Photoaddition to Benzene of *N*-Phenylmaleimides Substituted with Electron-Attracting Groups

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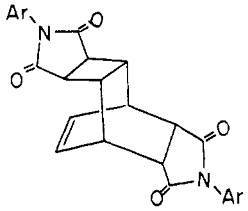
Photoadducts of benzene and *N*-phenylmaleimides substituted in the para position with electron-attracting groups were prepared, despite earlier reports that photoaddition does not occur when maleimide and benzene rings of *N*-phenylmaleimide derivatives can be coplanar. Photoadducts were also prepared from benzene and ortho-substituted *N*-phenylmaleimides.

It has been reported (*3, 5*) that *N*-phenylmaleimides having no substituents ortho to the imide nitrogen give little or no yield of photoadduct (**1**) with benzene. This has been attributed to the existence of low-lying excited states that quench the photoexcited maleimide when the phenyl and maleimide rings can be coplanar (*3, 5*). Nevertheless, in a recent study of polyimide synthesis via photoaddition of bismaleimides to benzene (*11*) and alkylbenzenes (*8*), we obtained high yields of polymer from 4,4′-bismaleimidodiphenyl sulfone. With 4,4′-bismaleimidodiphenyl ether and 4,4′-bismaleimidodiphenylmethane, which also have no substituents ortho to the maleimido group, the expected low yields of polyimide were realized (*11*). As expected, bismaleimides having ortho methyl groups (3,3′-dimethyl-4,4′-bismaleimidobiphenyl and 3,3′-dimethyl-4,4′-bismaleimidodiphenylmethane) gave good polymer yields (*8, 11*). These results indicated that strongly electron-attracting groups on the benzene ring of the maleimide derivative might prevent quenching of the photoexcited maleimide intermediate even though coplanarity is allowed.



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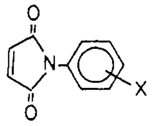
To test the generality of this photoaddition, we prepared some simple *N*-phenylmaleimides (**2**–**6**), substituted on the benzene ring with electron-attracting groups, and irradiated them in the presence of benzene. *N*-Phenylmaleimide (**7**) was included for comparison. Acetone and acetophenone were also added both as triplet sensitizers and cosolvents. (The maleimide derivatives had limited solubility in benzene alone.)



2 X = *p*-$SO_2C_6H_5$
3 X = *p*-CO_2CH_3
4 X = *p*-NO_2
5 X = *o*-CO_2CH_3
6 X = *o*-NO_2
7 X = H

Results of the experiments performed under different but arbitrary conditions of photolysis are given in Table I. The good yields of photoadduct obtained with **2**, **3**, and **4**, by use of a 450-W mercury lamp, are in accord with the reported polyimide synthesis. (Maleimide **2** was a model compound for the polyimide study.) With maleimides having ortho substituents (**5** and **6**), the yields were a little higher than those obtained from the correspondingly para-substituted reactants under the same conditions of photolysis. This may reflect an enhancement of reactivity owing to steric effects; however, the difference in yields is small enough that no definitive conclusions can be drawn. *N*-phenylmaleimide (**7**), as expected (*3, 5*), gave poor yields of photoadduct.

The possibility that the maleimide photoadditions might be proceeding via excited charge-transfer intermediates, as is the case with maleic anhydride photoaddition (*3, 4*), was considered; however, no charge-transfer complexes were detectable in ultraviolet spectra of benzene-maleimide derivative solutions, nor could a charge-transfer intermediate be trapped by conducting the photolysis of **3** in the presence of trifluoroacetic acid (*4*). In fact, trifluoroacetic acid suppressed the photoaddition.

On the basis of results obtained with maleimide derivatives **2**, **3**, and **4**, together with those reported earlier for polyimides prepared photochemically (*8, 11*), it appears that the conditions for photoaddition are satisfied by the presence of strongly electron-attracting para substituents, even though coplanarity of the benzene and maleimide rings is allowed.

Experimental

Melting points are uncorrected. Nmr spectra were run in deuterated dimethyl sulfoxide on a Varian A-60D spectrometer (tetramethylsilane internal standard). Ir spectra were run in KBr or Nujol on a Perkin-Elmer Model 257 spectrophotometer.

Preparation of maleimide derivatives. Maleimide derivatives were prepared in the following overall yields from maleic anhydride, and the corresponding amines by a procedure used to prepare bismaleimides (*10*): **2**, 66%, mp 166–168°C; **3**, 70%, mp 163–165°C; **4**, 83%, mp 166–169°C [lit. (*2*) 167–168°C]; **5**, 55%, mp 111–112°C [lit. (*9*) not reported]; **6**, 67%, mp 129–130°C [lit. (*2*) 130–131°C]. Maleimide **7** was prepared by a standard procedure (*6*).

Ir and nmr spectra of **2**, **3**, and **5** were consistent with assigned structure. Ir displayed broad imide carbonyl bands at 1690–1710 cm^{-1} (overlapping ester carbonyl); **2** had bands at 1360 and 1160 cm^{-1} (SO_2). Nmr: **2**, δ 7.31 (singlet, 2H), 7.75–8.25 (multiplet, 9H); **3**, δ 3.90 (singlet, 3H), 7.29 (singlet, 2H), 7.54–7.75 (doublet, 2H) 8.09–8.31 (doublet, 2H); **5**, δ 3.80 (singlet, 3H), 7.31 (singlet, 2H), 7.41–8.32 (multiplet, 4H).

