Light-induced and Related Reactions of Quinones. Part X.[1] Further Studies with Hydroxymethyl-, Vinyl-, and (2-Ethoxycarbonylethyl)-1,4-benzoquinones

By **J. Malcolm Bruce,* Arshad-ul-haq Chaudhry,** and (in part) **Keith Dawes,** Department of Chemistry, The University, Manchester M13 9PL

Irradiation of hydroxymethyl-1,4-benzoquinone in [$^2H_6$]benzene gave ([$^2H_5$]phenoxymethyl)-1,4-benzoquinone. with no incorporation of deuterium into the quinonoid nucleus. Irradiation of 2-hydroxymethyl-5- and 2-hydroxymethyl-6-methyl-1,4-benzoquinones in benzene gave the corresponding methyl homologues of phenoxymethyl-1,4-benzoquinone, but 3-methyl-2-phenoxymethyl-1,4-benzoquinone was not formed from 2-hydroxymethyl-3-methyl-1,4-benzoquinone.

Irradiation of [3,3,3-$^2H_3$]-2-(1,4-benzoquinonyl)propene in benzene gave 3-[$^2H_3$]methyl-5-hydroxybenzofuran with neither loss nor scrambling of the label. 1-(1,4-Benzoquinonyl)-1-phenylethylene behaved analogously, but vinyl-1,4-benzoquinone afforded only amorphous material.

Diethyl (1,4-benzoquinonylmethyl)malonate gave ethyl 6-hydroxycoumarin-3-carboxylate when irradiated in benzene containing a trace of oxygen.

The mechanistic significance of these results is discussed.

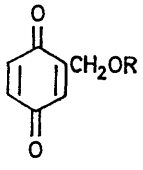
IRRADIATION of a benzene solution of hydroxymethyl-1,4-benzoquinone (1; R = H) with visible light gives,[2] in addition to the expected 2,5-dihydroxybenzaldehyde, a 10% yield of phenoxymethyl-1,4-benzoquinone (1; R = Ph), and it has been suggested [2,3] that a hydrogen atom is intramolecularly abstracted from the hydroxy-group by the excited quinonoid system to give an alkoxyl radical which adds to the solvent, re-aromatisation then occurring *via* intramolecular hydrogen transfer [as (2)]. Support for the formation of alkoxyl radicals under these conditions has been obtained [4] from studies with other hydroxyalkyl-1,4-benzoquinones, but the results do not bear on the mechanism of the re-aromatisation step. Direct evidence obtained by using [$^2H_6$]-benzene is now presented, together with data on the effect of a methyl group attached severally to the 2-, 5-, and 6-positions of hydroxymethyl-1,4-benzoquinone.

[1] Part IX, J. M. Bruce and A.-u.-h. Chaudhry, *J.C.S. Perkin I*, 1972, 372.

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

[3] J. M. Bruce in 'The Chemistry of the Quinonoid Compounds,' ed. S. Patai, Wiley, London and New York, in the press, ch. 9.

Visible-light irradiation of isopropenyl-1,4-benzoquinone (3; R = Me) in benzene gives a 60% yield of 5-hydroxy-3-methylbenzofuran, and mechanisms involving abstraction of hydrogen from the methyl group,



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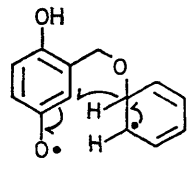


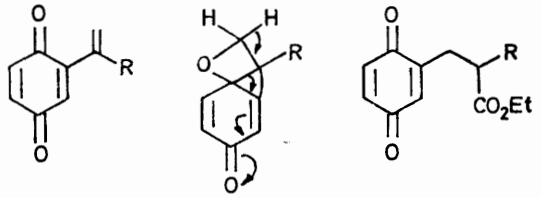
(2)

or rearrangement [as (4; R = Me)] of a spiro-oxetan were considered.[2,3,5] Neither *cis*- nor *trans*-styryl-1,4-benzoquinone gives a benzofuran,[5] although spiro-oxetan [as (4; R = Ph)] formation does not appear to be precluded. Further evidence, obtained by irradiation of the labelled quinone (3; R = CD_3), the phenylvinyl-

[4] J. M. Bruce, D. Creed, and K. Dawes, *J. Chem. Soc.* (*C*), 1971, 2244.

[5] J. M. Bruce, D. Creed, and K. Dawes, *J. Chem. Soc.* (*C*), 1971, 3749.

quinone (3; R = Ph), and vinyl-1,4-benzoquinone (3; R = H) is now presented.



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Diethyl (1,4-benzoquinonylmethyl)malonate (5; R = CO_2Et) is stable to irradiation with visible light in degassed benzene.[5] It is now shown that it affords ethyl 6-hydroxycoumarin-3-carboxylate when a trace of oxygen is present.

Preparation of Quinones.—Hydroxymethyl-1,4-benzoquinone was obtained from 2,5-dihydroxybenzaldehyde as previously described,[2] and by oxidation of *o*-hydroxymethylphenol (saligenin) with Frémy's salt. 2-Hydroxymethyl-6-methyl-1,4-benzoquinone was prepared analogously from 2-hydroxy-3-methylbenzyl alcohol, obtained by borohydride reduction of the corresponding aldehyde resulting from Reimer–Tiemann formylation of *o*-cresol. A similar route was used for the preparation of 2-hydroxymethyl-3- and 2-hydroxymethyl-5-methyl-1,4-benzoquinones, the required 2-hydroxy-6-methyl- and 2-hydroxy-4-methyl-benzaldehydes being obtained from *m*-cresol by the Reimer–Tiemann reaction, and separated by preparative g.l.c.; selective precipitation [6] of the calcium salts afforded only partial separation. It has been reported that treatment of *m*-cresol with hexamethylenetetramine and boric acid in glycerol,[7] or with ethylmagnesium bromide followed by triethyl orthoformate,[8] gives 2-hydroxy-4-methylbenzaldehyde exclusively, but we found that these methods gave, respectively, 1 : 1 and 3 : 2 mixtures of the 4- and 6-methyl isomers.

Phenoxymethyl-1,4-benzoquinone was required as a reference compound, and an alternative to the photochemical route [2] to it was oxidation of *o*-phenoxymethylphenol with Frémy's salt. However, although *o*-hydroxymethylphenol yields the corresponding *o*-alkoxymethylphenols when it is heated with alcohols,[9] the major product (up to 92%) obtained by heating it with phenol was 2,2′-dihydroxydiphenylmethane, possibly resulting from thermal rearrangement [10] of the *o*-phenoxymethylphenol formed initially.

Isopropenyl-1,4-benzoquinone [2] was conveniently obtained by oxidation with Frémy's salt of *m*-isopropenylphenol, prepared from *m*-(1-hydroxy-1-methylethyl)-phenol [2] by dehydration with acetic anhydride followed by alkaline hydrolysis to liberate the phenol from its acetate.

