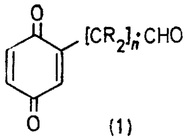
Light-induced and Related Reactions of Quinones. Part VI.[1] Reactions of Some *p*-Quinones carrying Formyl Groups

By **J. Malcolm Bruce*** and **David Creed,** Department of Chemistry, The University, Manchester M13 9PL

Preparations of formyl-1,4-benzoquinone, 1,4-benzoquinonylacetaldehyde, 3-(1,4-benzoquinonyl)propionaldehyde, 2-(1,4-benzoquinonyl)-2-methylpropionaldehyde, and 2-methyl-2-(1,4-naphthoquinon-2-yl)propionaldehyde are described. Irradiation of solutions of these quinones in benzene with visible light leads to the isolation of 2,5-dihydroxybenzoic acid from formyl-1,4-benzoquinone, and to the formation of 5-hydroxycoumaran-2-one and 3,4-dihydro-6-hydroxycoumarin from the next two quinones, respectively; the last two quinones in the series lose the elements of formaldehyde, and give 5-hydroxy-3-methylbenzofuran and 5-hydroxy-3-methylnaphtho-[1,2-*b*]furan, respectively. None of the irradiations prcceeded cleanly.

IRRADIATION of 1,4-benzoquinones having at least one free nuclear position in the presence of simple aliphatic aldehydes, especially acetaldehyde, gives the corresponding acylquinols, often in good yield.[2-4] 1,4-Naphthoquinone and 2-methyl-1,4-naphthoquinone similarly yield the corresponding acetylnaphthoquinols when they are irradiated in acetaldehyde.[5] These acylquinols are almost certainly formed[3] *via* attack of acyl radicals on ground-state quinone. However, in the absence of aldehydes, reactions which may involve intramolecular radical–radical combination, and intramolecular radical scavenging have been observed[6] for certain substituted 1,4-benzoquinones: thus, respectively, but-3-enyl-1,4-benzoquinone gives 1,4-dihydro-5,8-dihydroxynaphthalene, and benzyloxymethyl-1,4-benzoquinone yields 6-hydroxy-2-phenyl-1,3-benzodioxan.

The high selectivity of attack of acyl radicals on the quinonoid nucleus of partially substituted 1,4-benzo- and 1,4-naphtho-quinones suggested that quinones (1) carrying formyl groups in the side-chain might yield the corresponding cyclic ketones (2), and the preparation and irradiation of four representative benzoquinones and one naphthoquinone are now described.



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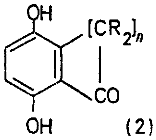

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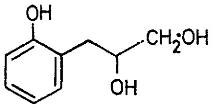
Preparation of Quinones.—The rather unstable formyl-1,4-benzoquinone (1; $n = 0$) was prepared by oxidation of 2,5-dihydroxybenzaldehyde with silver oxide.

1,4-Benzoquinonylacetaldehyde (1; R = H, $n = 1$) was obtained from *o*-allylphenyl acetate. Treatment of this with performic acid to give the glycol half formate, followed by alkaline hydrolysis of the two ester groupings, gave 3-*o*-hydroxyphenylpropane-1,2-diol (3) which with periodic acid afforded *o*-hydroxyphenylacetaldehyde as a relatively unstable oil which exists[7] in equilibrium with its cyclic hemiacetal, from which 5-hydroxybenzofuran is readily obtained by dehydration. Oxidation of the phenolic aldehyde with Frémy's salt gave only a trace of the required quinone, but treatment of the triol (3) with Frémy's salt readily gave 3-(1,4-benzoquinonyl)propane-1,2-diol, from which 1,4-benzoquinonylacetaldehyde was obtained in acceptable overall yield by treatment with periodic acid.



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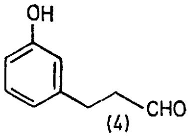

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The next higher homologue (1; R = H, $n = 2$) was synthesised from *m*-hydroxybenzaldehyde. Condensation[8] with cyanoacetic acid gave *m*-hydroxycinnamonitrile, which was reduced by Raney nickel alloy in aqueous formic acid directly to 3-*m*-hydroxyphenylpropionaldehyde (4), although this reagent has been reported[9] to reduce cinnamonitrile itself only as far as cinnamaldehyde. An alternative route to 3-*m*-hydroxyphenylpropionaldehyde involved Claisen–Schmidt condensation of *m*-hydroxybenzaldehyde with acetaldehyde to give *m*-hydroxycinnamaldehyde, followed by selective reduction[10] of the olefinic double bond over a soluble rhodium catalyst,[11] but this sequence was less satisfactory owing to low yields from the condensation reaction. Oxidation of the phenolic aldehyde (4) with Frémy's salt gave a poor yield of the quinone, and therefore the formyl group was protected by formation of its ethylene acetal; treatment with Frémy's salt gave a fair yield of 3-(1,4-benzoquinonyl)propionaldehyde ethylene acetal, from which the parent aldehyde (1; R = H, $n = 2$) was readily obtained by acidic hydrolysis.

