

tion of such an enormous rate enhancement for the hydrolysis of a five-membered cyclic ester which contains a heteroatom other than phosphorus. The origin of the extraordinary lability of catechol cyclic sulfate is now under study.

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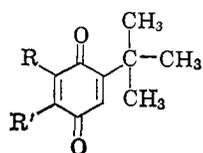
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Photorearrangement of Di-*t*-butyl-*p*-benzoquinones

Sir:

The current general interest in the photochemistry of carbonyl compounds has recently been extended to studies involving several *p*-benzoquinone systems. Some early work demonstrated the photoreduction of *p*-benzoquinone to hydroquinone in alcoholic solvents.¹ More recently, photodimerization² of some substituted *p*-benzoquinones and photocycloaddition with olefins³ has been observed. We wish to report here the photorearrangement of the di-*t*-butyl-*p*-benzoquinones Ia and Ib in alcohol solution.



Ia, R = *t*-Bu; R' = H
b, R = H; R' = *t*-Bu

Photolysis⁴ of a 0.2 *M* solution of Ia in ethanol for 24 hr. at 25–30° resulted in the isolation of an orange-red oil after solvent evaporation. Trituration of this oil with hexane provided a crystalline, white solid, 2.0 g. (38%), m.p. 128–130° (from hexane–benzene).

Elemental analysis (*Anal.* Calcd. for C₁₆H₂₆O₃: C, 72.10; H, 9.77. Found: C, 71.50; H, 9.92) and mass spectral determination of the molecular weight (mol. wt. 266) showed that this product (II) was a 1:1 adduct of the quinone and ethanol. An analogous product (III), m.p. 119.6–121.6°, was obtained in 50% yield when methanol was substituted for ethanol.

The infrared spectrum [λ_{\max} , μ : 2.97 (s), 3.17 (s) (OH); 6.24 (m) (aromatic C=C); 9.02 (s), 9.46 (s) (–C–O–C–)] and the ultraviolet spectrum [$\lambda_{\max}^{\text{THF}}$, $m\mu$: 238 (ϵ 16,000); 297 (ϵ 47,500)] were indicative of a hindered phenolic system.⁵ The n.m.r. spectrum provided confirmation for this structure: a broad peak at τ 5.0 (1 H) and a sharp singlet at τ 1.25 (1 H) found in the spectrum of IIa which disappeared on the addition of D₂O to the CDCl₃ solution pointed to the presence of one unhindered and one severely hindered hydroxyl group. Evidence for two mutually coupled aromatic protons

(1) (a) P. A. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **51**, 3546 (1929); (b) A. Schönberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).

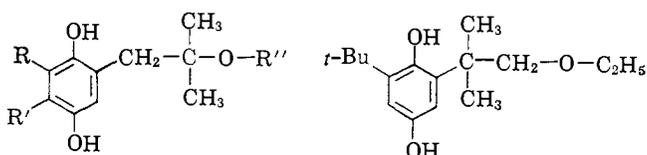
(2) (a) R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 11 (1959); (b) E. Zavarin, *J. Org. Chem.*, **23**, 47 (1958); (c) R. C. Cookson, D. A. Cox, and J. Hudec, *J. Chem. Soc.*, 4499 (1961); (d) D. Bryce-Smith and A. Gilbert, *ibid.*, 2428 (1964).

(3) (a) D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.*, 87 (1964); (b) D. Bryce-Smith and A. Gilbert, *Tetrahedron Letters*, 3471 (1964); (c) G. O. Schenck, I. Hartmann, and W. Metzner, *ibid.*, 347 (1965).

(4) Photolysis was carried out using a Pyrex vessel and a 275-w. G.E. sunlamp.

(5) C. D. Cook, R. G. Inskeep, A. S. Rosenberg, and E. C. Curtius, Jr., *J. Am. Chem. Soc.*, **77**, 1672 (1955).

was supplied by a pair of doublets (AB pattern) at τ 3.15 and 3.48. A quartet at τ 6.47 ($J = 8.5$ c.p.s., 2 H) and a triplet at 8.77 ($J = 8.5$ c.p.s., 3 H) constituted a clear indication for an ethoxy group. Taking into account the presence of two phenolic hydroxy groups, two aromatic protons, and two side chains, it became apparent that the ethoxy group could not be attached directly to the aromatic ring. Support for this conclusion was provided by the observation that two singlets at τ 8.40 (9 H) and 8.77 (6 H) account for only five of the six methyl groups that were present in Ia. A singlet was found at τ 7.20 (2 H) which signified that one of the original methyl groups had been converted into a methylene group. Hence, the adduct must be a hydroquinone which has one *t*-butyl side chain and one other side chain that contains an ethoxy group. Two reasonable structures (IIa and IIb) can be written for the adduct at this stage.



IIa, R = *t*-Bu; R' = H; R'' = C₂H₅
III, R = *t*-Bu, R' = H; R'' = CH₃
IV, R = H; R' = *t*-Bu; R'' = C₂H₅
V, R = H; R' = CH₂C(CH₃)₂OC₂H₅;
R'' = C₂H₅

Further structural information was sought by the acetylation and oxidation of II. Treatment with acetic anhydride–pyridine converted II into a monoacetate⁶ (VI), m.p. 63.5–65.5°. The n.m.r. spectrum of VI showed a sharp peak at τ 1.58 which disappeared very slowly on the treatment of a CDCl₃ solution of VI with D₂O. This behavior is in keeping with the hindered position of one of the hydroxyl groups in II.

Oxidation of II at 25° with chromic acid in acetic acid⁷ led to the quinone⁶ VII as a liquid. The n.m.r. spectrum of VII was very similar to that of II except in the aromatic region: in place of the distinct AB quartet of II there appeared one signal (2 H) of complex pattern centered at τ 3.00. This complexity must be caused by additional coupling through long-range spin–spin interaction. In structure VII the methylene group should undergo allylic coupling with the nearer of the two aromatic protons which are mutually coupled through the ketone. In the alternative structure (corresponding to IIb) neither allylic nor homoallylic coupling (H–C–C=C–C–H) is feasible. Irradiation of the methylene signal at τ 7.20 caused the multiplet at 3.00 in the high-frequency side band to resolve into a quartet (AB pattern), whereas irradiation of the τ 3.00 signal with the same decoupling frequency caused a sharpening of the methylene peak at 7.20 in the low-frequency side band. This double resonance experiment shows that the methylene group is coupled ($J < 1$ c.p.s.) with one of the aromatic protons and thus supports the structure VII. The coupling between the two aromatic protons ($J = 2.9$ c.p.s.) is consistent with their *meta* relationship to each other. If the molecular rearrangement had involved the migration of the side chain from one nuclear

(6) Satisfactory microanalyses were obtained for this compound.

(7) C. F. Koelsch and S. Wawzonek, *J. Am. Chem. Soc.*, **65**, 755 (1943).