[3,3,3-$^2H_3$]-2-(1,4-Benzoquinonyl)propene (3; R = CD_3) was prepared from *m*-(tetrahydropyran-2-yloxy)-acetophenone [4] by, successively, repeated exchange with deuterium oxide catalysed by lithium deuteroxide, treatment with methylenetriphenylphosphorane in tetrahydrofuran (conditions [11] which avoid scrambling of the label), removal of the protecting group by hydrolysis with dilute acid, and oxidation of the resulting phenol with Frémy's salt.

The very unstable vinyl-1,4-benzoquinone was prepared by oxidation of 2,5-dihydroxystyrene (vinylhydroquinone [12]) with silver oxide.

Ethyl 3-(1,4-benzoquinonyl)propanoate (5; R = H) and diethyl (1,4-benzoquinonylmethyl)malonate (5; R = CO_2Et) were prepared as previously described.[5] Condensation [13] of *m*-hydroxybenzaldehyde with ethyl acetoacetate followed by, successively, catalytic hydrogenation of the olefinic double bond and oxidation with Frémy's salt gave the corresponding quinone (5; R = Ac). An attempt to prepare the nitrile (5; R = CN) by an analogous route failed at the oxidation stage, only black tar being obtained.

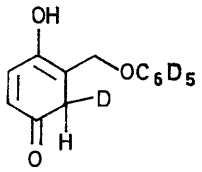
RESULTS AND DISCUSSION

Unless stated otherwise, degassed solutions of the quinones in dry benzene at 15° were irradiated with visible light. Yields are of purified products; tars were formed during all the irradiations.

Hydroxymethyl-1,4-benzoquinone (1; R = H) gave phenoxymethyl-1,4-benzoquinone (1; R = Ph) as previously described,[2] thus confirming the reproducibility of the reaction. When [$^2H_6$]benzene was used as solvent, the corresponding product (6% yield) was ([$^2H_5$]phenoxymethyl)-1,4-benzoquinone, this structure being confirmed by its mass spectrum [*m/e* 219 (no peak at 220 which would arise from a hexadeuterio-compound), and fragmentation pattern (see below)] and ^1H n.m.r. spectrum [ratio of quinonoid to methylene protons 3 : 2, methylene resonance a doublet (*J* 2 Hz) due to coupling [1,2] with quinonoid H-3]. If an intermediate such as (2) were involved, intramolecular transfer of deuterium would give (6), and conversion of this, *via* enolisation and oxidation,[2] into the corresponding quinone would involve appreciable retention of deuterium at C-3. The absence of label here suggests that an alternative mechanism operates, and this may involve intermolecular dehydrogenation of the cyclohexadienyl system [as (2)] by unchanged quinone; [14] the formation [2] of 2,5-dihydroxybenzyl alcohol would still be accounted for.

[6] P. Chuit and F. Bolsing, *Bull. Soc. chim. France*, 1906, **35**, 129.
[7] J. C. Duff, *J. Chem. Soc.*, 1941, 547.
[8] G. Casnati, M. Crisafulli, and A. Ricca, *Tetrahedron Letters*, 1965, 243.
[9] J. De Jonge and B. H. Bibo, *Rec. Trav. chim.*, 1955, **74**, 1448.
[10] H. J. Shine, 'Aromatic Rearrangements,' Elsevier, Amsterdam, 1967, ch. 2, p. 82, and references therein.
[11] *Cf.* T. B. Malloy, R. M. Hedges, and F. Fisher, *J. Org. Chem.*, 1970, **35**, 4256.
[12] I. H. Updegraff and H. G. Cassidy, *J. Amer. Chem. Soc.*, 1949, **71**, 407.
[13] R. K. Pandya and K. C. Pandya, *J. Indian Chem. Soc.*, 1957, **34**, 231.
[14] *Cf.* J. Saltiel and H. C. Curtis, *J. Amer. Chem. Soc.*, 1971, **93**, 2056; T. Nakota, K. Tokumaru, and O. Simamura, *Tetrahedron Letters*, 1967, 3303.

No evidence was obtained for the formation of 3-methyl-2-phenoxymethyl-1,4-benzoquinone when 2-hydroxymethyl-3-methyl-1,4-benzoquinone was irradiated; the major product (30%) was 2,5-dihydroxy-6-methylbenzaldehyde, possibly formed, at least in part,



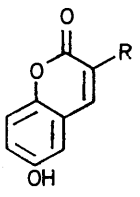
(6)

by oxidation of the corresponding benzyl alcohol during work-up. This result suggests that an *ortho*-effect may operate, since under similar conditions both 2-hydroxymethyl-5- and 2-hydroxymethyl-6-methyl-1,4-benzoquinone gave the corresponding phenoxymethyl-1,4-benzoquinone, although in low yield (2% and 1% respectively).

The mass spectrum of phenoxymethyl-1,4-benzoquinone showed the expected molecular ion (*M*) and a peak at *M* + 2 due to the hydroquinone resulting from reduction in the probe.[15] Also present was a relatively isolated group of three peaks with *m/e* 121, 122, and 123. That at *m/e* 121 can be attributed to loss of a phenoxy-group from the quinone, and the others to, respectively, loss of phenol and phenoxyl from the hydroquinone; the corresponding peaks at *m/e* 94 and 93 were present. Support for these assignments comes from the mass spectrum of ([$^2H_5$]phenoxymethyl)-1,4-benzoquinone which also shows the three peaks at *m/e* 121, 122, and 123, and from those of the 5- and 6-methyl homologues of phenoxymethyl-1,4-benzoquinone in which the members of the group are at *m/e* 135, 136, and 137.

Irradiation of isopropenyl-1,4-benzoquinone (3; R = Me) gave 5-hydroxy-3-methylbenzofuran as previously reported,[2] and the labelled quinone (3; R = CD_3) behaved analogously (52% yield), the mass and ^1H n.m.r. spectra of the product indicating that there had been neither loss nor scrambling of the label. This rules out mechanisms requiring abstraction from the allylic position of the side-chain,[2,3,5] and therefore indirectly supports a mechanism involving intramolecular addition to the olefinic double bond, possibly to give (4; R = Me or CD_3) as originally suggested.[2] It is of interest that abstraction from the potentially very reactive allylic position does not occur, since intramolecular abstraction of primary hydrogen from the t-butyl group of t-butyl-1,4-benzoquinone represents a major step in the photochemistry of this quinone.[1] The somewhat larger O · · · H distance in the transition state for intramolecular hydrogen transfer in the isopropenyl compound may be significant, although adoption of the s-*trans* conformation [as (3)] is probably more important. However, other factors may operate, since although the phenylvinylquinone (3; R = Ph) does give the corresponding benzofuran, the yield (33%) is reduced, and vinyl-1,4-benzoquinone itself affords only amorphous material.