2-(1,4-Benzoquinonyl)-2-methylpropionaldehyde (1; R = Me, $n = 1$) and the correspondingly substituted

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[1] Part V, J. M. Bruce and K. Dawes, preceding paper.

[2] H. Klinger and O. Standke, *Ber.*, 1891, **24**, 1340.

[3] J. M. Bruce and E. Cutts, *J. Chem. Soc.* (*C*), 1966, 449.

[4] J. M. Bruce, D. Creed, and J. N. Ellis, *J. Chem. Soc.* (*C*), 1967, 1486.

[5] G. O. Schenck and G. Koltzenburg, *Naturwiss.*, 1954, **41**, 452.

[6] J. M. Bruce and P. Knowles, *J. Chem. Soc.* (*C*), 1966, 1627.

[7] R. Aneja, S. K. Mukerjee, and T. R. Seshadri, *Tetrahedron*, 1958, **2**, 203.

[8] *Cf.* G. P. Schiemenz and H. Engelhard, *Chem. Ber.*, 1962, **95**, 967.

[9] T. van Es and B. Staskun, *J. Chem. Soc.*, 1965, 5775.

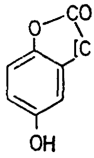
[10] F. H. Jardine and G. Wilkinson, *J. Chem. Soc.* (*C*), 1967, 270.

[11] J. W. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Comm.*, 1965, 131; A. J. Birch and K. A. M. Walker, *J. Chem. Soc.* (*C*), 1966, 1894.

1,4-naphthoquinone were prepared by treatment[12] of the unsubstituted quinones with *N*-2-methylpropenylmorpholine followed by oxidation of the adducts with aqueous iron(III) chloride.

Results of Irradiations.—Solutions of all the quinones in benzene were irradiated with visible light. Dark coloured tars were formed in every case.

Formyl-1,4-benzoquinone gave 2,5-dihydroxybenzaldehyde (11%) and 2,5-dihydroxybenzoic acid (37%) as the only pure products isolated. The fact that the next two higher homologues yield lactones (see later) suggests that the 2,5-dihydroxybenzoic acid may be formed from the strained lactone (5; $n = 0$), but direct evidence for this was not obtained. 1,4-Benzoquinonylacetaldehyde gave 5-hydroxycoumaran-2-one (5; $R = H$, $n = 1$) (24%). 3-(1,4-Benzoauinonyl)propionaldehyde gave 3-(2,5-dihydroxyphenyl)propionaldehyde (11%) in the form of its cyclic hemiacetal, and 3,4-dihydro-6-hydroxycoumarin (5; $R = H$, $n = 2$) (7%), identical with material synthesised from ethyl 3-(1,4-benzoquinonyl)-propionate[13] (6) by reduction to the quinol, acidic hydrolysis of the ester grouping, and thermal cyclisation.



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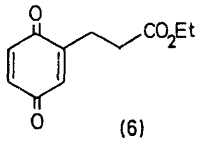

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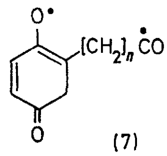

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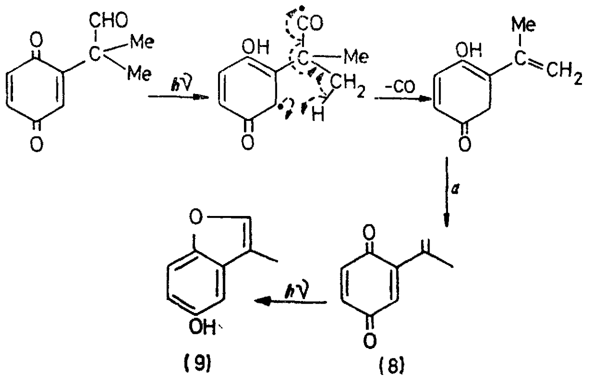
These products are not the ones to be expected by analogy with those obtained by purely intermolecular processes, in which the quinonoid and formyl portions are free, and their structures suggest that they may have been formed either *via* intermolecular abstraction of a formyl hydrogen atom followed by intramolecular scavenging of the resulting acyl radical at the adjacent oxygen of the still intact quinonoid moiety, or *via* intramolecular abstraction on to the quinone *nucleus* followed by cyclisation within the resulting diradical (7). The former route seems to be the more likely, and the direction of cyclisation could be a consequence of the smaller strain in the lactone (5) compared with that in the isomeric ketone (2).

The comparatively high yield of amorphous material formed from 1,4-benzoquinonylacetaldehyde may be due to the inherent instability of the quinone, and therefore two related systems in which the α-positions were blocked by methyl groups were used.

