Light-induced and Related Reactions of Quinones. Part I.[1] The Mechanism of Formation of Acetylquinol from 1,4-Benzoquinone and Acetaldehyde

By J. Malcolm Bruce and E. Cutts

Illumination of 1,4-benzoquinone in acetaldehyde with visible light yields acetylquinol which is shown by the use of 1,1-diphenylethylene as a scavenger to be formed *via* attack of acetyl radicals on the quinone. Supporting evidence is provided by reactions initiated in the dark by di-t-butyl diperoxalate.

MANY light-induced reactions between quinones and substrates carrying hydrogen atoms which can be fairly easily abstracted have been described during the last eighty years, but little is known of the principles which govern them and a further examination was therefore undertaken.

Light-induced reactions between *p*-quinones and aldehydes are particularly suitable for study since they usually yield acylquinols or quinol monoesters, neither of which is readily oxidised by the quinone, and complications due to the formation of large quantities of quinhydrones are therefore avoided. Tetrasubstituted *p*-benzoquinones yield the corresponding quinol monoesters,[2-4] but less highly substituted ones often give ketones in addition to or instead of esters. Thus irradiation of 1,4-benzoquinone in the presence of benzaldehyde yields both quinol monobenzoate and benzoylquinol,[5] but with acetaldehyde the major product is acetylquinol.[6] 1,4-Napthaquinone and its 2-methyl homologue similarly yield [7] the corresponding acetylnaphthaquinols and acetaldehyde, but quinizarinquinone gives [8] quinizarin monoacetate even though it contains an incompletely substituted 1,4-benzoquinone nucleus, suggesting that the formation of a quinol monoester followed by a light-induced Fries rearrangement, for which there are analogies,[9] could be the normal path for all the reactions which yield ketones, and that the quinizarin ester may have been isolated because the reaction conditions were unfavourable for the rearrangement. A similar argument would apply to the quinol monobenzoate formed from 1,4-benzoquinone and benzaldehyde. Such a rearrangement is now shown to be unlikely.

Mechanisms involving the combination of semiquinone and acyl radicals, formed simultaneously by interaction of the excited quinone with the aldehyde, have been suggested in order to account for the low quantum yields for the rections between chloranil and benzaldehyde [3] to give tetrachloroquinol monobenzoate, and between 1,4-naphthaquinone and acetaldehyde [7] to form 2-acetyl-1,4-naphthaquinol, but mechamisms involving attack of an acyl radical on a quinone molecule, for which there are analogies [10-12] involving radicals other than acyl, followed by disproportionation or crossed disproportionation are also possible, and a scheme for the light-induced formation of acetylquinol from 1,4-benzoquinone and acetaldehyde is supported by the work now described.

The visible absorption spectrum of 1,4-benzoquinone in cyclohexane contains at least five partially overlapping bands between 4000 and 5000 Å, but in acetaldehyde, used in the present work as both solvent and substrate, the fine structure is lost and only a broad absorption is observed, although in the same region. This absorption, which is probably due to an $n-\pi^*$ singlet transition,[13] and can cause, although not necessarily directly, reaction with the substrate to occur, lies in the region of emission of a tungsten filament lamp

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[1] Preliminary communication: J. M. Bruce and E. Cutts, *Chem. Comm.*, 1965, 2.

[2] R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 1953, 238.

[3] G. O. Schenck and G. Koltzenburg, *Angew. Chem.*, 1954, **66**, 475.

[4] A. Schönberg and M. M. Sidky, *J. Org. Chem.*, 1957, **22**, 1698.

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

[6] H. Klinger and W. Kolvenbach, *Ber.*, 1898, **31**, 1214.

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

[8] O. Dimroth and V. Hilken, *Ber.*, 1921, **54**, 3050.

[9] R. A. Finnegan and J. J. Mattice, *Tetrahedron*, 1965, **21**, 1015, and references therein.

[10] F. J. L. Aparicio and W. A. Waters, *J. Chem. Soc.*, 1952, 4666; A. F. Bickel and W. A. Waters, *ibid.*, 1950, 1764; L. F. Fieser *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3174; L. F. Fieser and A. E. Oxford, *ibid.*, 1942, **64**, 2060; L. F. Fieser and F. C. Chang, *ibid.*, p. 2043.

[11] Cf. C. C. Price, *J. Amer.. Chem. Soc.*, 1943, **65**, 2380.

[12] A. Rembaum and M. Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 4468.

[13] J. A. Barltrop and B. Hesp, *Proc. Chem. Soc.*, 1964, 195; J. M. Hollas, *Spectrochim. Acta*, 1964, **20**, 1563; Y. Kanda, H. Kaseda, and T. Matumura, *ibid.*, p. 1387; A. Kuboyama, *Bull. Chem. Soc. Japan*, 1962, **35**, 295.

which was therefore used as the source of light for most experiments. This also ensures that complications due to the direct excitation of species which absorb below 3500 Å are likely to be small.

Illumination of a 14% solution of 1,4-benzoquinone in outgassed acetaldehyde at 15—20° caused a colour change from yellow to dark brown, which faded towards the end of the reaction, and the formation of a precipitate of acetylquinol contaminated with quinhydrone. Work-up afforded quinol (15%) and acetylquinol (VII, 67%) as previously reported,[6] and quinol monoacetate (IV, 0·6%). Under these conditions a direct light-induced rearrangement (cf. ref. 9) of the monoacetate is unlikely since it does not absorb in the visible region, but this does not exclude it as an intermediate in the formation of acetylquinol since its rearrangement might be sensitised by 1,4-benzoquinone. This possibility was checked by irradiating a mixture of 1,4-benzoquinone and quinol monoacetate in acetaldehyde: acetylquinol was obtained in similar yield to that in the absence of the monoacetate, and the latter was quantitatively recovered. The possibility that the recovered ester contained acetyl or quinol residues different from those of the starting material, which would have implied a sensitised rearrangement involving a stationary concentration of the monoacetate, and could have been checked by the use of a labelled ester, was not tested. However, the similarity of the yields of acetylquinol formed in the presence or absence of the monoacetate, and the alternative evidence presented below, suggest that such a process is unlikely. Unsensitised rearrangements could, however, have occurred during some of the previously reported irradiations which used sunlight or mercury vapour lamps, and to check this a solution of quinol monoacetate in acetaldehyde was irradiated through Pyrex glass with light from a mercury arc: it was almost quantitatively recovered after a time for which a parallel irradiation of 1,4-benzoquinone in acetaldehyde had yielded 56% of acetylquinol.

These observations suggest that quinol monoacetate is not an important intermediate in the formation of acetylquinol, but they do not eliminate the possibility, previously suggested[12] for the interaction of methyl radicals with quinones, of the rearrangement of a radical such as (V), formed by addition of an acetyl radical to an oxygen atom of 1,4-benzoquinone, to one such as (II) from which the product could be derived. The possibility of such a rearrangement was tested by treating a solution of quinol monoacetate in acetaldehyde at room temperature with an excess of di-t-butyl diperoxalate[14] which decomposes under these conditions to yield carbon dioxide and t-butoxyl radicals which can react (see below) with the solvent to form acetyl radicals; either radical could then abstract a hydrogen atom from the hydroxyl group of the monoacetate (IV) to yield the radical (V). Quinol monoacetate was almost quantitatively recovered, suggesting that a rearrangement of the type (V) ⟶ (II) does not appreciably contribute to the formation of acetylquinol.