Ethyl 3-(1,4-benzoquinonyl)propanoate (5; R = H) behaves similarly to other systems having a potentially abstractable hydrogen atom at the β-position of the side-chain, and yields ethyl 5-hydroxy-2,3-dihydrobenzofuran-2-carboxylate when it is irradiated in degassed benzene, but diethyl (1,4-benzoquinonylmethyl)malonate (5; R = CO_2Et) is unusual in being stable under these conditions.[5] It has now been found that it yields ethanol and 45—50% of the coumarin (7; R = CO_2Et) when a catalytic amount of air or oxygen is present. The presence of oxygen partially suppresses the formation of the dihydrobenzofuran from the monoester (5; R = H), probably by scavenging intermediate radicals, but it does not induce formation of the corresponding coumarin (7; R = H). This suggests that photostability of the diester (5; R = CO_2Et) in the absence of air may be due to ready reversibility of abstraction of hydrogen from the β-position of the side-chain, or its failure (abstraction from positions α to electron-accepting groups is disfavoured [3]), and that coumarin formation occurs *via* a different, possibly competitive, mechanism which utilises the unique structural features of the malonate residue.



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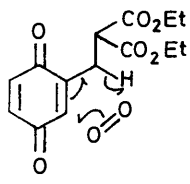

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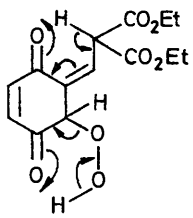

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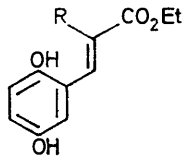

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It is possible that an ' ene reaction ' [as (8)] with singlet oxygen formed *in situ*, as suggested [16] for the photo-oxidation of phylloquinone, is involved. This would give the hydroperoxide (9) from which the diester (10; R = CO_2Et) could be formed as shown, tautomerism of the enone system being facilitated by the acidic character of the hydrogen involved, and loss of oxygen by concomitant generation of the benzenoid system. The diester (10; R = CO_2Et) contains an *o*-hydroxy-*cis*-cinnamate group, and would therefore readily cyclise to the coumarin (7; R = CO_2Et); a

[15] R. T. Alpin and W. T. Pike, *Chem. and Ind.*, 1966, 2009; J. Heiss, K.-P. Zeller, and A. Rieker, *Org. Mass Spec.*, 1969, **2**, 1325; J. M. Bruce in ' Rodd's Chemistry of Carbon Compounds,' ed. S. Coffey, 2nd edn., vol. IIIB, ch. 8, p. 35, in the press.

[16] C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, 1969, **91**, 731.

similar sequence with the monoester (5; R = H) would give the *trans*-cinnamate, from which a coumarin would not be expected. No attempt was made to independently generate singlet oxygen in the presence of the quinone (5; R = CO_2Et) (*cf.* ref. 16).

An alternative mechanism involving reduction of the quinone (5; R = CO_2Et) to the hydroquinone followed by successive cyclisation and dehydrogenation to give the coumarin can be discounted since the hydroquinone is stable under the conditions of the irradiation; it cyclises to ethyl 6-hydroxy-3,4-dihydrocoumarin-3-carboxylate when distilled at 180° and 10^{-2} mmHg.

Irradiation of the acetyl analogue (5; R = Ac) of the diester (5; R = CO_2Et) gave only tar.

EXPERIMENTAL

Irradiations were carried out as described previously.[2] Solutions were dried (Na_2SO_4), and solvents were removed under reduced pressure, usually below 60°. Bulb-to-bulb distillation temperatures are those of the heating bath. Unless stated otherwise, i.r. spectra were measured for films or Nujol mulls as appropriate. ^1H N.m.r. spectral bands (100 MHz) are singlets unless otherwise indicated (J in Hz); resonances assigned to OH groups were removed by addition of D_2O. Molecular weights were determined mass spectrometrically.

Hydroxymethyl-1,4-benzoquinone.—Frémy's salt (6 g) was added to a solution of *o*-hydroxymethylphenol (saligenin) (1·0 g) and potassium dihydrogen phosphate (3·5 g) in a mixture of methanol (30 ml) and water (400 ml), and the solution was stirred at room temperature for 4 h, and then extracted with ether (4 × 150 ml). The combined extracts were washed with water (3 × 20 ml), and dried. Removal of the solvent gave a brown oil which was chromatographed on Woelm polyamide (35 × 2·2 cm) using benzene as eluant, and the yellow fraction was sublimed at 140° and 10^{-2} mmHg to give the quinone (195 mg; 18%); after crystallisation from hexane it had m.p. 75—76° (lit.,[2] 74—75°), and was identical (i.r. and ^1H n.m.r. spectra) with authentic [2] material.

2-Hydroxy-3-methylbenzaldoxime.—*o*-Cresol (27 g) was added to a stirred solution of sodium hydroxide (80 g) in water (100 ml), and the solution was stirred at 65—70° during the slow addition of chloroform (41 ml). The mixture was then stirred for 1 h at 90—95°, cooled, and acidified with 10% sulphuric acid. The suspension was steam-distilled, and the distillate was extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate, then with water, and the solvent was removed. The residual oil was treated with a solution of hydroxylamine hydrochloride (10 g) and sodium hydroxide (5 g) in water (150 ml), and the mixture was refluxed for 30 min, and then cooled in ice. The oxime was collected, and crystallised from hexane to give needles (5 g, 13%), m.p. 99·5° (lit.,[17] 99°), τ (8% in $CDCl_3$) −0·28br (2-OH), 1·84br (2H, C*H*:N·O*H*), 2·85—3·31 (m, ArH_3), and 7·76 (Me).

2-Hydroxy-3-methylbenzaldehyde.—Copper(I) oxide (5 g) was added to a solution of the foregoing oxime (5 g) in aqueous 16% hydrochloric acid (50 ml), and the mixture was refluxed for 30 min and then steam-distilled. The distillate was extracted with ether, and the extract was washed with aqueous sodium hydrogen carbonate, then with water, and dried. Removal of the solvent, and distillation of the residue at 120° and 20 mmHg gave the aldehyde (4·2 g, 93%) as a viscous oil (lit.,[18] m.p. 17°), $\nu_{max.}$ 1599w, 1620s, 1660vs, and 3100w,br cm^{-1}, and τ (20% in CCl_4) −1·14 (OH), 0·23 (CHO), 2·70—2·85 (m, H-4 and H-6), 3·17—3·32 (m, H-5), and 7·84 (Me). The *2,4-dinitrophenylhydrazone*, orange crystals, had m.p. 259° (Found: C, 53·2; H, 3·8; N, 17·5%; M^+, 316. $C_{14}H_{12}N_4O_5$ requires C, 53·1; H, 3·8; N, 17·7%; M, 316).

