The Preparation and Structure of Alkylbenzene–Maleic Anhydride Photoadducts

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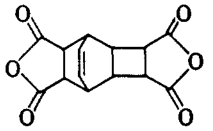
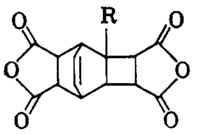
Dianhydrides from various alkylbenzenes and maleic anhydride were prepared. The nuclear magnetic resonance spectra of the tetramethyl esters (V) show that the dianhydrides have structure IV.

The photochemical addition of maleic anhydride to benzene, first reported by Angus and Bryce-Smith,[1b] has been studied in some detail. The reaction can be sensitized by benzophenone[2] and other photosensitizers.[3] Transfer of triplet energy by the sensitizer to a benzene–maleic anhydride charge-transfer complex appears to be the reaction mechanism.[3,4] Grovenstein and co-workers[5] made an extensive study of the structure and stereochemistry of the adduct and determined that it had structure I.


I

This study was carried out to prepare dianhydrides from various alkylbenzenes and to illucidate their structure. Of the three possible photoadditon products, structure IV was found to be consistent with the analytical data. As this work was being completed, others[6] reported that the maleic anhydride–biphenyl photoadduct also had structure IV.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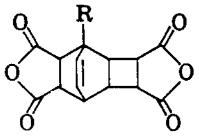
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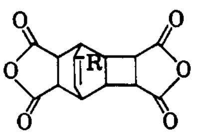
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Results and Discussion

Maleic anhydride was irradiated in the presence of alkylbenzene and a photosensitizer. The alkylbenzenes chosen for this study included toluene, ethylbenzene, cumene, *t*-butylbenzene, and long-chain alkylated benzenes. The results for the pure alkylbenzenes listed in Table I show a general decrease in yield as the size of the alkyl substituent is increased. This decrease may be due to added steric effects.

Acetone facilitated the reaction both as a sensitizer and as a solvent for the product. Table II shows that increasing amounts of acetone increased product yields. When little or no acetone was present, the product separated as a gum on the walls of the reaction vessel. This reduced the amount of light entering the reaction. As the amount of acetone was increased, the product became more soluble, the amount of light increased, and a greater yield was observed. The increased yields at short reaction times, where little or no product separated, indicate some sensitization by acetone. The greater sensitizing efficiency of benzophenone is shown by a significant increase in initial rate (run 4 of Table II).

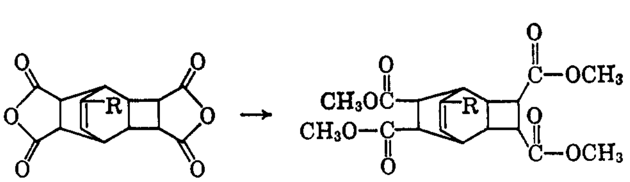
TABLE I

PRODUCTS OF THE ACETOPHENONE-PHOTOSENSITIZED REACTION OF MALEIC ANHYDRIDE AND ALKYLBENZENE IN PYREX GLASS

Alkylbenzene	Time, hr	Yield, %	Mp, °C	Equiv wt Calcd	Equiv wt Found
Benzene	18	41	350	68.6	69.6
Toluene	18	29	265–270	72.0	71.7
Ethylbenzene	18	24	250–255	75.5	74.5
Cumene	18	19	250–255	79.1	79.3
t-Butylbenzene	18	14	245–250	82.6	83.1
Branched C_5–C_6 alkylbenzene (oronite)	70	30	Gum	90[a]	96.1
n-C_{10}–C_{13} alkylbenzene (oronite)	47	14	180–200	108[b]	99.6

[a] Based on an average molecular weight of 164 for the alkylbenzene (C_6). [b] Based on an average molecular weight of 237 for the alkylbenzene.

