Light-induced and Related Reactions of Quinones. Part V.[1] Substituent Effects in Light-induced Reactions between *p*-Quinones and Aldehydes

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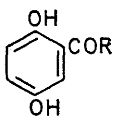
Irradiation of 1,4-benzoquinone with visible light in the presence of terephthaldehyde, *p*-cyanobenzaldehyde, and *p*-trifluoromethylbenzaldehyde yields the corresponding quinol monoaroyl esters as the major addition products. Similarly, naphthazarinquinone, 1,4-benzoquinone-2,3-dicarboxylic anhydride, and 2,3-dicyano-1,4-benzoquinone in acetaldehyde give the corresponding quinol monoacetates. 1,4-Benzoquinone gives quinol monoacrylate exclusively when it is irradiated in benzene containing acraldehyde, but in the presence of crotonaldehyde it yields both quinol monocrotonate and crotonylquinol. The significance of these results is discussed.

IRRADIATION of 1,4-benzoquinone with visible light in the presence of saturated aliphatic aldehydes leads to the formation of acylquinols as the only significant addition products.[1,2] In the presence of benzaldehydes, however, both aroylquinols and quinol monoaroyl esters are formed, the relative yields being influenced by *para*-substituents in the aldehyde. Quinizarinquinone anthracene-1,4:9,10-diquinone) gives[1] monoesters of 1,4-dihydroxy-9,10-anthraquinone with all types of aldehyde examined. 1,4-Benzoquinone and cinnamaldehyde yield only quinol monocinnamate. Results for three further *para*-substituted benzaldehydes, for three other high-potential quinones, anc for acraldehyde and crotonaldehyde are now presented.

Irradiation of 1,4-benzoquinone in benzene containing either terephthaldehyde or *p*-cyanobenzaldehyde gave both the aroylquinol (1; R = Ar) and, as the major product, the quinol monoaroyl ester (2; R = Ar); only the ester was obtained from *p*-trifluoromethylbenzaldehyde.



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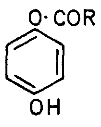

(2)

Irradiation of naphthazarinquinone (naphthalene-1,4:5,8-diquinone) (3) in acetaldehyde gave the monoacetate (4; R^1 = OAc, R^2 = H) and naphthazarin (4;

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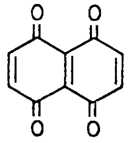
[1] Part IV, J. M. Bruce, D. Creed, and J. N. Ellis, *J. Chem. Soc.* (*C*), 1967, 1486.

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

$R^1 = OH$, $R^2 = H$) as the only products derived from the quinone, although paraldehyde was also produced. A parallel, but slower, reaction occurred in the dark, as previously described[1] for the structurally related quinizarinquinone (anthracene-1,4:9,10-diquinone) (5).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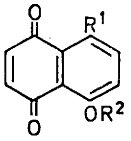
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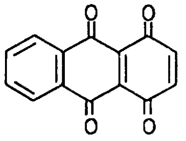
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Both naphthazarin (4; $R^1 = OH$, $R^2 = H$) and its monoacetate still contain *p*-quinonoid system, but, by analogy with the 9,10-anthraquinone system, where a hydroxy-group in the 1-position inhibits the photoreactivity,[3] it would be expected that these compounds would not react further. This was checked for juglone (5-hydroxy-1,4-naphthoquinone) (4; $R^1 = R^2 = H$), naphthazarin (4; $R^1 = OH$, $R^2 = H$), and for quinizarin (1,4-dihydroxy-9,10-anthraquinone) (*cf.* ref. 4): all were almost quantitatively recovered after irradiation under conditions similar to those used for naphthazarinquinone and quinizarinquinone, although with the first two hydroxy-compounds paraldehyde was formed quantitatively. As expected, irradiation of juglone acetate (4; $R^1 = H$, $R^2 = Ac$) readily gave a mixture of 2- and 3-acetyl-5-acetoxy-1,4-naphthoquinols, but, as with 1,4-naphthoquinone,[5] virtually no paraldehyde was formed.

1,4-Benzoquinone-2,3-dicarboxylic anhydride and 2,3-dicyano-1,4-benzoquinone behaved analogously, giving mixtures of the corresponding quinols and their monoacetates; there was no evidence for the formation of the acetylquinols. The acetaldehyde was quantitatively converted into paraldehyde in both cases.

