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THE PHOTOSENSITIZED ADDITION OF MALEIMIDE TO BENZENE IN THE ABSENCE OF A CHARGE-TRANSFER COMPLEX

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The photosensitized addition of maleic anhydride to benzene has been reported to involve a charge-transfer complex (1, 2). The ultraviolet spectrum of maleic anhydride shows only a low intensity absorption (ϵ <20) above 2500 Å in chloroform (3). A solution of maleic anhydride in aromatic solvents shows an absorption spectrum with a maximum at 2800 Å (ϵ ~1200). This latter maximum has been attributed to a charge-transfer complex (3). We wish to report that maleimide photochemically adds to benzene even though there appears to be no charge-transfer complex. The maximum in the absorption spectrum of freshly sublimed maleimide in both chloroform and chloroform-benzene solvents is at 2700 Å (ϵ = 720). Since maleimide shows exactly the same absorption in the presence and absence of aromatic hydrocarbon, it is likely that no charge-transfer complex is formed.

The product of the maleimide-benzene and maleimide-alkylbenzene photosensitized reaction is the imide analogue of the corresponding maleic anhydride photoproduct (4, 5). For example, a mixture of 1 g (0.01 mole) of maleimide, 2.5 ml acetophenone, 7 ml acetone, and 25 ml tert-butylbenzene was irradiated in a Pyrex reaction vessel for 18 hours with a Hanovia 450-watt lamp. White needles were isolated (1.1 g, 35%, m.p. 345-352°C) (6). The infrared spectrum of this material exhibited major bands at 3380, 3250, 3130, 1790, 1710, 1490, 1342, 1190, 1165, 1000, and 855 cm^{-1}. Photoadducts from other alkylbenzenes are listed in Table I.

TABLE I

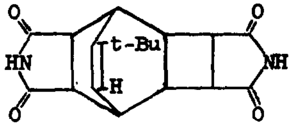
Alkylbenzene-Maleimide Photoadducts

Aromatic	Yield,[a] %	m.p.,[b] °C	Analysis Calculated N	Found N
Benzene	82	290-295	10.31	10.60
Toluene	84	330-335	9.78	9.91
Ethylbenzene	71	200-220	9.33	9.56
n-C_{10}-C_{13} Alkylbenzene	35	223-232	Not Analyzed	

[a] Irradiation times of 40-60 hours.

[b] Crude reaction product.

The nuclear magnetic resonance spectrum of the tert-butylbenzene adduct showed protons at δ 10.8 (2), 6.0 (1), 2.0-3.5 (8), and 1.0 (9). This spectrum is similar to that of the tetramethyl ester of alkylbenzene-maleic anhydride adducts (5). The ratio of vinyl proton (δ 6.0) to tert-butyl protons (δ 1.0) and to imide protons (δ 10.8) is correct for a single vinyl proton. The fact that there are two imide and one vinyl proton indicates that the gross structure of this adduct (I) is the same as that of the maleic anhydride-alkylbenzene photoadduct (4.5).



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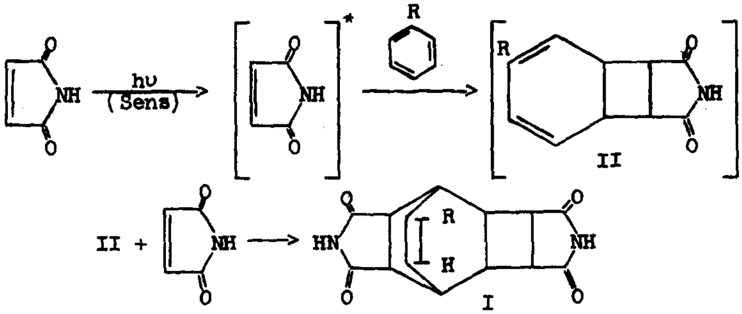
Conversion of the maleic anhydride photoadduct to the maleimide photoadduct provides more convincing evidence that these two classes of compounds have similar structures. For example, the toluene-maleic anhydride photoadduct (7) was treated with an excess of hot concentrated ammonia solution. The water was removed under vacuum and the resulting solid heated to 215°C in a stream of nitrogen. Ammonia was observed in the gas stream. A 60% yield of product was collected, m.p. 325-332°C (uncorrected). A mixture of this product and maleimide-toluene photoadduct melted at 330-335°C. The infrared spectrum of this material was the same as that of the maleimide-toluene photoadduct, except the presence of a small band at 1530 cm^{-1}. This band can be attributed to an amide II type absorption (8) of unreacted amide intermediate.

The photoreaction probably proceeds by the addition of electronically excited maleimide to the alkylbenzene. The intermediate diene II would react with a second molecule of



maleimide to form the observed product I. Steric hindrance and electronic effects probably direct the addition of the first molecule of maleimide to the 3-4 position. Since the reaction is photosensitized by acetophenone, triplet excitation must be involved (9).

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