The photoadducts were converted to the tetramethyl ester derivatives and subjected to nuclear magnetic resonance analysis. The results are listed in Table III. The ratio of vinyl protons (δ 6.0–6.2) to methyl ester protons (δ 3.5–3.7) is correct for a single vinyl proton for the alkylbenzene adducts. These results show that the tetramethyl ester is derived from a dianhydride of structure IV.[7,8]


IV V

The mechanism of the photoaddition has been reported to be a 1,2 addition of the first molecule of maleic anhydride followed by a 1,4 addition of the second.[1,5] The first addition probably involves the charge-transfer complex.[3,4] In general, an alkylbenzene with its increased ability to delocalize electronic charge is a better complexing agent than benzene.[9] The complex VI may then very well possess the correct steric orientation to give the observed product. (See Scheme I.)

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(1) (a) To whom correspondence should be addressed: Chemistry Department, Brigham Young University, Provo, Utah; (b) H. J. F. Angus and D. Bryce-Smith, *Proc. Chem. Soc.*, 326 (1959); *J. Chem. Soc.*, 4791 (1960).

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(5) E. Grovenstein, D. V. Rao, and J. W. Taylor, *J. Am. Chem. Soc.*, **83**, 1705 (1961).

(6) D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, 918 (1965).

(7) A similar structure was determined for the maleimide–alkylbenzene photoadducts: J. S. Bradshaw, *Tetrahedron Letters*, 2039 (1966).

(8) D. Bryce-Smith and A. Gilbert,[6] reported the same structure for the biphenyl–maleic anhydride photoadduct. Their assignment was based on a styrene-type ultraviolet absorption for the adduct.

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TABLE II

RELATIVE RATES OF THE ETHYLBENZENE–MALEIC ANHYDRIDE (MA) REACTION CARRIED OUT IN QUARTZ APPARATUS

	Reactants (molar ratio)				MA reacted,[a] %				
Run	MA	$C_6H_5C_2H_5$	Acetone	Benzophenone	4 hr	8 hr	11 hr	Yields, %	Remarks
1	1	24	0	0	21	28	31	17	Sides of reaction vessel became gummy
2	1	4	1	0	29	36	39	Not isolated	Sides of reaction vessel became gummy
3	1	4	7	0	36	72	83	63	Clear solution
4	1	4	7	0.2	49	74	87	62	Clear solution

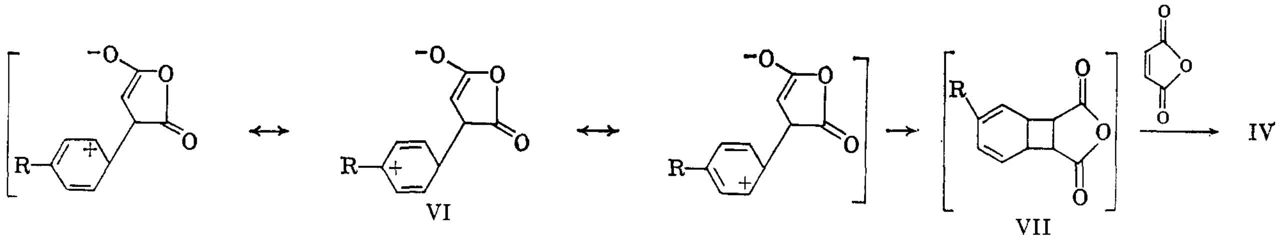
[a] Determined by vapor phase chromatography.

TABLE III

METHYL ESTERS OF THE AKLYLBENZENE–MALEIC ANHYDRIDE ADDUCTS

			Anal, %				
			Calcd		Found		
Alkylbenzene	Yield, %	Mp, °C	C	K	C	H	Nmr, δ (ratio)
Benzene	72	132–133					6.62 m (2) 3.75 d (12) 3.05 m (8)
Toluene	97	157–159	59.99	6.36	59.89	6.53	6.2 m (1) 3.6 s (12) 2.9 m (8) 2.15 s (3)
Ethylbenzene	98	100–102	60.90	6.64	60.93	6.71	6.2 m (1) 3.7 d (12) 3.0 m (8) 2.4 q (2) 1.3 t (3)
Cumene	70	107–108	61.75	6.91	61.66	6.79	6.0 m (1) 3.55 d (12) 2.8 m (8) 2.3 m (1) 1.1 d (3)
t-Butylbenzene	56	87–88	62.55	7.16	62.60	7.02	6.1 m (1) 3.5 d (12) 2.8 m (8) 1.1 s (9)

