Photolysis of t-Butyl-*p*-quinones: Competing 1,4- and 1,5-Dipolar Cycloadditions of the Photoproduct to Nitriles and Ketones

By S. FARID

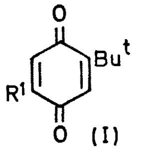
(*Research Laboratories, Eastman Kodak Company, Rochester, New York* 14650)

Summary Spirocyclopropyl ketones (XIV), obtained from the photolysis of t-butyl-*p*-quinones (I;R^1 = H or Bu^t), rearrange to (III) and (IV) and add nitriles and ketones in competitive 1,4- and 1,5-dipolar cycloadditions giving 6- and 7-membered heterocyclic compounds (VII)—(XII).

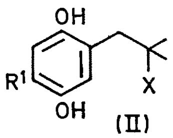
THE photolysis of the t-butyl-*p*-quinones (I) in alcohols or carboxylic acids are reported[1] to yield compounds of structure (II) as major products; (III) was also isolated, along with other compounds.

I report the isolation of cycloaddition products obtained by photolysis of solutions of (I) in nitriles or ketones. Irradiation ($\lambda \geqslant 436$ nm at *ca.* 10°) of (I; R^1 = H or Bu^t) in acetonitrile, benzonitrile, or acetone solution (0·05M) afforded the compounds (VIIa,b)—(IXa,b) and (X)—(XII), respectively, as well as the corresponding rearrangement products (III) and (IV).† The unsaturated quinone (V) and the hydroquinone (VI) were also present among the reaction products.

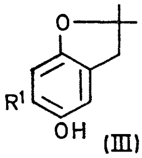
The intermediacy of a thermally unstable photoproduct in these addition and rearrangement reactions was shown by irradiation of (I) at −80° in 1,2-dimethoxyethane, followed by addition of ethanol, acetonitrile, or acetone and allowing to warm to +30°. In all cases the corresponding addition products were obtained. The ratio (III) : (IV) from irradiation of (I; R^1 = H) in dimethoxyethane is 0·8, in nitromethane 5·5. Irradiation of a dimethoxyethane solution of (I; R^1 = H) at −80° followed by 1 : 1 dilution with nitromethane gave a (III) : (IV) ratio of



(I)

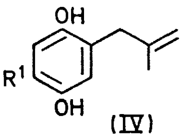


(II)

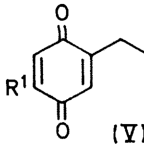


(III)

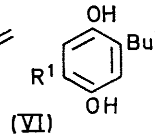
R^1 = H or Bu^t X = alkoxy- or acyloxy-group



(IV)



(V)



(VI)

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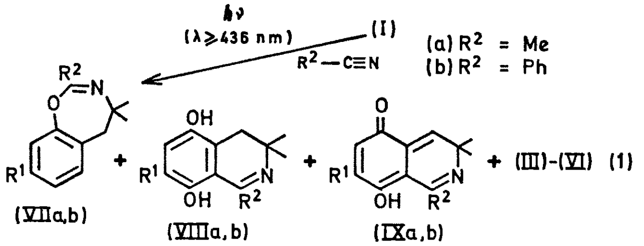
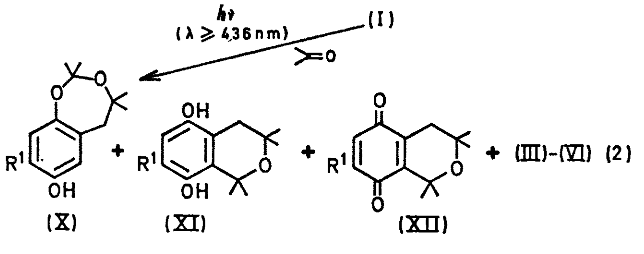
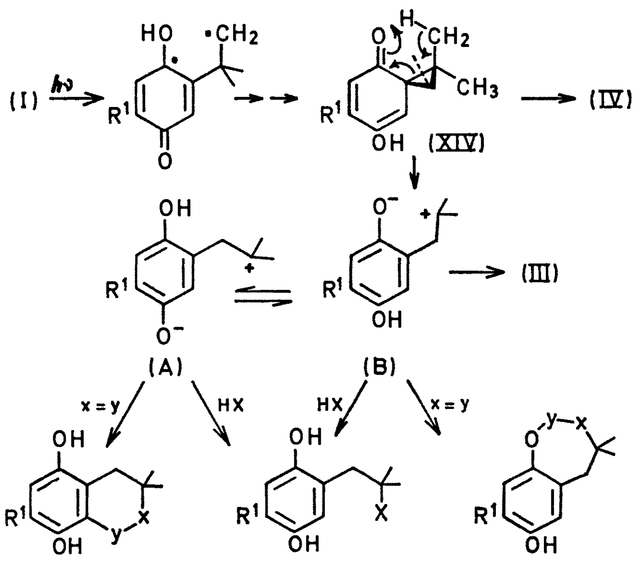
† In these reactions the ratio of addition to rearrangement products varies roughly between 1 : 2 and 2 : 1.

3·2. These results imply that an intermediate is formed photochemically, which can either rearrange to (III) and (IV) in different ratios depending on the solvent or react with alcohols, nitriles, or ketones giving addition products. As shown in the Scheme below, these results are best explained by assigning the structure (XIV), first postulated by Orlando *et al.*,[2] to this intermediate.



