Light-induced and Related Reactions of Quinones. Part IX.[1] t-Butyl-1,4-benzoquinones

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Irradiation of t-butyl-1,4-benzoquinone with visible light in dry acetaldehyde gives an 80% yield of 4,5-dihydro-2,4,4-trimethyl-1,3-benzodioxepin-7-ol, but irradiation in aqueous acetaldehyde yields 72% of 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol. The latter compound is also the major product when the quinone is irradiated in aqueous t-butyl alcohol, although only a poor yield results when the t-butyl alcohol is dry. With isopropyl alcohol, ethanol, and methanol the major products are the corresponding 2-alkoxy-1-(2,5-dihydroxyphenyl)-2-methylpropanes.

Irradiation of 2,5-di-t-butyl-1,4-benzoquinone in acetaldehyde gives the expected t-butyldihydrobenzodioxepin, although in low yield, but no dihydrobenzodioxepin was detected amongst the products similarly obtained from 2,6-di-t-butyl-1,4-benzoquinone.

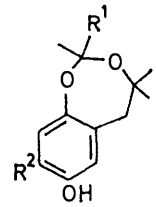
Irradiation of the quinones in dry benzene gives very low yields of 2,3-dihydro-2,2-dimethylbenzofuran-5-ols and 3-(2,5-dihydroxyphenyl)-2-methylpropenes.

Reorganisation of the carbon skeleton of a t-butyl group is involved in the formation of all these compounds, and mechanisms for this are discussed. Structural assignments are based on spectroscopic examination, and on comparison of derivatives with synthetic materials.

IRRADIATION of solutions of 1,4-benzoquinone [2] and its methyl homologues [3] in acetaldehyde with visible light gives the corresponding 2′,5′-dihydroxyacetophenones, often in good yield. When mono- and di-t-butyl-1,4-benzoquinones are irradiated [4,5] in solvents such as alcohols and carboxylic acids the main products are, respectively, ethers and 2,3-dihydrobenzofurans derived *via* reorganisation of the carbon skeleton of the side-chain. It was therefore of interest to irradiate t-butyl-1,4-benzoquinone and related compounds in acetaldehyde to determine whether the products were t-butyl-2′,5′-dihydroxyacetophenones or compounds containing reorganised t-butyl residues. The results obtained led to an extension of the study to include substrates other than aldehydes. While this work, now described, was in progress, the results of an independent investigation of the irradiation of t-butyl- and 2,5-di-t-butyl-1,4-benzoquinone in acetone were published,[6] and these corroborated the picture which had emerged from the studies with acetaldehyde. Additional examples of the reorganisation of t-butyl groups in related systems,[7] and further evidence concerning the mechanism [8] of the transformation have also appeared since the work described here was completed.

Results of Irradiations.—Solutions were irradiated with visible light. Tars were formed in all cases.

Irradiation of t-butyl-1,4-benzoquinone in acetaldehyde gave 4,5-dihydro-2,4,4-trimethyl-1,3-benzodioxepin-7-ol (1; $R^1 = R^2 = H$) as the major product (78% after purification), together with 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol (2; $R^1 = R^2 = R^3 = H$) and 2,3-dihydro-2,2-dimethylbenzofuran-5-ol (3; $R^1 = R^2 = H$) in yields of, respectively, 10 and 4%, estimated by ^1H n.m.r. spectroscopy of the total product. The alcohol (2; $R^1 = R^2 = R^3 = H$) appears to be a genuine photoproduct since the dihydrobenzodioxepin (1; $R^1 = R^2 = H$), a possible precursor of it, is stable



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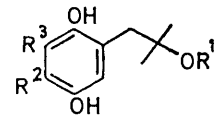

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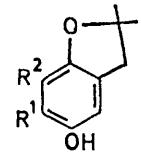
under the conditions used for irradiation and work-up even in the presence of water.



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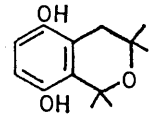

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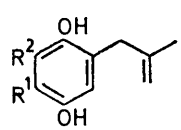
When the irradiation was performed in the presence of anhydrous magnesium sulphate, the yield of the dihydrobenzodioxepin was 80%, but 10% of the alcohol (2; $R^1 = R^2 = R^3 = H$) was still obtained. However, irradiation in aqueous acetaldehyde gave 72% of the alcohol (2; $R^1 = R^2 = R^3 = H$), and the dihydrobenzodioxepin (1; $R^1 = R^2 = H$) was not detected.

Irradiation in acetone containing anhydrous magnesium sulphate gave a mixture of products, shown, by spectroscopic comparison with authentic samples of the alcohol (2; $R^1 = R^2 = R^3 = H$) and the dihydrobenzofuran (3; $R^1 = R^2 = H$), and with data provided by Farid [9] for the dihydrobenzodioxepin (1; $R^1 = Me$,

[1] Part VIII, J. M. Bruce, D. Creed, and K. Dawes, *J. Chem. Soc.* (*C*), 1971, 3749.
[2] J. M. Bruce and E. Cutts, *J. Chem. Soc.* (*C*), 1966, 449.
[3] J. M. Bruce, D. Creed, and J. N. Ellis, *J. Chem. Soc.* (*C*), 1967, 1486.
[4] C. M. Orlando, H. Mark, A. K. Bose, and M. S. Manhas, *J. Amer. Chem. Soc.*, 1967, **89**, 6527.
[5] C. M. Orlando, H. Mark, A. K. Bose, and M. S. Manhas, *J. Org. Chem.*, 1968, **33**, 2512.
[6] S. Farid, *Chem. Comm.*, 1970, 303.
[7] I. Baxter and I. A. Mensah, *J. Chem. Soc.* (*C*), 1970, 2604.
[8] S. Farid, *Chem. Comm.*, 1971, 73.
[9] S. Farid, personal communication.

R^2 = H) and the dihydrobenzoxin (4), to contain these four compounds in the ratios 2 : 2 : 6 : 1, respectively. The alcohol (2; $R^1 = R^2 = R^3$ = H) and the dihydrobenzofuran (3; $R^1 = R^2$ = H) were isolated in yields of, respectively, 28 and 30% when the magnesium sulphate was omitted; when aqueous acetone was used, the isolated yield of the alcohol was 50%.

The only compounds identified (by ^{1}H n.m.r. spectroscopy) amongst the products obtained from irradiation in dry dioxan were the dihydrobenzofuran (3; $R^1 = R^2$ = H) and 3-(2,5-dihydroxyphenyl)-2-methylpropene (5; $R^1 = R^2$ = H), in the ratio 3 : 17. These were not detected in the products from irradiation in aqueous dioxan, but the alcohol (2; $R^1 = R^2 = R^3$ = H) was isolated in 11% yield; the quinone was consumed far more rapidly than in dry dioxan, and the major product was a light brown gum shown by ^{1}H n.m.r. spectroscopy to contain a high ratio of aliphatic to aromatic protons.



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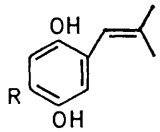

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Irradiation of t-butyl-1,4-benzoquinone in t-butyl alcohol alone or in the presence of anhydrous magnesium sulphate also gave the alcohol (2; $R^1 = R^2 = R^3$ = H) in yields of, respectively, 60 and 20%, but a 72% yield was obtained when the solvent was aqueous t-butyl alcohol. No additional products other than tars were detected. When dry isopropyl alcohol, ethanol, and methanol were used, severally, as solvents, the products were the expected ethers (2; R^1 = Pr^i, Et, and Me, respectively, $R^2 = R^3$ = H) in yields of 59, 63, and 38%, the ethyl ether being identical with, and formed in comparable yield to, that previously reported,[4] thus establishing the similarity of the irradiation conditions.