Alternative routes to acetylquinol (VII) could involve combination (cf. ref. 7) of semiquinone (I) and acetyl radicals to give (III), or attack (cf. refs. 11 and 12) of acetyl radicals on the quinone to yield (II). The former would involve a pair of radicals formed simultaneously close to each other, and could therefore be influenced by solvent-cage effects, whilst the latter should not be appreciably solvent-controlled and might therefore be affected by added scavengers. Illumination of a solution of 1,4-benzoquinone in acetaldehyde at −70° gave a yield of acetylquinol almost identical with that obtained by illumination of a similar solution at 15°, suggesting that a cage-controlled combination of radicals might not be important. Attention was therefore turned to the use of scavengers, the choice being limited by the facts that they should be essentially unreactive towards 1,4-benzoquinone in its ground or an excited state, and that they should preferably be capable of yielding recognisable products from any radicals, *e.g.*, acetyl, which they intercepted, although the latter criterion is not of paramount importance in distinguishing between cage- and non-cage-controlled processes. Olefinic systems carrying only vinylic, and consequently difficulty abstractable, hydrogen atoms were therefore chosen, it being considered that semiquinone radicals (I) were unlikely to be trapped as they would probably undergo efficient disproportionation,[15] but that acetyl radicals[16] or aryloxyl radicals,[17] *e.g.*, (V), might be scavenged by olefins such as styrene or 1,1-diphenylethylene. However, olefins of this type form charge-transfer complexes[18] with 1,4-benzoquinone, and complications could therefore arise because excitation of these might lead to the formation of oxetans,[19] or to a change in the path of the reaction involving acetaldehyde. However, it has been reported[20] that acetyl radicals, generated from acetaldehyde and benzoyl peroxide at 80—90°, will add to diethyl maleate, and that several other radicals will add[21,22] to maleic anhydride, and it therefore seemed appropriate to employ maleic anhydride as a scavenger since it contains only vinylic hydrogen atoms and does not readily undergo photo-addition[23] to 1,4-benzoquinone. However, irradiation of a mixture of 1,4-benzoquinone and maleic anhydride in the molar ratio 1 : 1·1 in acetaldehyde still led to the formation of

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

[15] E. Kilner and D. M. Samuel, " Applied Organic Chemistry," Macdonald and Evans, London, 1960, p. 365.

[16] Cf. G. Wittig and W. Gauss, *Chem. Ber.*, 1947, **80**, 363.

[17] Cf. F. Tüdös, *J. Polymer Sci.*, 1958, **30**, 343; J. C. Bevington, N. A. Ghanem, and H. W. Melville, *J. Chem. Soc*, 1955, 2822; *Trans.Faraday Soc.*, 1955, **51**, 946.

[18] R. Foster, *Tetrahedron*, 1960, **10**, 96; L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3776.

[19] Cf. D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.*, 1964, 87.

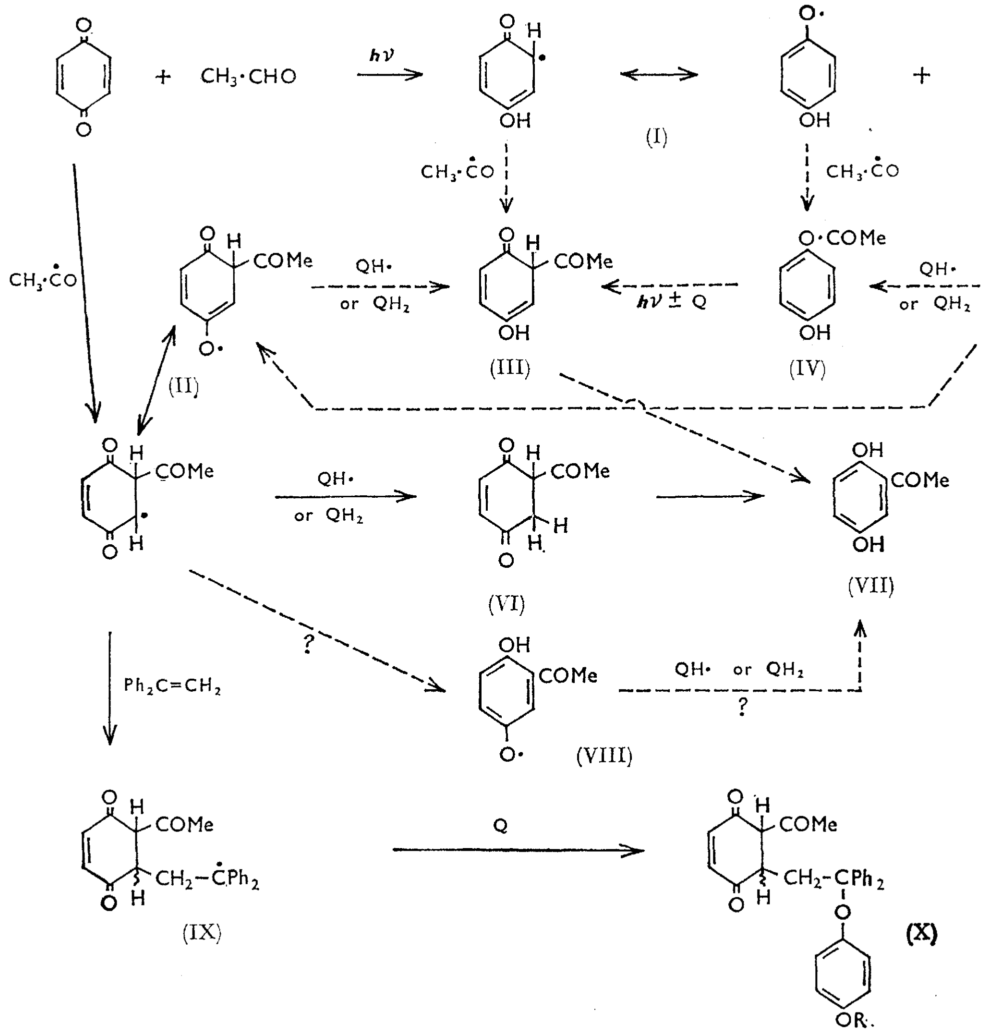
[20] T. M. Patrick, *J. Org. Chem.*, 1952, **17**, 1009.

[21] J. B. Conant and B. F. Chow, *J. Amer. Chem. Soc.*, 1933, **55**, 3475; R. L. Jacobs and G. G. Ecke, *J. Org. Chem.*, 1963, **28**, 3036.

[22] G. G. Ecke, L. R. Buzbee, and A. J. Kolka, *J. Amer. Chem. Soc.*, 1956, **78**, 79.

[23] D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, 1964, 2428.

71% of acetylquinol. Much of the maleic anhydride was recovered, but there was chromatographic evidence that at least four other products, which were not isolated, were formed in very low yield. Maleic anhydride therefore has little effect on the overall reaction.



Full arrows represent major routes, broken arrows with question marks represent paths which may be less important, and broken arrows represent paths which are probably of minor importance.

Q = 1,4-benzoquinone, QH· = 1,4-benzosemiquinone, and QH_2 = quinol.