SCHEME I



Experimental Section

Materials and Apparatus.—All organic chemicals were used as received: maleic anhydride, Pfanstiehl Laboratories; acetophenone, Eastman; benzene, toluene, and methanol, Allied Chemical; ethylbenzene, cumene, and *t*-butylbenzene, Eastman; *n*-C_{10}–C_{13} alkylbenzene and branched C_5–C_6 alkylbenzene, Oronite. A Hanovia quartz immersion reactor with a 450-w lamp was used in all experiments. The reactions were carried out in Pyrex test tubes or flasks unless otherwise specified.

Alkylbenzene–Maleic Anhydride Adduct.—The adducts of maleic anhydride, benzene, toluene, ethylbenzene, cumene, and *t*-butylbenzene were prepared as follows. Maleic anhydride (5 g, 0.05 mole) was dissolved in 5 ml of acetophenone in a large (25 × 200 mm) Pyrex test tube. To this solution was added 50 ml of the alkylbenzene. The tubes were stoppered and irradiated for 18 hr. The solids that formed were filtered and thoroughly washed with about 100–150 ml of dry ether. The yields, melting points, and equivalent weights of the products are listed in Table I. Greater yields (up to 84% in 90 hr in the case of toluene) were realized by running the reaction longer. No attempt was made to isolate unreacted starting materials. The infrared spectra of these compounds (KBr) were the same, except for differences in 1400–1500 cm^{-1} attributable to differences in alkyl groups. The branched C_5–C_6 alkylbenzene– and *n*-C_{10}–C_{13} alkylbenzene–maleic anhydride adducts were prepared in the same manner, except that a homogeneous mixture of 5 g of maleic anhydride, 15 ml of acetophenone, and 45 ml of alkylbenzene was used.

Ethylbenzene–Maleic Anhydride Reaction Run in Acetone.—Mixtures of maleic anhydride, ethylbenzene, acetone, and benzophenone were prepared. The exact amount of maleic anhydride was determined by quantitative vpc using a 15-ft 7% silicone on Fluoropak column at 90–95° with a known amount of *t*-butylbenzene as the internal standard. The reaction was carried out in a quartz immersion reactor equipped with a nitrogen gas inlet disk at the bottom. A weighed portion of the mixture (220–230 g) was added to the reaction vessel, saturated with nitrogen, and irradiated in a nitrogen atmosphere. Small portions of the reaction mixture were removed at specific intervals and analyzed. The product was isolated by evaporating the solvents and adding ethyl ether to the resulting gummy material. The solid which did not dissolve in ether had the correct infrared spectrum. The results are given in Table II.

Tetramethyl Esters.—Small amounts (1–4 g) of the alkylbenzene–maleic anhydride adducts were refluxed for 3–5 hr in methanol which was saturated with hydrogen chloride gas. Methanol was then evaporated under vacuum, leaving a gummy solid. Where possible, the gummy solid was recrystallized from methanol or methanol–petroleum ether (bp 30–60°) to yield white, crystalline solids. The yields, melting points, analytical, and nuclear magnetic resonance (CCl_4) data are given in Table III. In the case of the ethylbenzene and *t*-butylbenzene adducts, the esters were dissolved in benzene and chromatographed on alumina. The benzene eluants yielded solid material pure enough to be recrystallized from methanol–petroleum ether.

Tetracarboxylic Acids.—Tetracarboxylic acids were prepared by refluxing 10–12 g of the alkylbenzene–maleic anhydride adducts in 125 ml of 1.5 *M* potassium hydroxide solution for 4 hr. The cooled solutions were filtered and acidified with hydrochloric acid, yielding solids. The solids were separated, recrystallized from water, and dried. The yields and equivalent weights are given in Table IV.