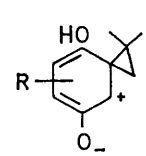
When t-butyl-1,4-benzoquinone was irradiated in dry benzene the products, identified in the mixture by ^{1}H n.m.r. spectroscopy, and separated by g.l.c. of their methyl ethers, were t-butylquinol, the dihydrobenzofuran (3; $R^1 = R^2$ = H), and the olefin (5; $R^1 = R^2$ = H) in yields of, respectively, 1, 1·5, and 4%.

Similar results were obtained with 2,5-di-t-butyl-1,4-benzoquinone, except that the reactions were slower. Irradiation in acetaldehyde gave 6% of 2,5-di-t-butylquinol and 38% of the dihydrobenzodioxepin (1; R^1 = H, R^2 = Bu^t). When benzene was used as solvent the products were 2,5-di-t-butylquinol and the olefin (5; R^1 = Bu^t, R^2 = H) in yields of 18 and 19%, respectively, but g.l.c.–mass spectroscopic examination of the material obtained by methylation of a sample of the total irradiation product also indicated the presence of the dihydrobenzofuran (3; R^1 = Bu^t, R^2 = H) and the olefins (5; $R^1 = CH_2{\cdot}CMe{:}CH_2$, R^2 = H), (6; R = Bu^t), and (6; R = $CH{:}CMe_2$), although it is not certain that the conjugated systems (6; R = Bu^t) and (6; R = $CH{:}CMe_2$) were formed during irradiation.

Photoreaction of 2,6-di-t-butyl-1,4-benzoquinone occurred extremely slowly, and the material was almost completely unchanged after irradiation under conditions which would have caused complete conversion of t-butyl-1,4-benzoquinone. Several products were formed in very low yield when it was subjected to prolonged irradiation in acetaldehyde, but none was characterised; the dihydrobenzofuran (3; R^1 = H, R^2 = Bu^t), and the olefin (5; R^1 = H, R^2 = Bu^t) were formed in low yield when benzene was used. The major ultimate product resulting from prolonged irradiation in either solvent was a brown tar. 2,6-Di-t-butyl-1,4-benzoquinone readily gave the ether (2; R^1 = Et, R^2 = H, R^3 = Bu^t), as previously reported,[4] when it was irradiated in ethanol.

Discussion of Results.—In no case when irradiation was carried out in acetaldehyde was evidence obtained for the formation of a t-butyl-2′,5′-dihydroxyacetophenone, indicating that the t-butyl-1,4-benzoquinones behave differently from 1,4-benzoquinone and its methyl homologues.

Formation of the dihydrobenzodioxepins (1; $R^1 = R^2$ = H) and (1; R^1 = H, R^2 = Bu^t), the alcohol (2; $R^1 = R^2 = R^3$ = H) and the related ethers (2; R^1 = Pr^i, Et, and Me, $R^2 = R^3$ = H) and (2; R^1 = Et, R^2 = H, R^3 = Bu^t), the dihydrobenzofurans (3; $R^1 = R^2$ = H) and (3; R^1 = Bu^t, R^2 = H), and the olefins [as (5) and (6)] requires rearrangement of the t-butyl side-chain, and this can be accounted for by intervention of a zwitterionic spirocyclopropane intermediate (7) as previously suggested for quinones carrying t-butyl [5,6,8] and related [10] side-chains. Opening of the three-membered ring of (7) would give the zwitterion (8) from which all the observed products could be derived by appropriate nucleophilic attack. The species (9) may also be involved since, as pointed out previously,[6] it could yield the olefin (5; $R^1 = R^2$ = H) *via* the abnormal Claisen rearrangement, and it might also suffer spontaneous or, more probably, reactant-promoted opening of the cyclopropane ring to give, ultimately, the dihydrobenzodioxepins [as (1)] and the ethers [as (2; R^1 = Alk)]. The possible intervention of a species such as (9) is supported [11] by the observation [6] that the same ultimate products can be formed by irradiating the quinone at −80° in 1,2-dimethoxyethane and then removing the light source and adding the appropriate reactants.



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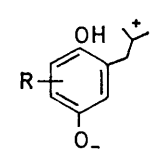

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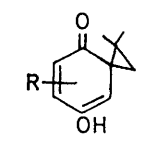

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The nature of the reaction medium exerts a controlling influence. Thus irradiation of t-butyl-1,4-benzoquinone

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

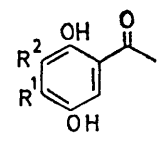
[11] *Cf.* E. Breuer and D. Melumad, *Tetrahedron Letters*, 1969, 1875.

in dry acetaldehyde gives 80% of the dihydrobenzodioxepin (1; $R^1 = R^2 = H$), but the alcohol (2; $R^1 = R^2 = R^3 = H$) is formed in 72% yield when aqueous acetaldehyde is used; in fact this medium is the best of those examined for the preparation of this alcohol, and the dihydrobenzodioxepin (1; $R^1 = R^2 = H$) is unlikely to be an intermediate since it is stable under the prevailing conditions. As expected, the alcohol (2; $R^1 = R^2 = R^3 = H$) is the major product when aqueous t-butyl alcohol is used as solvent. Only a poor yield of the alcohol was obtained when the quinone was irradiated in aqueous dioxan, although consumption of the quinone was rapid compared with that in dry dioxan, an observation reminiscent of an earlier one,[12] which is still unexplained, that 1,4-benzoquinone is photoreduced rapidly in aqueous dioxan but only slowly in dry dioxan. A particularly high proportion of tarry material was formed when t-butyl-1,4-benzoquinone was irradiated in dry benzene, supporting the view that clean reactions are to be expected in relatively polar media which favour the formation and subsequent reaction of zwitterionic species such as (7) and (8).

Similar arguments apply to 2,5- and 2,6-di-t-butyl-1,4-benzoquinone, although the 2,5-isomer reacts with acetaldehyde less rapidly, and the 2,6-isomer much less rapidly, than does t-butyl-1,4-benzoquinone. There appears to be little difference in reactivity towards ethanol. The reason for this is not clear, since the absorption spectra in the 450 nm region (ε 25—30) of solutions of the t-butyl-1,4-benzoquinones in acetaldehyde are very similar to those [4] of ethanolic solutions, and it is absorption in this region which generates the $^1(n,\pi^*)$ state from which the triplet, normally responsible [13] for reactions involving abstraction of hydrogen atoms, is generated. It may be significant that the 'forbidden' π–π^* transition lying in the 310—317 nm region (ε 183—464) for ethanolic solutions occurs at 335—345 nm (ε 106—224) for solutions in acetaldehyde, and hence becomes more important in relation to the emission of the tungsten filament lamps used in the present work, but this is unlikely to account for the marked difference in reactivity towards acetaldehyde between t-butyl- and 2,6-di-t-butyl-1,4-benzoquinone which have, in this solvent, respectively $\lambda_{max.}$ 342 (ε 220) and 342 nm (ε 224). It is possible, however, that the step following excitation, *i.e.* intramolecular abstraction of hydrogen from the t-butyl group on to the adjacent carbonyl group, may be reversible, and that reversal is facilitated by the steric effect of the 6-t-butyl group, either directly or by its influence on the orientation of the resulting hydroxy-group, or indirectly by its effect on solute–solvent interaction; the latter effect, although not the former, would also operate to some extent for 2,5-di-t-butyl-1,4-benzoquinone, and could therefore contribute to the intermediate position of this quinone on the reactivity scale. More quantitative data are required before firm conclusions can be drawn.

[12] J. M. Bruce and E. Cutts, unpublished work quoted in J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405.