Styrene was next examined as a scavenger. Solutions in cyclohexane containing both 1,4-benzoquinone (0·3%) and styrene (4%) showed light absorption in the 3500—3700 Å region which was absent from the spectrum of either component separately, indicating the presence of a complex, but at similar concentrations in acetaldehyde the spectrum of the mixture in the 3500—7000 Å region was identical with that of 1,4-benzoquinone alone, indicating that in the more polar acetaldehyde complex formation is small, and is therefore unlikely to appreciably influence the light-induced reaction. In the absence of specific information concerning the relative reactivities of 1,4-benzoquinone and olefins towards acetyl radicals it was considered, wrongly (see below), that these might be similar to their methyl affinities,[12,24] but addition, in separate experiments, of sufficient styrene calculated on this basis to reduce the yields of acetylquinol by 5 and 50% caused reductions of, respectively, 88 and 95%, and the mixtures remained homogeneous throughout the irradiations. Some styrene was recovered, and quinol and acetylquinol were isolated, but in each case the major product was a polymeric glass which from its infrared spectrum contained hydroxyl ($\nu_{max.}$ 3300, broad, cm.$^{-1}$) and carbonyl ($\nu_{max.}$ 1600, broad, and 1700 cm.$^{-1}$) groups. The proton magnetic resonance (p.m.r.) spectrum (in $CDCl_3$) contained incompletely resolved multiplets between τ 2·3 and 3·2 attributed to phenyl protons, and between τ 3·2 and 3·8, the latter group containing strong singlets at τ 3·37 and 3·46, assigned to the aromatic protons of acetylquinol and quinol residues; and singlets, attributed to acetyl groups, at τ 7·51

[24] F. Leavitt, M. Levy, M. Szwarc, and V. Stannett, *J. Amer. Chem. Soc.*, 1955, **77**, 5493.

and 7·55 superimposed on a broad absorption between τ 6·2 and 9·0 due to protons in the backbone of the polymer. The intensities of the absorptions indicated the presence of approximately three styrene residues per quinol residue. Treatment of the polymer with hydrobromic acid in acetic acid gave both quinol and acetylquinol, and, although these may have been trapped in the glass and therefore would not be structurally significant, in the light of the evidence presented below for the structures of the products obtained from reactions involving 1,1-diphenylethylene instead of styrene, the structure (XI) is suggested for the polymer formed in the irradiation, although the cyclohexenedione system would almost certainly have enolised during work-up.

In the probable absence of an appreciable concentration of a quinone–styrene complex the drastic reduction in the yield of acetylquinol, and the formation of a polymer, suggests that when styrene is not present the formation of acetylquinol is not a cage-controlled process, and that it does involve *free* radical intermediates. However, this evidence is not definitive of the intermediates involved, and it was therefore desirable to employ a trapping agent which would not yield polymeric products. 1,1-Diphenylethylene seemed suitable since in addition to its fulfilling the requirements outlined above, the steric effects of the two phenyl groups should prevent the formation of species higher than dimers [25] from reactions involving addition [26] of free radicals to the 2-position of the olefin, although disproportionation products [27] might be expected to predominate, *e.g.*,

$$2\mathrm{Ph_2C{=}CH_2} + 2\mathrm{R}\cdot \longrightarrow 2\mathrm{Ph_2\dot{C}{-}CH_2R} \longrightarrow \underset{\text{(XII)}}{\mathrm{Ph_2CH{-}CH_2R}} + \underset{\text{(XIII)}}{\mathrm{Ph_2C{=}CHR}}$$

As with styrene, mixtures of 1,1-diphenylethylene and 1,4-benzoquinone in cyclohexane showed spectroscopic evidence for complex formation, but no such evidence was obtained for mixtures in acetaldehyde. Illumination of a 10% solution of 1,4-benzoquinone in acetaldehyde containing, with respect to the quinone, 0·6 mol. of 1,1-diphenylethylene caused the colour to change from yellow to brown, characteristic of quinhydrone, but this eventually faded to pale yellow; there was no precipitate. Removal of the acetaldehyde left a gum from which, by solvent extraction and fractional sublimation at temperatures up to 200°, were obtained 1,1-diphenylethylene (23% recovery), acetylquinol (13%), quinol (47%), and a mixture of two isomeric yellow substances, *A* and *B* (total 24%), formed in roughly equal amounts, which were subsequently separated by chromatography. Analysis of these indicated the molecular formula $C_{22}H_{18}O_3$ suggesting the presence in each of one quinol, one acetaldehyde, and one diphenylethylene residue. Both were phenolic. The infrared spectrum of *A* indicated the presence of a non-hydrogen bonded hydroxyl group ($\nu_{max.}$ 3290 cm.$^{-1}$) and an intramolecularly hydrogen bonded carbonyl group ($\nu_{max.}$ 1610 cm.$^{-1}$), suggesting, in agreement with the yellow colour, that the molecule contained an acetylquinol residue. This was confirmed by the p.m.r. spectrum (12% in $CDCl_3$) which showed a singlet at τ −1·77 (1H) and a broad band at τ 5·0 (1H), both of which were rapidly removed by deuterium oxide indicating that they were due to the hydroxyl groups, that at lowest field being attributed to the intramolecularly hydrogen bonded one; [28] a singlet at τ 7·37 (3H) attributable to an acetyl group (cf. acetylquinol, τ_{Me} 7·47); and a group of bands between τ 2·61 and 3·29 (total 13H) due to aromatic and olefinic protons. Of the latter group four singlets at τ 2·96, 3·10, 3·15, and 3·29 constitute an AB quartet (*J* = 9 c./sec.) which, since the components do not show fine structure, can be attributed to the 5- and 6-protons in a 3-substituted acetylquinol; the absorption due to the 5-proton which occurs in a similar position in the spectrum of acetylquinol is split by coupling with both the 3- and 6-protons. A singlet at τ 3·06 (1H) suggests the presence of an isolated olefinic proton, and another singlet at τ 2·61 (5H) could be due to a phenyl group, with the remaining seven bands, lying between τ 2·70 and 2·87 (total 5H), being attributable to a second phenyl group in an environment which causes the protons to be non-equivalent. The structure (XV) accounts for these properties, and the spectroscopic assignments are supported by the spectrum of triphenylethylene ($PhCH{=}CPh_2$) which contains bands, each showing some fine structure, at τ 2·68 (10H) and 2·90 (5H) due to the phenyl groups, and a singlet at τ 3·00 (1H) due to the olefinic proton. Structure (XV) for compound *A* is further supported by permanganate oxidation, which yields benzophenone.

The infrared spectrum of compound *B* lacked sharp absorption in the 3300 cm.$^{-1}$ region, suggesting the absence of a non-hydrogen bonded hydroxyl group, but showed strong bands at 1630 and 1612 cm.$^{-1}$ characteristic of an intramolecularly hydrogen bonded carbonyl group in an acetylquinol derivative. The presence of such a system, which is also suggested by the yellow colour, is supported by the p.m.r. spectrum (12% in $CDCl_3$) which shows singlets at τ −2·18 (1H, removed by D_2O) and 7·43 (3H) attributed, respectively, to an intramolecularly hydrogen bonded hydroxyl group, and an acetyl group [cf. acetylquinol in dioxan, τ −1·55 (OH) and 7·47 (Me); and ref. 28]. The remainder of the spectrum contains a singlet at τ 5·84 (2H), which is in the region expected for absorption by the α-protons of an ether, and a group of at least sixteen bands lying between τ 2·39 and 3·27 (total 12H) due to aromatic protons. Of these, a pair at τ 3·10 and 3·27 (total 1H)

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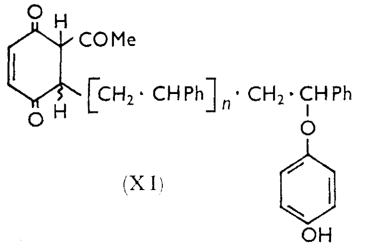
[25] C. E. Schildknecht, "Vinyl and Related Polymers," Wiley and Sons, New York, 1952, p. 156.

