Acid-catalysis of Photochemical Reactions

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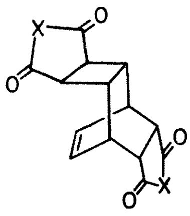
Summary Several examples of acid-catalysed photochemical reactions are reported, *e.g.* the formation of phenylsuccinic anhydride from benzene and maleic anhydride: these constitute a photochemical counterpart of the Friedel–Crafts reaction.

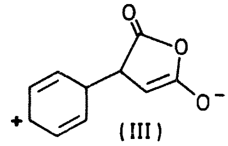
ALTHOUGH acid-catalysis is a common phenomenon in 'thermal' organic chemistry, surprisingly little is yet known of it in photochemistry. Exceptionally, Kropp has recently studied the acid-catalysed photoaddition of alcohols to certain cyclic olefins.[1] Photochemical acid-catalysis phenomena are in principle to be expected in view of the high rates of proton transfer which are possible relative to the lifetimes of many electronically excited molecules.

We report now the effects of acid on some photoaddition reactions involving donor-acceptor pairs where intermediates having a degree of charge separation, and hence susceptibility to protonation, were thought likely to be involved.

Photoaddition of maleic anhydride[2] and maleimides[3] to benzene is known to produce the 2 : 1 adducts (I) and (II) respectively. In the case of maleic anhydride, the excitation is of charge-transfer-type and the course of the reaction is insensitive to the presence of added tetracyanoethylene. These facts have led to the proposal[4] that a dipolar 1 : 1 intermediate (III), unreactive towards tetracyanoethylene, is involved in the unsensitised photoaddition of maleic anhydride, rather than the diene intermediate (IV) which was originally suggested.[2] On the other hand, the addition of maleimides to benzene involves excitation of the maleimide, rather than charge-transfer excitation, and the diene intermediate (V) can readily be trapped with tetracyanoethylene.[4] Confirmatory evidence for a dipolar intermediate of type (III) has been obtained by irradiation of benzene and maleic anhydride in the presence of 0·825M-trifluoroacetic acid at 20°.† Formation of adduct (I) was completely suppressed, and a new 1 : 1 adduct, phenylsuccinic anhydride, was obtained. This product is that which would be expected to result from protonation of intermediate (III), followed by deprotonation.

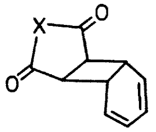


(I) X = O
(II) X = NH or NR

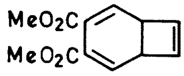


(III)

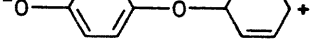
(and other canonical forms)



(IV) X = O
(V) X = NH or NR



(VI)



(VII)

(and other canonical forms)

In contrast, trifluoroacetic acid was virtually without effect on the photoaddition of *N*-n-butylmaleimide to benzene: specifically, no phenyl-*N*-n-butylsuccinimide was detected. This result conforms excellently with the previous conclusion that a dipolar intermediate is not involved.[4]

In corresponding benzophenone-sensitised additions of maleic anhydride to benzene, the yields of adduct (I) were reduced only to *ca.* 50% in the presence of 0·825-M-trifluoroacetic acid. This lower susceptibility of the triplet sensitised reaction to the effect of added acid is consistent

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† Benzene and trifluoroacetic acid alone undergo a relatively slow photoreaction leading to trifluoroacetophenone among other products. This will form the subject of a further Communication with Dr. G. B. Cox.

with the lower degree of dipolar character to be expected in a triplet than a singlet intermediate of type (III): spin considerations require the triplet to be formulated as a polarised diradical rather than a zwitter-ion.[5]‡

Similar effects of added trifluoroacetic acid have been found in the photoaddition of dimethyl acetylenedicarboxylate to benzene whereby dimethyl phenylfumarate and phenylmaleate are produced in place of dimethyl cyclo-octatetraene-1,2-dicarboxylate. Dimethyl phthalate is also produced from this irradiation both in the absence and presence of acid and is derived photochemically from the cyclo-octatetraene in each case, apparently by elimination of acetylene from an isomer such as (VI); it is interesting that this photoelimination reaction is also acid catalysed.

In the absence of acid, *p*-benzoquinone and benzene do not form an isolable photoadduct although the absorption spectrum of the mixture shows a charge-transfer band. Irradiation (> 280 nm) in the presence of trifluoroacetic acid led to the production of 4-phenoxyphenol in good yield as the only product, presumably by successive protonation-deprotonation of intermediate (VII). As in all the foregoing cases, no reaction occurred in the absence of u.v. radiation.

These new acid-catalysed photoreactions are in a sense analogous to thermal Friedel–Crafts reactions, although the products can be different: thus the aluminium chloride-catalysed thermal reaction of benzene and maleic anhydride gives benzoylacrylic acid, in sharp contrast with the present photochemical production of phenylsuccinic anhydride. They illustrate the profound influence which acids may have on the course of photochemical reactions, and provide the basis of a simple but sensitive mechanistic probe for polarised intermediates which should be capable of wide application.

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‡ Even for the singlet species, structures (III) and (VII) may exaggerate the actual degree of charge-separation which could be ustained in the absence of strong solvation.

[1] P. J. Kropp, *J. Amer. Chem. Soc.*, 1969, **91**, 5783: see also A. Stoll and W. Schlientz, *Helv. Chim. Acta*, 1955, **38**, 585; H. Hellberg *Acta Chem. Scand.*, 1957, **11**, 219; M. Kawanisi and H. Kato, *Tetrahedron Letters*, 1970, 721.

[2] H. J. F. Angus and D. Bryce-Smith, *Proc. Chem. Soc.*, 1959, 326; *J. Chem. Soc.*, 1960, 4791.

[3] D. Bryce-Smith and M. A. Hems, *Tetrahedron Letters*, 1966, 1895; J. S. Bradshaw, *ibid.*, p. 2039.

[4] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47.

[5] D. Bryce-Smith and A. Gilbert, *Chem. Comm.*, 1968, 1701.