The initial chemical step [2] in the light-induced reaction between 1,4-benzoquinone and acetaldehyde, which yields 2′,5′-dihydroxyacetophenone, is abstraction of the formyl hydrogen atom from the aldehyde, an energetically favourable process. However, no t-butyl-2′,5′-dihydroxyacetophenone could be detected in the products from the irradiation of t-butyl-1,4-benzoquinone in acetaldehyde, suggesting that intramolecular abstraction of hydrogen from the t-butyl group occurred to the exclusion of intermolecular abstraction from the solvent, although it was possible that acetyl radicals may have been formed, but that t-butyl-1,4-benzoquinone failed to scavenge them in the expected manner. Consequently, acetyl radicals were generated thermally [2] by allowing di-t-butyl diperoxyoxalate to decompose in the dark in acetaldehyde containing t-butyl-1,4-benzoquinone, with and without added t-butylquinol (*cf.* ref. 2), at a concentration similar to that used for the irradiation experiments. The reactions proceeded much less cleanly than those [2] with 1,4-benzoquinone, but the only products detected (and isolated) were 3′- and 4′-t-butyl-2′,5′-dihydroxyacetophenone, respectively (10; $R^1 = H$, $R^2 = Bu^t$) and (10; $R^1 = Bu^t$, $R^2 = H$), indicating that acetyl radicals can be scavenged at the nucleus of t-butyl-1,4-benzoquinone, and also that they are not involved in the formation of the dihydrobenzodioxepin (1; $R^1 = R^2 = H$).



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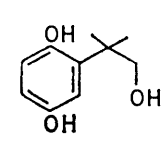

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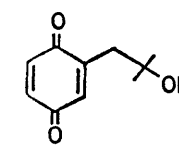

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Structures of Products.—The mass spectrum of the dihydrobenzodioxepin (1; $R^1 = R^2 = H$) showed the parent peak at *m/e* 208 as required, with the base peak at 164 corresponding to loss of C_2H_4O, the acetaldehyde fragment. The i.r. and ^1H n.m.r. spectra (see Experimental section) were in accord with expectation, in the latter the 2-methyl group giving a doublet, and the two non-equivalent 4-methyl groups each a separate singlet; the proton at C-2 gave a quartet at τ 4·91, and the two protons at C-5 gave the expected AB quartet.

Treatment of the dihydrobenzodioxepin (1; $R^1 = R^2 = H$) with Brady's reagent gave acetaldehyde 2,4-dinitrophenylhydrazone, and treatment with methanolic hydrochloric acid gave the alcohol (2; $R^1 = R^2 = R^3 = H$), thus confirming the presence of the acetal linkage. The dihydrobenzodioxepin (1; $R^1 = H$, $R^2 = Bu^t$) behaved analogously.

Cyclisation of the alcohols (2; $R^1 = R^2 = R^3 = H$) and (2; $R^1 = R^3 = H$, $R^2 = Bu^t$) gave the dihydrobenzofurans (3; $R^1 = R^2 = H$) and (3; $R^1 = Bu^t$, $R^2 = H$) in yields of, respectively, 90 and 74%. Treatment of the alcohol (2; $R^1 = R^2 = R^3 = H$) with di-

[13] J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405, and references therein.

methyl sulphate and aqueous sodium hydroxide gave the expected dimethyl ether (2; $R^1 = R^2 = R^3 = H$, OMe instead of OH), identical with material synthesised from 2,5-dimethoxyphenyl-lithium and 1,1-dimethyloxiran (isobutene oxide); when heated with toluene-*p*-sulphonic acid it gave 1-(2,5-dimethoxyphenyl)-2-methylpropene (6; R = H, OMe instead of OH), identical with material synthesised by treatment of 2,5-dimethoxybenzaldehyde with isopropylmagnesium bromide followed by dehydration of the resulting alcohol.

For comparison, the isomeric alcohol (11), which might have been obtained had the t-butyl group not undergone reorganisation, was prepared: acid-catalysed hydrolysis of 2,3-dihydro-3,3-dimethyl-2-morpholinobenzofuran-5-ol [14] gave 2-(2,5-dihydroxyphenyl)-2-methylpropanal, which was then reduced to the alcohol with sodium borohydride; both this alcohol and its 2′,5′-dimethyl ether were different from, respectively, the alcohol (2; $R^1 = R^2 = R^3 = H$) and its corresponding dimethyl ether.

Additional evidence was obtained from the ^{1}H n.m.r. spectra of the quinones (12; R = H, Me, Et, and Pr^i) obtained by oxidation of the corresponding quinols (2; R^1 = H, Me, Et, and Pr^i, $R^2 = R^3 = H$): allylic coupling between H-3 of the quinonoid portion and the CH_2 group of the side chain was observed, either as splitting (J 0·8 Hz) for (12; R = H) or as line broadening (confirmed by double irradiation) for (12; R = Me, Et, and Pr^i), for all the quinones, thus establishing the presence of the CH=C–CH_2 unit.

The orientations of the 3′- and 4′-t-butyl-2′,5′-dihydroxyacetophenones were also established by ^{1}H n.m.r. spectroscopy. In deuteriochloroform, the 4′-t-butyl compound (10; R^1 = Bu^t, R^2 = H) gave two singlets, at τ 3·10 and 3·04, due to the nuclear protons *para* to each other; the positions of these singlets changed to τ 2·95 and 4·05 when the spectrum was measured for a solution in hexadeuteriobenzene. In deuteriochloroform, the resonances due to the two nuclear protons of the 3′-t-butyl isomer (10; R^1 = H, R^2 = Bu^t) coincided to give a sharp singlet at τ 2·97, but when the spectrum was measured for a solution in hexadeuteriobenzene the resonances moved upfield, but unequally, and each proton now gave a well resolved doublet at, respectively, τ 3·16 and 3·53 with J 3 Hz, thus confirming their *meta* orientation and hence establishing the position of the t-butyl group.

EXPERIMENTAL

Acetaldehyde was freshly distilled. Acetone, alcohols, and dioxan were dried over, and distilled from, respectively, potassium carbonate, calcium oxide, and sodium. Irradiations were carried out as described previously.[15] Solutions were dried ($MgSO_4$), 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, and u.v. spectra for solutions in ethanol. ^{1}H N.m.r. spectral bands (at 100 MHz unless stated otherwise) 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.

t-Butyl-1,4-benzoquinone was prepared by oxidation of t-butylquinol with silver oxide, and after being sublimed at 55° and 10^{-2} mmHg had m.p. 59° (lit.,[4] 58—59°), $\lambda_{max.}$ (AcH) 342 and 443 nm (ε 220 and 25). 2,5-Di-t-butyl-1,4-benzoquinone was obtained from the corresponding quinol by oxidation with nitric acid,[16] and, after being crystallised from ethanol and sublimed at 120° and 10^{-2} mmHg, had m.p. 153° (lit.,[4] 150—151°), $\lambda_{max.}$ (AcH) 335 and 450 nm (ε 106 and 28). 2,6-Di-t-butyl-1,4-benzoquinone was prepared from 2,6-di-t-butylphenol *via* nitrosation and subsequent hydrolysis,[17] and after being sublimed at 60° and 10^{-2} mmHg had m.p. 66—67° (lit.,[17] 68°), $\lambda_{max.}$ (AcH) 342 and 450 nm (ε 224 and 30).

Irradiation of Quinones

t-Butyl-1,4-benzoquinone.—(*a*) The quinone (500 mg) was irradiated in acetaldehyde (50 ml) for 8 days, and the solvent was removed. ^{1}H N.m.r. spectroscopy of the residue showed the presence of the dihydrobenzodioxepin (1; $R^1 = R^2$ = H), the alcohol (2; $R^1 = R^2 = R^3 = H$), and the dihydrobenzofuran (3; $R^1 = R^2$ = H) in the ratios 21 : 3 : 1, respectively. Crystallisation from 3 : 1 cyclohexane–chloroform gave (i) the alcohol (57 mg, 10%), m.p. 164° (other properties as described later), and (ii) *4,5-dihydro-2,4,4-trimethyl-1,3-benzodioxepin-7-ol* (494 mg, 78%), plates (from cyclohexane), m.p. 150°, unchanged by sublimation at 150° and 10^{-2} mmHg (Found: C, 69·2; H, 7·9%; M, 208. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%; M, 208), $\nu_{max.}$ 3340s, 1620w, 1589w, 1495vs, 1341w, 1320w, 1287w, 1257m, 1209vs, 1196w, 1155w, 1145w, 1128w, 1109w, 1080s, 1070s, 1005w, 960m, 950s, 942m, 910m, 879w, 870w, 849w, 829w, 760m, and 683w cm^{-1}, τ (4% in $CDCl_3$) 3·19—3·53 (m, H-6 + H-8 + H-9), 4·91 (q, J 5, H-2), 5·06 (7-OH), 6·83 (d, J 15, H_a-5), 7·54 (d, J 15, H_b-5), 8·57 (d, J 5, 2-Me), 8·67 (4-Me), and 8·90 (4-Me). The mother liquor was not further examined.