The factors governing the formation of paraldehyde during the irradiation of some of the quinones have not been determined, but there may be a correlation with the acidity of the phenolic products.

Irradiation of 1,4-benzoquinone in benzene containing acraldehyde gave only quinol monoacrylate (2; $R = CH{=}CH_2$), but with crotonaldehyde crotonylquinol (1; $R = CH{=}CHMe$) and quinol monocrotonate (2; $R = CH{=}CHMe$) were formed in approximately equal amounts.

DISCUSSION

The above results confirm the reactivity trends for 1,4-benzoquinones with free nuclear positions which were becoming apparent from earlier work.[1,2] The products almost certainly arise *via* attack of excited quinone on the aldehyde to give an acyl or aroyl radical which is then scavenged by ground-state quinone, the position of scavenging depending on the nature of the radical and the oxidation potential of the quinone.

1,4-Benzoquinone scavenges acyl radicals almost exclusively at a nuclear carbon atom to yield, eventually,[1,2] the corresponding acylquinol (1; $R = Alk$), and benzoyl and *p*-substituted benzoyl radicals are similarly scavenged to yield the benzoylquinols (1; $R = Ar$) as major products when the *para*-substituents are electron donors (Me, Bu^t, MeO), although the corresponding quinol monobenzoates (2; $R = Ar$) are also obtained in up to 15% yield. When the *para*-substituents are electron acceptors (NO_2, CHO, CN, CF_3) the situation is reversed, and the monobenzoates become the predominant products. Thus, polar effects in the radicals appear to exert a controlling influence, which parallels that observed for ionic additions to 1,4-benzoquinone.

For the high-potential quinones quinizarinquinone, naphthazarinquinone, 1,4-benzoquinone-2,3-dicarboxylic anhydride, and 2,3-dicyano-1,4-benzoquinone even the acetyl radical, which with respect to 1,4-benzoquinone appears to be the most nucleophilic of those studied, is scavenged exclusively at oxygen to give the quinol monoacetates despite the availability of free nuclear positions. Electron-transfer from the radical ($R\dot{C}O$) to the quinone (Q) to give a radical-ion-pair type of intermediate $Q^{\overline{\cdot}}\overset{+}{R}CO$, in which $Q^{\overline{\cdot}}$ represents the semiquinone, may be the explanation (*cf.* ref. 1) since the acylium ion would now be located near to one of the oxygen atoms of the original quinone. Electron-transfer from ether radicals $EtO\dot{C}HMe$ to nitrobenzene has been detected,[6] that from a variety of carbon radicals to metal ions has been extensively studied,[7] and recently evidence has been presented[8] for electron-transfer from acetyl radicals to protonated quinolines.* Such a process would be particularly unfavourable for acyl radicals carrying substituents which would destabilise the incipient acylium ions, and the very low yield of quinizarin mono-*p*-nitrobenzoate obtained[1] from quinizarinquinone and *p*-nitrobenzaldehyde may be accounted for in these terms.

The exclusive formation of quinol monocinnamate (2; $R = COCH{=}CHPh$) from benzoquinone and cinnamaldehyde could also be a consequence of electron transfer, the relatively low potential quinone now sufficing since the incipient acylium ion can be appreciably stabilised by the adjacent olefinic π-system. In support of this, 1,4-benzoquinone and acraldehyde yield the ester (2; $R = COCH{=}CH_2$) exclusively; with crotonaldehyde both

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* Since the submission of this paper further evidence concerning electron transfer from radicals to quiones has appeared (H.-D. Becker, *J. Org. Chem.*, 1969, **34**, 1203).

[3] H. H. Dearman and A. Chan, *J. Chem. Phys.*, 1966, **44**, 416; D. Schulte-Frohlinde and C. v. Sonntag, *Z. Phys. Chem. (Frankfurt)*, 1965, **44**, 314; J. N. Pitts, H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, 1962, **66**, 2456.

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[5] G. O. Schenck and G. Koltzenburg, *Naturwiss.*, 1954, **41**, 452; E. Cutts, Ph.D. Thesis, University of Manchester, 1964.