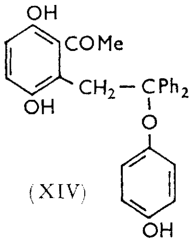
[26] Cf. K. W. Doak and D. L. Dineen, *J. Amer. Chem. Soc.*, 1951, **73**, 1084; C. S. Marvel, J. Dec, and J. O. Corner, *ibid.*, 1945, **67**, 1855.

[27] Cf. K. Ziegler, R. B. Whitney, and P. Herte, *Annalen*, 1942, **551**, 187; K. Ziegler, A. Seib, K. Knoevenagel, P. Herte, and F. Andreas, *ibid.*, p. 150; K. Ziegler, *ibid.*, p. 127.

[28] R. W. Hay and P. P. Williams, *J. Chem. Soc.*, 1964, 2270; S. Forsén and B. Åkermark, *Acta Chem. Scand.*, 1963, **17**, 1907; G. O. Dudek, *Spectrochim. Acta*, 1963, **19**, 691.

corresponds approximately in position with the resonances (τ 3·23) due to the 6-proton in acetylquinol, and is therefore attributed to such a proton in compound *B*; since $J = 10$ c./sec. the pair probably represents one half of a quartet due to the 5- and 6-protons in an acetylquinol derivative, and the absence of fine structure suggests the presence of a substituent at the 3-position. The doublet due to the 5-proton is largely obscured by the other aromatic resonances, the intensity of which indicates the presence of two phenyl groups. This information could be accounted for by structure (XVII), which might arise *via* scavenging [17] of a radical such as (II) or its enol, although models indicate that the acetyl methyl group would probably lie between the planes of the phenyl groups and be appreciably shielded, and its resonance would therefore be expected at higher field than that observed, *viz.*, τ 7·43, which is close to the value 7·47 for the methyl group in acetylquinol which cannot be so shielded. However, the properties of compound *B* could also be accounted for by the isomeric structure (XVI) since this would not involve abnormal shielding of the acetyl group, and the methylene protons could, as indicated by models, be appreciably deshielded by the phenyl groups thereby causing their resonance to be at an unusually low field (τ 5·84; cf. τ 7·38 for the methylene protons in ethylbenzene). The correctness of structure (XVI) was established by the quantitative formation of substance *B* when compound *A* (XV) was treated with toluene-*p*-sulphonic acid in toluene.[29]


(XI)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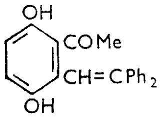
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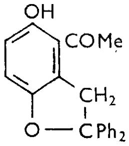
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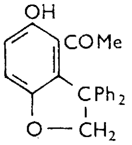
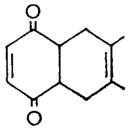

(XVII)


(XVIII)

The formation of these compounds could be explained by scavenging of radical (II) by 1,1-diphenylethylene to yield the radical (IX) which then loses a hydrogen atom either before or after cyclisation to give, respectively, an olefin or a dihydrofuran from which (XV) and (XVI) could be derived by enolisation. If the loss of hydrogen occurred by disproportionation the dihydro-derivative of the olefin (XV) would have been expected as a product, but it was not detected. However, radicals similar to (IX) or its cyclisation product which carry a hydrogen atom β to the carbon atom bearing the unpaired electron are known to be dehydrogenated by quinones,[30,31] and, since they would be formed in the presence of 1,4-benzoquinone, might have been dehydrogenated in the present case. This would account for the comparatively high (47%) yield of quinol, but it was felt that it was not necessarily the correct explanation since the physical properties, particularly solubility, of compounds (XV) and (XVI) were different from those of the crude product obtained by removal of the acetaldehyde from the mixture resulting from the irradiation, and it was thus possible that they were artefacts formed subsequently, *e.g.*, at the sublimation stage. The irradiation was therefore repeated, using a greater proportion of 1,1-diphenylethylene in order to further reduce the formation of acetylquinol, but after removal of the acetaldehyde the residue was fractionated by solvent, including chloroform, extraction at room temperature: an almost white compound *C* was obtained in 47% yield (based on the structure suggested in the sequel). This material analysed for $C_{28}H_{24}O_5$. Its infrared spectrum showed rather broad absorption in the 3000—3500 cm.$^{-1}$ region (OH) and a sharp peak at 1645 cm.$^{-1}$ attributable to a carbonyl group less strongly hydrogen bonded than those in compounds (XV) and (XVI). The p.m.r. spectrum (12% in dioxan; the compound was sparingly soluble in $CDCl_3$) contained singlets at τ 2·15 and 2·50 (each 1H, removed by addition of D_2O) attributed to hydroxyl protons, an incompletely resolved multiplet between τ 2·55 and 3·1 (total 13H, reduced to 12H by addition of D_2O) ascribed to a further hydroxyl and two phenyl groups, singlets at 3·43 and 3·49 (total 3H), and an incompletely resolved doublet ($J \sim 2$ c./sec.) at τ 3·61 (3H) which became a sharp singlet of undimished intensity after the solution had been treated with deuterium oxide. The latter bands are in the region expected for the nuclear protons in a quinol (cf. quinol, in dioxan, τ 3·40), and, since their total intensity corresponds with the presence of six such protons, two quinol residues, either both monosubstituted or, in view of the general nature of the reaction, more probably one disubstituted, are indicated. That the doublet at τ 3·61 collapses to a singlet after addition of deuterium oxide suggests that it arises from coupling between nuclear and hydroxyl protons, the latter presumably giving a resonance obscured by those due to the two phenyl groups since the other absorptions due to hydroxyl groups are singlets; coupling between nuclear and phenolic hydroxyl protons has been observed previously.[32] The remainder of the spectrum of compound *C* consists of singlets at τ 5·50 (2H) and 7·97 (3H) which are attributed, respectively, to methylene and acetyl groups. These features are explained by the structure (XIV), the benzylic protons (τ 5·50) being deshielded by the phenyl groups [cf. τ 5·84 for the benzylic protons of compound (XVI)]. The acetyl resonance at

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[29] Cf. R. C. Elderfield and V. B. Meyer, in R. C. Elderfield (ed.), "Heterocyclic Compounds," Wiley and Sons, Inc., New York, 1951, vol. 2, p. 10.

[30] R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 1953, 3405.

[31] K. Ziegler and W. Deparade, *Annalen*, 1950, **567**, 123.

[32] S. Forsén, *J. Phys. Chem.*, 1963, **67**, 1740.

τ 7·97 is particularly high (cf. acetylquinol, τ 7·47), and is in the region expected for that of an aliphatic acetyl group (cf. acetone, τ 7·90). Models show that the large substituent at the 3-position of the acetylquinol nucleus in compound (XIV) can force the acetyl group out of conjugation with the quinol ring to which it is attached, and this would account for the observed resonance position. This explanation is supported by the pale colour of the compound, by its infrared spectrum in the carbonyl region, by the absence of a hydroxyl resonance below τ 2·15 (cf. τ −1·55 for the intramolecularly hydrogen bonded hydroxyl group in acetylquinol), and by the comparatively high field (τ 3·4—3·6) of the resonances due to the aromatic protons other than those of the phenyl groups. Structure (XIV) for compound *C* is confirmed by its thermal decomposition which at 100° under reduced pressure occurs quantitatively to yield quinol and approximately equal amounts of the olefin (XV) and the dihydrobenzofuran (XVI).