2-Hydroxy-3-methylbenzyl Alcohol.—Sodium borohydride was added in portions to a stirred, ice-cooled solution of 2-hydroxy-3-methylbenzaldehyde (2·1 g) in a mixture of methanol (10 ml) and water (15 ml) until the yellow colour was just discharged. The solution was saturated with ammonium chloride, and extracted with ether (3 × 50 ml), and the combined extracts were washed with saturated ammonium chloride, and dried. Removal of the solvent, finally at 60° and 10^{-2} mmHg, gave the alcohol (2·03 g, 97%) as an oil (lit.,[19] m.p. 32°) which polymerised on attempted distillation. It had $\nu_{max.}$ 1600s and 3360s,br cm^{-1}, τ (4% in CCl_4) 3·06—3·56 (m, ArH_3), 5·42br [$(OH)_2$], 5·48 (CH_2), and 7·90 (Me).

2-Hydroxymethyl-6-methyl-1,4-benzoquinone.— Frémy's salt (6 g) was added to a stirred solution of 2-hydroxy-3-methylbenzyl alcohol (1 g) and potassium dihydrogen phosphate (3·5 g) in a mixture of methanol (50 ml) and water (400 ml), stirring at room temperature was continued for 1 h, and the mixture was extracted with ether. The extract was washed with water, dried, and the solvent was removed. Chromatography of the residual brown oil on Woelm polyamide (35 × 2·2 cm) using benzene as eluant followed by sublimation of the yellow fraction at 110° and 10^{-2} mmHg and crystallisation of the sublimate from 1 : 4 benzene–hexane gave the *quinone* (0·4 g, 36%) as yellow needles, m.p. 77° (Found: C, 62·9; H, 5·1%; M^+, 152. $C_8H_8O_3$ requires C, 63·0; H, 5·2%; M, 152), $\nu_{max.}$ 792w, 910m, 920vs, 978w, 1020m, 1068vs, 1165s, 1198s, 1295vs, 1620vs, and 3260vs,br cm^{-1}, τ (8% in $CDCl_3$) 3·26 (m, H-3, changed to d, J 3 by irradiation at τ 5·49), 3·44 (m, H-5, changed to d, J 3, by irradiation at τ 7·99), 5·49br (CH_2, sharpened by irradiation at τ 3·26), 7·08br (OH), and 7·99 (d, J 2, Me, changed to s by irradiation at τ 3·44).

2-Hydroxy-4-methyl- and 2-Hydroxy-6-methyl-benzaldehyde.—*m*-Cresol (27 g) was formylated as described above for the preparation of 2-hydroxy-3-methylbenzaldehyde oxime, and the resulting mixture of oximes was hydrolysed as described for the preparation of 2-hydroxy-3-methylbenzaldehyde. Preparative g.l.c. of the product on a 6 ft Carbowax column at 200° gave, first, 2-hydroxy-4-methylbenzaldehyde (2 g), and then 2-hydroxy-6-methylbenzaldehyde (1·5 g). 2-Hydroxy-4-methylbenzaldehyde, needles from water, m.p. 59—60° (lit.,[6-8] 60°), had $\nu_{max.}$ 1578m, 1632s, 1664vs, and 3200m,br cm^{-1}, τ (12% in $CDCl_3$) −1·22 (OH), 0·08 (CHO), 2·50 (d, J 8, H-6), 3·1 (m, H-3 and H-5), and 7·65 (Me); oxime, m.p. 109° (lit.,[20] 108—109°), τ (10% in $CDCl_3$) 0·02 (2-OH), 1·80 (CH:N), 1·90br (N·OH), 2·94 (d, J 8, H-6), 3·25—3·36 (m, H-3 and H-5), and 7·70 (Me); *2,4-dinitrophenylhydrazone*, orange crystals, m.p. 267° (Found: C, 52·9; H, 3·7; N, 17·6%; M^+, 316. $C_{14}H_{12}N_4O_5$ requires 53·1; H, 3·8; N, 17·7%; M, 316). 2-Hydroxy-6-methylbenzaldehyde, needles from aqueous ethanol, m.p. 32—33° (lit.,[6] 31·4—31·9°), had $\nu_{max.}$ 1580s, 1622vs, 1645vs, 1670vs,

[17] E. Paschen, *Ber.*, 1891, **24**, 3667.
[18] F. Tiemann and C. Schotten, *Ber.*, 1878, **11**, 767.
[19] P. Marchand and J. B. Grenet, Rhone-Poulene S.A. Fr.P. 1,328,945/1963 (*Chem. Abs.*, 1964, **60**, 2831f).
[20] O. Anselmino, *Ber.*, 1917, **50**, 395.

and 3100w,br cm^{-1}, τ (12% in $CDCl_3$) −1·98 (OH), −0·25 (CHO), 2·58 (q, *J* 8, H-4), 3·05—3·35 (m, H-3 and H-5), and 7·39 (Me); oxime, m.p. 116° (lit.,[6] 118·5—119·5°), τ (3% in $CDCl_3$) −0·32 (2-OH), 1·45 (CH:N), 2·3br (N·OH), 2·68—3·35 (m, ArH_3), and 7·60 (Me); 2,4-*dinitrophenylhydrazone*, orange-red, m.p. 266° (Found: C, 53·0; H, 3·8; N, 17·6%; M^+, 316. $C_{14}H_{12}N_4O_5$ requires C, 53·1; H, 3·8; N, 17·7%; *M*, 316).

2-*Hydroxy*-4-*methylbenzyl Alcohol*.—2-Hydroxy-4-methylbenzaldehyde (1 g) was reduced with sodium borohydride as described above for the 3-methyl isomer, and the resulting alcohol (0·82 g, 81%) was purified by distillation (bulb-to-bulb) at 180° and 10^{-2} mmHg, m.p. 100° (lit.,[21] 108°), $\nu_{max.}$ 1592w, 1625w, and 3150w,br cm^{-1}, and τ [12% in $(CD_3)_2CO$] 0·4 (2-OH), 2·85 (d, *J* 8, H-6), 3·30 (m, H-3 and H-5), 5·25 (CH_2), 6·85 (CH_2OH), and 7·75 (Me).

2-*Hydroxymethyl*-5-*methyl*-1,4-*benzoquinone*.—The foregoing phenol (1 g) was oxidised as described above for the preparation of 2-hydroxymethyl-6-methyl-1,4-benzoquinone. Distillation (bulb-to-bulb) of the crude product at 140° and 10^{-2} mmHg followed by crystallisation from hexane gave the *quinone* (0·22 g, 20%) as yellow needles, m.p. 74° (Found: C, 62·8; H, 5·1%; M^+, 152. $C_8H_8O_3$ requires C, 63·0; H, 5·2%; *M*, 152), $\nu_{max.}$ ($CHCl_3$) 912s, 1005s, 1088s, 1140m, 1345m, 1620s, 1655vs, 2910m, and 3400s cm^{-1}, τ (6% in $CDCl_3$) 3·25 (m, H-3), 3·44 (m, H-6), 5·51 (d, *J* 2, CH_2), 7·5br (OH), and 7·97 (d, *J* 2, Me).