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[7] J. K. Kochi, A. Bemis, and C. L. Jenkins, *J. Amer. Chem. Soc.*, 1968, **90**, 4616; J. K. Kochi and A. Bemis, *J. Amer. Chem. Soc.*, 1968, **90**, 4038; and references therein.

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the ester (2; R = COCH=CHMe) and the ketone (1; R = COCH=CHMe) are formed, suggesting that the methyl group enhances the nucleophilic character of the derived acyl radical so that both the electron-transfer and the polar-radical mechanisms can occur competitively.

EXPERIMENTAL

Irradiations were carried out as described previously.[1,2,9] Terephthaldehyde and *p*-cyanobenzaldehyde were sublimed, and *p*-trifluoromethylbenzaldehyde [10] was fractionally distilled. Quinones were purified by sublimation. Solvents were removed under reduced pressure, usually below 60°, and the products were isolated by chromatography and/or fractional sublimation. Yields are based on quinone consumed. I.r. spectra were measured for Nujol mulls, and u.v. spectra for solutions in ethanol. ^{1}H N.m.r. spectra were measured for solutions (concentration, %, given) in $(CD_3)_2CO$ unless stated otherwise; peaks are singlets unless indicated by d = doublet, t = triplet, q = quartet, m = multiplet; *J* in c./sec. Resonances assigned to OH groups were removed by D_2O. Molecular weights were determined mass spectrometrically.

1,4-*Benzoquinone and Substituted Benzaldehydes*.—(*a*) Irradiation of a solution of the quinone (2 g.) and terephthaldehyde (2·48 g.) in benzene (35 c.c.) caused precipitation of a solid which after 1 week completely covered the walls of the vessel. Removal of the solvent from the mother liquor and fractional sublimation of the residue gave 1,4-benzoquinone (0·60 g., 30% recovery) and terephthaldehyde (1·26 g., 51% recovery). Crystallisation of the precipitate from benzene gave *quinol mono*-p-*formylbenzoate* which, after sublimation at 140°/10^{-4} mm., formed white crystals, m.p. 189—191° (Found: C, 69·3; H, 4·5%; *M*, 242. $C_{14}H_{10}O_4$ requires C, 69·3; H, 4·1%; *M*, 242); $\nu_{max.}$ 3450s, 1705br,s, 1600m cm.$^{-1}$, $\lambda_{max.}$ 249·5—252, 277, 301 nm. (ε 20,500, 5390, 2510); τ (12%) −0·25 (CHO), 1·60 (d, *J* 10, 3′-H + 5′-H), 1·88 (d, *J* 10, 2′-H + 6′-H), 2·75 (d, *J* 11, 2-H + 6-H), 3·0 (d, *J* 11, 3-H + 5-H), 6·9 (OH). The solvent was removed from the mother liquor from this crystallisation, and the residue was sublimed, first at 110—120°/10^{-3} mm. to give a mixture of the foregoing ester and the yellow *p*-formylbenzoylquinol, and then at 140—150°/10^{-3} mm. to give more ester (0·45 g.). Analysis of the mixture from the sublimation by ^{1}H n.m.r. spectroscopy showed that it contained ester (0·27 g.) and *p*-formylbenzoylquinol (0·06 g., 2%) which had τ −1·20 (1-OH) and 3·28 (H-3) with other bands overlapping those due to the ester. The total yield of quinol mono-*p*-formylbenzoate was 40% (0·84 g.). The 2,4-*dinitrophenylhydrazone* of quinol mono-*p*-formylbenzoate had m.p. 281° (decomp.) (Found: C, 56·8; H, 3·1; N, 13·5. $C_{20}H_{14}N_4O_7$ requires C, 56·8; H, 3·3; N, 13·4%), and $\nu_{max.}$ 3390m, 3200w, 1710s, 1620s, and 1590s cm.$^{-1}$.

