, 1600 cm^{-1}), of the dimer VIII (Ar = C_6H_4Cl), identical (IR) with that obtained by reaction of the dichloroquinone with Ag (see below).

3-(α-Chloro-1-naphthylmethyl)-2-methyl-1,4-naphthaquinone. This was obtained, as above, from 2-methyl-1,4-naphthaquinone (5 g) and 1-naphthaldehyde (7 g) by treatment, in CH_3COOH, with HCl. It crystallised from EtOAc as yellow scales, m.p. 150°, yield 48%. (Found: C, 76·2; H, 4·7; Cl, 10·3. $C_{22}H_{15}ClO_2$ requires C, 76·2; H, 4·3; Cl, 10·2%).

2-Methyl-3-(1-naphthylmethyl)-1,4-naphthaquinone. Hydrogenolysis of the above chloroquinone, followed by chromic acid oxidation, gave a product, most of which crystallised from EtOAc as yellow plates, m.p. 162°, yield 82%. (Found: C, 84·4; H, 5·3. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%); ν_{max}(KBr) 1662, 1601 cm^{-1}. The less-soluble fraction (20 mg) separated from C_6H_6 as yellow plates, m.p. 290° (ν_{max} 1662, 1600 cm^{-1}), identical (m. m.p., IR) with the dimer obtained by reaction of the chloroquinone with Ag (see below).

3-Methoxymethyl-2-methyl-1,4-naphthaquinone. 3-Chloromethyl-2-methyl-1,4-naphthaquinone (0·5 g) in MeOH (50 ml) was treated with a cold soln of NaOMe (1 mol) in MeOH (10 ml). A bluish-green colour appeared and then faded, and after 5 min the soln was poured into H_2O. The ppt crystallised from MeOH in yellow leaflets, m.p. 95°, yield 56%. (Found: C, 71·8; H, 5·2; OMe, 13·7. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6; OMe, 14·4%); ν_{max} 1670, 1625, 1600 cm^{-1}.

Binaphthaquinones

These were obtained by two methods: (a) autoxidation in basic soln, (b) by reaction of 2-(α-chloroalkyl)-1,4-naphthaquinones with Ag. The examples below are typical.

(a) To 3-ethyl-2-methyl-1,4-naphthaquinone (200 mg) in EtOH (20 ml) was added 5N aq NaOH (2 ml). The soln turned purple and then blue, and in 5 min the colour had almost vanished and a yellow ppt appeared. After 15 min this was collected, and crystallised from CH_3COOH to give 1,2-bis(3-ethyl-1,4-naphthaquinon-2-yl)ethane VII (R = Et) as yellow needles, m.p. 267° (lit.[8] m.p. 267°) (yield 48%), τ ($CDCl_3$) 8·78 (t, 6H, Q—$CH_2C\underline{H}_3$), 7·19 (m, 8H, Q—CH_2—) + ArH signals. Less-soluble starting quinones were dissolved in EtOH/EtOAc (1:1).

(b) 2-Chloromethyl-3-ethyl-1,4-naphthaquinone (0·5 g) was refluxed in dry C_6H_6 (20 ml) with Ag powder (2 g) for 10 hr, filtered, concentrated and allowed to cool. The binaphthaquinone which separated (yield 60%) had m.p. 267° and was identical (IR, m. m.p.) with that prepared in (a).

The following binaphthaquinones were obtained by both methods from the appropriate starting materials.

1,2-Bis-(3-benzyl-1,4-naphthaquinon-2-yl)ethane. (VII; R = CH_2Ph) yellow plates, m.p. 280° (from C_6H_6) (lit.[10] m.p. 273–274°), (Found: C, 82·9; H, 5·4%; M, 522·1824. Calc. for $C_{36}H_{26}O_4$ C, 82·7; H, 5·0%; M, 522·1831); ν_{max} (KBr) 1658, 1598 cm^{-1}, λ_{max} ($CHCl_3$) 270, 330 nm (log ε 4·51, 3·87). *Leucoacetate*, plates, m.p. 225° (from CH_3COOH). (Found: C, 76·1; H, 5·7. $C_{44}H_{38}O_8$ requires C, 76·1; H, 5·5%).

When 3-benzyl-2-methyl-1,4-naphthaquinone (200 mg) in EtOH (50 ml) was treated with 10N aq KOH (5 ml) the dimer was obtained in 63% yield. Also 3-benzyl-2- methyl-1,4-naphthaquinone (500 mg) in EtOH (100 ml) was treated with 10N aq KOH (10 ml) under N_2 and the soln acidified after 5 min. Part of the ppt dissolved in EtOH (20 ml), and the insoluble portion was crystallised from C_6H_6 to give the dimer (45%). The EtOH soln was evaporated leaving a red residue which was taken up in ether and shaken with AgO to give starting material (120 mg).

