

The Mechanism of the Light-induced Reaction Between 1,4-Benzoquinone and Acetaldehyde

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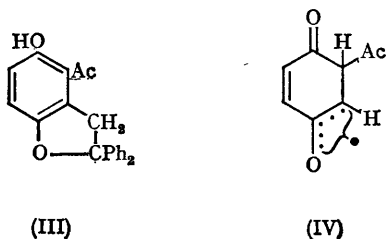
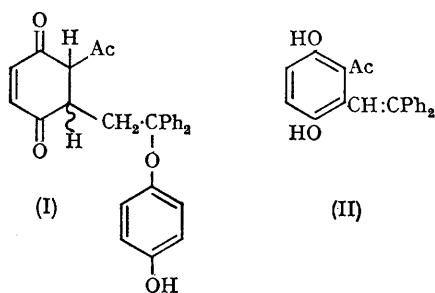
ILLUMINATION of mixtures of certain 1,4-quinones and aldehydes yields^{1,2} the corresponding acyl-quinols which could arise either by combination³

Irradiation of 1,4-benzoquinone in outgassed acetaldehyde with light from a tungsten filament lamp affords 70% of acetylquinol, but the formation of this is largely suppressed when 1,1-diphenylethylene is present, and the proton magnetic resonance spectrum of the solution indicates that only one major product, the rather unstable enedione (I), accumulates. In ethanolic solution this enolises to the corresponding quinol which on being heated decomposes quantitatively to a mixture of quinol, the olefin (II), and the dihydrobenzofuran (III), the relative proportions of (II) and (III) depending on the decomposition temperature. Permanganate oxidation of (II) yields benzophenone, and treatment with toluene-*p*-sulphonic acid in boiling toluene affords (III). Proton magnetic resonance and infrared spectra confirm these structures.

The formation of the enedione (I) may be accounted for by a sequence of selective scavenging reactions involving addition of an acetyl radical to a quinone molecule to give the radical (IV) which is trapped in the enedione form by 1,1-diphenylethylene to give a comparatively unreactive alkyldiphenylmethyl radical which, like the triphenylmethyl radical,⁴ adds to the oxygen of another quinone molecule. The hydrogen then required to complete the formation of (I) may be provided by the semiquinone formed concomitantly with the acetyl radical, or by quinol derived from the semiquinone.

The production of (I) indicates that, in the absence of 1,1-diphenylethylene, acetylquinol probably arises from the radical (IV) by processes

of acyl and semiquinone radicals or by a sequence involving attack of acyl radicals on the quinone³. Support for the latter mechanism has now been obtained.



¹ H. Klinger and O. Standke, *Ber.*, 1891, **24**, 1340; H. Klinger and W. Kolvenbach, *Ber.*, 1898, **31**, 1214.

² G. O. Schenck and G. Koltzenburg, *Naturwiss.*, 1954, **41**, 452.

³ Cf. C. C. Price, *J. Amer. Chem. Soc.*, 1943, **65**, 2380; A. Rembaum and M. Szwarc, *ibid.*, 1955, **77**, 4468.

⁴ J. Schmidlin, J. Wohl, and H. Thommen, *Ber.*, 1910, **43**, 1298.

involving enolisation and disproportionation, rather than by direct union of acetyl and semi-quinone radicals.

That radical intermediates are involved is further indicated by reactions in acetaldehyde initiated in the dark by di-*t*-butyl diperoxalate, which leads *via t*-butoxyl⁵ to acetyl radicals. With 1,4-benzoquinone and the perester in the molar ratio 2:1 acetylquinol can be isolated in 37% yield, but in the presence of added quinol

and a sufficient excess of perester to oxidise it completely to quinone the yield is increased to 69%, thus supporting sequences involving disproportionation of radicals such as (IV) or the corresponding enol. With only 0.1 molar equivalent of the perester the yield of acetylquinol falls to 6% indicating that if (IV) or its enol abstracts hydrogen from acetaldehyde the resulting chains must be short.

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⁵ P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, 1960, **82**, 1762.