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MECHANISM OF THE PHOTOADDITION OF MALEIC ANHYDRIDE TO BENZENE

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Although the 2:1 photoaddition of maleic anhydride to benzene was first reported in 1959,[1a] the nature of the 1:1 intermediate(s) has until recently been in question: cf. refs. 1 and 2. The bicyclo-octadiene (I) originally proposed[1a] had subsequently appeared unlikely in view of the failure by several workers[2a] to intercept it with tetracyanoethylene, and an alternative zwitter-ionic intermediate (IIa) has been suggested:[2b] this latter was consistent with the charge-transfer nature of the excitation process.[2c] Hartmann et al. have recently revived interest in the original proposal[1a] by their discovery that the trapping product (III) of (I) with tetracyanoethylene can be obtained, albeit in modest yield unless dichloromethane is used as a co-solvent.[3] The previous failures to obtain (III) resulted from an unexpectedly low dienophilic reactivity of tetracyanoethylene towards (I) in the presence of benzene.[3] Tetracyanoethylene is apparently completely complexed in benzene solution.[4]

Although Hartmann's findings effectively reinstate the bicyclo-octadiene (II) as an intermediate, high trapping efficiency with tetracyanoethylene requires the presence of dichloromethane - which is evidently affecting the course of the reaction. Moreover, this intermediate could not readily give rise to the results reported from trapping experiments with acids.[2b]

We now report evidence which, in conjunction with our previous findings,[2b] suggest that bicyclo-octadiene (I) is the immediate precurosor of the 2:1 adduct (IV) in unsensitised and sensitised reactions in the absence of dichloromethane, and that zwitter-ion (IIa) is the precursor of (I) in unsensitised reactions. We also find that dibromomethane, but not dichloromethane, as a solvent can effectively promote a triplet process.

Thus the relative quantum yields of (IV) from 0.29-M maleic anhydride in benzene + diluent (3:4 by vol.) were 1.0 : 1.1 : 1.05 : 1.7 for cyclohexane, acetonitrile, dichloromethane, and dibromomethane respectively.* It is noteworthy that dibromomethane enhances the adduct formation to a degree similar to that which results from incorporation of 0.06-M benzophenone into the cyclohexane solution. This effect is attributed to $S_1 \rightarrow T_1$ intersystem crossing in the excited benzene-maleic anhydride complex under the influence of the heavy atom solvent. As the benzophenone-sensitised triplet pathway is less sensitive than the unsensitised route to diversion by proton donors (giving phenylsuccinic anhydride),[2b] the observation that the unsensitised reaction is similarly less

