

Light-induced Cleavage of the Side-chain of Some 1'-Hydroxyalkyl-1,4-benzoquinones

By J. MALCOLM BRUCE,* DAVID CREED, and K. DAWES

(Department of Chemistry, The University, Manchester M13 9PL)

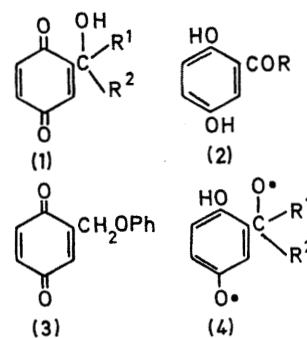
Summary Light-induced fragmentation of 1'-hydroxyalkyl-1,4-benzoquinones to acylquinols occurs when suitable free radical leaving groups are present at the 1-position.

OXIDATION of the side-chain and reduction of the quinonoid nucleus occurs readily¹ when 1'-hydroxyethyl-1,4-benzoquinone (1; R¹ = Me, R² = H) and α -hydroxybenzyl-1,4-benzoquinone (1; R¹ = Ph, R² = H) are irradiated in benzene with visible light, the products being acetylquinol (2; R = Me) and benzoylquinol (2; R = Ph), respectively. However, hydroxymethyl-1,4-benzoquinone (1; R¹ = R² = H) gives a poor yield of the corresponding oxidation-reduction product, gentisaldehyde (2; R = H), but phenoxymethyl-1,4-benzoquinone (3) is also formed, and it has been suggested¹ that this arises *via* intramolecular abstraction of hydrogen from the *hydroxy*-group to give the biradical (4; R¹ = R² = H), the alkoxy-moiety of which then attacks the solvent.

The formation of alkoxy-radicals by direct removal of hydrogen atoms from the hydroxy-groups of alcohols is not a well established process, and further evidence is now presented for its occurrence in quinonoid systems.

Irradiation¹ of 1'-hydroxy-2'-phenylethyl-1,4-benzoquinone (1; R¹ = H, R² = CH₂Ph) gave the expected oxidation-reduction product, phenylacetylquinol (2; R = CH₂Ph), in 15% yield, the major product (24%) being gentisaldehyde (2; R = H), indicating loss of the benzyl group, probably as a radical since significant amounts (7% and 4%, respectively) of 3-benzylgentisaldehyde and 3,5-(or 3,6-)dibenzylgentisaldehyde were also formed, together with a trace of

toluene; scavenging of benzyl radicals at the nucleus of *p*-quinones is to be expected,² and under the conditions of the irradiation the products would be oxidised to the corresponding quinones which could themselves undergo elimination of the 1'-benzyl group.



Irradiation of the methyl homologue (1; R¹ = Me, R² = CH₂Ph) also caused loss of the benzyl group, giving acetylquinol (2; R = Me) (37%), and oxidation of the side-chain, but with concomitant reorganisation³ to give 1-(2,5-dihydroxyphenyl)-1-phenylacetone (43%). The formation of acetylquinol supports the view that the excited quinonoid moiety can abstract from the hydroxy-group to give the alkoxy-radical [4; R¹ = Me(or H), R² = CH₂Ph] from which the product is derived *via* β -elimination⁴ of a benzyl radical. Similar cleavage occurs with the allyl analogues

(1; $R^1 = H$, $R^2 = CH_2CH:CH_2$) and (1; $R^1 = Me$, $R^2 = CH_2CH:CH_2$) which give, respectively, gentisaldehyde and acetylquinol, and, in the latter case, some allyl, suggesting that the process may be general when a suitable radical leaving group is present.

Alternative mechanisms involving abstraction of the 1'-hydrogen (the usual path⁵ for reactions of excited quinones with "free" alcohols) from side-chains in which $R = H$ are largely ruled out by the observation that the deuterium-labelled quinone (1; $R^1 = D$, $R^2 = CH_2Ph$) gives the

corresponding gentisaldehyde (2; $R = D$) and its 2-benzyl homologue with >90% retention of the label.

Preliminary experiments with diphenylmethyl systems (e.g. 1; $R^1 = H$, $R^2 = CHPh_2$) in which steric effects are appreciable suggest that abstraction of hydroxy-hydrogen may only occur when hydrogen bonding with the adjacent carbonyl group is possible.

(Received, April 3rd, 1969; Com. 475.)

¹ J. M. Bruce and P. Knowles, *J. Chem. Soc. (C)*, 1966, 1627.

² Cf. L. F. Fieser and F. C. Chang, *J. Amer. Chem. Soc.*, 1942, **64**, 2043; E. S. Huyser and B. Amini, *J. Org. Chem.*, 1968, **33**, 576.

³ Cf. C. M. Orlando, H. Mark, A. K. Bose, and M. S. Manhas, *J. Org. Chem.*, 1968, **33**, 2512.

⁴ Cf. K. Maruyama and K. Murakami, *Bull. Chem. Soc. Japan*, 1968, **41**, 1401, and references therein.

⁵ J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405, and references therein.