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PHOTOCHEMICAL REACTION OF BENZENE WITH DIMETHYL ACETYLENEDICARBOXYLATE[1]

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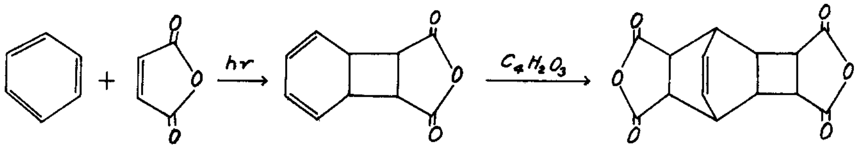
The photochemical reaction of benzene with maleic anhydride has been shown to give an adduct of structure II[2,3]. This reaction evidently proceeds[1] by a photochemically activated 1,2-addition to give intermediate I followed by a 1,4-addition of maleic anhydride to give II. Similar photochemical reactions of maleic anhydride appear to occur with toluene, _o_-xylene, and chlorobenzene, especially in presence of a photosensitizer such as benzophenone[4]. We now wish to report a photochemical reaction of benzene with dimethyl acetylenedicarboxylate.



I

II

Irradiation at room temperature of a solution of dimethyl acetylenedicarboxylate (5.0 ml) in benzene (300 ml) with ultraviolet light for

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[1] This research was supported by the Office of Ordnance Research, U. S. Army.

[2] H. J. F. Angus and D. Bryce-Smith, _Proc. Chem. Soc._ 326 (1959); _J. Chem. Soc._ 4791 (1960).

[3] E. Grovenstein, Jr. and D. V. Rao, _J. Amer. Chem. Soc._ in press.

[4] G. O. Schenck and R. Steinmetz, _Tetrahedron Letters_ No. 21, 1 (1960).

47 hours in a quartz apparatus previously described[5] gave, in addition to a difficulty volatile residue, 0.56 g. of yellow crystals (m.p. 109.4-110.4°. Found: C, 65.39; H, 5.35; sapn. equiv., 107; mol. wt., 254. Calcd. for $C_{12}H_{12}O_4$: C, 65.43; H, 5.49; sapn. equiv., 110; mol. wt., 220). This methyl ester was purified by crystallization from methanol and sublimation at a bath temperature of 102° and a pressure of 0.03 mm. Saponification of the ester gave an acid which after recrystallization from water was isolated as yellow crystals of m.p. 206.5-208° (dec.) (Found: C, 62.34; H, 4.18. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20). The acid sublimed at a bath temperature of 190° and a pressure of 0.05 mm. The acid and the methyl ester readily decolorized a solution of potassium permanganate. The acid in acetic acid solution with a 5% Pt on carbon catalyst at room temperature and atmospheric pressure absorbed 3.0 moles of hydrogen per mole of acid in 4 hours and 0.6 additional moles in 91 hours. The acid in ethanol had ultraviolet absorption (shoulder) at 300 mμ (log ϵ = 2.84) and a maximum at 227 mμ (log ϵ = 4.20). The color of the acid and its ultraviolet absorption spectrum are similar to those reported for cycloöctatetraenecarboxylic acid which has λ_{max}^{EtOH} 306 mμ (log ϵ = 2.92) and end-absorption at 220 mμ with log ϵ = 4.3. Also the infrared absorption spectra of the acid and its methyl ester are similar to those reported for cycloöctatetraenecarboxylic acid and its methyl ester (note especially that the acid has C=C absorption at 6.14 μ while absorption at longer wavelength is expected for planar conjugated olefinic bonds or an aromatic ring). Moreover cycloöctatetraenecarboxylic acid rather rapidly absorbs three molar equivalents of hydrogen and more slowly absorbs a fourth molar equivalent upon hydrogenation overa platinum

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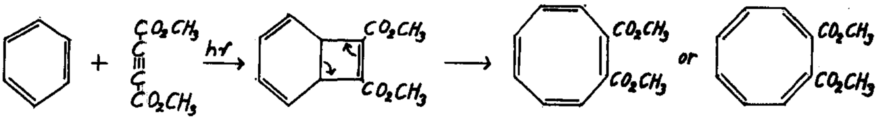
[5] E. Grovenstein, Jr. and S. P. Theophilon, J. Amer. Chem. Soc. 77, 3795 (1955).

catalyst in acetic acid solution[6].

The similarity in physical and chemical properties of the acid from reaction of benzene with dimethyl acetylenedicarboxylate with the known cycloöctatetraenecarboxylic acid and the lack of similarity with phenylmaleic and phenylfumaric acids strongly implies that the photochemical product has the structure IV and /or V of dimethyl cycloöctatetraene-1,2-dicarboxylate. A structure of this type can be formed by way of an intermediate III resembling that (II) proposed for the photochemical reaction of benzene with maleic anhydride. Intermediate III, however, undergoes isomerization to IV or V which is expected to be thermodynamically more stable than II and to be comparatively unreactive toward dimethyl acetylenedicarboxylate at room temperature[7].



III IV V

D. Bryce-Smith has kindly informed us that he has obtained 1 to 1 photo-adducts of acetylene derivatives with benzene etc. and that these appear to be derivatives of cycloöctatetraene. Moreover G. Büchi has considered a substituted cycloöctatetraene as one of several possible structures for a photo-adduct derived from benzonitrile and an acetylene derivative[9].

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[6] A. C. Cope, M. Burg and S. W. Fenton., ibid. 74, 173 (1952).

[7] Note that no appreciable amount of bicyclo[4.2.0]octa-2,4,7-triene appears to be in equilibrium with cycloöctatetraene. A temperature of 160-170° was used to effect reaction between cycloöctatetraene and diethyl acetylenedicarboxylate (W. Reppe, O. Schichting, K. Klager and T. Toepel, Ann. 560 1 (1948).

[8] D. Bryce-Smith, personal communication.

[9] G. Büchi, Seventh Reaction Mechanisms Conference, University of Chicago, Sept. 5, 1958.