3-Benzyl-2-methyl-1,4-naphthaquinone (1 g) in tBuOH (30 ml) was treated with N tBuOK (15 ml) and shaken in an atmosphere of O_2 until 1 mol was absorbed (~5 min), the colour of the soln changing from deep blue to red. The mixture was acidified, diluted with H_2O and extracted with ether. The latter was shaken with aq $NaHCO_3$ which yielded, after acidification, phthiocol, m.p. 173° (10%) identical (m m.p., IR) with authentic material. On keeping the ethereal soln for some time the dimer VII (R = CH_2Ph) (100 mg) began to separate. Benzaldehyde was identified in the filtrate as its 2,4-dinitrophenylhydrazone.

1,2-Bis-(3-chloro-1,4-naphthaquinon-2-yl)ethane. (VII; R = Cl) yellow leaflets, m.p. 303° (lit.[8] m.p. 302°). In method (a) NaOMe (>1 mol) in MeOH was used as base. This compound was also prepared* as follows: To a solution of 1,2-di-β-naphthylethane (1 g) in CH_3COOH (22 ml) was added CrO_3 (8 g) in H_2O (6 ml) and CH_3COOH (6 ml), in 10 min. The mixture was kept at 60° for 12 hr and then diluted with H_2O. The precipitated 1,2-bis-(1,4-naphthaquinon-2-yl)ethane crystallised from CH_3COOH in yellow needles, m.p. 225–227°, yield 23%. (Found: C, 77·1; H, 4·2. $C_{22}H_{14}O_4$ requires C, 77·1; H, 4·1%); ν_{max}(KBr) 1665, 1598 cm^{-1}, λ_{max}($CHCl_3$) 258, 268, 337 nm (log ε 4·52, 4·48, 4·07). *Leuco-acetate*, needles, m.p. 208–210° (from dilute CH_3COOH). (Found: C, 70·1; H, 5·1. $C_{30}H_{26}O_8$ requires C, 70·05; H, 5·1%). Chlorine was passed into a soln of the biquinone (100 mg) in CH_3COOH (30 ml) at 25–30° for 2½ hr. The soln was left overnight and poured onto ice to precipitate the colourless tetrachloride (m.p. 251–253°). This (123 mg) in CH_3COOH (25 ml) was refluxed for 1 hr with anhyd. NaOAc (200 mg). Dilution with H_2O gave 1,2-bis-(3-chloro-1,4-naphthaquinon-2-yl)ethane, m.p. 303° (from dimethylformamide) (50%), identical (IR, m.m.p.) with that described above.

* With M. R. Akhtar.

The following binaphthaquinones were made by method (a) only.

1,2-*Bis*-(3-*diphenylmethyl*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII; R = $CHPh_2$). Lemon-yellow plates, m.p. 318° identical (IR, m.m.p.) with a sample prepared by Dean *et al.*[9]

1,2-*Bis*-[3-(4-*chlorobenzyl*)-1,4-*naphthaquinon*-2-*yl*]*ethane*. (VII; R = $CH_2C_6H_4Cl$). Yellow plates, m.p. 220° (from C_6H_6). (Found: C, 72·9; H, 4·5; Cl, 12·0; M, 590·1056. $C_{36}H_{24}{}^{35}Cl_2O_4$ requires C, 73·1; H, 4·1; Cl, 12·0%; M, 590·1053), τ ($CDCl_3$) 7·14 (s, 4H, Q—CH_2CH_2—Q), 5·83 (s, 4H, Q—CH_2—Ar) + ArH signals.

1,2-*Bis*-[3-(1-*naphthylmethyl*)-1,4-*naphthaquinon*-2-*yl*]*ethane*. (VII; R = $CH_2C_{10}H_7$). Yellow needles, m.p. 306° (from C_6H_6). (Found: C, 84·5; H, 5·1%; M, 622·2156. $C_{44}H_{30}O_4$ requires C, 84·9; H, 4·8%; M, 622·2144).

1,2-*Bis*-(3-*p*-*tolyl*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII; R = C_6H_4Me). Yellow plates, m.p. 224° (from C_6H_6). (Found: C, 82·8; H, 5·0%; M, 522·1830. $C_{36}H_{26}O_4$ requires C, 82·5; H, 5·2%; M, 522·1831), τ ($CDCl_3$) 7·74 (s, 6H, CH_3—Ar), 7·18 (s, 4H, Q—CH_2CH_2—Q) + ArH signals. *Leuco-acetate*, leaflets, m.p. 205°. (Found: C, 76·0; H, 5·6. $C_{44}H_{38}O_8$ requires C, 76·1; H, 5·5%).

