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PHOTOCHEMICAL REACTIONS BETWEEN DIBROMOMALEIC ANHYDRIDE AND BENZENE OR ITS HOMOLOGUES

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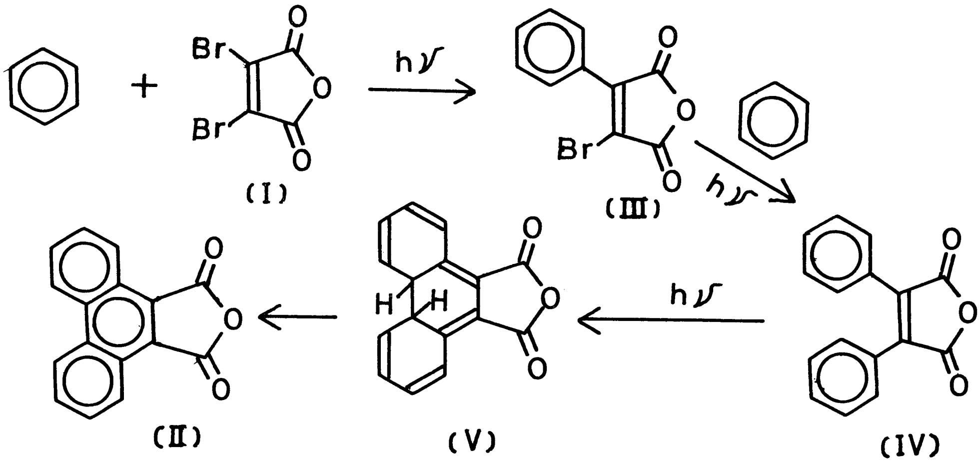
On the irradiation of dibromomaleic anhydride in benzene or its substituted derivatives, α-aryl-α'-bromomaleic anhydrides were obtained. Further irradiation of the solution afforded phenanthrene-9,10-dicarboxylic anhydrides. In the first step, charge-transfer complexes also were found to participate in the reaction.

The photochemical addition between maleic anhydride and benzene is a well known example where charge-transfer complexes determine the course of photochemistry.$^{1)}$ On the other hand, the initial product of the photosensitized reaction of dichloromaleic anhydride with benzene has been reported to be α-phenyl-α'-chloromaleic anhydride, which successively undergoes sensitized addition to benzene yielding a tricyclic dianhydride in a way analogous to the case of maleic anhydride-benzene system.$^{2)}$ In the case of dibromomaleic anhydride and benzene (or its substituted homologues), here investigated however, we found that both of the two bromine atoms were photochemically substituted with aryl groups at first and the successive photochemical cyclization of the intermediate afforded phenanthrene-9,10-dicarboxylic dianhydride as the final product of the unsensitized reaction. This is the first example of the case where maleic anhydride homologue is found to undergo a direct, photochemical transformation into polycyclic aromatic hydrocarbons.

On the irradiation of benzene solution (300 ml) of dibromomaleic anhydride (I) (3.6 gr) with a high-pressure mercury lamp (Riko-Sha UVL-700P) in nitrogen atmosphere, fume of hydrogen bromide evolved and yellow crystals separated out of the solution as the time elapsed. White crystalline material (72 mg) was obtained as the final product, which was identified with phenanthrene-9,10-dicarboxylic anhydride (II). The same product (II) was also obtained when the reaction was carried out by the use of a 30 W low-pressure mercury lamp (Riko-Sha UVL-303Q). In this case, however, another product (III) was obtained in much larger amount (420 mg) than II (133 mg). Irradiation of the benzene solution of III afforded compound II, and compound III was identified with α-phenyl-α'-bromomaleic anhydride. Hence, the formation of the final product (II) may be described by the scheme shown in the next page. From mechanistic view-point, the formation of III



might be closely related to that of α-phenyl-α'-chloromaleic anhydride from dichloromaleic anhydride and benzene.2) It should be reminded however that no sensitizer is required in the photochemistry of dibromomaleic anhydride while dichloromaleic anhydride does not react in the absence of any sensitizer.2) Photochemical transformation from IV to II was previously studied by Sargent and Timmons.3) In our case, however, IV was not isolated as an intermediate probably because the photochemical cyclization of IV followed immediately after it had been formed.