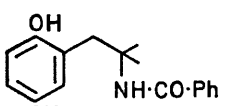




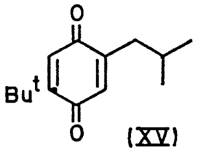
SCHEME

The first step is an intramolecular hydrogen abstraction. (XIV) can then be formed by hydrogen migration in the resultant semiquinone radical and addition of the side-chain radical to the ring. The rearrangement (XIV) → (IV) has obvious analogy to the reported "abnormal Claisen rearrangement."[3] The two tautomeric zwitterions [(A) and (B)] lead, in 1,4- and 1,5-dipolar cycloadditions, to the 6- and 7-membered heterocyclic compounds, respectively. (V), (IX), and (XII) are presumably formed from the corresponding hydroquinones (IV), (VIII), and (XI), respectively in oxidation–reduction reactions, in which (I) is reduced to (VI).

The reaction products have been separated and purified by g.l.c. and/or thin-layer or column chromatography using silica gel. The structure elucidation was based on n.m.r. and mass spectra. The structural data of the products from the reaction of (I; $\mathrm{R}^1 = \mathrm{H}$) with benzonitrile are: (VIIb; $\mathrm{R}^1 = \mathrm{H}$): n.m.r. ($\mathrm{CDCl_3}$): τ 8·68 [$\mathrm{C(CH_3)_2}$], 6·95 ($\mathrm{C}H_2$); *m/e* (relative intensity) 267 (M^+) (0·4), 164 ($M - \mathrm{C_6H_5CN^+}$) (100), 149 ($M - \mathrm{C_6H_5CN} - \mathrm{CH_3^+}$) (68); on chromatographic work-up (silica gel) (VIIb; $\mathrm{R}^1 = \mathrm{H}$) undergoes hydrolysis to (XIII): (VIIIb; $\mathrm{R}^1 = \mathrm{H}$): n.m.r. ($\mathrm{CDCl_3}$): τ 8·71 [$\mathrm{C(C}H_3)_2$], 7·30 ($\mathrm{C}H_2$), 2·45 ($\mathrm{C_6H_5}$) 3·20 and 3·39 (aromatic protons, *J* 9·1 Hz); *m/e* (relative intensity) 267 (M^+) (55), 266 ($M - H^+$) (100), 252 ($M - \mathrm{CH_3^+}$) (13), 210 (8); (VIIIb; ($\mathrm{R}^1 = \mathrm{H}$) is readily oxidized to (IXb; $\mathrm{R}^1 = \mathrm{H}$) on being treated with chloranil in acetone: (IXb; $\mathrm{R}^1 = \mathrm{H}$): dark red crystals, m.p. 238—242° (decomp.); n.m.r. ($\mathrm{CDCl_3}$): τ 8·55‡ [$\mathrm{C(C}H_3)_2$], 3·70 (olefinic proton of the heterocyclic ring, d, *J* 2·1 Hz, due to coupling with the OH proton§), 3·25 (2H), 2·56 ($\mathrm{C_6}H_5$); *m/e* (relative intensity) 265 (M^+) (6), 250 ($M - \mathrm{CH_3^+}$) (100), 165 (2), 124 1/2 (6), 110 1/2 (4), 89 (4), 83 1/2 (3); $\lambda_{\max}$ (dioxan) 465 (ϵ 3100) and 382 nm (4050); $\lambda_{\max}$ (EtOH) 488 and 385 nm; ν_{OH} (in benzene or nitromethane) 3380 cm^{-1}.



(XIII)



(XV)

Another type of rearrangement of (I; $\mathrm{R}^1 = \mathrm{Bu}^t$) takes place on irradiation in 1,2-dichloroethane at elevated temperatures (60°), giving (XV) as the major photoproduct (*ca.* 90%), The ratio (XV): (III) — (VI) decreases with decreasing temperature. At −40° in the same solvent (XV) is formed in *ca.* 10% yield. Since (XV) and (I) absorb in the same region, further photolysis products from (XV), (III), and (IV) ($\mathrm{R}^1 = \mathrm{Bu}^t$), were formed on prolonged irradiation at high temperatures.

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‡ In $\mathrm{C_6D_6}$ the corresponding signal is strongly shifted to τ 9·24.

§ The corresponding compounds derived from 2,5-di-t-butylquinone (I; $\mathrm{R}^1 = \mathrm{Bu}^t$) have to be shaken for several minutes with $\mathrm{D_2O}$ to accomplish the H/D exchange

[1] C. M. Orlando, jun., H. Mark, A. K. Bose, and M. S. Manhas, *J. Amer. Chem. Soc.*, 1967, **89**, 6527, and references therein; *cf.* also A. T. Shulgin and H. O. Kerlinger, *Tetrahedron Letters*, 1965, 3355.

[2] C. M. Orlando, jun., H. Mark, A. K. Bose, and M. S. Manhas, *Tetrahedron Letters*, 1966, 3003.

[3] E. N. Marvel, D. R. Anderson, and J. Ong, *J. Org. Chem.*, 1962, **27**, 1109; W. M. Lauer and T. A. Johnson, *ibid.*, 1963, **28**, 2913; R. M. Roberts, R. G. Landolt, R. N. Greene and E. W. Heyer, *J. Amer. Chem. Soc.*, 1967, **89**, 1404.