TABLE IV
TETRACARBOXYLIC ACIDS OF THE ALKYLBENZENE–MALEIC ANHYDRIDE ADDUCTS

Alkylbenzene	Yield, %	Mp, °C	Equiv wt Calcd	Equiv wt Found
Benzene	90	120–350[a]	77.6	78.6
Toluene	58	197–200	81.1	83.0
Cumene	41	182–184	88.1	88.3
C_{10}–C_{13} alkylbenzene	60	258–260	117[b]	115.1

[a] The acid melts, loses water, and forms the anhydride. [b] Based on molecular weight 237 for the alkylbenzene.

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Three-Membered Rings. II. Conjugative Properties and Electronic Spectra of Substituted Stilbene Oxides[1]

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The ultraviolet spectra of a series of *para*-substituted stilbene oxides demonstrate that oxirane transmits electronic effects *via* second-order conjugation from one phenyl group to the other. The spectra of the corresponding bibenzyls and particularly the *para*-substituted styrene oxides serve as references. This transmissive effect of the oxirane ring is found to be consistent with the hyperconjugation description of the *extension* of conjugation in the styrene oxide series. The spectra of some substituted *cis*-stilbene oxides show the expected steric inhibition of conjugative transmission. The thiirane ring in *cis*- and *trans*-stilbene sulfide behaves like the electron-accepting oxirane.

It has recently been shown[2] that oxiranyl and thiiranyl groups act as electron acceptors relative to the benzene ring. This was demonstrated by the ultraviolet spectra of *p*-methoxy and *p*-nitrostyrene oxides and sulfides. The observed red shifts and enhancements of the "first primary" benzene transition[3] were of a magnitude compatible with significant participation in electron delocalization which has been referred to as "extension of conjugation."

The perturbation theory of Petruska[4] and Stevenson[5] lends further support to the qualitative use of electron donor–acceptor resonance structures[6,2] to rationalize the observed conjugative extension of benzene by the three-membered rings when donor or acceptor substituents are present in the *para* position.

We here seek to determine whether "transmission of conjugation" in correspondingly substituted stilbene oxides can be equally satisfactorily demonstrated.

The spectra of *para*-substituted stilbene oxides do show unequivocal conjugative effects beyond the chromophoric expectations from the simply additive constituent-substituted styrene oxides. It is thus possible to ascribe the observed spectroscopic perturbations to "second-order conjugative transmission."

It was found convenient to prepare several of the stilbene oxides from the stilbenes *via* the bromohydrins or in one case from the dibromide. Only 4-methoxy-4′-nitrobibenzyl has not been previously described. This was prepared by reduction of the corresponding stilbene to 4-amino-4′-methoxybibenzyl followed by reoxidation of the amino group with either peracetic or trifluoroperacetic acid.[7]

Experimental Section[8]

Materials.—All of the compounds studied were recrystallized to constant physical properties (melting point, ultraviolet, and infrared spectra), all of which agree with the literature values. The following compounds were obtained commercially or prepared according to published methods: *cis*- and *trans*-stilbene oxide,[9] bibenzyl, 4-nitrobibenzyl,[10] *cis*- and *trans*-4,4′-dinitrostilbene oxide,[11] 4,4′-dinitrobibenzyl,[12] 4-methoxybibenzyl,[13] and 4,4′-dimethoxybibenzyl.[14]

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[1] Preliminary reports of part of this work have been given at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1963, and at the 9th Spectroscopicum Internationale, June 1961, Lyons, France. This work was supported in part by Cancer Research Funds, University of California, and by an Institutional Cancer Research Grant, IN-33D, Allocation 8, from the American Cancer Society. Abstracted, in part, from the Ph.D. thesis of D. Jambotkar.

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[3] The "first primary" benzene band ($^1A_{1g}$–$^1B_{1u}$) which appears at about 210 mμ is labeled ^1A–^1L_a in Platt's nomenclature: J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

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[7] (a) W. Emmons, *J. Am. Chem. Soc.*, **76**, 3470 (1954); (b) *ibid.*, **79**, 5528 (1957). It is interesting that, although a methoxy substituent in the same ring as the amino function is known to cause the reaction to fail, the 4′-methoxy substituent did not produce an untoward effect on the oxidation.

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