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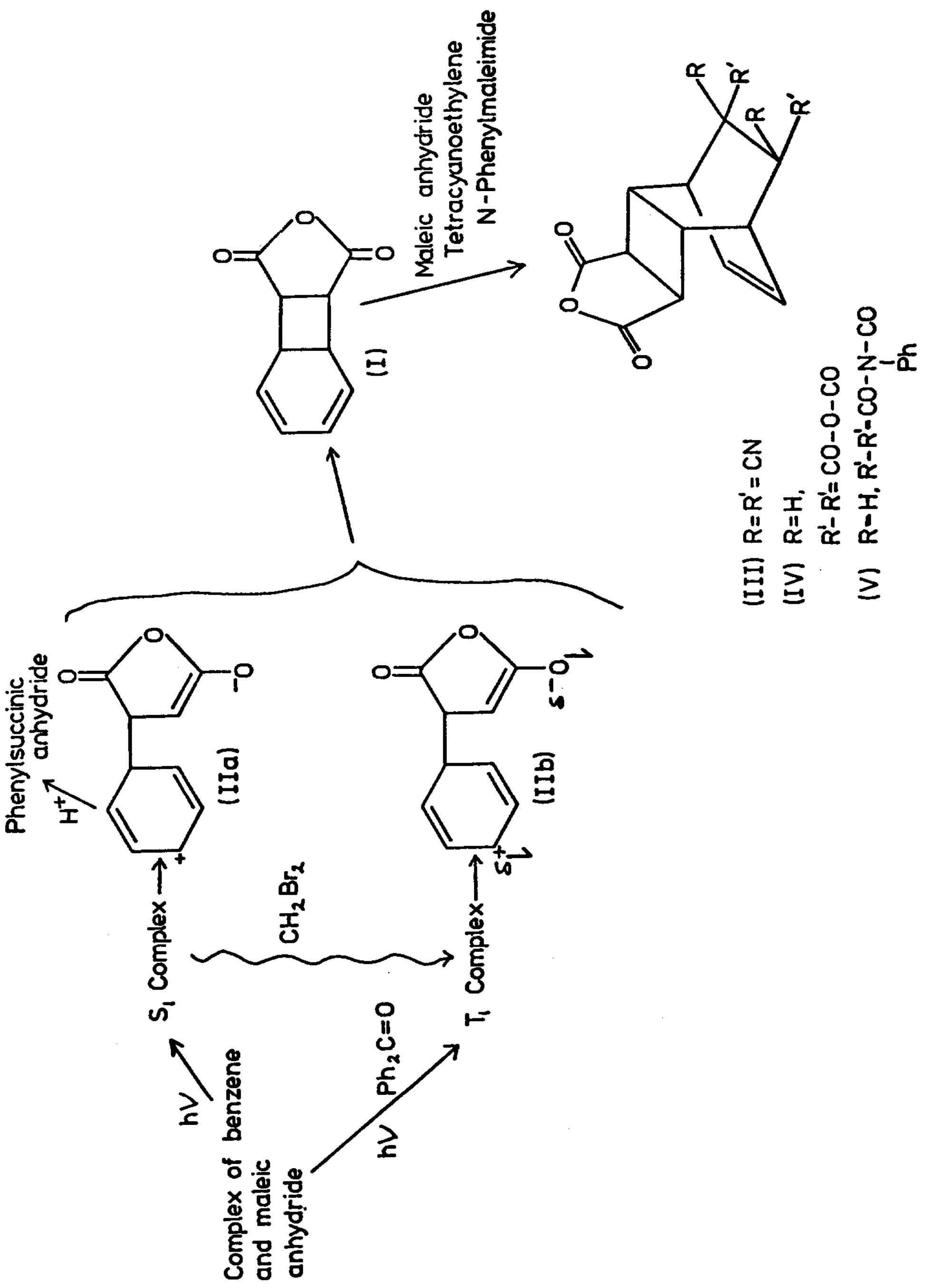
* Footnote. All irradiations were carried out in pyrex apparatus at 20° under argon using light from a medium pressure mercury arc lamp.


Complex of benzene and maleic anhydride
hν
hν
Ph₂C=O
S₁ Complex
T₁ Complex
CH₂Br₂
H⁺
Phenylsuccinic anhydride
(IIa)
(IIb)
(I)
Maleic anhydride
Tetracyanoethylene
N-Phenylmaleimide
R
R'
(III) R=R'=CN
(IV) R=H,
R'-R'=CO-O-CO
(V) R=H, R'-R'=CO-N-CO
Ph

sensitive in dibromomethane further suggests that dibromomethane acts by inducing a triplet pathway, and that the unsensitised process occurs by a singlet mechanism in the absence of heavy atom solvents.

Chemical, as distinct from physical, effects of heavy atom solvents have hitherto only been observed in the photoreactions of acenaphthylenes.[5]

It is possible to reconcile the evidence of (II_a_, _b_) on the one hand, with that for (I) on the other by the reasonable postulate that the former can cyclise into (I) unless intercepted by a proton donor, and that (II_a_) is more readily protonated than the inductively polarised (II_b_).

We find that N-phenylmaleimide is much more effective than tetracyanoethylene as a trap for (I). Irradiation of a benzene solution 0.17M in maleic anhydride and 0.0846 M in N-phenylmaleimide in the presence and absence of dibromomethane gave the 1:1:1 adduct (V) as the only detectable product. The yields of (V) were comparable with those of (IV) obtained in the absence of N-phenylmaleimide. As expected, in the presence of 0.825M trifluoroacetic acid, the rate of formation of (V) was reduced drastically (8-fold), but when dibromomethane (19M) was also present, the reduction was much less (2.2-fold). Since efficient formation of (V) by addition of N-phenylmaleimide to (II_a_ and _b_) seems highly improbable, these results strongly support the proposal that (II_a_ and _b_) are produced in the singlet and triplet processes respectively, and that each transforms into (I). We agree with Hartmann[3] that (I) is the immediate precursor of (IV) in the sensitised and unsensitised photoadditions of maleic anhydride to benzene. The zwitterionic precursor of (I), namely (II_a_), is evidently involved in the unsensitised singlet reaction, but to a smaller extent, if at all, in the triplet process induced by benzophenone or dibromomethane.

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