The formation of the ether (XIV) is consistent with scavenging of a radical such as (IX) at an oxygen of a 1,4-benzoquinone molecule (addition [33] of the triphenylmethyl radical to 1,4-benzoquinone provides an analogy) to give the radical (X; R = •) from which (XIV) can be derived by enolisation and addition of a hydrogen atom. However, it was of interest to determine whether this was a genuine product from the light-induced reaction or whether, like compounds (XV) and (XVI), it was an artefact produced during work-up. The latter possibility was suggested by the observation that the total crude product remaining after removal of the acetaldehyde was readily soluble in chloroform, and that the ether (XIV) slowly separated when the solution was allowed to stand: it might have been formed *via* a compound such as (X; R = H) since exposure of the chloroform solution to daylight could have produced sufficient hydrogen chloride to catalyse such a transformation. Accordingly, mixtures of 1,4-benzoquinone and 1,1-diphenylethylene in the molar ratio 1 : 2 in outgassed acetaldehyde were sealed in p.m.r. spectrometer sample tubes, and the spectrum was measured initially and then after one week's storage in the dark: there was no change in the intensity, measured by comparative integration against an external standard, of the resonances (quoted in c./sec. downfield from the acetaldehyde doublet) at 316 and 204 due, respectively, to the aromatic and methylene protons of the diphenylethylene, or of that at 279 due to 1,4-benzoquinone. The solutions were then irradiated at 20° until the spectra, measured at intervals, showed no further significant change. The absorption at 316 became broader, and fine structure developed on the low-field side of it, whilst the bands at 279 and 204 progressively decreased in intensity until the final spectra indicated that quinone and diphenylethylene had been consumed in the molar ratio 2 : 1, as required for the formation of a compound such as (XIV). However, although new bands appeared at 284 and 271, there was no absorption in the 200—40 region characteristic of (XIV) which, in acetaldehyde, gives a singlet at 119 attributable to the methylene group (the phenyl and hydroxyl protons give a complex multiplet between 325 and 295, and the nuclear protons of the quinol residues give singlets at 274 and 263). After the solution had been kept in the dark for several weeks a new band at 128 appeared in the spectrum, in approximately the correct position (119) for the methylene resonance of compound (XIV); separate experiments showed that the positions of the resonances for acetaldehyde solutions were somewhat shifted by the presence of 1,1-diphenylethylene.

These results indicate that the ether (XIV) is not produced during the light-induced reaction, and therefore the products from a larger-scale, but otherwise similar, irradiation were fractionated using only acid-free [34] hydrocarbon solvents. A pale yellow compound, slightly contaminated with quinol, was obtained. This had infrared absorption at 3700 cm.$^{-1}$ attributable to a phenolic hydroxyl group, and carbonyl bands at 1710 and 1680 cm.$^{-1}$ which are similar to those (1720 and 1680 cm.$^{-1}$) of the enedione (XVIII). The p.m.r. spectrum (20% in acid-free [34] $CDCl_3$) showed a multiplet between τ 2·4 and 2·9 attributed to two phenyl groups; a small singlet at 3·31 which was removed by addition of deuterium oxide, and may have been due to a hydroxylic impurity; a rather broad singlet at τ 3·47 (6H) corresponding in position with that expected for the olefinic protons in cyclohexenedione systems [cf. τ 3·68 for compound (XVIII), and values between 3·0 and 3·4 for related systems [35]], and for the nuclear protons in a quinol; a broad band at τ 4·03 removed by deuterium oxide, and attributed to a hydroxyl group; poorly defined multiplets centred at, respectively, τ 6·60, 7·27, and 7·50 (total ~4H); and a singlet at τ 8·14 (3H) assigned to an acetyl group. These features can be accounted for by a structure of the type (X; R = H), possibly as a mixture of stereoisomers, and this formulation is supported by the quantitative transformation of the substance into the quinol (XIV) when its solution in ethanol is kept at room temperature. The enolisation is catalysed by traces of acid.

A solution of the enedione (X; R = H) in acetaldehyde containing 1,1-diphenylethylene at a concentration comparable with that remaining at the end of the irradiations which were followed spectroscopically showed singlets at 318 (with surrounding fine structure), 286, 272, and 251 c./sec. downfield from the acetaldehyde doublet, in good agreement with the results obtained during the irradiation, and indicating that the enedione is not an artefact produced during work-up.

The formation of the enedione (X; R = H) can be accounted for by a sequence of selective scavenging reactions involving addition of an acetyl radical, produced concomitantly with 1,4-benzosemiquinone by

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[33] J. Schmidlin, J. Wohl, and H. Thommen, *Ber.*, 1910, **43**, 1298.

[34] J. M. Bruce and P. Knowles, *J.*, 1964, 5900.

[35] M. F. Ansell, J. W. Lown, D. W. Turner, and D. A. Wilson, *J. Chem. Soc.*, 1963, 3036.

abstraction of a hydrogen atom from acetaldehyde by the excited quinone, to a quinone to give the radical (II) which is trapped in the enedione form by 1,1-diphenylethylene to form the comparatively unreactive alkyldiphenylmethyl radical (IX) which with another quinone molecule yields (cf. ref. 33) the aryloxyl radical (X; R = •) from which (X; R = H) can be derived by addition of a hydrogen atom. This may be provided by the semiquinone, or by quinol derived from it. The considerable selectivity of these reactions follows if the acetyl radical has nucleophilic character[36] $(CH_3\dot{C}{=}O \longleftrightarrow CH_3\bar{C}{=}\dot{O}^+)$ and therefore preferentially attacks a nuclear position of the quinone, and the radical (II) has electrophilic character and is scavenged by the olefin before it can enolise to the semiquinone (VIII). Similar selectivity has been observed for free radical-initiated reactions involving mixtures of olefins and αβ-unsaturated carbonyl compounds from which alternating copolymers are obtained.[37] In the absence of 1,4-benzoquinone, and therefore of an efficient competitive scavenger, 1,1-diphenylethylene in acetaldehyde reacts with acetyl radicals generated *via* the decomposition of di-t-butyl diperoxalate to yield[38] a mixture of 4,4-diphenylbutanone (XII; R = Ac) and 4,4-diphenylbut-3-enone (XIII; R = Ac), as expected.

The production of the enedione (X; R = H) indicates that in the absence of 1,1-diphenylethylene acetylquinol (VII) probably arises from the radical (II) by processes involving enolisation and addition of hydrogen, the latter being provided *via* disproportionation of (II) or its enol (VIII), in which case acetylquinone would be involved, or by crossed disproportionation with benzosemiquinone formed in the initial light-induced step, or from quinol which could arise from the semiquinone; the formation of quinol has already been noted.