2-*Hydroxy*-6-*methylbenzyl Alcohol*.—2-Hydroxy-6-methylbenzaldehyde (1 g) was reduced with sodium borohydride as described above for the 3-methyl isomer, and the resulting alcohol (0·64 g, 63%) was distilled (bulb-to-bulb) at 160° and 10^{-2} mmHg, m.p. 101° (lit.,[22] 80°), $\nu_{max.}$ 1595s, 1610m, and 3260s,br cm^{-1}, τ [6% in $(CD_3)_2CO$] 2·72—3·34 (m, ArH_3), 5·60 (CH_2), 6·01br (2 × OH), and 7·72 (Me).

2-*Hydroxymethyl*-3-*methyl*-1,4-*benzoquinone*.—The foregoing phenol (1 g) was oxidised as described above for the preparation of 2-hydroxymethyl-6-methyl-1,4-benzoquinone. Distillation (bulb-to-bulb) of the crude product at 120° and 10^{-2} mmHg gave the *quinone* (0·11 g, 10%) as a yellow oil (Found: C, 63·0; H, 5·3%; M^+, 152. $C_8H_8O_3$ requires C, 63·0; H, 5·2%; *M*, 152), $\nu_{max.}$ 752m, 840s, 1002s, 1122m, 1301s, 1605s, 1652vs, and 3450s,br cm^{-1}, τ (2% in $CDCl_3$) 3·24 (H-5 and H-6), 5·45 (CH_2), 7·25br (OH), and 7·90 (Me).

2,2′-*Dihydroxydiphenylmethane*.—A degassed solution of *o*-hydroxybenzyl alcohol (1·24 g) in phenol (14·1 g) was heated in a sealed tube at 210° for 12 h. The excess of phenol was then removed at 80° and 10^{-2} mmHg and the residue was distilled at 200° and 10^{-2} mmHg. Crystallisation of the distillate from water gave the dihydroxydiphenylmethane (1·9 g, 95%) as needles, m.p. 119—120° (lit.,[23] 118—120°); dimethyl ether, prisms from aqueous ethanol, m.p. 58° (lit.,[24] 66°); diacetate, needles from pentane, m.p. 43—44° (lit.,[25] 47—47·5°).

m-*Isopropenylphenyl Acetate*.—A solution of *m*-(1-hydroxy-1-methylethyl)phenol [2] (10 g) in freshly distilled acetic anhydride (43 ml) was refluxed for 10 h, the excess of anhydride was removed by distillation, and the residue was distilled at 70° and 10^{-2} mmHg to give the *ester* (9·4 g, 81%) as an oil (Found: C, 75·1; H, 6·6%; M^+, 176. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%; *M*, 176), $\nu_{max.}$ 1580s, 1608m, and 1770vs cm^{-1}, τ (4% in CCl_4) 2·8—3·2 (m, ArH_4), 4·72br (olefinic H), 5·00 (q, *J* 2, olefinic H), 7·88 (OAc), and 7·94 (d, *J* 2, Me).

m-*Isopropenylphenol*.—The foregoing ester (5·6 g) was refluxed with aqueous 25% sodium hydroxide (25 ml) for 4 h, and, after cooling and acidification with 20% sulphuric acid, the crude product was isolated by extraction with ether and then distilled at 160° and 10^{-2} mmHg to give the *phenol* (3·9 g, 92%) as an oil (Found: C, 80·4; H, 7·6%; M^+, 134. $C_9H_{10}O$ requires C, 80·6; H, 7·5%; *M*, 134), $\nu_{max.}$ 1580vs, 1610m, and 3320s,br cm^{-1}, τ (10% in $CDCl_3$) 2·8—3·4 (m, ArH_4), 3·84 (OH), 4·72br (olefinic H), 5·00 (m, olefinic H), and 7·96br (Me).

Isopropenyl-1,4-*benzoquinone*.—Frémy's salt (6 g) was added to a solution of *m*-isopropenylphenol (1 g) and potassium dihydrogen phosphate (3·5 g) in a mixture of methanol (50 ml) and water (400 ml), and the mixture was stirred at room temperature for 2 h. The crude product was isolated by extraction with ether and chromatographed on Woelm polyamide (25 × 2·2 cm) using benzene as eluant. Distillation (bulb-to-bulb) of the yellow fraction at 140° and 10^{-2} mmHg gave the quinone (265 mg, 26%) as a viscous yellow oil identical (i.r. and ^{1}H n.m.r. spectra) with material prepared as previously described.[2]

[2,2,2-$^2H_3$]-3′-(*Tetrahydropyran*-2-*yloxy*)*acetophenone*.—*m*-(Tetrahydropyran-2-yloxy)acetophenone [4] (6 g) in tetrahydrofuran (6 ml) was shaken for 24 h with a solution of lithium (10 mg) in 99·5% deuterium oxide (6 ml), and the product was isolated by extraction with ether. The process was repeated four times more, and the trideuterioacetophenone was then distilled at 140° and 10^{-2} mmHg. Its ^{1}H n.m.r. spectrum indicated >97% α-deuteriation.

[3,3,3-$^2H_3$]-2-(1,4-*Benzoquinonyl*)*propene*.—Powdered methyltriphenylphosphonium bromide (18 g) was added to n-butyl-lithium (17·5 ml of 0·025M-solution in ether) in dry tetrahydrofuran (100 ml), and the solution was then stirred at room temperature for 2 h. The foregoing trideuterioacetophenone (5·5 g) in tetrahydrofuran (25 ml) was then added dropwise, and stirring was continued at room room temperature for 2 h. The ether was distilled off through a 12 in Vigreux column, and simultaneously replaced by tetrahydrofuran, the process being continued until the temperature at the top of the column had reached 64°. The mixture was then refluxed for 4 h, after which the solvent was removed by distillation, finally at 80° (bath) and 20 mmHg. The residue was treated with water (200 ml), and extracted with ether (4 × 100 ml). The combined extracts were washed with water, concentrated to 55 ml, and then shaken for 24 h with 20% sulphuric acid (100 ml). The ethereal phase was separated, and extracted with aqueous 10% sodium hydroxide (3 × 10 ml). The combined alkaline extracts were washed with ether (3 × 10 ml), and then acidified with 20% sulphuric acid and extracted with ether (3 × 25 ml), the combined extracts being washed with aqueous sodium hydrogen carbonate, then with water, and dried. Removal of the solvent left a brown oil (3 g) shown by ^{1}H n.m.r. spectroscopy to be a 3 : 17 mixture of *m*-hydroxyacetophenone and the required [3,3,3-$^2H_3$]-2-*m*-hydroxyphenylpropene. Since oxidation of *m*-hydroxyacetophenone with Frémy's salt affords only tarry ma-