1,2-*Bis*-(3-*isopropyl*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII; R = i-Pr). Yellow needles, m.p. 253° (from C_6H_6). (Found: C, 78·9; H, 6·1%; M, 426·1824. $C_{28}H_{26}O_2$ requires C, 78·7; H, 6·3%; M, 426·1831), τ ($CDCl_3$) 8·54 (d, 12H, $CH(C\underline{H}_3)_2$), 7·17 (s, 4H, Q—CH_2CH_2—Q), 6·63 (m, 2H, $C\underline{H}(CH_3)_2$) + ArH signals. *Leuco-acetate*, plates, m.p. 240°. (Found: C, 72·0; H, 6·2. $C_{36}H_{38}O_8$ requires C, 72·2; H, 6·4%).

1,2-*Bis*-(3-γγ-*dimethylallyl*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII; R = $CH_2CH{=}CMe_2$). This reaction was conducted in EtOH using aq KOH as base. The colour changed from blue to red but the dimer did not precipitate. The soln was acidified and extracted with ether which was shaken with aq $NaHCO_3$. Acidification of the alkaline soln gave phthiocol (10%) (m.m.p., IR). Concentration of the ether soln gave the dimer which crystallised from EtOAc as yellow rods, m.p. 206° (15%). (Found: C, 80·1; H, 6·6%, M, 478·2133. $C_{32}H_{30}O_4$ requires C, 80·3; H, 6·3%; M, 478·2144). The biquinone gave a positive Dam-Karrer Test.

1,2-*Bis*-(3-*bromo*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII: R = Br). Yellow plates, m.p. 290° (from $CHCl_3$). (Found: C, 52·8; H, 2·4; Br, 32·2%; M, 497·9102. $C_{22}H_{12}Br_2O_4$ requires C, 52·8; H, 2·4; Br, 32·0%; $C_{22}H_{12}{}^{79}Br_2O_4$ requires M, 497·9101).

1,2-*Bis*-(3-*methoxy*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII; R = OMe). This was obtained by treatment of 3-chloro(or bromo)-2-methyl-1,4-naphthaquinone with NaOMe (2 mol) in MeOH. It formed yellow needles, m.p. 212° (EtOAc). (Found: C, 71·7; H, 4·6; OMe, 14·3%; M, 402·1116. $C_{24}H_{18}O_6$ requires C, 71·6; H, 4·5; OMe, 15·4%; M, 402·1103).

1,2-*Bis*-(3-*ethoxy*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII; R = OEt). Prepared as above, using NaOEt in EtOH, it crystallised from EtOAc in yellow needles, m.p. 225°. (Found: C, 72·7; H, 5·1; OEt, 19·4%; M, 430·1410. $C_{26}H_{22}O_6$ requires C, 72·6; H, 5·1; OEt, 20·9%; M, 430·1416).

1,2-*Bis*-(3-*hydroxy*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII; R = OH). 3-Chloro-2-methyl-1,4-naphthaquinone (0·5 g) in EtOH (50 ml) was treated with 5N NaOH (10 ml). After 30 min the red soln was acidified, and the ppt was crystallised from C_6H_6 as yellow plates, m.p. 270°, yield 25%. (Found: C, 70·4; H, 4·1%; M, 374·0781. $C_{22}H_{14}O_6$ requires C, 70·6; H, 3·7%; M, 374·0790); ν_{max} (KBr) 3320, 1645, 1594 cm^{-1} (cf. phthiocol, 3315, 1655, 1598 cm^{-1}). λ_{max} (EtOH) 251, 277, 330 nm (log ε 4·52, 4·50, 3·67) [cf. phthiocol, 251, 277, 330 nm (log ε 4·24, 4·22, 3·38)]. The same compound was obtained by heating the above dimethoxy (or diethoxy) binaphthaquinone with HBr in CH_3COOH.

1,2-*Bis*-(3-*methoxymethyl*-1,4-*naphthaquinon*-2-*yl*)*ethane* (VII; R = CH_2OMe). This was obtained by autoxidation of 3-methoxymethyl-2-methyl-1,4-naphthaquinone in the usual way and similarly, from 3-chloromethyl-2-methyl-1,4-naphthaquinone using NaOMe (3 and 4 mol respectively) in MeOH. It crystallized from C_6H_6 in yellow needles, m.p. 230°. (Found: C, 72·2; H, 5·3; OMe, 13·1. $C_{26}H_{22}O_6$ requires C, 72·1; H, 5·1; OMe, 14·4%); ν_{max} (KBr) 1665, 1622, 1598 cm^{-1}.