2-(1,4-Benzoquinonyl)-2-methylpropionaldehyde (1; $R = Me$, $n = 1$) gave 5-hydroxy-3,3-dimethylcoumaran-2-one (5; $R = Me$, $n = 1$) (6%), the cyclic hemiacetal of 2-(2,5-dihydroxyphenyl)-2-methylpropionaldehyde (43%), and 5-hydroxy-3-methylbenzofuran (9) (25%). The first two products are analogous to those obtained from 1,4-benzoquinonylacetaldehyde, but the benzofuran represents a system formed by a new type of light-induced reaction of a substituted 1,4-benzoquinone, and requires an overall loss of the elements of formaldehyde. A possible route is indicated in the Scheme. Abstraction of formyl hydrogen would be favoured, and would be expected to occur intramolecularly, as shown, since the acyl radical which would result from intermolecular abstraction is the probable precursor of the coumaranone (5; $R = Me$, $n = 1$) which, as described, is also formed. Decarbonylation would be facilitated by the stability of the resulting tertiary allylic radical, and additional driving force would be available from concomitant hydrogen transfer to give the isopropenyl group (both factors may be important since pivaloyl radicals can be efficiently scavenged[4] by 1,4-benzoquinone at the same temperature). Tautomerism and oxidation would then yield isopropenyl-1,4-benzoquinone (8), which is known[6] to cyclise in at least 60% yield to 5-hydroxy-3-methylbenzofuran when irradiated under similar conditions.



SCHEME

[a] Tautomerism followed by oxidation by ground-state quinone

An alternative mechanism would involve intramolecular abstraction from a methyl group (known[14] to occur with alkyl-1,4-benzoquinones) followed by β-elimination of a formyl radical to give the isopropenyl group. No attempt has been made to distinguish between these and other possible mechanisms.

2-Methyl-2-(1,4-naphthoquinon-2-yl)propionaldehyde behaved similarly to the corresponding benzoquinone in that it gave 5-hydroxy-3-methylnaphtho[1,2-*b*]-furan (26%) by loss of the elements of formaldehyde, but differently in yielding a rather unstable dimer (23%) to which structure (10) is tentatively assigned on the basis of its spectroscopic properties (see Experimental section); in solution it exists in equilibrium with the corresponding phenolic aldehyde resulting from ring-opening of the hemiacetal group. The dimer (10) may be formed by intermolecular scavenging of a derived acyl radical at the free, although appreciably hindered, 3-position of another molecule of the

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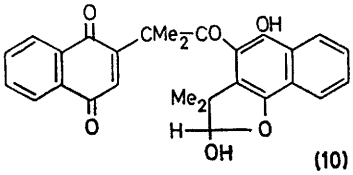
[12] K. Ley and R. Nast, *Angew. Chem.*, 1967, **79**, 150.

[13] J. M. Bruce and K. Dawes, unpublished work.

[14] C. M. Orlando, H. Mark, A. K. Bose, and M. S. Manhas, *J. Amer. Chem. Soc.*, 1967, **89**, 6527; *J. Org. Chem.*, 1968, **33**, 2512.

quinone to give, eventually (see ref. 3 for an analogous mechanism), the corresponding quinol grouping from which the cyclic hemiacetal unit is derived.



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EXPERIMENTAL

Irradiations were carried out as described previously.[1,3,4] Solvents were removed under reduced pressure, usually below 60°, and the products were isolated by chromatography (t.l.c. where necessary) and/or fractional sublimation. I.r. spectra were measured for Nujol mulls unless stated otherwise, and u.v. spectra for solutions in ethanol. ^{1}H N.m.r. spectral bands are singlets unless otherwise indicated (J in c./sec.). Resonances assigned to OH groups disappeared on addition of D_2O. Molecular weights were determined mass spectrometrically.

Preparation of Materials

Formyl-1,4-*benzoquinone*.— 2,5-Dihydroxybenzaldehyde (0·2 g.) in dry benzene (6 c.c.) was added to silver oxide (1·6 g.) and anhydrous sodium sulphate (1 g.) in dry benzene (7 c.c.), and the mixture was shaken at room temperature for 3 hr., then filtered through Woelm polyamide (3 g.) with benzene as eluant. The solvent was removed at 20°, and the residue was sublimed at 90—100°/10 mm. to give the unstable *quinone* (0·065 g., 32%) as orange needles, m.p. 90—94° (Found: M, 136·01555. $C_7H_4O_3$ requires M, 136·01604), $\nu_{max.}$ 3035m, 1707s, 1658br,s, and 1610s cm.$^{-1}$, τ[8% in $(CD_3)_2CO$] −0·41 (CHO) and 2·7—3·1 (m, quinonoid H_3).

