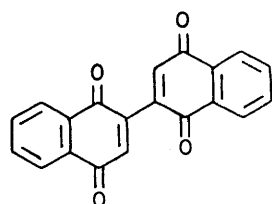


Further Conversions of Naphthoquinones into Dinaphthofuranquinones

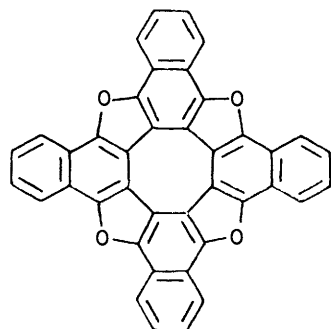
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1,4-Naphthoquinone is in part converted by aluminium chloride in carbon disulphide into the *ortho*-quinone (3; R = H). Thermal isomerisation of the binaphthylidiquinone (1) in 2-methoxynaphthalene gives the hydroxyquinone (4; R = H) but in 1-nitronaphthalene produces the dihydroxydiquinone (7; R = H).

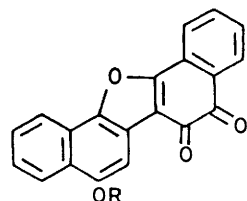
WHILE examining the reactions of veratrole with quinones¹ we observed that 1,4-naphthoquinone undergoes self-condensation on treatment, in carbon disulphide, with anhydrous aluminium chloride. The products isolated were the binaphthylidiquinone (1) (18%),



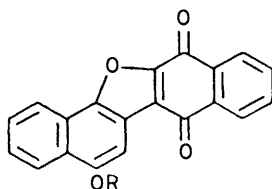
(1)



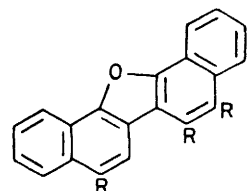
(2)



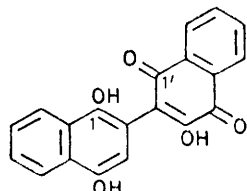
(3)



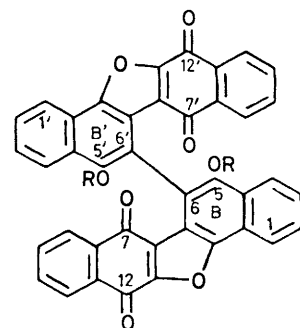
(4)



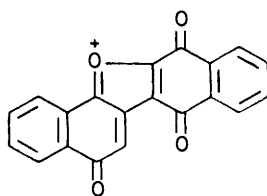
(5)



(6)



(7)



(8)

the tetrameric compound (2) (2%), which is the major product obtained from a similar reaction in nitrobenzene,^{2,3} naphthalene-1,4-diol (6%), and a new red quinone, C₂₀H₁₀O₄ (5%). The last-named forms a monoacetate and shows i.r. absorption in the carbonyl region which is typical⁴ of a 4-alkoxy-1,2-naphthoquinone, and we formulate it accordingly as the dinaphthofuran derivative (3; R = H). In agreement with this its red acetate (3; R = Ac) shows light absorption in the visible at longer wavelength than is shown⁵ by the isomeric 1,4-quinone derivative (4; R = Ac), while the u.v. spectrum of its leucoacetate (5; R = OAc) resembles closely that⁶ of the dinaphthofuran (5; R = H). In the mass spectrometer the new quinone behaves as expected,^{7,8} the molecular ion losing carbon monoxide much more readily than does that from the isomeric 1,4-quinone (4; R = H). It does not show a significant (M + 2H)⁺ ion, presumably because of the effect of the furan ring on the 1,2-quinone system.⁸ We suggest that the first step in the formation of this quinone is the addition of water (which is formed during the reaction) to the binaphthylidiquinone (1) to give the trihydroxyquinone (6), the more stable of the two possible internal quinhydrone. Aluminium chloride forms a chelate complex with the two adjacent oxygen functions on the quinone ring⁹ and subsequent cyclisation can occur only between the hydroxy-group at C-1 and the quinone carbonyl group at C-1'. Finally, cleavage of the aluminium complex and subsequent dehydration affords the 1,2-quinone (3; R = H).