The above results strongly indicate the intervention of *free* radicals, and supporting evidence was obtained from reactions involving the independent generation of acetyl radicals in the dark. Acetyl radicals have previously been generated non-photolytically *via* the decomposition[20,39] of peroxides in acetaldehyde at 80—100°, but reactions under these conditions would not be comparable with the present irradiations, and an alternative source of radicals for use at 15—20° was required. *N*-Nitrosoacetanilide decomposes in solution at this temperature, but in the presence of acetaldehyde and 1,4-benzoquinone only black tars were obtained. However, di-t-butyl diperoxalate[14] decomposes cleanly in cumene at room temperature to yield carbon dioxide and, *via* cumyl radicals, bicumyl, and a solution of this compound in acetaldehyde was therefore a potential source of acetyl radicals. In order to check this the decomposition was carried out in acetaldehyde alone: paraldehyde, t-butyl alcohol, and biacetyl were detected in the products, the biacetyl presumably having been formed by dimerisation of acetyl radicals. When the decomposition was carried out in acetaldehyde containing 1,4-benzoquinone (0·5 mol. with respect to peroxide since each molecule is potentially capable of generating two acetyl radicals) a considerable amount of tar was produced and acetylquinol was isolated in 37% yield, but in the presence of added quinol and a sufficient excess of perester to oxidise it completely to quinone (*i.e.*, quinone : quinol : perester = 2 : 1 : 2 mol.) the yield was increased to 69%. This supports sequences in which radicals such as (II) or (VIII) gain hydrogen from quinol or 1,4-benzosemiquinone; in the absence of a suitable source of hydrogen disproportionation of (II) or (VIII) would yield acetylquinol and acetylquinone, the latter possibly being responsible for the tars which are formed. It follows from this that acetaldehyde probably cannot serve as an efficient source of hydrogen, and therefore as a chain carrier, and this view is supported by the observation that with only 0·1 mol. of perester the yield of acetylquinol falls to 6%. The intermediate formation of acetylquinone by disproportionation of (II) or (VIII) cannot be excluded, however, since this quinone is readily reduced[40] by quinol in acetaldehyde solution.

Support for the above sequence leading to the enedione (X; R = H) *via* radicals, rather than *via* 1 : 1 quinone–olefin photoadducts which could be envisaged as intermediates, was obtained by decomposition, in the dark, of di-t-butyl diperoxalate in an acetaldehyde solution containing 1,4-benzoquinone, 1,1-diphenylethylene (respectively 1 : 2 mol.), and a trace of quinol: a brown tar was produced from which neither the enedione (X; R = H) nor its enol (XIV) could be isolated, but when it was fractionally sublimed at 100—180°/10^{-4} mm. quinol (36%) and a mixture (total 9%) of approximately equal amounts of the olefin (XV) and the dihydrobenzofuran (XVI) were obtained, as expected from the thermolysis of the ether (XIV). In an attempt to obtain a cleaner total product (cf. the perester experiments not involving diphenylethylene), quinol equivalent to the quinone used was added to the reaction mixture: 92% of the olefin was recovered, and acetylquinol was obtained in 65% yield, indicating that hydrogen-transfer from quinol or 1,4-benzosemiquinone to the radical (II) to give the enedione (VI) is much more efficient than scavenging of it by 1,1-diphenylethylene.

The above sequence of events involving several artefacts indicates the care which should be exercised in drawing mechanistic conclusions from the structures of compounds isolated by normal procedures, and underlines the value of studying light-induced transformations *in situ* by spectroscopic techniques.

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[36] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, 1959, p. 748; J. I. G. Cadogan, Royal Institute of Chemistry Lecture Series, 1961, No. 6, p. 5.

[37] M. G. Baldwin, *J. Polymer Sci.*, *Part A*, *General Papers*, 1965, **3**, 703; J. M. Barton, G. B. Butler, and E. C. Chapin, *ibid.*, p. 501; C. C. Price, *J. Chem. Educ.*, 1965, **42**, 14, and references therein.

[38] J. M. Bruce and J. N. Ellis, unpublished work.

[39] H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Amer. Chem. Soc.*, 1963, **85**, 1437.

[40] J. M. Bruce, unpublished work.

EXPERIMENTAL

Apparatus used for handling reactants and for irradiations was thoroughly washed with distilled water, then with distilled acetone, and dried. Reactants were purified immediately before use, 1,4-benzoquinone by sublimation, and acetaldehyde, styrene, and 1,1-diphenylethylene by fractional distillation (b. p., respectively, 21—22°/760 mm., 52°/30 mm., and 110°/2 mm.).

Solutions to be irradiated were placed in a vertical Pyrex tube of 16 mm. internal diameter and 280 mm. effective length which could be connected *via* a tap to a pumping system, and degassed at 10^{-2} mm. by the cool–pump–warm method. Solid carbon dioxide–acetone, which is at a temperature above the m. p. of acetaldehyde, was used as the cooling agent since with liquid nitrogen the acetaldehyde frequently polymerised [41] when the solid melted, giving a viscous mass even in the presence of 1,4-benzoquinone and styrene. With the tap closed, the apparatus was removed from the pumping system, and the tube containing the solution was surrounded by a concentric Pyrex jacket through which tap-water at approximately 15° was passed during the irradiation. For the reaction at −70° the water-jacket was replaced by a clear-walled Dewar flask containing solid carbon dioxide–acetone. Unless stated otherwise the solutions were irradiated with two 300w tungsten filament lamps placed close to the cooling jacket, the whole apparatus being surrounded by a polished aluminium reflector. A similar procedure was adopted for the irradiations which were followed spectroscopically, except that the solutions were contained in p.m.r. spectrometer sample tubes of 4 mm. i.d. which after being degassed were fusion-sealed.

P.m.r. spectra were measured with a Varian A-60 spectrometer with tetramethylsilane as internal standard except for solutions in acetaldehyde when the solvent resonances were used. Sublimation and bulb-to-bulb distillation temperatures are those of the heating-bath.

Quinol Monoacetate.—A mixture of quinol monobenzyl ether (10 g.), acetic anhydride (50 c.c.), and anhydrous sodium acetate (0·5 g.) was heated on the steam-bath for 5 hr., the acetic anhydride was removed, finally at 20 mm., and the residue was triturated with water. Sublimation of the insoluble material at 60°/0·05 mm. gave quinol monoacetate monobenzyl ether (9·7 g.), m. p. 112·5—114·5°. This material (1·22 g.) in ethanol (50 c.c.) was shaken with 5% palladium-on-charcoal (1 g.) under hydrogen at N.T.P. until hydrogen uptake ceased, the catalyst and solvent were removed, and the residue was sublimed at 0·05 mm. on to a cold-finger. Crystallisation of the sublimate from light petroleum (b. p. 40—60°) gave quinol monoacetate (0·59 g.) as needles, m. p. 59—60·5° (lit.,[42] 62—63°). It had $\nu_{\max.}$ (in Nujol) 3400 and 1720 cm.$^{-1}$.

Irradiations of 1,4-*Benzoquinone in Acetaldehyde.*—(*a*) A solution of 1,4-benzoquinone (3 g.) in acetaldehyde (22 c.c.) was irradiated for 4 weeks, and the resulting dark precipitate was collected by filtration and sublimed, first at 20°/0·15 mm. to give, on a cold-finger at −78°, metaldehyde (0·01 g.) identical (infrared spectrum) with authentic material, and then at 90—130°/0·15 mm. to give acetylquinol (0·31 g.), m. p. 201—202·5°, identical (mixed m. p. and infrared spectrum) with authentic [43] material. The acetaldehyde and other relatively volatile products such as paraldehyde were distilled from the filtrate, finally at 30°/2·5 mm., and the residue was fractionally sublimed at 0·05 mm. to give (i) at 60—90°, a solid from which, by treatment with hot light petroleum (b. p. 40—60°), quinol (0·01 g.) and quinol monoacetate (0·02 g.) identical (mixed m. p. and infrared spectrum) with authentic material were obtained; (ii) at 70—90°, quinol (0·02 g.); and (iii) at 90—140°, a mixture of quinol (0·39 g.) and acetylquinol (0·36 g.) which was separated by treatment with water to remove the quinol. Additional acetylquinol (0·5 g.) was obtained by more vigorous heating of the tarry residue.