(*b*) Repetition of experiment (*a*), but in the presence of anhydrous magnesium sulphate (5 g) gave the alcohol (87 mg) and the dihydrobenzodioxepin (507 mg, 80%).

(*c*) The quinone (500 mg) was irradiated in a mixture of acetaldehyde (50 ml) and water (0·8 ml) for 4 days, the solvent was removed, and the residual oil was triturated with hot carbon tetrachloride until it solidified. Crystallisation from benzene and sublimation at 150° and 10^{-2} mmHg then gave 1-*(2,5-dihydroxyphenyl)-2-methylpropan-2-ol* (405 mg, 72%) as white prisms, m.p. 164° (Found: C, 65·6; H, 7·8%; M, 182. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%; M, 182), $\nu_{max.}$ 3370s, 3200br,s, 1622w, 1611m, 1508s, 1326w, 1293m, 1271w, 1249m, 1220m, 1187m, 1258m, 1133m, 1100w, 1010w, 964s, 914m, 892w, 878s, 831m, 796m, 784w, 766w, 742w, 726w, 712w, and 672w cm^{-1}, τ [4% in $(CD_3)_2CO$] 1·44 (5′-OH), 2·38 (2′-OH), 3·43—3·53 (m, H-3′ + H-4′ + H-6′), 5·12 (2-OH), 7·30 (2 × H-1), and 8·75 (2 × Me).

4,5-Dihydro-2,4,4-trimethylbenzo-1,3-dioxepin-7-ol was recovered almost quantitatively after being similarly irradiated in aqueous acetaldehyde.

[14] J. M. Bruce and D. Creed, *J. Chem. Soc.* (*C*), 1970, 649, and references therein.

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

[16] G. R. Barrett, U.S.P. 2,577,505 (*Chem. Abs.*, 1952, **46**, 5617e).

[17] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, 1962, **27**, 651.

(*d*) The quinone (500 mg) was irradiated in dry acetone (20 ml) for 44 h, the solvent was removed, finally at 80° and 20 mmHg, and the residual oil was triturated with hot carbon tetrachloride until it solidified. Crystallisation from benzene gave 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol (154 mg, 28%), m.p. 164°, identical (mixed m.p. and i.r. spectrum) with material obtained as described under (*c*). Removal of the solvent from the benzene mother liquor and chromatography of the residue on silica gel (36 × 2·6 cm) (4 : 1 chloroform–carbon tetrachloride as eluant) gave 2,3-dihydro-2,2-dimethylbenzofuran-5-ol (150 mg, 30%), needles (from cyclohexane), m.p. 101°, identical (mixed m.p. and i.r. spectrum) with authentic [4] material.

When the irradiation was repeated in the presence of anhydrous magnesium sulphate (5 g), ^{1}H n.m.r. spectroscopy of the total residue remaining after removal of the magnesium sulphate and the excess of acetaldehyde indicated the presence of the alcohol (2; $R^1 = R^2 = R^3 = H$), the dihydrobenzofuran (3; $R^1 = R^2 = H$), the dihydrobenzodioxepin (1; $R^1 = Me$, $R^2 = H$), and the dihydrobenzoxin (4) in the ratios 2 : 2 : 6 : 1, respectively; data for compounds (1; $R' = Me$, $R^2 = H$) and (4) were provided by Farid.[9]

(*e*) The quinone (1·7 g) was irradiated in a mixture of acetone (75 ml) and water (2·5 ml) for 3 days, the solvent was removed, and the residue was triturated with hot cyclohexane. Crystallisation of the insoluble material from benzene gave 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol (0·92 g, 50%), m.p. 164·5°, identical with material obtained as described under (*c*). The cyclohexane washings and the benzene mother liquors yielded tarry material, from which a small amount of unchanged quinone was recovered by t.l.c.

(*f*) The quinone (500 mg) was irradiated in dry dioxan (40 ml) containing anhydrous magnesium sulphate (5 g) for 2 days. Removal of the solvent left an oil, shown by comparison of the characteristic methylene ^{1}H n.m.r. resonances (in $CDCl_3$) at τ 7·08 and 6·74 to contain, respectively, the dihydrobenzofuran (3; $R^1 = R^2 = H$) and the olefin (5; $R^1 = R^2 = H$) in the ratio 3 : 17. Neither was isolated. Several unidentified compounds were also present.

(*g*) Repetition of (*f*), but with water (0·8 ml) instead of magnesium sulphate, gave the alcohol (2; $R^1 = R^2 = R^3 = H$) (64 mg, 11%), m.p. 163°, isolated by washing the product with chloroform and recrystallising the insoluble material from benzene.

(*h*) The quinone (500 mg) was irradiated in dry t-butyl alcohol (20 ml) for 24 h, the solvent was removed, and the residue was distilled (bulb-to-bulb) at 180° and 10^{-2} mmHg to give an oil which solidified. Crystallisation from benzene afforded 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol (330 mg, 60%), m.p. 164°, identical with material prepared by method (*c*).

The yield was only 20% when anhydrous magnesium sulphate (5 g) was present. When the solvent was a mixture of t-butyl alcohol (22 ml) and water (3 ml), and the irradiation time 3 weeks, the product, isolated by trituration with hot carbon tetrachloride followed by crystallisation from 99 : 1 cyclohexane–acetone, was the same alcohol (396 mg, 72%), m.p. 164°.

(*i*) The quinone (500 mg.) was irradiated in dry isopropyl alcohol (50 ml) for 24 h, the solvent was removed, and the residue was triturated with warm pentane (3 × 10 ml). The insoluble material was crystallised from 1 : 1 benzene–hexane and then sublimed at 130° and 10^{-2} mmHg to give 1-(2,5-*dihydroxyphenyl*)-2-*isopropoxy*-2-*methylpropane* (405 mg, 59%) as white crystals, m.p. 133° (Found: C, 69·9; H, 8·7%; *M*, 224. $C_{13}H_{20}O_3$ requires C, 69·6; H, 8·9%; *M*, 224), $\nu_{max.}$ 3380s, 3080m,br, 1625w, 1500s, 1250s, 1210s, 1110s, 990s, 865m, and 840m cm^{-1}, τ (2% in $CDCl_3$) 1·25 (2′-OH), 3·2—3·6 (m, 3 × ArH), 5·10 (5′-OH), 6·15 (heptet, *J* 6, O·CH), 7·30 (2 × H-1), 8·87 (3 × H-3 + 2-Me), and 8·85 (d, *J* 6, O·CMe_2).

(*j*) Experiment (*i*) was repeated, but with dry ethyl alcohol (25 ml). 1-(2,5-Dihydroxyphenyl)-2-ethoxy-2-methylpropane (440 mg, 63%) had m.p. 144—146° (lit.,[4] 144—147°), τ (2% in $CDCl_3$) 1·39 (2′-OH), 3·30—3·56 (m, 3 × ArH), 5·20 (5′-OH), 6·54 (q, *J* 6, O·CH_2), 7·25 (2 × H-1), and 8·8 (m, 3 × Me).