Preparation of photoadducts. Solutions consisting of 0.5 gram of maleimide derivative, 2 ml of acetophenone, 7 ml of acetone, and 45 ml of benzene were irradiated 22 hr with a Hanovia 450-W mercury lamp in borosilicate

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Table I. Yields and Melting Points of Photoadducts

Maleimide	Adduct yield, %[a]	Adduct mp, °C[b]
2	68	400
3	69 (23)	345
4	76 (30)	392
5	(28)	303–305
6	(34)	340–343
7	20	390

[a] Initial yields after irradiation for 22 hr with a Hanovia 450-W medium-pressure mercury lamp in borosilicate glass test tubes. Numbers in parentheses are yields obtained after irradiating 17 hr with an Ultra-Violet Products PCQ-X1 low-pressure lamp in quartz tubes. [b] All melted with decomposition.

glass test tubes or for 17 hr with an Ultra-Violet Products PCQ-X1 lamp in quartz tubes. The former were irradiated at refluxing benzene temperature; the latter were at about 40°C. No external cooling was employed. Products precipitated on the walls of the test tubes in all cases except with that from maleimide **5** which was remarkably soluble in the reaction medium. The latter was isolated by evaporating the solvent, stirring the residue with boiling ethanol, and filtering off the insoluble adduct. Photoadducts were identical (mp, ir) with bisimides prepared from maleic anhydride–benzene photoadduct (*1, 7*) and the corresponding amines by heating the two together at 200°C until gas evolution ceased (*5*).

Ir: **2** (KBr), 3040, 2920, 1770, 1700, 1590, 1485, 1440, 1370, 1290, 1150, 1105, 1070, 1000, 885, 840, 790, 760, 740, 730, 710, 695, 682, 630 cm^{-1}; **3** (KBr), 2950, 1770, 1700, 1600, 1500, 1475, 1432, 1410, 1365, 1275, 1170, 1110, 1020, 960, 863, 770, 740, 730, 685, 630 cm^{-1}; **4** (KBr), 3100, 2910, 1770, 1700, 1590, 1500, 1370, 1335, 1180, 1155, 1110, 1000, 860, 755, 730, 700, 685, 655 cm^{-1}; **5** (Nujol) 1765, 1700, 1600, 1578, 1490, 1300, 1270, 1190, 1160, 1130, 1085, 1000, 960, 890, 850, 827, 805, 750, 730, 695, 680, 655, 620 cm^{-1}; **6** (Nujol), 1765, 1715, 1600, 1580, 1520, 1348, 1300, 1270, 1243, 1220, 1180, 1150, 860, 848, 790, 783, 755, 724, 705, 690, 650 cm^{-1}.

Irradiation of **3** in benzene in the presence of 0.825*M* trifluoroacetic acid resulted in no photoadduct and quantitative recovery of starting material.

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Synthesis of *cis*- and *trans*-1,2-Dimethoxyethylene by Thermal Demethanolization of 1,1,2-Trimethoxyethane

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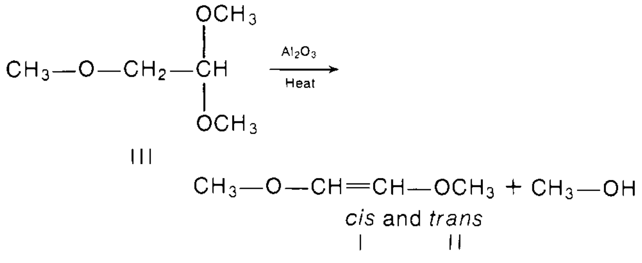
The vapor-phase pyrolysis of 1,1,2-trimethoxyethane over alumina at 300°C is used to produce a cis-rich mixture of *cis*- and *trans*-1,2-dimethoxyethylene in conversions approaching 90%. The cis-trans ratios are typically around eight. The trans-isomer is best prepared by equilibration from the cis-isomer with mercuric acetate catalyst at elevated temperatures (175°C). Some physical properties, including nmr, infrared, and Raman spectra of these isomers, are also reported.

In the course of studying olefin isomerization reactions, we required pure samples of *cis*- and *trans*-1,2-dimethoxyethylene (I and II, respectively). This material was reported in a U.S. Patent (*8*) and by German, Russian, and Japanese workers (*2, 11, 12, 14, 17*). Two main preparative methods were reported: dechlorination of 1,2-dichloro-1,2-dimethoxyethane with Mg (*2, 12, 17*) and pyrolysis of 1,1,2-trimethoxyethane (III) over solid catalysts (*8, 11, 14*). Since we had a supply of III, we decided to use the pyrolytic method originally reported by McElvain and Stammer (*13*) for the preparation of 1,2-diethoxyethylene. It was apparent that we could make substantial improvements in the reported pyrolysis procedures, and we are reporting our results here. In addition, some physical and spectral properties of I and II are also reported.

Results and Discussion

The catalytic decomposition of III proceeds according to the following equation:



$$\underset{\text{III}}{CH_3-O-CH_2-\underset{OCH_3}{\overset{OCH_3}{CH}}} \xrightarrow[\text{Heat}]{Al_2O_3} \underset{\substack{cis \text{ and } trans\\ \text{I} \quad \text{II}}}{CH_3-O-CH{=}CH-OCH_3} + CH_3-OH$$

This is entirely analogous to the pyrolysis of 1,1,2-triethoxyethane reported by McElvain and Stammer (*13*).

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