Similar results were obtained when the irradiation was stopped after 1 week, but some (<2%) quinone was recovered as quinhydrone.

(*b*) 1,4-Benzoquinone (0·5 g.) in acetaldehyde (22 c.c.) was irradiated at −78 to −70° for 79 hr., and the mixture was worked-up as described under (*a*) to give acetylquinol (0·23 g., 72%). A parallel irradiation at 15° afforded acetylquinol (0·27 g., 76%).

Irradiations Involving Quinol Monoacetate.—(*a*) A mixture of 1,4-benzoquinone (0·18 g.) and quinol monoacetate (0·50 g.) in acetaldehyde (5 c.c.) was irradiated for 1 week, acetaldehyde and paraldehyde were removed, finally at 50°/20 mm., and the residue was distilled (bulb-to-bulb) at 0·05 mm. to give, at 60—90°, an oil (0·50 g., 100%) which solidified, and from which quinol monoacetate (0·35 g., 70%), m. p. 58·5—60° undepressed on admixture with authentic material, was obtained, and, at 90—120°, acetylquinol (0·14 g., 55%), m. p. 198—202° undepressed by authentic material.

(*b*) A solution of quinol monoacetate (0·50 g.) in acetaldehyde (5 c.c.) was irradiated with a 125w medium pressure mercury vapour lamp for 5 days. Removal of the acetaldehyde and bulb-to-bulb distillation of the residue at 90—110°/0·15 mm. gave quinol monoacetate (0·50 g.) slightly contaminated by green material which was not characterised. A parallel irradiation using 1,4-benzoquinone (0·36 g.) instead of quinol monoacetate afforded, by a procedure similar to that described above for irradiation with visible light, acetylquinol (0·28 g., 56%).

Irradiation in the Presence of Maleic Anhydride.—A mixture of 1,4-benzoquinone (0·25 g.) and maleic anhydride (0·25 g., freshly sublimed) in acetaldehyde (22 c.c.) was irradiated for 7 days, and then distilled to give acetaldehyde, paraldehyde, maleic anhydride (0·11 g.), and a solid residue. This was sublimed at 0·05 mm. to yield, at up to 70°, a mixture (0·15 g.) containing acetylquinol and, as shown by thin-layer chromatography, at least four other components; at 70—100° a mixture of quinol (0·03 g.) and acetylquinol (0·14 g.); and, at 100—150°, acetylquinol (0·12 g.).

Irradiations in the Presence of Styrene.—(*a*) A solution of 1,4-benzoquinone (0·25 g.) and styrene (2·50 g.) in acetaldehyde (22 c.c.) was irradiated for 7 days and then distilled, finally at 50°/20 mm., to remove acetaldehyde and a mixture (estimated by vapour-phase chromatography) of paraldehyde (0·55 g.) and styrene (1·56 g.). Sublimation at 100—130°/10^{-4} mm. then gave a mixture (estimated by ultraviolet spectroscopy) of quinol (0·02 g., 9%) and acetylquinol (0·01 g., 3%), and a brown glassy residue (0·73 g.).

(*b*) The foregoing irradiation was repeated, but using one tenth of the amount of styrene. A similar polymer

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[41] J. Furukawa and T. Saegusa, in H. F. Mark and E. H. Immergut (eds.), " Polymer Reviews," Interscience Publ., New York, 1963, **3**, 77.

[42] H. S. Olcott, *J. Amer. Chem. Soc.*, 1937, **59**, 392.

[43] E. Kurosawa, *Bull. Chem. Soc. Japan*, 1961, **34**, 300.

(0·42 g.) was obtained together with quinol (0·03 g., 11%) and acetylquinol (0·03 g., 9%).

Irradiations in the Presence of 1,1-*Diphenylethylene*.—(*a*) A solution of 1,4-benzoquinone (2·50 g.) and 1,1-diphenylethylene (2·50 g.) in acetaldehyde (22 c.c.) was irradiated for 7 days. The initially yellow solution became brown, but the colour then faded to pale yellow. There was no precipitate. Acetaldehyde and paraldehyde were distilled off, finally at 30°/20 mm., and the residue was extracted with boiling pentane (2 × 50 c.c.). Concentration of the first extract to 10 c.c. followed by standing at 20° gave a precipitate of acetylquinol (0·1 g.); the mother-liquor was combined with the second extract, and the solvent was removed to give 1,1-diphenylethylene (0·47 g.). The pentane-insoluble material was sublimed at 10^{-4} mm. to give (i) at up to 130°, a yellow solid *D*, and (ii) at 130—200°, a yellow solid *E*. The solid *D* was re-sublimed to give (iii) at up to 80°, a yellow solid which was chromatographed in benzene (75 c.c.) on silica gel (Sorbsil, 230 × 20 mm.) to give in the first 200 c.c. of eluate an unidentified material (0·01 g.), in the next 440 c.c. acetylquinol (0·16 g.), and then, eluted by chloroform (400 c.c.), quinol (0·73 g.); (iv) at 80—100°, a mixture of quinol (0·50 g.) and acetylquinol (0·20 g.); (v) at 100—150° a mixture (1·38 g.) of which a portion (1·28 g.) in benzene (175 c.c.) was chromatographed on silica gel (Sorbsil, 400 × 25 mm.) to give an unidentified material (0·01 g.) eluted by 350 c.c. of 1 : 1 benzene–light petroleum (b. p. 60—80°), a yellow substance *F* (0·52 g.) eluted by 2200 c.c. of this mixture, and another yellow substance *G* (0·72 g.) eluted by benzene (3000 c.c.). Sublimation of *F* at 140—160°/10^{-5} mm. and crystallisation of the sublimate from ethanol gave 4-*acetyl*-5-*hydroxy*-1,2-*diphenyl*-2,3-*dihydrobenzofuran* (XVI) as yellow crystals, m. p. 172—174° [Found: C, 79·9; H, 5·6%; *M* (Rast), 330. $C_{22}H_{18}O_3$ requires C, 80·0; H, 5·6%; *M*, 330]. Sublimation of *G* at 140—160°/10^{-5} mm. and crystallisation of the sublimate from carbon tetrachloride gave 1,1-*diphenyl*-2-(2-*acetyl*-3,6-*dihydroxyphenyl*)-*ethylene* (XV) as yellow crystals, m. p. 169—172° [Found: C, 80·2; H, 5·7%; *M* (Rast), 330. $C_{22}H_{18}O_3$ requires C, 80·0; H, 5·6%; *M*, 330]. Solid *E* was sublimed at 150°/10^{-5} mm. and the sublimate was crystallised from carbon tetrachloride to give more of the olefin (XV) (0·20 g.), and the carbon tetrachloride-soluble portion was crystallised from ethanol to give further dihydrobenzofuran (XVI) (0·10 g.). Repetition of this crystallisation sequence gave additional (XV) (0·52 g.) and (XVI) (0·04 g.).