(*b*) The reaction was carried out as in (*a*), but with quinone (1 g.) and *p*-cyanobenzaldehyde (1·36 g.) to give a precipitate which was extracted (Soxhlet) with light petroleum (b.p. 80—100°). The material extracted was sublimed at 80°/10^{-4} mm. to give *p*-cyanobenzaldehyde (0·05 g.), and then at 130—140°/10^{-4} mm. to yield *quinol mono*-p-*cyanobenzoate* (0·15 g.), m.p. 187—189° (Found: C, 70·5; H, 3·5; N, 5·6%; *M*, 239. $C_{14}H_9NO_3$ requires C, 70·3; H, 3·8; N, 5·9%; *M*, 239); $\nu_{max.}$ 3490s, 2235m, 1600w cm.$^{-1}$; $\lambda_{max.}$ 238, 248, 281—282 nm. (ε 33,700, 22,150, 4210) and τ (16%) 1·61 (d, *J* 11, 3′-H + 5′-H), 1·96 (d, *J* 11, 2′-H + 6′-H), 2·75 (d, *J* 12, 2-H + 6-H), 3·04 (d, *J* 12, 3-H + 5-H) and 6·95br (OH). The solvent was removed from the benzene solution remaining from the irradiation, and the residue was sublimed at 90°/10^{-4} mm. to give 1,4-benzoquinone (0·09 g., 9% recovery) and *p*-cyanobenzaldehyde (0·76 g.), and then at 130—140°/10^{-4} mm. to give a mixture of the foregoing ester and *p*-cyanobenzoylquinol which was shown by its ^{1}H n.m.r. spectrum [τ (10%) −1·06 (OH) with other bands overlapping those due to the ester] to contain ester (0·42 g.) and ketone (0·10 g.). The total yields were *p*-cyanobenzaldehyde (0·81 g., 61% recovery), quinol mono-*p*-cyanobenzoate (0·56 g., 56%), and *p*-cyanobenzoylquinol (0·1 g., 10%).

(*c*) A mixture of 1,4-benzoquinone (0·71 g.) and *p*-trifluoromethylbenzaldehyde (1·27 g.) in benzene (25 c.c.) was irradiated: a black precipitate was formed during the first day; the irradiation was stopped after 1 week. The precipitate (0·16 g.) was quinhydrone. The solvent was removed from the mother liquor, and the residue was chromatographed on silica gel to yield (i) with benzene, *p*-trifluoromethylbenzaldehyde (0·37 g., 22% recovery), (ii) with 10% ether in benzene, quinhydrone (0·44 g.; total 0·60 g., 84%), and (iii) with 20% ether in benzene a mixture which was separated by preparative t.l.c. into *p*-trifluoromethylbenzoic acid (0·07 g.) and *quinol mono*-p-*trifluoromethylbenzoate* (0·15 g., 12%) which had m.p. 165—165·5° (Found: C, 59·6; H, 3·2%; *M*, 282. $C_{14}H_9F_3O_3$ requires C, 59·6; H, 3·1%; *M*, 282) which had $\nu_{max.}$ 3390s, 1735s cm.$^{-1}$, and τ (10%) 1·15—1·55 (m, 2′-H + 6′-H + OH), 1·60—1·91 (m, 3′-H + 5′-H) and 2·42—2·97 (m, 2-H + 3-H + 5-H + 6-H), and (iv) with ether, more *p*-trifluoromethylbenzoic acid (0·1 g.; total 0·17 g., 13%).

High-potential Quinones and Acetaldehyde.—(*a*) Naphthazarin [11] was sublimed at 95—100°/5 × 10^{-5} mm. to give red crystals with a green lustre, m.p. 200—205° (decomp.); this compound (1 g.) in glacial acetic acid (8 c.c.) was treated portionwise with lead tetra-acetate until the red colour had been discharged after which the mixture was shaken for 10 min. The precipitate was collected and extracted with hot benzene (4 × 20 c.c.): removal of the solvent gave naphthazarinquinone [12] (0·52 g., 52%) as dark green crystals. The quinone (0·28 g.) was irradiated in acetaldehyde (170 c.c.) for 18 hr.; the colour changed to bright red after 30 min. Removal of the solvent and chromatography of the residue on activated [13] neutral silica gel gave (i) with benzene, naphthazarin (0·05 g., 16%), and (ii) with 30% ether in benzene followed by sublimation at 70—75°/5 × 10^{-3} mm., naphthazarin monoacetate (0·12 g., 36%), m.p. 140—141° (lit.,[14] 137—138°) (Found: C, 61·9; H, 3·8%; *M*, 232. Calc. for $C_{12}H_8O_5$; C, 62·1; H, 3·5%; *M*, 232); $\nu_{max.}$ 1760s, 1650s, 1200s, 870m cm.$^{-1}$; τ (10% in $CDCl_3$) −2·43 (OH), 2·65 (2-H + 3-H), 3·06 (d, 6-H + 7-H) and 7·58 (Ac). When a solution of naphthazarinquinone (0·20 g.) in acetaldehyde (110 c.c.)

