

in general agreement with Witanowski's observation<sup>3</sup> that the influence of *meta* and *para* substituents on nitrogen chemical shifts in nitrobenzene are nearly equal.

The bulk of the evidence now available suggests that the inductive effect may influence these nitrogen chemical shifts more than the mesomeric effect, a conclusion already reached by Witanowski.<sup>8</sup> The remaining effects which might be mesomeric in nature probably can be associated with the paramagnetic term arising from the mixing of the ground and excited electronic states.<sup>9</sup> Unfortunately, this is not easy to test because determination of the mean electronic excitation energy of the  $n \rightarrow \pi^*$  transition is difficult in nitrobenzenes because of masking by the  $\alpha$  band.<sup>10</sup>

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Wolfgang Bremser, Jacqueline I. Kroschwitz, John D. Roberts

Contribution No. 3918, Gates and Crellin Laboratories of Chemistry  
California Institute of Technology, Pasadena, California 91109

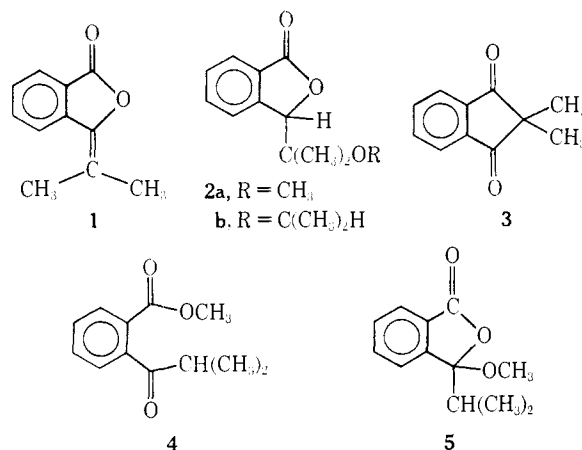
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### Photoaddition of Alcohols to Isopropylidene-phthalide

Sir:

The photoaddition of alcohols to olefins in Markovnikov fashion to give ethers<sup>1</sup> seems to be limited to six- and seven-membered ring cases, and is usually accepted as proceeding through protonation of a highly strained *trans*-cycloalkane or orthogonal triplet. Additions of the oxygen of alcohols to the  $\beta$  position of  $\alpha$ - and  $\beta$ -unsaturated ketones which have this double bond in a six- or seven-membered ring are also well documented,<sup>2</sup> and mechanistic similarity to the additions to cyclic olefins has been suggested.<sup>2,3</sup> The photoaddition of methanol to crotonic acid<sup>4</sup> is a well-reviewed counter-example to the necessity of having a cyclic double bond for the addition, but Kropp and Krauss reinvestigated this case and have convincingly shown<sup>4</sup> that there is no photoaddition of methanol here, and that acid-catalyzed reaction was probably responsible for the earlier result. More recently, however, the photoaddition of methanol to benzoylacrylic acid to give 2-methoxy-3-benzoylpropionic acid was reported.<sup>5</sup> We report here that alcohols add to the exocyclic double bond of isopropylidene-phthalide (**1**),<sup>6</sup> a case of addition to a non-cyclic double bond  $\gamma, \delta$  to a carbonyl group. There is no chance of an ionic dark reaction being responsible here, since different products are formed under such conditions. Irradiation of **1** in methanol ( $1.4 \times 10^{-2} M$ ) for 14 hr with a 450-W Hanovia lamp converted about 39% of the starting material to the methanol adduct **2a**: nmr ( $CDCl_3$ )  $\tau$  1.8–2.6 (complex, 4 aromatic H), 4.25 (s, 1 methine H), 6.35 (s, 3 methoxyl H), 8.38

and 8.50 (2, s, 3 methyl H each); mass spectrum (15 eV) 206 (P, <1%), 191 (<1), 175 (12), 133 (100), 132 (20), 77 (28), 76 (20), all others <15%. The remainder of the photolysis mixture consisted of **1**, **3**,<sup>7</sup>



and a small amount of dimeric material. Control experiments showed that **1** does not react with methanol in the dark, even upon 24-hr reflux, and that treatment with methanolic sulfuric acid, sodium hydroxide, and sodium methoxide gives only mixtures of **4** and **5**, and the **4/5** ratio varying from 2.1 to 3.9 depending upon conditions.

Similarly, photolysis in 2-propanol gave **2b** as the major product: nmr ( $CDCl_3$ )  $\tau$  1.9–2.8 (complex, 4 aromatic H), 4.08 (s, 1 ring methine H), 5.72 (heptet, 1 isopropoxyl H), 8.40 and 8.52 (2 s, each 3 H), 8.70 and 8.73 (2, d, each 3 H); mass spectrum (15 eV) 234 (P, <1%), 133 (100), 132 (55), 77 (26), all others <15%.

Neither photoreduction nor radical addition of the alcohol occurs with **1**, even in 2-propanol, in contrast to the behavior of a steroidal acetylcyclopentene<sup>8</sup> and the sensitized behavior of several unsaturated acids.<sup>9</sup> Photolysis of **1** must lead to an intermediate with considerable polarization of the isopropylidene bond, possibly by protonation of the carbonyl carbon; enhanced basicities for some excited states are known.<sup>10</sup> We conclude that alcohol addition to olefins does not always require great strain in an orthogonal or *trans* intermediate if the double bond is conjugated with a carbonyl group.

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(7) Rearrangement to **3** is the predominant reaction at low concentration in nonhydroxylic solvents. Similar reactions in aliphatic examples are well documented; see H. U. Hostettler, *Tetrahedron Lett.*, 1941 (1965); H. Nozaki, A. Yamaguti, and R. Noyori, *ibid.*, 37 (1965); H. Nozaki, *Tetrahedron*, **23**, 3933 (1967), and references therein.

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S. F. Nelsen, P. J. Hintz

Department of Chemistry, University of Wisconsin  
Madison, Wisconsin 53706

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