(*k*) Experiment (*i*) was repeated, but with dry methanol. The solvent was removed, the residue was distilled (bulb-to-bulb) at 160° and 10^{-2} mmHg, and the distillate was triturated with light petroleum (b.p. 40—60°) until it solidified. Fractional crystallisation from 1 : 1 hexane–benzene followed by sublimation at 110° and 10^{-2} mmHg gave 1-(2,5-*dihydroxyphenyl*)-2-*methoxy*-2-*methylpropane* (226 mg, 38%), m.p. 118—119° (Found: C, 67·2; H, 8·1%; *M*, 196. $C_{11}H_{16}O_3$ requires C, 67·4; H, 8·2%; *M*, 196), $\nu_{max.}$ 3380s, 3150m,br, 1590w, 1505s, 1215s, 1060s, and 820 s cm^{-1}, τ (2% in $CDCl_3$) 1·51 (2′-OH), 3·2—3·6 (m, 3 × ArH), 4·90 (5′-OH), 6·78 (OMe), 7·27 (2 × H-1), and 8·80 (3 × H-3 + 2-Me).

(*l*) The quinone (3·33 g) was irradiated in dry benzene (75 ml) for 7 days, the solvent was removed, and the residue was distilled (bulb-to-bulb) at 160° and 10^{-2} mmHg. The distillate was dissolved in air-free aqueous 10% sodium hydroxide (25 ml) under nitrogen, and the solution was treated with dimethyl sulphate (3·5 ml) in one portion, then shaken vigorously for 30 min, and finally heated at 100° for 30 min. After being cooled, the mixture was extracted with ether (3 × 25 ml); the combined extracts were washed with water, dried, and evaporated and the residue was distilled at 180° and 10^{-2} mmHg. Preparative g.l.c. of the distillate (6 ft × ⅜ in column packed with 3% SE30 on Chromosorb G at 175°) gave (i) 2,3-dihydro-5-methoxy-2,2-dimethylbenzofuran (53 mg, 1·5%), identical with material prepared as described below; (ii) t-butylquinol dimethyl ether (38 mg, 1%), an oil,[18] $\nu_{max.}$ 2830m, 1610w, 1584m, 1488vs, 1464m, 1283s, 1250m, 1220vs, 1179m, 1148m, 1088m, 1058s, 1031s, 876m, 858w, 800m, 731m, and 692w cm^{-1}, τ (1% in $CDCl_3$) 3·10—3·45 (m, 3 × ArH), 6·13 (OMe), 6·60 (OMe), and 8·64 (Bu^t); (iii) 3-(2,5-*dimethoxyphenyl*)-2-*methylpropene* (146 mg, 4%) as an oil (Found: C, 75·0; H, 8·4%; *M*, 192. $C_{12}H_{16}O_2$ requires C, 74·9; H, 8·3%; *M*, 192), $\nu_{max.}$ 2990w, 2940m, 2910m, 2835m, 1605w, 1592w, 1508s, 1458m, 1280m, 1228s, 1055s, 1030m, 890w, 800w, and 730w cm^{-1}, τ (3% in $CDCl_3$) 3·29br (3 × ArH), 5·23br (*cis*- or *trans*-H-1), 5·37br (*trans*- or *cis*-H-1), 6·26 (2′-OMe + 5′-OMe), 6·71 (2 × H-3), and 8·29br (2-Me).

2,5-*Di-t-butyl*-1,4-*benzoquinone*.—(*a*) The quinone (1 g) was irradiated in acetaldehyde (75 ml) for 4 days, the solvent was removed, and the residue was crystallised from cyclohexane to give a white solid mixture (750 mg). A portion (100 mg) of this was chromatographed as described under (*l*) to yield (i) 2,5-di-t-butylquinol (8 mg, equivalent to 6%

[18] M. L. Clemens ,U.S.P. 2,776,321 and B.P. 763,146 (*Chem. Abs.*, 1957, **51**, 9690h); M. R. Brimer, B.P. 774,018 (*Chem. Abs.*, 1957, **51**, 17,994i).

overall), identical with authentic [19] material, and (ii) *4,5-dihydro-2,4,4-trimethyl-8-t-butyl-1,3-benzodioxepin-7-ol* (60 mg; equivalent to 38% overall), m.p. 143—144·5° (Found: C, 72·6; H, 9·7%; *M*, 264. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%; *M*, 264), $\nu_{max.}$ 3430s, 1624w, 1518m, 1416s, 1348s, 1291w, 1282w, 1258w, 1222m, 1201m, 1191s, 1177s, 1138m, 1092s, 1086s, 1054m, 1028w, 1012w, 980m, 964s, 936s, 900s, 882m, 858m, 798w, 770m, 741w, and 671m cm^{-1}, τ (2% in $CDCl_3$) 3·17 (H-9), 3·68 (H-6), 4·85 (q, *J* 5, H-2), 5·27 (OH), 6·86 (d, *J* 15, H_a-5), 7·52 (d, *J* 15, H_b-5), 8·52 (d, *J* 5, 2-Me), 8·62 (4-Me_a + Bu^t), and 8·86 (4-Me_b).

(*b*) The quinone (4 g) was irradiated in dry benzene (75 ml) for 7 days, and the solution was then concentrated to 12 ml: 2,5-di-t-butylquinol (397 mg, 10%) separated. Concentration of the mother liquor gave further solid (1·02 g), which after several crystallisations from cyclohexane had m.p. 128—135°, and was shown by ^1H n.m.r. spectroscopy to be a 3 : 17 mixture of 2,5-di-t-butylquinol and the olefin (5; $R^1 = Bu^t$, $R^2 = H$).

The solvent was removed from the benzene mother liquor, and the residue was methylated as described under (*l*); g.l.c.–mass spectrometry indicated the presence of five components: (i) *m/e* 248, 233, 218, 145, and 91 (60, 100, 20, 20, and 20%), probably the dimethyl ether of compound (5; $R^1 = CH_2{\cdot}CMe{:}CH_2$, $R^2 = H$); (ii) *m/e* 234, 220, 219, 204, 191, 145, and 91 (80, 20, 100, 20, 20, and 20%), probably the monomethyl ether of (5; $R^1 = Bu^t$, $R^2 = H$) with OMe *meta* to Bu^t; (iii) *m/e* 248, 223, 218, 145, and 91 (60, 100, 20, 40, and 30%), probably the dimethyl ether of compound (6; $R = CH{:}CMe_2$); (iv) *m/e* 234, 220, 219, 205, 145, and 91 (40, 60, 70, 100, 40, and 20%), probably the methyl ether of (3; $R^1 = Bu^t$, $R^2 = H$); (v) *m/e* 234, 220, 219, 145, and 91 (65, 20, 100, 40, and 20%), probably the monomethyl ether of (6; $R = Bu^t$) with OMe *meta* to Bu^t.

2,6-Di-t-butyl-1,4-benzoquinone.—(*a*) The quinone (2 g) was irradiated in acetaldehyde (150 ml) for 4 weeks, and the solvent was then removed, leaving a dark oil from which the starting quinone could be recovered (51 and 53%, respectively) either by preparative t.l.c. on silica gel (99 : 1 benzene–triethylamine as eluant) or by steam distillation. No other material was characterised. The quinone was recovered almost quantitatively when the irradiation time was reduced to 4 days.

(*b*) The quinone (1 g) was irradiated in dry benzene (25 ml) for 3 weeks, the solvent was removed, and the residue was steam distilled to give unchanged quinone (0·34 g). The material involatile in steam was isolated by extraction with ether and shown by ^1H n.m.r. spectroscopy to contain small amounts of the dihydrobenzofuran (3; $R^1 = H$, $R^2 = Bu^t$) and the olefin (5; $R^1 = H$, $R^2 = Bu^t$), together with unidentified material.