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[10] R. Filler and H. Novar, *J. Org. Chem.*, 1960, **25**, 733.

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[12] *Cf.* K. Zahn and P. Ochwat, *Annalen*, 1928, **462**, 72.

[13] H. Brockmann and W. Müller, *Chem. Ber.*, 1958, **91**, 1920.

[14] L. A. Cort and P. A. B. Rodriguez, *J. Chem. Soc.* (*C*), 1967, 949.

was kept in the dark for 4 days and then worked up as described above it gave naphthazarin (0·03 g., 14%), and naphthazarin monoacetate (0·11 g., 46%).

(*b*) 3,6-Dihydroxyphthalic anhydride, obtained by sublimation of 3,6-dihydroxyphthalic acid [15] in small batches at 190°/10^{-4} mm., was oxidised to 1,4-benzoquinone-2,3-dicarboxylic anhydride by treatment of its suspension in dry carbon tetrachloride with nitrogen oxides; [16] sublimation at 150°/10^{-4} mm. gave the brick-red quinone; $\nu_{\text{max.}}$ 1863s, 1803—1790br, s, 1675—1660s, 1590m cm.$^{-1}$. Irradiation of the quinone (0·07 g.) in acetaldehyde (10 c.c.) for 10 days, removal of paraldehyde, extraction of the residue with light petroleum (b.p. 60—80°), and sublimation of the insoluble material at 80—90°/10^{-4} mm. gave a yellow solid (0·04 g.) which contained 3-acetoxy-6-hydroxyphthalic anhydride as shown by its spectra: $\nu_{\text{max.}}$ 3580m, 3500—3300m, 1850—1840s, 1770—1750s cm.$^{-1}$; τ 0·00br (OH), 2·54 (centre of AB quartet, *J* 8, 4-H + 5-H), 7·70 (Ac); *M*, 222 ($C_{10}H_6O_6$ requires *M*, 222). The compound was not obtained in a pure state; the absence of aromatic proton resonances in the τ 1·5—2·4 region indicates the absence of 4-acetyl-3,6-dihydroxyphthalic anhydride.

(*c*) 2,3-Dicyano-1,4-benzoquinone, obtained by oxidation [16] of the quinol with nitrogen oxides, was sublimed at 110—120°/10^{-2} mm. A solution of it (0·64 g.) in acetaldehyde (30 c.c.) was irradiated for 4 weeks; the paraldehyde was removed and the residue was chromatographed on silica gel to give (i) with 30% ether in benzene followed by sublimation at 110—120°/10^{-4} mm., 2,3-*dicyanoquinol monoacetate* (0·51 g., 64%), m.p. 163·5—165° (Found: C, 59·2; H, 3·1; N, 13·5%; *M*, 202. $C_{10}H_6N_2O_3$ requires C, 59·4; H, 3·0; N, 13·4%; *M*, 202); $\nu_{\text{max.}}$ 3290s, 2240m, 1780s, 1760m, 1590m cm.$^{-1}$; $\lambda_{\text{max.}}$ 224, 238, 330 nm (ε 15,350, 9400, 6040), and τ (6%) 2·48 ("d", "*J*" 2, 5-H + 6-H) and 7·67 (Ac); acetylation of the monoacetate gave the diacetate, m.p. 167—168° (lit.,[15] 165—166°), identical with authentic material prepared from 2,3-dicyanoquinol; and (ii) with ethyl acetate, 2,3-dicyanoquinol (0·22 g., 35%).