3-o-*Hydroxyphenylpropane*-1,2-*diol*.—*o*-Allylphenyl acetate [15] (24·5 g.) was added [16] dropwise during 20 min. to a mixture of hydrogen peroxide (100 vol; 25 c.c.) and formic acid (98%; 100 c.c.) maintained at 40—45°. The temperature was held at 40° for 1 hr. more, and the mixture was then kept overnight at room temperature. The solvent was removed, and the residue was heated on a steam-bath for 30 min. with a solution of sodium hydroxide (10 g.) in water (150 c.c.). The solution was cooled, acidified (HCl) to pH 1, and then extracted with ethyl acetate (6 × 100 c.c.); the combined extracts were washed with saturated aqueous sodium hydrogen carbonate (3 × 100 c.c.), and then dried ($MgSO_4$). Removal of the solvent and distillation of the residue gave 3-*o*-hydroxyphenylpropane-1,2-diol (16·6 g., 68%) as a pale yellow viscous oil, b.p. 164—166°/10^{-1} mm. (lit.,[17] 175°/1·2 mm.) (Found: C, 63·6; H, 6·9%. Calc. for $C_9H_{12}O_3$: C, 64·3; H, 7·1%), $\nu_{max.}$ (film) 3300br,s, 2930m, 1585m, and 753s cm.$^{-1}$, τ[10% in $(CD_3)_2CO$] 1·3 (ArOH), 2·8—3·4 (m, ArH_4), 6·1 (m, –CH–), 6·5 (d, J 5, terminal CH_2), 6·9 (AlkOH), and 7·2 (*d*, J 5, benzylic CH_2).

o-*Hydroxyphenylacetaldehyde*.—Periodic acid (4·33 g. of aq. 50% $HIO_4,2H_2O$) was added at room temperature to 3-*o*-hydroxyphenylpropane-1,2-diol (1·31 g.) in water (100 c.c.), and the mixture was shaken for 1 min. and then extracted with benzene (3 × 25 c.c.). The combined extracts were washed with water (100 c.c.), then with saturated aqueous sodium hydrogen carbonate (2 × 10 c.c.), and dried ($MgSO_4$). Removal of the solvent and distillation (bulb-to-bulb) of the residue at 75—80° (bath)/10^{-2} mm. (lit.,[18] 90°/' vacuum ') gave the aldehyde (0·75 g., 71%) as an oil, $\nu_{max.}$ (film) 3420br,s, 1718s, 1598s, and 753s cm.$^{-1}$, τ(8% in CCl_4) 0·50 (t, J 2·5, CHO), 2·8—3·5 (m, ArH_4), 4·13 (q, α-H of hemiacetal form, *i.e.* H_X of ABX system, J_{AX} 3, J_{BX} 6), 5·56 (OH), 6·50 (d, J 2·5, CH_2 of aldehyde form), and 6·5—7·4 (octet, CH_2 of hemiacetal form, *i.e.* H_A and H_B, J_{AB} 17). The 2,4-*dinitrophenylhydrazone*, orange crystals, m.p. 165—168° (Found: C, 52·8; H, 3·6; N, 17·0. $C_{14}H_{12}N_4O_5$ requires C, 53·2; H, 3·8; N, 17·7%), had $\nu_{max.}$ 3500m, 3300m, 1625s, and 1590m cm.$^{-1}$, τ(10% in $CDCl_3$) −0·1 (NH, removed by D_2O), 1·1 (d, J_m 3, H-5′), 1·5 (OH), 1·6 (q, J_o 10, J_m 3, H-3′), 2·0 (t, J 6, –CH=), 2·05 (d, J_o 10, H-2′), 2·6—3·3 (m, 2-, 3-, 4-, and 5-H), and 6·28 (d, J 6, CH_2).

3-(1,4-*Benzoquinonyl*)*propane*-1,2-*diol*.— 3-*o*-Hydroxyphenylpropane-1,2-diol (0·93 g.) in water (10 c.c.) was added to a solution of potassium dihydrogen phosphate (3·8 g.) in water (150 c.c.), the mixture was vigorously stirred, and Frémy's salt (5·0 g.) was added. Vigorous stirring was continued for 1 hr., and the solution was then saturated with ammonium sulphate and extracted with ether (8 × 50 c.c.). The combined extracts were dried ($MgSO_4$), the solvent was removed, and the residue was filtered through Woelm polyamide (10 g.) with benzene as eluant. Removal of the benzene at 20° left the *quinone* (0·77 g., 79%) as an orange oil which rapidly darkened in air; it formed hexagonal prisms (from benzene), m.p. 81—82° (Found: C, 59·3; H, 5·5. $C_9H_{10}O_4$ requires C, 59·3; H, 5·5%), $\nu_{max.}$ 3330s, 3250s, 1657vs, and 1600w cm.$^{-1}$, $\lambda_{max.}$ 245, 300, 335, and 435 nm.(ε 11,000, 780, 400, and 50), τ[10% in $(CD_3)_2CO$] 3·3—3·5 (m, quinonoid H_3), 6·0—6·6 (m, H-2 and OH), 6·59 (d, J 5, terminal CH_2), 7·15 (OH), and 7·48 [octet, H_A and H_B of ABX system (H_X≡H-2), J_{AB} 14·5, J_{AX} 5·5, J_{BX} 8, in-chain CH_2].