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[23] C. A. Buehler, D. E. Cooper, and E. O. Scrudder, *J. Org. Chem.*, 1943, **8**, 316.
[24] O. Kruber and H. Lauenstein, *Ber.*, 1941, **74**, 1693.
[25] H. L. Bender, A. G. Farnham, and J. W. Guyer, Bakelite Corp., U.S.P. 2,464,207/1949 (*Chem. Abs.*, 1949, **43**, 4698e).

terial,[26] no attempt was made to separate the mixture, and a portion (1 g) of it was oxidised with Frémy's salt as described above for the preparation of isopropenyl-1,4-benzoquinone; an analogous isolation procedure afforded [3,3,3-$^2H_3$]-2-(1,4-*benzoquinonyl*)*propene* (0·22 g, 22%) as a viscous yellow oil (Found: M^+, 151. $C_9H_5D_3O_2$ requires M, 151), $\nu_{max.}$ 680w, 695w, 815w, 870m, 910s, 968s, 1035s, 1075s, 1105m, 1122m, 1180m, 1200m, 1288s, 1358m, 1440m, 1590w, 1660vs, 2200vw, and 2220vw cm^{-1}, τ (4% in C_6D_6) 3·30—3·45 (m, quinonoid H_3), 4·38 (d, J 2, olefinic H), 4·52 (d, J 2, olefinic H), and 7·76 (0·2 H, m, due to incompletely deuteriated methyl group).

1-m-*Acetoxyphenyl*-1-*phenylethylene*.— *m*-(Tetrahydropyran-2-yloxy)acetophenone [4] (11 g) in dry ether (50 ml) was added dropwise to a stirred, ice-cooled solution of phenylmagnesium bromide [from bromobenzene (10·5 ml) and magnesium (2·5 g)] in ether (125 ml), the temperature of the mixture not being allowed to exceed 20°. The solution was then stirred at room temperature for 2 h, and decomposed at 0° by the addition of ice-cold aqueous 10% ammonium chloride. The ethereal phase was separated, combined with ether extracts of the aqueous phase, and washed with aqueous 10% sodium hydroxide followed by water. The ethereal solution was concentrated to 55 ml and then shaken with 20% sulphuric acid (100 ml) at room temperature for 24 h. The ethereal phase was separated and extracted with aqueous 10% sodium hydroxide (4 × 10 ml), and the combined alkaline extracts were washed with ether and then acidified with 20% sulphuric acid. Extraction with ether (5 × 50 ml) followed by washing of the combined extracts with, successively, aqueous sodium hydrogen carbonate and water, followed by drying and removal of the solvent gave an oil (10 g) which was refluxed with acetic anhydride (45 ml) for 20 h. Removal of the excess of anhydride followed by distillation of the residue at 150° and 10^{-2} mmHg gave 1-m-*acetoxyphenyl*-1-*phenylethylene* (8·34 g, 76%) as a viscous oil (Found: C, 79·9; H, 5·9%; M^+, 238. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%; M, 238), $\nu_{max.}$ 1499s, 1582m, 1610m, and 1770vs cm^{-1}, τ (8% in CCl_4) 2·70—3·25 (m, ArH_9), 4·64 (CH_2), and 7·82 (OAc).

1-m-*Hydroxyphenyl*-1-*phenylethylene*.—The foregoing ester (5 g) was hydrolysed as described above for *m*-isopropenylphenyl acetate. Distillation of the crude product at 140° and 10^{-2} mmHg gave 1-m-*hydroxyphenyl*-1-*phenylethylene* (4·06 g, 90%) as a viscous oil (Found: C, 84·9; H, 6·0%; M^+, 196. $C_{14}H_{12}O$ requires C, 85·5; H, 6·1%; M, 196), $\nu_{max.}$ 1498m, 1595s, 1610m, and 3350s,br cm^{-1}, τ (8% in C_6D_6) 2·65—3·45 (ArH_9), 4·62 (m, CH_2), and 4·87br (OH).

1-(1,4-*Benzoquinonyl*)-1-*phenylethylene*.—Frémy's salt (6 g) was added to a solution of the foregoing phenol (1 g) and potassium dihydrogen phosphate (3·5 g) in a mixture of methanol (75 ml) and water (400 ml), and the mixture was stirred at room temperature for 4 h. Extraction with ether, chromatography on Woelm polyamide (30 × 2·2 cm) using pentane as eluant, and distillation (bulb-to-bulb) at 140° and 10^{-2} mmHg gave the *quinone* (145 mg, 15%) as a yellow oil which soon decomposed (Found: C, 79·7; H, 5·2%; M^+, 210. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%; M, 210), $\nu_{max.}$ 710m, 778m, 840m, 912s, 1028m, 1038m, 1095m, 1399m, 1599w, 1615w, and 1670vs cm^{-1}, τ (12% in C_6D_6) 2·98 (Ph), 3·62 (m, quinonoid H), 3·94br (2 × quinonoid H), 4·63br (olefinic H), and 4·72br (olefinic H).

Vinyl-1,4-*benzoquinone*.—A mixture of 2,5-dihydroxystyrene [12] (100 mg), anhydrous sodium sulphate (1 g), and silver oxide (1 g) in dry benzene (10 ml) was shaken in the dark at room temperature for 2 h. The mixture was filtered, the filter cake washed with benzene (3 × 5 ml), and the combined filtrate and washings were concentrated in the dark at 20° to 1 ml, and then chromatographed on Woelm polyamide (20 × 2·2 cm) using benzene as eluant. Removal of the solvent from the yellow fraction, finally at 20° and 10^{-2} mmHg, gave the *quinone* (20 mg, 21%) as a yellow solid which very rapidly decomposed; its solution in benzene was relatively stable (Found: M^+, 134. $C_8H_6O_2$ requires M, 134), $\nu_{max.}$ 830m, 855m, 916m, 1022m, 1108m, 1280m, 1600s, 1620s, and 1650s cm^{-1}, τ (4% in CCl_4) 3·20—3·46 (m, quinonoid H_3 and vinyl H-1), 3·90 (q, J_1 17, J_2 2, vinyl H_A-2 or H_B-2), and 4·42 (q, J_1 12, J_2 2, vinyl H_B-2 or H_A-2).

