Photoreactions:[1] Rearrangement of Thymoquinone

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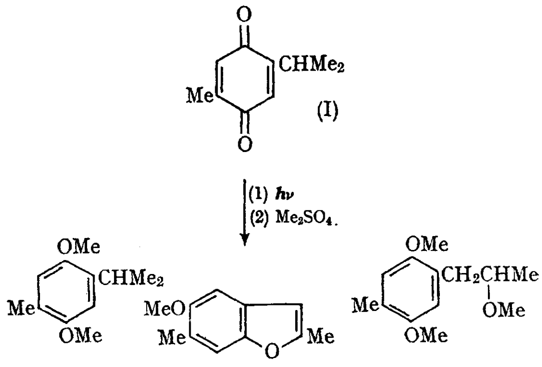
REARRANGEMENT of the side chain of t-butyl-*p*-benzoquinone during photolysis in various solvents has been reported.[1,2] To determine the scope of this photorearrangement, a 1% solution of thymoquinone (I) in methanol was irradiated[3] for 53 hr. and the reaction mixture was then subjected to methylation with alkaline dimethyl sulphate. Using preparative gas chromatography on a 2 ft. silicone-rubber column at 150°, three phenolic products were isolated as methyl ethers. One of these, obtained in 15% yield, was shown to be the dimethyl ether of thymohydroquinone (II) by comparison with an authentic sample.

The second product, formed in 13% yield, was identified as 2,6-dimethyl-5-methoxybenzofuran (III) on the basis of the following data: *M*; Calc. 176; Found: 176 (mass spectral); n.m.r.[4] (in $CDCl_3$, τ): 7·70, 7·55 (6H, Ar–CH_3); 6·18 (3H, Ar–OCH_3), 3·75 (1H, β-furan H), 2·85, 3·14 (2H, *p*-Ar-*H*). The major product (20%) from this photoreaction was assigned the dimethylhydroquinone structure (IV). The following data are cited in support of this assignment: mass spectrum: molecular ion, *m/e* 224 (*M*, Calc. for $C_{13}H_{20}O_3$), base peak, *m/e* 165 $[M - CH(OCH_3)CH_3]^+$; n.m.r. (in $CDCl_3$, τ): 8·91 (doublet, 3H, CH_3–CH), 7·88 (3H, Ar–CH_3), 7·38 (multiplet, 2H, Ar–CH_2), 6·78 (3H, OCH_3), 6·52 (multiplet, 1H, *H*C–OCH_3), 6·35 (6H, Ar–OCH_3), 3·55 (2H, Ar–*H*).



(II) (III) (IV)

Previous reports[5] on the photochemical reactions of thymoquinone have been primarily concerned with dimerization. The present investigation shows that the isopropyl side chain in (I) undergoes the same type of photorearrangement as the t-butyl group in t-butyl-*p*-benzoquinone. Probably a spirocyclopropyl intermediate is involved in both cases.[1] In the photolysis of t-butyl-*p*-benzoquinones, dihydrobenzofurans (coumarans) were among the products of the reactions. In the photolysis of thymoquinone, the isolation of the benzofuran (III) and not the corresponding dihydrobenzofuran can be reasonably ascribed to the ease of aromatization of the latter in the presence of quinones.

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[1] For the previous Paper in this series, see: C. M. Orlando, Jr., H. Mark, A. K. Bose, and M. S. Manhas, *Tetrahedron Letters*, 1966, 3003.

[2] C. M. Orlando, Jr., and A. K. Bose, *J. Amer. Chem. Soc.*, 1965, **87**, 3782.

[3] The photolysis was carried out at 25—30° in a Pyrex vessel using a 275 w G. E. sunlamp as the light source.

[4] For the chemical shifts of protons in the furan ring system see: A. R. Katritzky, "Physical Methods of Heterocyclic Chemistry," Academic Press, New York, 1963, Vol. II, p. 124. Unless mentioned otherwise, the n.m.r. peaks appeared as singlets.

[5] A. Lallemand, *Ann. Chim. Phys.*, 1857, **49**, 167; L. I. Smith and R. W. H. Tess, *J. Amer. Chem. Soc.*, 1944, **66**, 1323, E. Zavarin, *J. Org. Chem.*, 1958, **23**, 47; R. C. Cookson, J. J. Frankel, and J. Hudec, *Chem. Comm.*, 1965, 16.