1,4-*Benzoquinonylacetaldehyde*.—Periodic acid (0·49 g. of aq. $HIO_4,2H_2O$) was added at room temperature to a solution of the quinone just described (0·168 g.) in water (20 c,c,), and the mixture was shaken and extracted at 5 min. intervals with benzene (10 c.c.) during the course of 1 hr. The combined extracts were washed with water (3 × 20 c.c.) and dried ($MgSO_4$), and the solvent was removed at 20° to give a brown oil which was filtered through Woelm polyamide (2 g.) with benzene–pentane (1 : 1) as eluant. Removal of the solvent from the eluate at 20° left the *quinone* (0·08 g., 58%) as an orange oil which rapidly darkened in air (Found: M, 150·03151. $C_8H_6O_3$ requires M, 150·03169), $\nu_{max.}$ (CCl_4) 2880w, 1733s, 1665vs, 1635sh, and 1595s cm.$^{-1}$, τ(4% in $CDCl_3$) 0·28 (t, J *ca.* 1, CHO), 3·2—3·4 (m, quinonoid H_3), and 6·47br (CH_2).

m-*Hydroxycinnamonitrile*.—Condensation of *m*-hydroxybenzaldehyde (12·4 g.) with cyanoacetic acid (9·4 g.) by a procedure analogous to that described by Patterson [19] gave *trans*-*m*-hydroxycinnamonitrile (7·96 g., 59%) which,

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[15] R. Adams and R. E. Rindfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 648.

[16] A. Roebuck and H. Adkins, *Org. Synth.*, 1948, **28**, 35.

[17] B. I. Nurunnabi, *Pakistan J. Sci. Ind. Res.*, 1960, **3**, 108 (*Chem. Abs.*, 1961, **55**, 25903e).

[18] I. J. Rinkes, *Rec. Trav. chim.*, 1926, **45**, 819.

[19] J. M. Patterson, *Org. Synth.*, 1960, **40**, 46.

from aqueous ethanol, formed buff crystals, m.p. 147—149° (lit.,[20] 148°), $\nu_{max.}$ 3350br,m, 3290m, 3060w, 2210s, 1617s, and 1582 cm.$^{-1}$, $\lambda_{max.}$ 236, 278, and 321 nm. (ε 10,700, 14,300, and 3900), τ[16% in $(CD_3)_2CO$] 1·4 (OH), 2·44 (d, J_{trans} 17, Ar–CH=), 2·5—3·1 (m, ArH_4), and 3·80 (J_{trans} 17, =CH·CN).

m-*Hydroxycinnamaldehyde*.—Freshly distilled acetaldehyde (4 c.c.) was added to a solution of *m*-hydroxybenzaldehyde (7·62 g.) and sodium hydroxide (2·5 g.) in water (150 c.c.), and the mixture was stirred overnight at room temperature, extracted with ethyl acetate (3 × 40 c.c.), acidified with concentrated hydrochloric acid and again extracted with ethyl acetate (3 × 40 c.c.). The latter extracts were combined, washed successively with water (15 c.c.) and saturated aqueous sodium hydrogen carbonate (3 × 15 c.c.), and dried ($MgSO_4$). Removal of the solvent and chromatography of the residue on silica gel (200 g.) with 5% ether–benzene as eluant gave *m*-hydroxybenzaldehyde (3·2 g.), and then a mixture of *m*-hydroxybenzaldehyde (0·79 g.) and trans-m-*hydroxycinnamaldehyde* (0·92 g., 11%), from which the latter was isolated by fractional sublimation (85—105°/5 × 10^{-2} mm.) as pale yellow crystals, m.p. 116—119° (Found: C, 72·8; H, 5·0%; *M*, 148. $C_9H_8O_2$ requires C, 73·0; H, 5·4%; *M*, 148), $\nu_{max.}$ 3190s, 1655vs, 1624s, and 1580s cm.$^{-1}$, $\lambda_{max.}$ 240 and 290 nm. (ε 7100 and 16,000), τ[10% in $(CD_3)_2CO$] 0·6 (d, J' 7, CHO), 2·57 (d, J_{trans} 15, Ar–CH=), 2·8—3·3 (m, ArH_4), 3·48 (q, J_{trans} 15, J' 7, =CH–), and 6·2—7·4 (OH).

3-m-*Hydroxyphenylpropionaldehyde*.—(*a*) A mixture of *m*-hydroxycinnamonitrile (1 g.), Raney nickel–aluminium alloy (1 g.), and 75% aqueous formic acid (15 c.c.) was refluxed for 1 hr., cooled, and filtered; the filtrate was diluted with water (30 c.c.) and extracted with ethyl acetate (2 × 15 c.c.). The combined extracts were washed with water (2 × 10 c.c.), then with saturated aqueous potassium hydrogen carbonate (2 × 10 c.c.), and dried ($MgSO_4$). Removal of the solvent, and chromatography of the residue on silica gel (50 g.) with 5% ether–benzene as eluant, followed by distillation (bulb-to-bulb) at 130—135° (bath)/5 × 10^{-2} mm., gave the aldehyde (0·45 g., 43%), identical with material prepared as follows.