For comparison with the above quinone we required a specimen of the isomeric 1,4-quinone (4; R = H) and sought to prepare this by the thermal isomerisation¹⁰ of the binaphthylidiquinone (1) in 1-nitronaphthalene. Brief heating (0.5 min at 300 °C, or 6 min at 265 °C) afforded mixtures which we could not separate easily but longer heating (20 min at 300 °C) gave a more readily purified product. This proved to be not the desired quinone but a compound C₄₀H₁₈O₈ which forms a dimethyl ether, a diacetate, and a leucohexa-acetate and is therefore a dihydroxydiquinone. It must result from the oxidative coupling of two molecules of the hydroxyquinone (4; R = H) and we formulate it as the symmetrical dihydroxydiquinone (7; R = H). Its spectroscopic properties and those of its derivatives are consistent with this structure. Thus the i.r. spectrum of the parent compound shows bands in the carbonyl region resembling those exhibited by the hydroxyquinone (4; R = H) (see below). In its mass spectrum the base

peak appears to result from cleavage of the aryl-aryl linkage with the formation of an ion of m/e 313 which we formulate as (8), while the virtual absence of an $(M - CO)^+$ ion indicates that the compound contains 1,4- rather than 1,2-quinone systems. As expected, the u.v.-visible light absorption of the corresponding diacetate (7; R = Ac) is similar to that⁵ of the acetoxyquinone (4; R = Ac). The n.m.r. spectrum of the leucohexa-acetate shows the presence of three types of acetoxy-group in the molecule, for two of which the proton signals appear at unusually high fields, at δ 0.90 and 1.48. A model of the leucohexa-acetate reveals that the two dinaphthofuran units are constrained to lie in planes which are nearly perpendicular to each other. The protons of the acetoxy-groups at C-5 and -5' and at C-7 and -7' [see structure (7)], lie above or below, and close to, the aromatic rings B' and B, and in consequence are highly shielded. In the mass spectrometer the leucohexa-acetate undergoes repeated loss of keten followed by cleavage of the aryl-aryl linkage.

The oxidising agent involved in the formation of the dihydroxydiquinone (7; R = H) appears to be the solvent, 1-nitronaphthalene, because when we heated the binaphthyldiquinone (1) at 260 °C in 2-methoxynaphthalene, a high-boiling solvent without oxidising properties, we obtained the desired hydroxyquinone (4; R = H) without difficulty. The structure of the latter follows from its conversion into its known¹¹ methyl ether. When heated at 300 °C in 1-nitronaphthalene the hydroxyquinone readily underwent oxidation to give the dimeric product (7; R = H). Presumably the nitro-compound abstracts an electron from the hydroxynaphthofuran system of (4; R = H) and the resulting cation-radical dimerises and then loses two protons.

Boiling nitrobenzene (b.p. 211 °C) converts 1-hydroxy-2-methoxyanthrone into the corresponding helianthone¹² but the possibility that, like 1-nitronaphthalene, it might effect the dehydromerisation of other phenols with low ionisation potentials does not appear to have been considered. Thus the photochemical isomerisation of the binaphthyldiquinone (1) gave a product formulated¹³ as the hydroxyquinone (4; R = H) and an alternative synthesis of the methyl ether of the latter seemed to confirm the proposed structure. The purification of the photo-compound had however involved crystallisation from nitrobenzene and we have established that the product is not the monomer but the dihydroxydiquinone (7; R = H). The final stage of the apparently unambiguous synthesis of the methyl ether was effected using anhydrous aluminium chloride and nitrobenzene, reagents which can bring about a Scholl reaction,¹⁴ and the compound produced is, in fact, the dimethoxydiquinone (7; R = Me).

EXPERIMENTAL

The identity of high-melting, poorly soluble compounds with authentic specimens was usually established by comparison of their i.r., u.v., visible, and mass spectra.