1,2-*Bis*-(3-*methyl*-1,4-*naphthaquinon*-2-*yl*)*ethane*. (VII; R = Me). 2,3-Dimethyl-1,4-naphthaquinone (200 mg) in ether (200 ml) was treated with NaOMe (from 2 g Na) in MeOH (50 ml). After 24 hr the green soln was poured into water and the ether layer was evaporated leaving the biquinone, yellow leaflets, m.p. 269° (from CH_3COOH). A further quantity was obtained by aeration of the aqueous alkaline layer, and acidification, total yield 35%; τ ($CDCl_3$) 7·63 (s, 6H, Q—CH_3), 7·18 (s, 4H, Q—CH_2CH_2—Q) + ArH signals.

The following binaphthaquinones were prepared by method (b) only.

1,2-*Bis*-(3-*methyl*-1,4-*naphthaquinon*-2-*yl*)-1,2-*diphenylethane*. (VIII; Ar=Ph). Lemon-yellow plates, m.p. 318° (from C_6H_6). (Found: C, 82·6; H, 4·9%; M, 522·1840. $C_{36}H_{26}O_4$ requires C, 82·8; H, 5·0%; M, 522·1831), λ_{max} ($CHCl_3$) 274, 340 nm (log ε 4·41, 3·81). The same compound was obtained by hydrogenolysis

of 3-α-chlorobenzyl-2-methyl-1,4-naphthaquinone (1 g) in CH_3COOH (40 ml) containing anhyd. NaOAc (1 g) in the presence of 5% palladised $BaSO_4$ (0·2 g). Working up as before[8] gave 3-benzyl-2-methyl-1,4-naphthaquinone, λ_{max} ($CHCl_3$) 274, 340 nm (log ε 4·19, 3·57) (95% yield) which crystallised from EtOH. The residual yellow solid (15 mg), insoluble in EtOH, crystallized from C_6H_6 in yellow plates, m.p. 318°, identical with the dimer reported above. The *leuco-acetate* formed plates, m.p. 245° (CH_3COOH). (Found: C, 75·8; H, 5·6. $C_{44}H_{38}O_8$ requires C, 76·1; H, 5·5%).

1,2-*Bis*-(3-*methyl*-1,4-*naphthaquinon*-2-*yl*)-1,2-*di*-(4-*chlorophenyl*)*ethane*. (VIII; Ar = C_6H_4Cl). Yellow prisms, m.p. 250° (from C_6H_6). (Found: C, 72·9; H, 4·1; Cl, 12·0; M, 590·1039. $C_{36}H_{24}{}^{35}Cl_2O_4$ requires C, 73·1; H, 4·1; Cl, 12·0%; M, 590·1053). The same dimer was obtained as a minor product in the hydrogenolysis of 3-(4-chlorobenzyl)-2-methyl-1,4-naphthaquinone (see above).

1,2-*Bis*-(3-*methyl*-1,4-*naphthaquinon*-2-*yl*)-1,2-*di*-(1-*naphthyl*)*ethane*. (VIII; Ar = $C_{10}H_7$). Yellow plates, m.p. 290° (from C_6H_6). (Found: C, 84·5; H, 4·7: $C_{44}H_{30}O_4$ requires C, 84·9; H, 4·8%). The same compound was obtained as a minor product in the hydrogenolysis of[8]3-(α-chloro-1-naphthylmethyl)-2-methyl-1,4-naphthaquinone (see above).

Oxidation of 2-*hydroxy*-1,4-*naphthaquinones*.* The following is typical: to a solution of 2-hydroxy-1,4-naphthaquinone (5 g, 0·028 mole) in H_2O (50 ml) and 4N NaOH (7 ml, 0·028 mole), stirred at 95°, was added potassium persulphate (7·56 g, 0·028 mole) in H_2O (25 ml) during 30 min. The soln was stirred at 95° for 90 min more, cooled, and extracted with $CHCl_3$ which was dried (Na_2SO_4) and evaporated. The residue was washed well with ether to remove monomer, chromatographed on silica gel–oxalic acid in C_6H_6–HCOOEt (10:3), and crystallized from CH_3COOH to give 2,2'-dihydroxy-3,3'-bi-1,4-naphthaquinonyl in yellow needles, m.p. 280–281° (lit.[28] 270–275°), λ_{max} (EtOH) 252, 274, 329 nm (log ε 4·50, 4·42, 3·76), λ_{max} ($EtOH/HO^-$) 274, 299, 506 nm (log ε 4·48, 4·38, 3·61), ν_{max} (KBr) 3310, 1675, 1641, 1590 cm^{-1}.

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