Ethyl 2-(m-*Hydroxybenzyl*)-3-*oxobutanoate*.—A solution of ethyl 2-(*m*-hydroxybenzylidene)-3-oxobutanoate [13] (6 g) in ethanol (100 ml) was hydrogenated over 5% palladium–charcoal (100 mg) at normal temperature and pressure, the catalyst and solvent were removed, and the residue was distilled at 170° and 10^{-2} mmHg to give the *ester* (5·9 g, 95%) as an oil (Found: C, 65·9; H, 6·9%; M^+, 236. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%; M, 236), $\nu_{max.}$ 1590s, 1620s, 1725vs, and 3400vs cm^{-1}, τ (12% in $CDCl_3$) 2·75—3·35 (m, ArH_4), 5·82 (q, J 7, OCH_2), 6·14 (m, H-2), 6·84 (m, $ArCH_2$), 7·31 (COMe), and 8·79 (t, J 7, ester Me).

Ethyl 2-(1,4-*Benzoquinonylmethyl*)-3-*oxobutanoate*.—The foregoing phenol (1 g) was oxidised with Frémy's salt as described for the preparation of 1-(1,4-benzoquinonyl)-1-phenylethylene, and the yellow fraction from the chromatography was distilled at 160° and 10^{-2} mmHg to give the *quinone* (286 mg, 26%) as a yellow oil (Found: C, 62·1; H, 5·5%; M^+, 250. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6%; M, 250), $\nu_{max.}$ 782m, 912s, 1020m, 1085m, 1150m, 1290m, 1360s, 1602s, 1660vs, 1720vs, and 1740vs cm^{-1}, τ (20% in $CDCl_3$) 3·22br (quinonoid H_2), 3·36 (m, quinonoid H), 5·83 (q, J 7, OCH_2), 6·18 (m, H-2), 7·10 ($ArCH_2$), 7·78 (COMe), and 8·76 (t, J 7, ester Me).

Ethyl m-*Hydroxybenzylidene*(*cyano*)*acetate*.—A solution of *m*-hydroxybenzaldehyde (12·2 g), ethyl cyanoacetate (11·3 g), and piperidine (10 drops) in benzene (100 ml) was refluxed (Dean–Stark) for 2 h, cooled, and diluted with ether (100 ml). The solution was washed successively with 1% hydrochloric acid (3 × 10 ml), saturated aqueous sodium hydrogen carbonate (3 × 15 ml), and water (3 × 25 ml), and then dried. Removal of the solvent and crystallisation of the residue from benzene gave the *ester* (20·1 g, 95%) as pale yellow needles, m.p. 89—90° (Found: C, 66·3; H, 4·8; N, 6·7%; M^+, 217. $C_{12}H_{11}NO_3$ requires C, 66·4; H, 5·1; N, 6·5%; M, 217), $\nu_{max.}$ 1595m, 1618m, 1700s, 2220w, and 3370m cm^{-1}, τ [12% in $(CD_3)_2CO$] 1·63 (benzylidene CH), 2·19—3·07 (m, ArH_4), 5·55 (q, J 7, OCH_2), 6·85br (OH), and 7·60 (t, J 7, Me).

Ethyl m-*Hydroxybenzyl*(*cyano*)*acetate*.—The foregoing ester (6 g) was hydrogenated as described above for the 3-oxobutanoate to give the *ester* (4·95 g, 82%) as an oil (Found: C, 65·3; H, 5·3; N, 6·6%; M^+, 219. $C_{12}H_{13}NO_3$ requires C, 65·6; H, 5·9; N, 6·4%; M, 219), $\nu_{max.}$ 1591s, 1742vs, 2250m, and 3400vs cm^{-1} τ (14% in $CDCl_3$) 2·69—3·35 (m, ArH_4), 3·45 (OH), 5·80 (q, J 7, OCH_2), 6·24 (H-2), 6·84 (m, $ArCH_2$), and 8·80 (t, J 7, Me).

Diethyl 2,5-*Dihydroxybenzylmalonate*.—Zinc dust was

[26] R. Al-Hamdany, R. Brown, and J. M. Bruce, unpublished work.

added in portions to a solution of diethyl (1,4-benzoquinonylmethyl)malonate[5] (100 mg) in acetic acid (5 ml) at 80° until the yellow colour was just discharged. The excess of zinc was removed by filtration, the filtrate was diluted with water (100 ml), and the product was isolated by extraction with ether. Crystallisation from benzene gave the *hydroquinone* (93 mg, 92%) as needles, m.p. 92—93° (Found: M^+, 282·1069. $C_{14}H_{18}O_6$ requires M, 282·1103), $\nu_{max.}$ 1510s, 1610w, 1730vs, and 3400vs,br cm^{-1}, τ (3% in $CDCl_3$) 3·24 (m, ArH_3 and 1 × OH), 4·03br (remaining OH), 5·73 (q, J 7, 2 × OCH_2), 6·13 (m, H-2), 6·83 (m, $ArCH_2$), and 8·80 (t, J 7, 2 × Me). Identical material (93% yield) was obtained by hydrogenation of an ethanolic solution of the quinone over platinum.

Ethyl 6-Hydroxy-3,4-dihydrocoumarin-3-carboxylate.—The foregoing hydroquinone (150 mg) was distilled (bulb-to-bulb) at 180° and 10^{-2} mmHg, and the distillate was crystallised from 1 : 4 benzene–hexane to give the *dihydrocoumarin* (80 mg, 64%) as needles, m.p. 104° (Found: C, 60·9; H, 5·2%; M^+, 236. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·2%; M, 236), $\nu_{max.}$ 1608w, 1700s, 1730s, and 3350s cm^{-1}, τ (4% in $CDCl_3$) 3·08 (q, $J_{7,8}$ 7, $J_{5,7}$ 2, H-7), 3·30 (m, H-7 and H-8), 4·41br (OH), 5·82 (q, J 7, OCH_2), 6·27 (q, $J_{3,4A}$ 8, $J_{3,4B}$ 6, H-3), 6·80 (m, changed to q, J 16, by irradiation at τ 6·27, 2 × H-4), and 8·79 (t, J 7, Me).

Irradiation of Quinones.—Hydroxymethyl-1,4-benzoquinone. The quinone (200 mg) was irradiated in 99·7% [$^2H_6$]benzene (10 ml) for 6 days, the solvent was removed, and the brown residue was chromatographed on Woelm polyamide (35 × 2·2 cm) using benzene as eluant. Sublimation of the first (yellow) fraction at 150° and 10^{-2} mmHg, and crystallisation of the sublimate from 1 : 9 benzene–cyclohexane gave ([$^2H_5$]*phenoxymethyl*)-1,4-*benzoquinone* (20 mg, 6%), as yellow crystals, m.p. 136—138° (Found: C, 70·9; H, 2·5; D, 4·8%; M^+, 219. $C_7H_5D_5O_3$ requires C, 71·3; H, 2·3; D, 4·6%; M, 219), $\nu_{max.}$ 750m, 805m, 818m, 922s, 1018s, 1052m, 1195m, 1570w, 1650s, and 2270w cm^{-1}, τ (4% in C_6D_6) 3·11br (H-3), 3·30 (H-5 and H-6), and 5·16 (d, J 2, CH_2).