(*b*) A solution of tristriphenylphosphoniumrhodium chloride [11] (0·093 g.) in benzene (30 c.c.) was shaken under hydrogen for 1 hr. *m*-Hydroxycinnamaldehyde (0·20 g.) in ethyl acetate (7 c.c.) was then added, and shaking under hydrogen was continued for a further 2 hr. The solvent was removed, the residue was extracted with ether, and the material extracted was distilled (bulb-to-bulb) at 130—135° (bath)/5 × 10^{-2} mm. to give 3-*m*-hydroxyphenylpropionaldehyde (0·12 g., 59%) as a colourless oil, $\nu_{max.}$ (film) 3490s, 3040m, 2980—2820m, 2720m, 1720vs, 1598s, and 1587vs cm.$^{-1}$, $\lambda_{max.}$ 218, 277, and 284 nm. (ε 5100, 1900, and 1700), τ(12% in $CDCl_3$) 0·40 (t, J 1, CHO), 2·8—3·5 (m, ArH_4), 3·06 (OH), and 7·1—7·6 (m, CH_2·CH_2). The 2,4-*dinitrophenylhydrazone* had m.p. 168—170° (Found: C, 54·5; H, 4·2; N, 16·7. $C_{15}H_{14}N_4O_5$ requires C, 54·5; H, 4·2; N, 16·9%), $\nu_{max.}$ 3470br,s, 3300s, 3105m, 1617s, 1593s, and 1583s cm.$^{-1}$, τ[8% in $(CD_3)_2SO$] – 1·08 (NH, removed by D_2O), 1·24 (d, J_m 3, H-5′), 1·77 (q, J_o 10, J_m 3, H-3′), 2·11 (t, J 5, CH=N), 2·34 (d, J_o 10, H-2′), 2·8—3·5 (m, ArH), and 7·1—7·5 (m, CH_2·CH_2).

3-(1,4-*Benzoquinonyl*)*propionaldehyde Ethylene Acetal*.—A mixture of 3-*m*-hydroxyphenylpropionaldehyde (0·422 g.), ethylene glycol (0·8 c.c.), toluene-*p*-sulphonic acid (0·01 g.), and benzene (50 c.c.) was refluxed (Dean–Stark) for 2 hr., cooled, diluted with ether (10 c.c.), and then washed successively with saturated aqueous sodium hydrogen carbonate (2 × 20 c.c.), saturated aqueous sodium hydrogen sulphite (2 × 10 c.c.), and water (10 c.c.), and then dried ($MgSO_4$). Removal of the solvent left a colourless oil (0·392 g.) which was dissolved in methanol (10 c.c.) and added to a mixture of potassium dihydrogen phosphate (1·1 g.) and Frémy's salt (1·1 g.) in water (120 c.c.). The mixture was stirred for 2 hr. and extracted with ether (4 × 30 c.c.), and the combined extracts were washed with water (2 × 20 c.c.) and dried ($MgSO_4$). Removal of the solvent and crystallisation of the residue from benzene–light petroleum (b.p. 60—80°) gave the *quinone* 0·241 g., 41%) as yellow crystals, m.p. 49—51° (Found: C, 63·6; H, 6·0%; *M*, 208. $C_{11}H_{12}O_4$ requires C, 63·4; H, 5·8%; *M*, 208), $\nu_{max.}$ 3060w, 1670sh, 1659vs, and 1598s cm.$^{-1}$, $\lambda_{max.}$ 246, 310, and 425 nm. (ε 18,100, 620, and 35), τ(12% in $CDCl_3$) 3·2—3·5 (m, quinonoid H_3), 5·1 (t, –O–CH–O–), 6·0—6·2 (m, CH_2·CH_2 of dioxolan ring), 7·3—7·6 (m, 'allylic' CH_2), and 7·9—8·4 (m, remaining CH_2).

3-(1,4-*Benzoquinonyl*)*propionaldehyde*.— 6N-Sulphuric acid (10 c.c.) was added to a solution of the acetal just described (0·617 g.) in tetrahydrofuran (8 c.c.), and the mixture was stirred at room temperature for 2 hr. and then extracted with ether (4 × 5 c.c.). The combined extracts were washed with water (4 × 3 c.c.) and dried ($MgSO_4$), and the solvent was removed. Distillation (bulb-to-bulb) of the residue at 100—105° (bath)/10^{-1} mm. gave the *quinone* (0·373 g., 76%) as an orange oil (Found: *M*, 164·05711. $C_9H_8O_3$ requires *M*, 164·04734), $\nu_{max.}$ (film) 3070w, 3000—2800m, 2730w, 1720s, 1658vs, and 1600s cm.$^{-1}$, $\lambda_{max.}$ 247, 305, 320sh, and 428 nm. (ε 21,400, 780, 750, and 25), τ(6% in $CDCl_3$) 0·21 (CHO), 3·2—3·4 (m, quinonoid H_3), and 7·2 (CH_2·CH_2).