Juglone Acetate and Acetaldehyde.—This quinone [17] (0·87 g.) was irradiated in acetaldehyde (100 c.c.) for 3 weeks, the solvent was removed, and the residue was sublimed at 140—150°/5×10^{-4} mm. to give a mixture (0·66g., 64%) of 2- and 3-acetyl-5-acetoxy-1,4-naphthoquinol which was not separated (Found: *M*, 260. $C_{14}H_{12}O_5$ requires *M*, 260); $\nu_{\text{max.}}$ 3400—3100s, 1765s, 1740m, 1640s 1600s cm.$^{-1}$; $\lambda_{\text{max.}}$ 218, 257, 303, 317, 390 nm (ε 31,330, 34,140, 3060, 3250, 7020); τ (12%) 1·10 (OH), 1·84 (q, J_1 8, J_2 2), 2·32 (t, *J* 8), 2·77, 2·82 (q, J_1 8, J_2 2), 6·99 (OH), 7·30 (Ac), 7·37 (Ac), 7·58 (OAc) and 7·68 (OAc); integration showed that the ratio of the components was 4 : 1, but insufficient evidence was available to allow precise assignment.

1,4-*Benzoquinone and Acraldehyde.*—A solution of the quinone (2 g.) and acraldehyde (1·2 c.c.) in benzene (35 c.c.) was irradiated for 3 weeks; the solvent and excess of acraldehyde were removed and the residue was chromatographed on silica gel (100 g.) with chloroform as eluant to give (i) 1,4-benzoquinone (0·58 g., 29% recovery), and (ii) *quinol monoacrylate* (1·16 g., 38%) as an orange oil which was distilled (bulb-to-bulb) at 110° (bath)/0·5 mm. (Found: C, 65·5; H, 4·9%; *M*, 164. $C_9H_8O_3$ requires C, 65·9; H, 4·9%; *M*, 164); $\nu_{\text{max.}}$ (film) 3400br,s, 1740—1710vs, 1635m, 1600m, 1510vs cm.$^{-1}$, and τ (10% in $CDCl_3$) 3·10 (d, *J* 9, 2-H + 6-H), 3·30 (d, *J* 9, 3-H + 5-H), 3·28—4·12 (m, $CH{=}CH_2$), 4·34—4·94br, (OH).

1,4-*Benzoquinone and Crotonaldehyde.*—(*a*) A solution of the quinone (2 g.) and crotonaldehyde (1·5 c.c.) in benzene (35 c.c.) was irradiated for 3 weeks: a dark crystalline precipitate soon formed. Removal of the solvent and excess of aldehyde, and chromatography of the residue on silica gel (150 g.) with 5% ether in chloroform as eluant gave (i) 1,4-benzoquinone (0·86 g., 43% recovery) and (ii) a mixture (1·64 g., 50%) which was separated by fractional crystallisation from light petroleum into *quinol monocrotonate*, m.p. 111—112° (Found: C, 67·1; H, 5·6%; *M*, 178. $C_{10}H_{10}O_3$ requires C, 67·3; H, 5·6%; *M*, 178); $\nu_{\text{max.}}$ 3430s, 1720s, 1655s cm.$^{-1}$; $\lambda_{\text{max.}}$ 221, 278 nm (ε 11,000, 3000); τ (3% in $CDCl_3$) 2·84 (q, J_{AB} 16, J_{AMe} 7, H_A of $CH_A{=}CH_BMe$), 3·10 (d, *J* 9, 2-H + 6-H), 4·00 (q, J_{AB} 16, J_{BMe} 1·5, H_B), 4·42 (OH), and 8·04 (q, J_{AMe} 7, J_{BMe} 1·5, Me); and crotonylquinol, yellow, m.p. 140—142° (lit.,[18] 154·5°) (Found: C, 67·3; H, 5·5%; *M*, 178); $\nu_{\text{max.}}$ 3350s, 1652, 1597s, 1560s cm.$^{-1}$; τ (4% in $CDCl_3$) −2·24 (2-OH), 2·69—3·23 (m, aromatic and olefinic H_5), 4·95br (5-OH), and 7·99 (d, *J* 6, Me). Analysis of the mixture from the irradiation by ^1H n.m.r. spectroscopy showed that it contained quinol monocrotonate and crotonylquinol in the ratio 4 : 5.

(*b*) No precipitate was formed when the quinone (1 g.) was irradiated in crotonaldehyde (25 c.c.) in the absence of benzene, and the quinone was completely consumed to give a mixture of quinol monocrotonate (0·8 g., 50%) and crotonylquinol (0·8 g., 50%).

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