Peroxyoxalate Experiments

(*a*) A solution of t-butyl-1,4-benzoquinone (1·64 g) and di-t-butyl diperoxyoxalate [20] (1·17 g) in acetaldehyde (50 ml) was kept in the dark at 20° for 11 days, carbon dioxide being allowed to escape *via* a mercury seal. The solvent was then removed: analytical g.l.c. and t.l.c. did not indicate the presence of either the dihydrobenzodioxepin (1; $R^1 = R^2 = H$) or the dihydrobenzofuran (3; $R^1 = R^2 = H$) in the residual oil. Unchanged quinone (0·61 g) was removed by steam distillation, and the residue was sublimed at 120° and 0·03 mmHg to give a mixture of viscous brown oil and yellow crystals which was crystallised from light petroleum (b.p. 60—80°) to give a mixture (30 mg) of yellow felted needles and pale yellow plates; the brown oil, which remained in the mother liquors, was not examined. The needles and the plates were roughly separated mechanically, and each fraction was then recrystallised from light petroleum (b.p. 60—80°). Appropriate single crystals were used as seeds, and advantage was taken of the fact that the needles separated from solution much more rapidly than did the plates; pure samples of each component were obtained. *2′,5′-Dihydroxy-3′-t-butylacetophenone* (7mg) formed yellow needles, m.p. 141—142° (Found: C, 69·1; H, 7·7%; *M*, 208. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%; *M*, 208), $\nu_{max.}$ 3440s, 1630m, 1603s, 1590s, 1250w, 1238m, 1216s, 1140w, 1039w, 983w, 977m, 878w, 858m, 800s, and 678w cm^{-1}, $\lambda_{max.}$ 264 and 371 nm (ε 5550 and 3470), τ (2% in $CDCl_3$) −2·64 (2′-OH), 2·97 (H-4′ + H-6′), 5·38br (5′-OH), 7·43 (COMe), and 8·62 (Bu^t), τ (2% in C_6D_6) −3·20 (2′-OH), 3·16 (d, *J* 3, H-4′), 3·53 (d, *J* 3, H-6′), 6·08 (5′-OH), 8·08 (COMe), and 8·64 (Bu^t). *2′,5′-Dihydroxy-4′-t-butylacetophenone* (5 mg) formed pale yellow plates, m.p. 195—196·5° (Found: C, 69·3; H, 7·5%; *M*, 208. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%; *M*, 208), $\nu_{max.}$ 3360sh, 3280s, 1630m, 1608s, 1560w, 1510w, 1329w, 1310w, 1232m, 1210s, 1020m, 962m, 886s, 860m, 851s, 811m, 758m, 730w, and 670w cm^{-1}, $\lambda_{max.}$ 267 and 366 nm (ε 6400 and 3040), τ (1·2% in $CDCl_3$) −1·7 (2′-OH), 3·04 (H-6′?), 3·10 (H-3′?), 5·28br (5′-OH), 7·47 (COMe), and 8·62 (Bu^t), τ (1·2% in C_6D_6) −2·31 (2′-OH), 2·95 (H-3′), 4·05 (H-6′), 6·19 (5′-OH), 8·04 (COMe), and 8·66 (Bu^t).

(*b*) A solution of t-butyl-1,4-benzoquinone (1·64 g), t-t-butylquinol (0·83 g) and di-t-butyl diperoxyoxalate (1·76 g) in acetaldehyde (50 ml) was treated as described under (*a*), giving an identical mixture (17 mg) of yellow felted needles and pale yellow plates.

Experiments relating to the Structures of Irradiation Products

1-(2,5-Dihydroxyphenyl)-2-methylpropan-2-ol.—A mixture of 4,5-dihydro-2,4,4-trimethyl-1,3-benzodioxepin-7-ol (100 mg), methanol (2 ml), and concentrated hydrochloric acid (0·2 ml) was refluxed for 30 min, the solvent was removed, and the residue was washed with boiling pentane (3 × 10 ml). Crystallisation of the residue from benzene followed by sublimation at 150° and 10^{-2} mmHg gave the *alcohol* (65 mg, 75%), m.p. 164° (Found: C, 65·6; H, 7·8%; *M*, 182; $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%; *M*, 182), $\nu_{max.}$ 3370s, 3200br,s, 1622w, 1611m, 1508s, 1326w, 1293m, 1271w, 1249m, 1220m, 1187m, 1158m, 1133m, 1100w, 1010w, 964s, 914m, 892w, 878s, 831m, 796w, 784w, 766w, 742w, 726w, 712w, and 672w cm^{-1}, τ [4% in $(CD_3)_2CO$] 1·44 (5′-OH), 2·38 (2′-OH), 3·43—3·53 (3 × ArH), 5·12 (2-OH), 7·30 (2 × H-1), and 8·75 (2 × Me).

Treatment of the dihydrobenzodioxepin with hot Brady's reagent gave acetaldehyde 2,4-dinitrophenylhydrazone, identical with authentic material.

2,3-Dihydro-2,2-dimethylbenzofuran-5-ol.—A mixture of 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol (100 mg), toluene-*p*-sulphonic acid (5 mg), and dry benzene (2·5 ml) was refluxed for 2 h, cooled, and then washed with saturated aqueous sodium hydrogen carbonate followed by water.

[19] R. Stroh, R. Seydel, and W. Hahn, *Angew. Chem.*, 1957, **69**, 699.

[20] P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, 1960, **82**, 1762.

The benzene was removed, and the residue distilled (bulb-to-bulb) at 220° and 10^{-2} mmHg. Crystallisation of the distillate from 9 : 1 hexane–benzene gave the dihydrobenzofuran (80 mg, 90%) as white crystals, m.p. 101—101·5°, identical with authentic [4] material which also had m.p. 101—101·5°. It showed τ (4% in $CDCl_3$) 3·37—3·48 (m, 3 × ArH), 5·35 (OH), 7·08 (2 × H-3), and 8·56 (2 × Me). The *methyl ether*, prepared by treatment of the dihydrobenzofuranol (150 mg) with aqueous sodium hydroxide and dimethyl sulphate, was obtained by distillation (bulb-to-bulb) at 140° and 10^{-2} mmHg as an oil (122 mg, 75%) (Found: C, 74·3; H, 8·0%; *M*, 178. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%; *M*, 178), $\nu_{max.}$ 2970m, 2930m, 2830w, 1600w, 1490s, 1225s, 1208m, 1148s, 1032s, 880m, 785m, and 730m cm^{-1}, τ (5% in $CDCl_3$) 3·30—3·48 (m, 3 × ArH), 6·29 (OMe), 7·40 (2 × H-3), and 8·60 (2 × Me).

1-(2,5-*Dimethoxyphenyl*)-2-*methylpropan*-2-*ol*.—(*a*) A solution of 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol (910 mg) in freshly boiled-out aqueous 10% sodium hydroxide (5 ml) at 15° was treated with dimethyl sulphate (1 ml) in one portion, shaken at 15° for 30 min, and then heated at 100° for 1 h. Water (10 ml) was added, and the product was isolated by extraction with ether and then distilled (bulb-to-bulb) at 120° and 0·05 mmHg to give the *dimethyl ether* (753 mg, 72%) as an oil (Found: C, 68·7; H, 8·4%; *M*, 210. $C_{12}H_{18}O_3$ requires C, 68·7; H, 8·6%; *M*, 210), $\nu_{max.}$ 3440vs, 2840vs, 1608m, 1590s, 1507vs, 1320w, 1300w, 1288s, 1227vs, 1184vs, 1162vs, 1140w, 1134s, 1115w, 1108w, 1054vs, 1032vs, 985w, 975m, 943m, 908vs, 880m, 812vs, 776m, 730w, 718vs, 710s, and 672w cm^{-1}, τ (4% in $CDCl_3$) 3·24—3·34 (m, 3 × ArH), 6·24 (OMe), 6·27 (OMe), 7·19 (2 × H-1), and 8·78 (2 × Me); no peak was observed for 2-OH, probably because the band was very broad, but the expected exchange peak appeared at τ 5·38 after treatment with D_2O. The ether also showed τ [8% in $(CD_3)_2SO$; 60 MHz)] 3·00—3·10 (m, 3 × ArH), 5·74 (OH), 6·21 (2 × OMe), 7·23 (2 × H-1), and 8·89 (2 × Me); addition of ethanol to the solution and remeasurement of the spectrum gave the same bands together with those due to ethanol, including τ 5·58 (t, *J* 5·5, OH of EtOH), indicating that the solvent conditions were adequate to reveal C*H*·O*H* coupling.

