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PHOTOADDITION OF MALEIMIDE AND SOME N-SUBSTITUTED MALEIMIDES TO BENZENE

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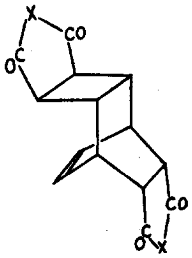
Previous workers have reported the photodimerisation of various substituted maleimides to cyclobutanes,[1,2] and their cycloaddition to certain olefins and acetylenes.[2,3]

We wish to report that maleimide and some, but not all, N-substituted maleimides readily form 2 : 1 photoadducts with benzene. The reactions can be weakly photosensitised by benzophenone. The adducts have been formed from maleimide, N-n-butyl-, N-benzyl-, N-o-tolyl-, and N-2,6-xylylmaleimide. N-phenyl, N-p-tolyl-, and N-p-methoxyphenylmaleimide did not form photoadducts with benzene. It can be inferred from a result given in ref. 1 that dimethylmaleimide does not photoadd to benzene, although the authors do not explicitly state this. In the five cases specified above the adducts have the structures (I) - (V) respectively. This has been shown by their independent synthesis from the benzene-maleic anhydride adduct for which the stereochemical structure (VI) has been established.[4] Thus,



(I) : $\mathrm{X = NH}$
(II) : $\mathrm{X = NBu^{n}}$
(III) : $\mathrm{X = NBz}$
(IV) : $\mathrm{X = N(\underline{o}\text{-}MeC_6H_4)}$
(V) : $\mathrm{X = N(2,6\text{-}Me_2C_6H_3)}$
(VI) : $\mathrm{X = O}$

the benzene-maleic anhydride adduct formed the benzene-maleimide adduct, m.p. > 400°, when heated with urea at 140°. No epimerisation would be expected under these conditions. The benzene-N-benzylmaleimide adduct, m.p. 285°, was obtained similarly by the use of benzylamine. The benzene-N-$\underline{n}$-butylmaleimide adduct, m.p. 175.5°, was prepared from the maleimide adduct by reaction of the potassio-derivative with n-butyl iodide. The two further adducts referred to above, (IV) and (V), were prepared from the benzene-maleic anhydride adduct (VI) by heating with the corresponding amines at 200°: they had m.ps. 382° (dec.) and > 400° respectively. All of these new adducts had the correct elemental analyses and gave n.m.r. and infrared spectra consistent with the assigned structures.

Although cyclopentene-3,5-dione and $\Delta^{\alpha,\beta}$-butenolide are isoelectronic with maleimide and maleic anhydride, neither formed a photoadduct with benzene with or without the use of benzophenone as a sensitiser.

The rate of unsensitised addition of maleic anhydride to benzene has previously been reported to be unaffected by the use of oxygen-saturated solutions, and from this and other evidence the 2 : 1 adduct has been concluded to arise via a 1 : 1 adduct formed by collapse of an excited singlet maleic anhydride-benzene charge-transfer complex.[5] This conclusion has recently been disputed by Hardham on the basis of an observed small (ca. 25%) decrease of the rate in the presence of oxygen; but the same author found that other efficient triplet quenchers such as azulene and ferric dibenzoylmethide had little or no effect on the rate, and indeed under certain conditions actually increased it by up to 50%.[6] Our experience with the maleimide-benzene system suggests that the results of oxygen-quenching experiments should be interpreted with caution. In one set of experiments, oxygen had no detectable effect on the rate: in other experiments performed at another time under seemingly identical conditions, the rate was reduced to ca. 20% of that found in the absence of oxygen. Some unusual critical factor seems to be involved and attempts to identify it are in progress.

Regarding the mechanism of the unsensitised addition of maleimide to benzene, it can only be said at this time that at least part of the product seems to be formed via triplet intermediates under certain conditions. Solutions of maleimide in benzene (examined in 0.0004 cm. films) show abnormally strong absorption over the region 230 - 280 mμ, but the absorption due to maleimide at longer wavelengths is identical with that found with solutions of maleimide in chloroform. The abnormal absorption may be attributable to a charge-transfer transition. Since the rate of the unsensitised addition was not reduced by more than 10% with the use of a Pyrex filter essentially opaque to radiation of wavelengths shorter than 280 mμ (medium pressure Hanovia S500 lamp), it seems probable that absorption of energy via a charge-transfer transition plays much less of a part than in the corresponding addition of maleic anhydride to benzene.[5,6] This does not imply that complexing of maleimide with benzene is unimportant in the photoaddition process. Polarisation complexes, not readily detectable by ultraviolet spectroscopy, may well be involved.

The rate of the benzophenone-sensitised addition of maleimide to benzene was consistently reduced to *ca*. 20% by the use of oxygen-saturated solutions, so can reasonably be considered to involve energy transfer from triplet benzophenone, probably to maleimide complexed with benzene in some way as in the corresponding case of maleic anhydride and benzene.[5]

The inability of N-phenylmaleimide to photoadd to benzene, and the ability of N-benzylmaleimide to do so, suggested that N-phenylmaleimide might be quenching some excited intermediate by virtue of the existence of low-lying excited states while the molecule is in planar and near-planar conformations. Strong support for this belief comes from the observation that normal addition to benzene occurs with N-*o*-tolyl- and N-2,6-xylylmaleimide where models show that the attainment of a planar conformation should be hindered by the methyl groups. Further, N-*p*-tolylmaleimide, where there is no such hindrance, resembled N-phenylmaleimide in its failure to add to benzene.

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