2-*Methyl*-2-(1,4-*naphthoquinon*-2-*yl*)*propionaldehyde*.—This had m.p. 162—164° (lit.,[12] 160—163°), $\nu_{max.}$ 2715w, 1726vs, 1662vs, 1608s, and 1591s cm.$^{-1}$, $\lambda_{max.}$ 245, 251, 262sh, 333, and 420sh nm. (ε 23,400, 22,000, 12,000, 3480, and 40), τ(10% in $CDCl_3$) 0·29 (CHO), 1·9—2·1 (m, H-6′ + H-7′), 2·1—2·4 (m, H-5′ + H-8′), 3·09 (H-3′), and 8·58 (Me_2).

2-(1,4-*Benzoquinonyl*)-2-*methylpropionaldehyde*.—5-Hydroxy-3,3-dimethyl-2-morpholinocoumaran was prepared (*cf.* ref. 12) from 1,4-benzoquinone and *N*-2-methylpropenylmorpholine; m.p. 188—191° (lit.,[21] 187—191°). A suspension of this compound (4 g.) in water (20 c.c.) and benzene (20 c.c.) was added dropwise during 15 min. to a vigorously shaken solution of iron(III) chloride (8·64 g. $FeCl_3,6H_2O$) in water (12 c.c.). The benzene layer was separated, the aqueous phase was extracted with benzene (2 × 10 c.c.), and the combined extracts were washed with water (3 × 10 c.c.) and saturated aqueous sodium chloride (10 c.c.), and then dried ($MgSO_4$). Removal of the solvent, elution of the residue through Woelm polyamide (10 g.) with benzene–pentane (1 : 1), and then crystallisation from hexane–ether gave the *quinone* (1·98 g., 69%) as yellow crystals, m.p. 51·5—53° (Found: C, 67·2; H, 6·0%; *M*, 178. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%; *M*, 178), $\nu_{max.}$ 1725s, 1655sh, 1645vs, and 1595s cm.$^{-1}$, $\lambda_{max.}$ 246, 325sh, and 430 nm. (ε 18,500, 600, and 30), τ(8% in $CDCl_3$) 0·38 (CHO), 3·2—3·3 (m, quinonoid H_3), and 8·65 (Me_2).

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Formyl-1,4-*benzoquinone*.—The quinone (0·072 g.) in benzene (25 c.c.) was irradiated for 1 week, giving a dark solution and a brown precipitate, which was collected. The material obtained by removal of the benzene was sublimed at 85—90°/5 × 10^{-4} mm. to give 2,5-dihydroxybenzaldehyde (0·008 g., 11%), m.p. 99—100°, identical (mixed m.p. and i.r. spectrum) with authentic material. Sublimation of the precipitate gave 2,5-dihydroxybenzoic acid (0·028 g., 37%), m.p. 200—204°, similarly identical with authentic material.

1,4-*Benzoquinonylacetaldehyde*.—The quinone (0·230 g.) in benzene (30 c.c.) was irradiated for 3 weeks. The colour of the solution changed from orange to red, and a finely divided black precipitate separated. The solvent was removed from the mother liquor, and the residue was chromatographed on silica gel (10 g.) with 5% ether–benzene as eluant. Sublimation of the eluted material at 110—115°/5 × 10^{-2} mm. gave 5-hydroxycoumaran-2-one (0·055 g., 24%), m.p. 190—192° (lit.,[22] 189—190°) (Found: C, 64·2; H, 3·8%; *M*, 150. Calc. for $C_8H_6O_3$: C, 64·0; H, 4·0%; *M*, 150), $\nu_{max.}$ 3335s, 1762vs, 1606m, and 1150—1080s cm.$^{-1}$, τ[6% in $(CD_3)_2CO$] 1·7br (OH), 2·9—3·3 (m, ArH_3), and 6·21 (CH_2).

3-(1,4-*Benzoquinonyl*)*propionaldehyde*.— Irradiation of the quinone (0·373 g.) in benzene (25 c.c.) caused the initial yellow colour of the solution to fade and a brown solid was precipitated. The total product was separated by preparative t.l.c. on silica gel with 10% ether–benzene eluant into the following compounds.

(*a*) 3-(2,5-Dihydroxyphenyl)propionaldehyde (0·042 g., 11%), white crystals from benzene, m.p. 104—106° (Found: C, 65·0; H, 6·2%; *M*, 166. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%; *M*, 166). It existed as the cyclic hemiacetal, $\nu_{max.}$ 3350—3200s and 1660m cm.$^{-1}$, τ[5% in $(CD_3)_2CO$] 2·41 (OH), 3·48 (ArH_3), 4·35 (d, *J* 4, OH), 4·56 (m, changing to t with *J* 4 after addition of D_2O, –O–CH–O–), 6·9—7·6 (m, Ar–CH_2), and 8·0—8·3 (m, remaining CH_2). Treatment with silver oxide in ether regenerated the starting quinone.