(*b*) 1,1-Dimethyloxiran (isobutene oxide) (3·6 g) in ether (50 ml) was added slowly to a stirred solution of 2,5-dimethoxyphenyl-lithium [from [21] 1,4-dimethoxybenzene (5·8 g)] in ether (275 ml) at 5°, and stirring was continued for 24 h. The mixture was cooled to 0° and decomposed with ice–water (200 ml), and the ethereal phase was separated and combined with ether (4 × 100 ml) extracts of the aqueous phase. The combined extracts were dried, the solvent was removed, and the residue was chromatographed on silica gel (36 × 2·4 cm) (benzene as eluant) until no further 1,4-dimethoxybenzene was removed; elution with ether and distillation at 160° and 10^{-2} mmHg then gave 1-(2,5-dimethoxyphenyl)-2-methylpropan-2-ol as an oil (5·4 g, 61%), identical (i.r. and ^1H n.m.r. spectra) with material prepared by method (*a*).

1-(2,5-*Dimethoxyphenyl*)-2-*methylpropan*-1-*ol*.— 2,5-Dimethoxybenzaldehyde (8 g) in ether (50 ml) was added with stirring at −10 to −5° to a solution of isopropylmagnesium bromide [from isopropyl bromide (5 ml)] in ether (20 ml), and stirring was then continued at room temperature for 1 h. The mixture was decomposed with aqueous 10% ammonium chloride (100 ml), and the ethereal phase was separated and combined with ether (4 × 50 ml) extracts of the aqueous phase. The ethereal solution was washed with aqueous 10% sodium hydroxide, dried, and evaporated. The residual oil was heated on a steam-bath with saturated aqueous sodium hydrogen sulphite (50 ml), and then extracted with light petroleum (3 × 25 ml; b.p. 40—60°), the combined extracts being washed with saturated aqueous sodium hydrogen sulphite (2 × 25 ml), then with water (3 × 25 ml), dried, and evaporated. The residue was distilled at 100° and 10^{-2} mmHg, to give the *alcohol* (5·9 g, 59%) as an oil which solidified, m.p. 52—54° (Found: C, 68·3; H, 8·5%; *M*, 210. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6; *M*, 210), $\nu_{max.}$ (film) 3440br,s, 2960s, 2870w, 2840m, 1610w, 1590w, 1500vs, 1470s, 1280s, 1220vs, 1180s, 1050s, 1030s, 815m, 720m, and 710m cm^{-1}, τ (2% in CCl_4) 3·24 (d, *J* 2, H-6′), 3·42 (m, H-3′ + H-4′), 6·56 (ill-defined m, changed by addition of D_2O to d, *J* 6, H-1), 6·29 (OMe), 6·33 (OMe), 8·1 (irregular m, becoming symmetrical after addition of D_2O, *J* 6, H-2 + OH), 9·10 (d, *J* 6, Me), and 9·20 (d, *J* 6, Me).

1-(2,5-*Dimethoxyphenyl*)-2-*methylpropene*.—(*a*) A mixture of 1-(2,5-dimethoxyphenyl)-2-methylpropan-2-ol (170 mg) and toluene-*p*-sulphonic acid (10 mg) was heated in a bulb-to-bulb distillation apparatus at 120° and 760 mmHg for 1 h, and then distilled at 115° and 0·03 mmHg to give the *olefin* (55 mg, 36%) as an oil (Found: C, 74·6; H, 8·5%; *M*, 192. $C_{12}H_{16}O_2$ requires C, 74·9; H, 8·5%; *M*, 192), $\nu_{max.}$ 2835m, 1606w, 1583m, 1495s, 1468m, 1428w, 1417w, 1378w, 1350w, 1303w, 1284m, 1229s, 1200w, 1180m, 1165m, 1133w, 1119w, 1058s, 1032m, 890w, 878w, 830w, 809m, 799w, 732w, 719w, 707w, and 671m cm^{-1}, τ (4% in $CDCl_3$) 3·26br (3 × ArH), 3·73br (H-1), 6·24 (2 × OMe), 8·08 (d, *J* 2·1 Me), and 8·18 (d, *J* 1·9, Me). The residue from the distillation was a brown glass.

(*b*) A mixture of 1-(2,5-dimethoxyphenyl)-2-methylpropan-1-ol (200 mg), toluene-*p*-sulphonic acid (10 mg), and dry benzene (10 ml) was refluxed for 4 h, cooled, and diluted with ether (25 ml). The solution was washed with saturated aqueous sodium hydrogen carbonate, then with water, dried, and evaporated. Distillation (bulb-to-bulb) of the residue at 120° and 10^{-2} mmHg gave the olefin (65 mg, 35%) as an oil, identical (i.r. and ^1H n.m.r. spectra) with material prepared by method (*a*).

2-(2,5-*Dihydroxyphenyl*)-2-*methylpropanal*.—2,3-Dihydro-3,3-dimethyl-2-morpholinobenzofuran-5-ol [14] (1 g) was stirred with 5% sulphuric acid (20 ml) at 60° for 5 min, and the solution was cooled and extracted with ether (3 × 50 ml). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate, then with water, dried, and evaporated. Distillation (bulb-to-bulb) of the residue at 160° and 10^{-2} mmHg gave the aldehyde (600 mg, 80%) as a thick oil which eventually solidified, m.p. 103° (from hexane) (lit.,[14] oil) (Found: C, 66·5; H, 6·8%; *M*, 180. Calc. for $C_{10}H_{12}O_3$: C, 66·6; H, 6·6%; *M*, 180), $\nu_{max.}$ 3200br,w, 1605w, 1285m, 1185s, 1082s, 960s, 890s, 820s, 795w, and 730w cm^{-1}, τ (4% in $CDCl_3$) 3·42 (m, 3 × ArH), 4·52 ('H-1'), 7·84 (2 × OH), 8·71 (Me), and 8·76 (Me), indicating that the compound existed predominantly as the cyclic hemiacetal, as previously described.[14]

2-(2,5-*Dihydroxyphenyl*)-2-*methylpropanol* —The foregoing aldehyde (645 mg) was dissolved in warm water (20 ml), and the solution was cooled to room temperature, stirred, and treated with sodium borohydride (50 mg). After 15 min the solution was saturated with sodium chloride and extracted with ether (4 × 50 ml); the combined

[21] J. M. Bruce, *J. Chem. Soc.*, 1959, 2366.

extracts were dried and evaporated. Sublimation of the residue at 135° and 10^{-2} mmHg gave the *alcohol* (625 mg, 96%), m.p. 138—139° (Found: C, 65·6; H, 7·6%; *M*, 182. $C_{10}H_{14}O_3$ requires C, 65·8; H, 7·7%; *M*, 182), $\nu_{max.}$ 3375s, 3200m, 1615w, 1595w, 1500m, 1262m, 1210s, 1050s, 820m, and 780m cm^{-1}, τ [4% in $(CD_3)_2CO$] 1·50br (5′-OH), 2·55br (2′-OH), 3·28 (d, *J* 3, H-6′), 3·40 (d, *J* 8, H-3′), 3·52 (q, J_1 8, J_2 3, H-4′), 5·44br (1-OH), 6·27 (2 × H-1), and 8·78 (2 × Me).

