Tetrahedron Letters No.26, pp. 3003-3006, 1966. Pergamon Press Ltd.
Printed in Great Britain.

PHOTOREACTIONS II. 2,2-DIMETHYL-5-HYDROXYCOUMARANS FROM t-BUTYL-p-BENZOQUINONES (1,2)

C.M. Orlando, Jr. and H. Mark
Kay-Fries Chemicals, Inc.
West Haverstraw, New York

Ajay K. Bose and M.S. Manhas
Department of Chemistry and Chemical Engineering
Stevens Institute of Technology
Hoboken, New Jersey

(Received 7 April 1966; in revised form 28 April 1966)

In an earlier communication, we reported the photorearrangement of the quinones Ia and Ib in alcoholic solution to the hydroquinones IIa and IIb, respectively. On the basis of n.m.r. spectra, we concluded that the t-butyl side chain had undergone rearrangement during the photoreaction. In subsequent studies we have found that the photolysis of Ia in glacial acetic acid, aqueous dioxane or dimethyl malonate affords a colorless compound, m.p. 150-152.5°, in less than 15% yield*. Elemental analyses (Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.36; H, 909. Found: C, 75.70; H, 9.28) and mass spectral determination of the molecular weight (mol. wt. 220) showed this product to be isomeric with the starting quinone. The infrared spectrum indicated the absence of carbonyl groups but the presence of hydroxyl functionality. The n.m.r. spectrum was best interpreted as that of the 2,2-dimethyl-5-hydroxycoumaran structure IVa: multiplet at τ 3.48 (2H, aromatic protons), very broad band centered at τ 5.30 (1H, -OH), singlet at τ 7.10 (2H, $-CH_2-$), singlet at τ 8.58 (6H, $-C(CH_3)_2$), and a singlet at τ 8.70 (9H, $-C(CH_3)_3$). The alternative structure

---

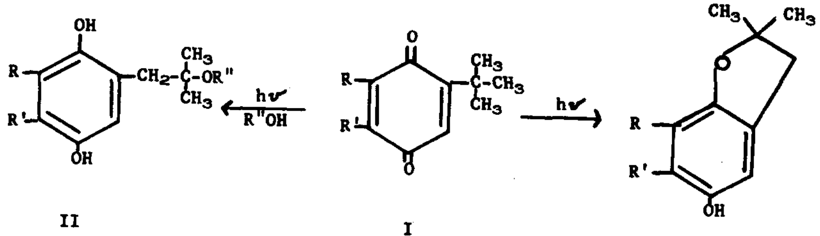
*These photoreactions were carried out in pyrex vessels at 25-30° using a 275 W. G.E. sunlamp as a light source.

Va was not favored since the chemical shift of a methylene group adjacent to an ether oxygen would be expected to be at about τ 6.0. It is interesting to note that the photochemical formation of IVa from Ia is apparently independent of the acidity of the solvent. Photolysis of Ia in trifluoroacetic acid afforded the trifluoroacetate of IVa which on exposure to the atmosphere rapidly formed IVa.

While this investigation was in progress a report (3) appeared in which a substituted coumaran and an ether obtained in the photolysis of Ib in alcohol were assigned the structures Vb and IIIb, respectively. It was also shown that IIIb could be converted to Vb with aqueous hydriodic acid. Since in these structures no rearrangement of the t-butyl group was indicated, we found it desirable to collect further evidence for the structure of the photoreaction products of Ib.

Photolysis of Ib in glacial acetic acid provided the same product, m.p. 155-157°, obtained earlier by Shulgin and Kerlinger (3) from the photorearrangement of Ib in methanol and ethanol. A by-product from the acetic acid photolysis was an acetate, m.p. 105-108°, the molecular formula of which was established to be $C_{16}H_{24}O_4$ (Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.57; H, 8.57. Found: C, 68.47; H, 8.55). The n.m.r. spectrum of the acetate displayed a methylene peak at τ 7.13; this chemical shift is consistent with the benzylic methylene group in IIb ($R''=CH_3CO-$). The methylene group of a primary acetate as in IIIb ($R''=CH_3CO-$) however, should show a chemical shift in the τ 5.7-6.1 range.

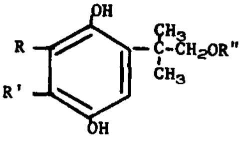
We prepared the β-methallyl hydroquinone VI (4) and confirmed its structure by examining its n.m.r. spectrum. Treatment with hot aqueous hydriodic acid converted VI into 2,2-dimethyl-5-hydroxycoumaran (IVc). Photolysis of t-butyl-p-benzoquinone (Ic) in ethanol afforded an ether which was converted



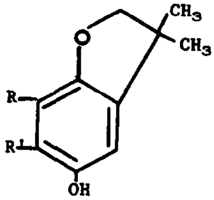
II

I

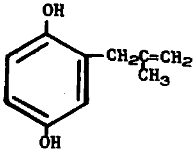
IV



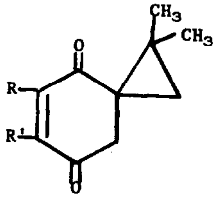
III



V



VI

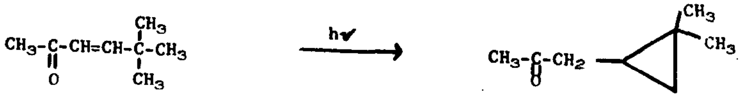


VII

a, R=t-Bu, R'=H

b, R=H, R'=t-Bu

c, R=R'=H



VIII

IX

to IVc by heating in aqueous hydriodic acid. In addition, direct formation of IVc was achieved by photolysis of Ic in glacial acetic acid. The methylene group in the n.m.r. spectrum of IVc obtained by these methods appeared at τ 7.05. The structure IIc can be unequivocally assigned to this ether from Ic. We find, therefore, that the ethers and coumarans obtained so far by the photolysis of t-butyl-p-benzoquinones are characterized by the rearrangement of the t-butyl side chain in each case. Very recently, several dialkylamino-p-benzoquinones have been found to undergo photocyclization without rearrangement (5).

The rearrangement of the t-butyl side chain during the photolysis of these alkyl-p-benzoquinones can be reasonably interpreted by assuming the formation of a spiro-cyclopropyl intermediate (such as VII or tautomers). This is reminiscent of the formation of the cyclopropyl ketone IX as a photoproduct from the α, β-unsaturated ketone VIII (6). The monitoring of the photoreaction of Ia in methanol by n.m.r. spectroscopy reveals a sequence of intermediates and a multiplicity of products. Our finding from the investigation of the mechanism of the photorearrangement of p-benzoquinones will be reported in due course.

REFERENCES

1. For Part I see, C.M. Orlando, Jr. and A.K. Bose, J. Am. Chem. Soc., 87, 3782 (1965).
2. Presented in part at The First Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb. 3, 1966, Abstracts p. 133.
3. A.T. Shulgin and H.O. Kerlinger, Tetrahedron Letters, 38, 3355 (1965).
4. A. Gaydasch and W.K.T. Gleim, U.S. Patent, 2,681,371, June 15, 1954; C.A. 49, 7595c (1955).
5. D.W. Cameron and R.G.F. Giles, Chem. Comm. 22, 573 (1965).
6. M.J. Jorgenson and N.C. Yang, J. Am. Chem. Soc., 85, 1698 (1963).