2-Hydroxymethyl-3-methyl-1,4-benzoquinone. The quinone (80 mg) was irradiated in benzene (6 ml) for 6 days, the solvent was removed, and the brown residue was chromatographed on Woelm polyamide (45 × 2·2 cm) using first benzene, and then ethanol as eluant. The first fraction afforded starting material (4 mg). Removal of the ethanol from the second fraction, and sublimation of the residue at 160° and 10^{-2} mmHg gave 2,5-*dihydroxy-6-methylbenzaldehyde* (24 mg, 30%), yellow crystals, m.p. 206° (decomp.) (Found: C, 62·8; H, 5·4%; M^+, 152. $C_8H_8O_3$ requires C, 63·0; H, 5·2%; M, 152), $\nu_{max.}$ 1578s, 1625s, 3100w, 3250s cm^{-1}, τ [2% in $(CD_3)_2CO$] −1·48 (2-OH), −0·41 (CHO), 2·84 (d, J 8, H-4), 3·35 (d, J 8, H-3), 7·1br (5-OH), and 7·49 (Me).

2-Hydroxymethyl-5-methyl-1,4-benzoquinone. The quinone (150 mg) was irradiated in benzene (10 ml) for 7 days, the solvent was removed and the brown residue was chromatographed on Woelm polyamide (40 × 2·2 cm) using benzene as eluant. Sublimation of the first fraction at 160° and 10^{-2} mmHg, and crystallisation of the sublimate from cyclohexane afforded 5-*methyl-2-phenoxymethyl-1,4-benzoquinone* (14 mg, 2%), yellow needles, m.p. 133—135° (Found: M^+, 228·078642. $C_{14}H_{12}O_3$ requires M, 228·078559), $\nu_{max.}$ 690m, 755m, 808s, 932m, 1010s, 1042m, 1092m, 1260s, 1500m, 1589m, 1601m, and 1660s cm^{-1}, τ (1% in $CDCl_3$) 2·68—3·22 (m, H-6 and Ph), 3·48 (t, J 2, H-3), 5·19 (d, J 2, CH_2), and 8·02 (d, J 2, Me).

2-Hydroxymethyl-6-methyl-1,4-benzoquinone. The quinone (400 mg) in benzene (20 ml) was irradiated for 16 days, and the dark brown solution was worked up as described in the foregoing experiment. Sublimation at 150° and 10^{-2} mmHg and crystallisation from hexane gave 6-*methyl-2-phenoxymethyl-1,4-benzoquinone* (6 mg, *ca.* 1%), as yellow needles, m.p. 104—105° (Found: C, 73·4; H, 5·5%; M^+, 228. $C_{14}H_{12}O_3$ requires C, 73·6; H, 5·3%; M, 228), $\nu_{max.}$ 692w, 756s, 910s, 919m, 938w, 1060m, 1080w, 1252s, 1299m, 1498m, 1601s, and 1655vs, cm^{-1}, τ (1% in CCl_4) 2·70—3·26 (m, H-3 and Ph), 3·50 (m, H-5), 5·19 (d, J 2, CH_2), and 7·99 (d, J 2, Me).

[3,3,3-$^2H_3$]-2-(1,4-*Benzoquinonyl*)*propene.* The quinone (150 mg) was irradiated in benzene (10 ml) for 4 h, the solvent was removed, and the brown residue was subjected to p.l.c. on silica gel (20 × 20 × 0·2 cm) using 4 : 1 benzene–acetic acid as eluant. Extraction of the main band, distillation at 120° and 10^{-2} mmHg, and crystallisation from hexane gave 3-[$^2H_3$]*methyl-5-hydroxybenzofuran* (78 mg, 52%), as plates, m.p. 88—91° (Found: C, 71·6; H, 3·3; D, 3·8%; M^+, 151. $C_9H_5D_3O_2$ requires C, 71·5; H, 3·3; D, 3·9%; M, 151), $\nu_{max.}$ 1490s, 1610m, 1630w, 2060w, 2120w, 2220w, and 3300m,br cm^{-1}, τ (2% in C_6D_6) 2·85 (d, J 8, H-7), 3·20 (H-2), 3·35—3·55 (m, H-4 and H-6), 5·65br (OH), and 8·20 (0·2H, m, due to undeuteriated Me).

1-(1,4-*Benzoquinonyl*)-1-*phenylethylene.* The quinone (145 mg) in benzene (10 ml) was irradiated for 3 h; the solution became colourless after 1 h. Work-up as described in the foregoing experiment, and distillation at 180° and 10^{-2} mmHg gave 5-hydroxy-3-phenylbenzofuran (49 mg, 33%) as an oil (lit.,[27] oil) (Found: M^+, 210. Calc. for $C_{14}H_{10}O_2$: M, 210), $\nu_{max.}$ 1470s, 1500w, 1610w, and 3350s,br cm^{-1}, τ (5% in CCl_4) 2·44 (H-2), 2·55—2·95 (m, H-4, H-7, and Ph), and 3·30 (q, J_1 9, J_2, 2, H-6).

Diethyl (1,4-*Benzoquinonylmethyl*)*malonate.* The quinone (320 mg) in dry benzene (25 ml) which had been saturated with oxygen was irradiated for 14 days; yellow crystals began to separate after 2 days. The precipitate (110 mg, 42%) was collected, rinsed with dry benzene, and dried. It was identical (mixed m.p., t.l.c., and i.r. and ^1H n.m.r. spectra) with authentic[28] ethyl 6-hydroxycoumarin-3-carboxylate (m.p. 187—188°), and after sublimation at 180° and 10^{-2} mmHg had m.p. 187—188° (lit.,[28] 192°) (Found: C, 61·1; H, 4·5%; M^+, 234. Calc. for $C_{12}H_{10}O_5$, C, 61·5; H, 4·3%; M, 234), $\nu_{max.}$ 1570s, 1680w, 1750vs, and 3320s cm^{-1}, τ [10% in $(CD_3)_2CO$] 1·25br (OH), 1·52 (H-4), 2·80 (m, H-5, H-7, and H-8), 5·69 (q, J 7, CH_2), and 8·67 (t, J 7, Me). The mother liquor was shown by g.l.c. to contain ethanol, and further coumarin (total yield 47%) and unchanged quinone (80 mg) were isolated from it by chromatography on silica gel.

Similar results were obtained when the benzene solution was saturated with air, but the quinone remained almost unchanged when the solution was rigorously degassed prior to irradiation.

Irradiation of ethyl 2-(1,4-benzoquinonylmethyl)-3-oxobutanoate under similar conditions afforded only tarry material.

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