(*b*) The foregoing irradiation was repeated, but using a larger quantity (7·51 g.) of 1,1-diphenylethylene. After the acetaldehyde and paraldehyde had been removed the viscous residue was extracted with light petroleum (3 × 25 c.c., b. p. 60—80°) to remove 1,1-diphenylethylene (5·13 g.), and the insoluble material was triturated with chloroform (25 c.c.) at room temperature for 1 hr. in daylight to give a solid (3·92 g.). A portion (2·97 g.) of this in ethanol (10 c.c.) was treated with water (15 c.c.), giving an almost white precipitate *H* (1·72 g.). Removal of the ethanol from the mother-liquor by distillation under reduced pressure at room temperature gave further *H* (0·1 g.), and, by extraction with ether, quinol (0·9 g.). Traces of quinol were removed from *H* either by reprecipitation or, more efficiently, by heating at 70°/10^{-5} mm., the resulting almost white microcrystalline material (total 2·28 g.) being 1-(4-*hydroxyphenoxy*)-1,1-*diphenyl*-2-(2-*acetyl*-3,6-*dihydroxyphenyl*)*ethane* (XIV) (Found: C, 75·4; H, 5·6. $C_{28}H_{24}O_5$ requires C, 76·4; H, 5·9%). It gave a very pale yellow solution in dioxan, and decomposed at ~100°.

(*c*) A mixture of 1,4-benzoquinone (0·05 g.) and 1,1-diphenylethylene (0·17 g.) in acetaldehyde (0·5 c.c.) was sealed in a p.m.r. spectrometer tube and treated as described in the discussion. The bands in each spectrum were integrated against the methylene resonance of an external standard consisting of 1,1-diphenylethylene (0·18 g) in acetaldehyde (0·5 c.c.) contained in a similar, sealed, tube. The standard had previously been checked for constancy by comparative integration against a sealed sample of dioxan in carbon tetrachloride. Concordant results were obtained from three separate experiments.

(*d*) A solution of 1,4-benzoquinone (2·50 g.) and 1,1-diphenylethylene (2·25 g.) in acetaldehyde (22 c.c.) was irradiated for 7 days, the solvent was removed at 20°, finally at 20 mm., and the residue was stirred with benzene (10 c.c.) at 20°. A small quantity of acetylquinol was filtered off and the filtrate was added to pentane (30 c.c.) to give a semi-solid precipitate. This was collected and dissolved in benzene (15 c.c.) and the solution was added to pentane (100 c.c.) to give a solid which was similarly precipitated five times more to give 1-(4-*hydroxyphenoxy*)-1,1-*diphenyl*-2-(2-*acetyl*-3,6-*dioxocyclohex*-4-*enyl*)*ethane* (X; R = H) (2 g.) as a pale yellow solid which readily decomposed when heated (Found: C, 74·3; H, 5·8. $C_{28}H_{24}O_5$ requires C, 76·5; H, 5·9%). Acid-free [34] benzene and pentane were used throughout. When a solution of (X; R = H) in ethanol was kept in the dark at room temperature for 7 days, and the solvent then removed, finally at 20°/0·01 mm., the infrared spectrum of the residue was identical with that of the ether (XIV).

Thermolysis of the Ether (XIV).—The compound (0·200 g.) was heated at 100°/10^{-4} mm. in a vertical tube to give a sublimate of quinol (0·049 g., 100%) and a residue from which a mixture (0·139 g., 95%) of the olefin (XV) and the dihydrobenzofuran (XVI) was obtained by sublimation at 130°/10^{-4} mm. The proportions in the mixture, determined by p.m.r. spectroscopy, were, respectively, 56 and 44%. When the thermolysis was effected at 150° using a preheated bath the decomposition was again quantitative, but the proportions of (XV) and (XVI) in the mixture were 51 and 49%.

Oxidation and Cyclisation of the Olefin (XV).—(*a*) Saturated aqueous potassium permanganate was added dropwise to a solution of the olefin (0·12 g.) in acetone (5 c.c.) at room temperature until the purple colour persisted, and sulphur dioxide was then passed in until a colourless solution was obtained. Water (10 c.c.) was added, most of the acetone was distilled off, and the residue was extracted with ether. The extract was washed with water, dried ($MgSO_4$), and the solvent was removed and the residue was sublimed on to a cold-finger to give benzophenone (0·024 g.), m. p. 47—49°, identical (mixed m. p. and infrared spectrum) with authentic material.

(*b*) A solution of the olefin (0·091 g.) and toluene-*p*-sulphonic acid (5 mg.) in dry toluene (10 c.c.) was refluxed for 12 hr., cooled, and washed with aqueous sodium hydrogen carbonate and then with water. The toluene was removed, finally at 20 mm., and the residue was sublimed at 120—140°/10^{-4} mm. to give the dihydrobenzofuran (XVI) (0·088 g., 97%), m. p. 172—174°, identical (mixed m. p. and infrared spectrum) with material prepared as described above.

Reactions Involving Di-t-butyl Diperoxalate.[14]—(*a*) A mixture of quinol monoacetate (0·19 g.) and the perester

(0·22 g.) in acetaldehyde (5 c.c.) was kept in the dark at 20° for 7 days, carbon dioxide being allowed to escape *via* a mercury seal. The solvent was then removed, and the residue was crystallised from pentane to give quinol monoacetate (0·16 g.) identical (mixed m.p. and infrared spectrum) with the starting material.

(*b*) A solution of 1,4-benzoquinone (0·50 g.) and the perester (0·51 g.) in acetaldehyde (50 c.c.) was kept for 5 days as described under (*a*), and the solvent was then distilled off. Fractional sublimation of the residue gave, at 80—120°/0·01 mm., acetylquinol (0·26 g., 37%) identical with authentic material. There was an appreciable quantity of dark brown tar.

(*c*) The foregoing experiment was repeated using less (0·046 g.) of the perester. Fractional sublimation afforded 1,4-benzoquinone (0·34 g., 67% recovery) and acetylquinol (0·036 g., 6%).

(*d*) A solution of 1,4-benzoquinone (0·50 g.), quinol (0·25 g.), and the perester (0·71 g.) in acetaldehyde (50 c.c.) was kept as above for 5 days, the solvent was removed, and the residue was sublimed at 100°/25 mm. to give 1,4-benzoquinone (0·05 g.) and then at 90—120°/0·05 mm. to give a mixture which was separated by treatment with water into quinol (0·09 g.) and acetylquinol (0·49 g., 69%).

(*e*) A mixture of 1,4-benzoquinone (0·51 g.), quinol (0·006 g.), 1,1-diphenylethylene (1·60 g.), and the perester (0·48 g.) in acetaldehyde (50 c.c.) was kept as described under (*a*) for 7 days, the acetaldehyde was removed, and the residue was freed from 1,1-diphenylethylene (1·22 g.) by extraction with pentane (100 c.c.), and then sublimed, first at 100°/10^{-4} mm. to give quinol (0·18 g.) and then at 100—180°/10^{-4} mm. to give a yellow mixture (0·14 g.) whose infrared and p.m.r. spectra were identical with those of a mixture containing equal quantities of the olefin (XV) and the dihydrobenzofuran (XVI). There was an involatile brown residue (0·53 g.).

(*f*) A mixture of 1,4-benzoquinone (0·12 g.), quinol (0·12 g.), 1,1-diphenylethylene (0·40 g.), the perester (0·17 g.), and acetaldehyde (20 c.c.) was treated as described under (*e*) to give, by extraction with pentane (25 c.c.), 1,1-diphenylethylene (0·37 g.), and, by sublimation, quinol (0·06 g.) and acetylquinol (0·11 g.).

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