2-(2,5-*Dimethoxyphenyl*)-2-*methylpropanol*.—A solution of 2-(2,5-dihydroxyphenyl)-2-methylpropanol (910 mg) in freshly boiled-out aqueous 10% sodium hydroxide (10 ml) at 15° was treated with dimethyl sulphate (1·5 ml) in one portion, shaken for 30 min at 15°, and then heated on a steam-bath for 1 h. The suspension was cooled and diluted with water (10 ml), and the oil which separated was isolated by extraction with ether and distilled (bulb-to-bulb) at 170° and 10^{-2} mmHg to give the *dimethyl ether* (710 mg, 68%) as an oil (Found: C, 68·2; H, 8·7%; *M*, 210. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·6%; *M*, 210), $\nu_{max.}$ 3400br,w, 2830m, 1605w, 1585m, 1490m, 1225s, 1050s, 1030s, 805m, and 735m cm^{-1}, and τ (4% in $CDCl_3$) 3·13 (d, *J* 3, H-6′), 3·22 (d, *J* 8, H-3′), 3·32 (q, J_1 8, J_2 3, H-4′), 6·27 (OMe), 6·29 (OMe), 8·20 (1-OH), and 8·66 (2 × Me), τ [10% in $(CD_3)_2SO$; 60 MHz] 2·90—3·30 (m, 3 × ArH), 5·48 (t, *J* 5·5, OH), 6·19 (OMe), 6·23 (OMe), 6·31 (d, *J* 5·5, 2 × H-1), and 8·72 (2 × Me).

1-(1,4-*Benzoquinonyl*)-2-*methylpropan*-2-*ol*.—A mixture of 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol (100 mg), silver oxide (500 mg), anhydrous sodium sulphate (500 mg), and dry ether (10 ml) was shaken at room temperature for 2 h, filtered, and evaporated. Distillation (bulb-to-bulb) of the residue at 140° and 10^{-2} mmHg gave the yellow *quinone* (55 mg, 55%) as an oil which solidified, m.p. 45—49° (Found: C, 67·0; H, 7·0%; *M* + 2, 182. $C_{10}H_{12}O_3$ requires C, 66·8; H, 6·7%; *M* + 2, 182), $\nu_{max.}$ 3460s, 1660vs, 1620w, 1600s, 1298s, 1238w, 1221w, 1205m, 1128s, 1079s, 1010w, 986m, 976m, 922s, 903w, 888w, 847vs, 790w, 761w, 719w, and 672w cm^{-1}, $\lambda_{max.}$ 248, 322, and 429 nm (ε 17,500, 884, and 35), τ (6% in $CDCl_3$) 3·25—3·33 (m, quinonoid 3 × H), 7·38 (d, *J* 0·8, 2 × H-1), 7·76 (OH), and 8·76 (2 × Me). This hydroxyalkylquinone was very much less stable than its methyl, ethyl, and isopropyl ethers, which are described below.

1-(1,4-*Benzoquinonyl*)-2-*methoxy*-2-*methylpropane*.—Oxidation of 1-(2,5-dihydroxyphenyl)-2-methoxy-2-methylpropane (125 mg) with silver oxide (1 g) in the presence of anhydrous sodium sulphate (1 g) as described in the previous preparation gave, by distillation (bulb-to-bulb) at 120° and 10^{-2} mmHg, the *quinone* (102 mg, 85%) as a yellow oil (Found: C, 68·0; H, 7·3%; *M*, 194. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%; *M*, 194), $\nu_{max.}$ 3310w, 3260w, 2980s, 2920s, 2830m, 1660vs, 1600s, 1385s, 1370s, 1295vs, 1220s, 1122s, 1080vs, 1068vs, 912s, and 830s cm^{-1}, $\lambda_{max.}$ 249, 320, and 432 nm (ε 12,600, 750, and 30), τ (10% in $CDCl_3$) 3·28 (quinonoid 3 × H), 6·78 (OMe), 7·36 (2 × H-1, sharpened and increased in amplitude by irradiation at τ 3·28), and 8·82 (2 × Me).

1-(1,4-*Benzoquinonyl*)-2-*ethoxy*-2-*methylpropane*.— Oxidation of 1-(2,5-dihydroxyphenyl)-2-ethoxy-2-methylpropane (200 mg) as just described for the methoxy-analogue gave, by distillation (bulb-to-bulb) at 180° and 10^{-2} mmHg, the *quinone* (156 mg, 79%) as a yellow oil (Found: C, 69·4; H, 7·8%; *M*, 208. $C_{12}H_{16}O_3$ requires C, 69·3; H, 7·7%; *M*, 208), $\nu_{max.}$ 3305w, 3270w, 2980vs, 2930s, 1660vs, 1600s, 1368s, 1294vs, 1220s, 1122vs, 1070vs, and 912s cm^{-1}, $\lambda_{max.}$ 248, 321, and 430 nm (ε 14,800, 780, and 33) τ (10% in $CDCl_3$) 3·30 (quinonoid 3 × H), 6·60 (q, *J* 6, O·CH_2), 7·39 (2 × H-1, sharpened and increased in amplitude by irradiation at τ 3·30), and 8·84 (m, 3 × Me).

1-(1,4-*Benzoquinonyl*)-2-*isopropoxy*-2-*methylpropane*.— Oxidation of 1-(2,5-dihydroxyphenyl)-2-isopropoxy-2-methylpropane (200 mg) as described for the methoxy-analogue gave, by distillation (bulb-to-bulb) at 180° and 10^{-2} mmHg, the *quinone* (166 mg, 85%) as a yellow oil (Found: C, 70·4; H, 8·1%; *M*, 222. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%; *M*, 222), $\nu_{max.}$ 3310w, 3260w, 2975vs, 2930s, 1660vs, 1600s, 1465m, 1380s, 1370s, 1290s, 1175s, 1115vs, 1072s, 1010s, 913s, and 850m cm^{-1}, $\lambda_{max.}$ 248, 321, and 430 nm (ε 12,000, 720, and 31), τ (6% in $CDCl_3$) 3·19 (quinonoid H-3, sharpened and increased in amplitude by irradiation at τ 7·40), 3·28 (quinonoid H-5 + H-6), 6·20 (m, O·CH), 7·40 (2 × H-1, sharpened and increased in amplitude by irradiation at τ 3·19), 8·86 (3 × H-3 + 2-Me), and 8·90 (d, *J* 6, Me_2CH).

1-(2,5-*Dihydroxy*-4-*t-butylphenyl*)-2-*methylpropan*-2-*ol*.— Hydrolysis of 4,5-dihydro-2,4,4-trimethyl-8-t-butyl-1,3-benzodioxepin-7-ol with methanolic hydrochloric acid as described for the preparation of 1-(2,5-dihydroxyphenyl)-2-methylpropan-2-ol gave, after crystallisation from cyclohexane and sublimation at 130° and 10^{-2} mmHg, the *alcohol*, m.p. 133·5° (Found: C, 70·7; H, 9·0%; *M*, 238. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·2%; *M*, 238), $\nu_{max.}$ 3440s, 3270br,m, 3150br,m, 1635w, 1582w, 1520m, 1296w, 1285w, 1222s, 1199w, 1190s, 1160s, 1120m, 1052w, 1030w, 975w, 920m, 895m, 888m, 869m, 850w, 808w, 799w, 768m, 739w, 706w, and 671w cm^{-1}, τ (2% in $CDCl_3$) 2·08 (2′-OH), 3·16 (H-3′), 3·68 (H-6′), 5·32 (5′-OH), 7·31 (2 × H-1), 7·70 (2-OH), 8·62 (Bu^t), and 8·70 (2 × Me).

2,3-*Dihydro*-2,2-*dimethyl*-6-*t-butylbenzofuran*-5-*ol*.— A mixture of the foregoing alcohol (20 mg), toluene-*p*-sulphonic acid (2 mg), and dry benzene (1·5 ml) was refluxed for 2·5 h, cooled, and diluted with benzene (1·5 ml). The solution was washed with aqueous 5% sodium hydrogen carbonate, then with water, and dried. Removal of the solvent, and sublimation of the residue at 120° and 10^{-2} mmHg gave the dihydrobenzofuran (13 mg, 74%), m.p. 158—159°, identical with authentic [4] material.

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