Reaction of 1,4-Naphthoquinone with Aluminium Chloride.—A mixture of 1,4-naphthoquinone (15.8 g), anhydrous aluminium chloride (16.75 g), and carbon disulphide (250 ml) was stirred at room temperature for 27 h. Ice (120 g) and 5M-hydrochloric acid (100 ml) were added and the mixture was stirred for 2 h and filtered. The residue was extracted with acetone to remove naphthoquinone (5.0 g) and the resulting solid (3.5 g) in chloroform was separated by column chromatography on silica gel (chloroform) into 2,2'-binaphthyl-1,4 : 1',4'-diquinone (1) (2.8 g), m.p. 270 °C (decomp.) (lit.,¹⁰ 270–280 °C) and tetranaphthylene[5,6-bcd : 11,12-b'c'd' : 17,18-b''c''d'' : 23,24-b'''c'''d''']tetra-furan (2)¹⁵ (0.3 g) which sublimed at 490 °C and 2×10^5 mmHg. The filtrate from the reaction mixture was steam-distilled to remove carbon disulphide and the mixture was filtered. Extraction of the aqueous filtrate with ether afforded naphthalene-1,4-diol (1 g). Repeated purification of the residual violet solid (2 g) by t.l.c. on silica gel [benzene-*NN*-dimethylformamide (6 : 1)] gave 8-hydroxydinaphtho-[1,2-b : 2',1'-d]furan-5,6-quinone (3; R = H) (0.8 g) which crystallised from chloroform-ethanol containing some *NN*-dimethylformamide as dark red needles, m.p. >350 °C (Found: *M*, 314.057 1. $C_{20}H_{10}O_4$ requires *M*, 314.057 9), ν_{max} (Nujol) 3360 (phenolic OH), 1690w, 1655, and 1642 cm^{-1} (quinone C=O); λ_{max} (EtOH) 279 (log ϵ 4.77), 332 (3.90), 348 (3.90), and 530 nm (3.51); λ_{inf} 260 (log ϵ 4.63), 273 (4.74), and 314 nm (3.98); m/e 314 [70%, $(M)^+$], 286 [100%, $(M - CO)^+$], and 258 [14%, 286 - CO]. Reaction of this hydroxyquinone with acetic anhydride and a little concentrated sulphuric acid at 40 °C gave the corresponding acetate (3; R = Ac) which crystallised from benzene as red rhombohedra, m.p. 261.5–263 °C (Found: *M*, 356.068 6. $C_{22}H_{12}O_5$ requires *M*, 356.068 5), ν_{max} (KBr) 1765 (aryl acetate C=O), 1698w, 1667, and 1650 cm^{-1} (quinone C=O); λ_{max} (CHCl₃) 266 (log ϵ 4.68), 276 (4.73), 336 (3.76), and 476 nm (3.48); λ_{inf} 255 (log ϵ 4.61), 290 (4.30), 299 (4.26), 319 (3.91), and 380 nm (3.26); m/e 356 [14%, $(M)^+$], 314 [100%, $(M - CH_2CO)^+$], and 286 (61%, 314 - CO). Reductive acetylation of the hydroxyquinone with acetic anhydride, zinc dust, and triethylamine at 140 °C gave the corresponding leucotriacetate (5; R = OAc) which separated from chloroform-ethanol as needles, m.p. 270–271 °C (Found: *C*, 70.4; *H*, 3.8; *AcO*, 36.5%; *M*, 442. $C_{26}H_{18}O_7$ requires *C*, 70.6; *H*, 4.1; 3AcO, 40.05%; *M*, 442), ν_{max} (Nujol) 1765 cm^{-1} (aryl acetate C=O), λ_{max} (CHCl₃) 263 (log ϵ 4.83), 271 (4.80), 281 (4.76), 318 (4.12), 331 (4.26), and 344 nm (4.05); λ_{inf} 299 (log ϵ 4.20), 304 (4.13), and 352 nm (3.30); δ (CDCl₃) 2.49, 2.49, and 2.54 (each s, 3 H, CH₃CO₂Ar), 7.4–7.8 (m, 5 H, H-2, -3, -7, -10, and -11), 7.8–8.0 (m, 2 H, H-4 and -9), and 8.4–8.6 (m, 2 H, H-1 and -12); m/e 442 [24%, $(M)^+$], 400 [21%, $(M - CH_2CO)^+$], 358 (70%, 400 - CH₂CO), and 316 (100%, 358 - CH₂CO).