(*b*) 3,4-Dihydro-6-hydroxycoumarin (0·028 g., 7%), white crystals, m.p. 160—162° (from hexane–acetone), identical (mixed m.p. and i.r. spectrum) with material prepared as follows. A solution of ethyl 3-(1,4-benzoquinonyl)propionate[13] (0·100 g.) in a mixture of 1,2-dimethoxyethane (3 c.c.) and water (2 c.c.) was treated with concentrated hydrochloric acid (0·5 c.c.) followed by zinc dust (0·200 g.). The suspension was stirred for 5 min. then filtered, and the filtrate was refluxed (steam-bath) for 4 hr., cooled, diluted with water (5 c.c.), and extracted with ether. The combined extracts were washed with water (3 × 2 c.c.), and dried ($MgSO_4$). Removal of the solvent, and sublimation of the residue at 125—130°/10^{-1} mm. gave 3,4-dihydro-6-hydroxycoumarin (0·032 g., 41%) as white crystals, from hexane–acetone, m.p. 160—162° (lit.,[23] 163°) (Found: C, 65·6; H, 4·5%; *M*, 164. Calc. for $C_9H_8O_3$: C, 65·8; H, 4·9%; *M*, 164), $\nu_{max.}$ 3290s, 1736vs, and 1598s cm.$^{-1}$.

2-(1,4-*Benzoquinonyl*)-2-*methylpropionaldehyde*.— The quinone (0·500 g.) in benzene (30 c.c.) was irradiated for 1 week, the colour changing from yellow to light brown. The solvent was removed, and the residue was subjected to preparative t.l.c. on silica gel with 10% ether–benzene as eluant to give the following products.

(a) 5-*Hydroxy*-3,3-*dimethylcoumaran*-2-*one* (0·030 g., 6%), white crystals by sublimation at 100—105°/5 × 10^{-5} mm., m.p. 139—141° (Found: C, 66·9; H, 5·6%; *M*, 178. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%; *M*, 178), $\nu_{max.}$ 3370s, 1763vs, and 1608m cm.$^{-1}$, τ(2% in $CDCl_3$) 3·05 (d, J_o 10, H-7), 3·2—3·4 (m, H-4 and H-6), 4·42 (OH), and 8·53 (Me_2).

(b) The *cyclic hemiacetal* of 2-(2,5-dihydroxyphenyl)-2-methylpropionaldehyde (0·215 g., 43%), an oil (Found: *M*, 180·07942. $C_{10}H_{12}O_2$ requires *M*, 180·07864), $\nu_{max.}$ (film) 3500—3300vs, 2970s, and 1610m cm.$^{-1}$. Treatment with silver oxide in benzene regenerated the starting quinone.

(c) 5-Hydroxy-3-methylbenzofuran (0·104 g., 25%), crystals, from light petroleum (b.p. 60—80°), m.p. 90—91°, identical (mixed m.p. and i.r. spectrum) with authentic[6] material.

2-*Methyl*-2(1,4-*naphthoquinon*-2-*yl*)*propionaldehyde*.— Irradiation of the quinone (0·312 g.) in benzene (15 c.c.) for 4 days gave a light brown solution from which preparative t.l.c. on silica gel with 10% ether–benzene as eluant gave the following products.

(*a*) 5-Hydroxy-3-methylnaphtho[1,2-*b*]furan (0·071 g., 26%) as off-white crystals, m.p. 153—156° (lit.,[24] 145—146°) (Found: C, 78·4; H, 5·2%; *M*, 198. Calc. for $C_{13}H_{10}O_2$: C, 78·8; H, 5·1%; *M*, 198), $\nu_{max.}$ 3500s, 1640w, 1603m, 1588m, and 1570m cm.$^{-1}$, $\lambda_{max.}$ 260, 300, 314, 328, 344, 367, and 388 nm. (ε 40,000, 3260, 3200, 3150, 3060, 460, and 550), τ[8% in $(CD_3)_2CO$] 1·26 (OH), 1·6—1·9 (m, H-7 and H-8), 2·3—2·6 (m, H-2, H-6, and H-9), 2·92 (H-4), and 7·76 (d, *J* 1, Me).

(*b*) 1-(2,3-*Dihydro*-2,5-*dihydroxy*-3,3-*dimethylnaphtho*-[1,2-*b*]*furan*-4-*yl*)-2-*methyl*-2-(1,4-*naphthoquinon*-2-*yl*)-1-*oxopropanealdehyde* (?) (0·072 g., 23%) (Found: *M*, 456·15728. $C_{28}H_{24}O_6$ requires *M*, 456·15759), $\nu_{max.}$ ($CHCl_3$) 3610vs, 3440br,m, 1719s (CHO of aldehyde form), 1694vs, and 1665vs cm.$^{-1}$, $\lambda_{max.}$ 246, 250sh, and 263sh nm. (ε 38,000 36,000, and 8000), τ(3% in $CDCl_3$) 0·37 (weak, CHO of aldehyde form), 1·9—2·8 (m, ArH_8 and OH), 3·44 (H-3 of quinonoid ring), 4·39 (–O–CH–O–), and 8·6—8·9 (m, Me_4); absorption due to the hydroxy-proton of the hemiacetal was not detected, but it may have been very broad. The u.v. spectrum showed similar features to those of the starting quinone.

We thank the S.R.C. for a research studentship (to D. C.).

[9/1213 *Received, July* 17*th*, 1969]

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