5-Hydroxydinaphtho[1,2-b : 2',3'-d]furan-7,12-quinone (4; R = H).—A mixture of 2,2'-binaphthyl-1,4 : 1',4'-diquinone (50 mg) and 2-methoxynaphthalene (1 g) was heated at 260 °C for 15 min, cooled, and treated with chlorobenzene (5 ml). The resulting solid was collected, washed with chlorobenzene and with ethanol, and crystallised from ethanol-pyridine to give the red hydroxyquinone (42 mg), m.p. >355 °C (lit.,⁵ 360 °C) (Found: *M*, 314.058 3. $C_{20}H_{10}O_4$ requires *M*, 314.057 9), ν_{max} (Nujol) 3300 (phenolic OH), 1675, 1660, and 1595 cm^{-1} (quinone C=O and C=C); m/e 314 [100%, $(M)^+$], 286 [5%, $(M - CO)^+$], 258 (10%, 286 - CO), 230 (10%, 258 - CO), and 202 (18%, 230 -

CO). Methylation of the hydroxyquinone with freshly distilled dimethyl sulphate and anhydrous potassium carbonate in dry acetone gave the corresponding methyl ether (4; R = Me) which crystallised from chloroform-ethanol as orange-red needles, m.p. 296–297 °C (lit.,¹¹ 293–295 °C).

5,5'-Dihydroxybi(dinaphtho[1,2-b:2',3'-d]furan-6-yl)-7,12:7',12'-diquinone (7; R = H).—(a) A mixture of 2,2'-binaphthyl-1,4:1',4'-diquinone (100 mg) and 1-nitronaphthalene (1 g) was heated at 300 °C for 20 min, cooled, and chlorobenzene (5 ml) was added. The solid was collected, washed with ethanol and with chloroform, and crystallised from ethanol-pyridine to give the red dihydroxydiquinone (26 mg), m.p. >360 °C (Found: *M*, 626.100 4. C₄₀H₁₈O₈ requires *M*, 626.100 2), ν_{\max} (Nujol) 3 330 (phenolic OH), 1 675, 1 655, and 1 597 cm⁻¹ (quinone C=O and C=C); *m/e* 626 [79%, (M)⁺], 313 [100%, (M - C₂₀H₉O₄)⁺], 285 (26%, 313 - CO), 257 (13%, 285 - CO), 229 (7%, 257 - CO), and 200 (8%, 229 - CHO).

(b) A similar reaction with 5-hydroxydinaphtho[1,2b:2',3'-d]furan-7,12-quinone (4; R = H) (40 mg) gave the same product (25 mg).

(c) Photolysis of the binaphthylidiquinone (1) and crystallisation of the product from nitrobenzene¹³ gave the same compound.

Reaction of the dihydroxydiquinone with acetyl chloride in pyridine gave the corresponding diacetate (7; R = Ac), m.p. >345 °C, which crystallised from chloroform-ethanol (Found: *M* - CH₂CO, 668.111 5. C₄₂H₂₀O₉ requires *M*, 668.110 7), ν_{\max} (Nujol) 1 768 (aryl acetate C=O), 1 675 and 1 600 cm⁻¹ (quinone C=O and C=C); λ_{\max} (CHCl₃) 266 (log ϵ 5.01) and 425 nm (4.01); λ_{infl} 260 (log ϵ 4.96), 283 (4.52), 293 (4.38), 306 (4.15), and 334 nm (3.85); *m/e* 710 [0.5%, (M)⁺], 668 [44%, (M - CH₂CO)⁺], 626 [100%, (M - 2CH₂CO)⁺], and 313 (40%, 626 - C₂₀H₉O₄).

Methylation of the dihydroxydiquinone as described earlier gave the corresponding dimethyl ether (7; R = Me) which crystallised from chloroform-ethanol as orange needles, m.p. >348 °C (Found: *M*, 654.131 5. C₄₂H₂₂O₈ requires *M*, 654.131 4), ν_{\max} (Nujol) 1 668 cm⁻¹ (quinone C=O); λ_{\max} (CHCl₃) 267.5 (log ϵ 5.08), and 446 nm (4.03); λ_{infl} 263 (log ϵ 5.07), 298 (4.41), 312 (4.16), 325 (3.96), and 338 nm (3.86); *m/e* 654 [100%, (M)⁺], 639 [5%, (M - Me)⁺], 621 (4%, 639 - H₂O), and 608 (71%, 639 - MeO).

The same compound resulted from the attempted synthesis¹³ of the methoxy-quinone (4; R = Me) in the presence of nitrobenzene and anhydrous aluminium chloride.

Reductive acetylation of the dihydroxydiquinone as described earlier gave the corresponding leucohexa-acetate, m.p. 301–303 °C which crystallised from chloroform-ethanol (Found: *M* - CH₂CO, 840.184 3. C₅₀H₃₂O₁₃ requires *M*, 840.184 3), ν_{\max} 1 767 cm⁻¹ (aryl acetate C=O); λ_{\max} (CHCl₃) 269 (log ϵ 5.27), 323 (4.39), 337 (4.43), 360 (4.20), and 377 nm (4.33); λ_{infl} 302 nm (log ϵ 4.50); δ (CDCl₃) 0.90, 1.48, and 2.70 (each s, 6 H, CH₃CO₂ at C-5 and -5', -7 and -7', -12 and -12', respectively), 7.2–8.1 and 8.5–8.7 (m, 16 H, ArH); *m/e* 882 [0.3%, (M)⁺], 840, 798, 756, 714, 672, 630 [10–40%, (M - nCH₂CO)⁺], and 315 (100%, 630 - C₂₀H₁₁O₄).

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REFERENCES

- 1 R. Buchan and O. C. Musgrave, *J.C.S. Perkin I*, 1975, 2185.
- 2 C. Marschalk, *Bull. Soc. chim. France*, 1938, 5, 304.
- 3 H. Erdtman and H.-E. Högberg, *Tetrahedron Letters*, 1970, 3389.
- 4 R. H. Thomson, 'Naturally Occurring Quinones,' Academic Press, London, 1971, 2nd edn., p. 64; A. R. Burnett and R. H. Thomson, *J. Chem. Soc. (C)*, 1967, 1261.
- 5 D. Schulte-Frohlinde and V. Werner, *Chem. Ber.*, 1961, 94, 2726.
- 6 H.-E. Högberg, *Acta Chem. Scand.*, 1972, 26, 309.
- 7 T. Hayashi, Y. Inouye, M. Ohashi, H. Kakisawa, A. Tate-matsu, and T. Kinoshita, *Org. Mass Spectrometry*, 1970, 3, 1293.
- 8 R. W. A. Oliver and R. M. Rashman, *J. Chem. Soc. (B)*, 1971, 341.
- 9 Cf. S. R. Gupta, K. K. Malik, and T. R. Seshadri, *Indian J. Chem.*, 1969, 7, 457.
- 10 R. Punmerer, A. Pfaff, G. Riegelbauer, and E. Rosenhauer, *Ber.*, 1939, 72, 1623.
- 11 O. C. Musgrave and D. Skoyles, *J.C.S. Perkin I*, 1979, 2679.
- 12 G. F. Attree and A. G. Perkin, *J. Chem. Soc.*, 1931, 144.
- 13 A. J. Shand and R. H. Thomson, *Tetrahedron*, 1963, 19, 1919.
- 14 A. T. Balaban and C. D. Nenitzescu in 'Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, Vol. 2, p. 979.
- 15 H. Erdtman and H.-E. Högberg, *Chem. Comm.*, 1968, 773.