Unlike the case of dichloromaleic anhydride,2) reaction products of the same type as described above were also obtained when dibromomaleic anhydride was irradiated in the presence of toluene, xylene, tetraline, or naphthalene. In the case of dibromomaleic anhydride-anisole system, on the other hand, the correspondingly substituted phenanthrene-9,10-dicarboxylic anhydride was not obtained. Instead, small quantity of α-(p-methoxyphenyl)-α'-(o-methoxyphenyl)maleic anhydride (VII) (yield, 0.8 %) was obtained together with α-(p-methoxyphenyl)-α'-bromomaleic anhydride (VIIIa) (yield, 2%) and α-(o-methoxyphenyl)-α'-bromomaleic anhydride (VIIIb) (yield, 9 %) on the internal irradiation of I (5.0 gr) in anisole (150 ml) with a 100 W high-pressure mercury lamp for 30 hr.

In any case, the first step of the formation of the above reaction products is the substitution of a bromine atom in dibromomaleic anhydride by an aryl group. Then, the first step was further studied to clarify the reaction mechanism. At the concentration of the present experiment, anisole by itself does not absorb light at the wavelength longer than 320 nm, and the absorption due to dibromomaleic anhydride also becomes negligible at approximately 370 nm. When the two components are mixed together however, a tail of the absorption band is extended beyond 470 nm, which indicates the formation of charge-transfer complexes between dibromomaleic anhydride and anisole. By the use of an aqueous potassium chromate filter solution (0.2 g/l) in a glass vessel, the exciting light at 365 nm was completely removed from the radiation emitted by the high-pressure mercury lamp. Most of the light at 405 nm and a part of that at 313 nm also were absorbed by the same filter. Under this condition, the yield of VIIIb was reduced to approximately 40 % of that of the case without the filter. When the acetone filter was used on the other hand, the light at 313 nm was eliminated but the intensities of the incident radiation at the wavelength longer than 365 nm remained unchanged. In this case, the yield of VIIIb decreased only slightly from the value in the absence of the filter solution. The yield of VIIIa, which is about one fifth of that of VIIIb, varies analogously on the change of the filter solutions. On the basis of these observations, it is concluded that the lights in the wavelength region between 310 and 460 nm are equally important for the present experiment. Because the exciting lights with wavelength longer than 400 nm are still effective in the formation of VIII, it is strongly suggested that charge-transfer complexes participate in the first step of the reaction. One should remember also, however, that the irradiation of I in benzene with a low-pressure mercury lamp yielded III as mentioned previously. In other words, α-aryl-α'-bromomaleic anhydride is also produced even on the direct excitation of either dibromomaleic anhydride or benzene (or its substituted homologue) by itself.

The photochemical reactions between dibromomaleic anhydride and toluene analogously were found to be strongly affected by the intensity of the exciting light at 405 nm, which is situated on the charge-transfer band of this system. All of three isomeric α-tolyl-α'-bromomaleic anhydrides were obtained with the ratio [ortho(IXa) : meta (IXb) : para (IXc) = 1 : 4 : 4], which is considerably different from the corresponding ratio in the case of anisole-dibromomaleic anhydride system (ortho : meta : para = 5 : 0 : 1). In addition to these tolyl-substituted derivatives, α-benzyl-α'-bromomaleic anhydride (X) was obtained. Although the rate of formation of the three isomers IXa, IXb and IXc exceeds that of X in the beginning, the situation is reversed as the irradiation time is prolonged (Fig. 1). This is probably because IX is successively transformed into methyl-substituted phenanthrene-9,10-dicarboxylic anhydrides, while X remains unchanged even under the irradiation. The rate of formation of X appears to be affected only by the concentration of dibromomaleic anhydride remaining in the solution. It is not clear at present whether the precursor excited state of X

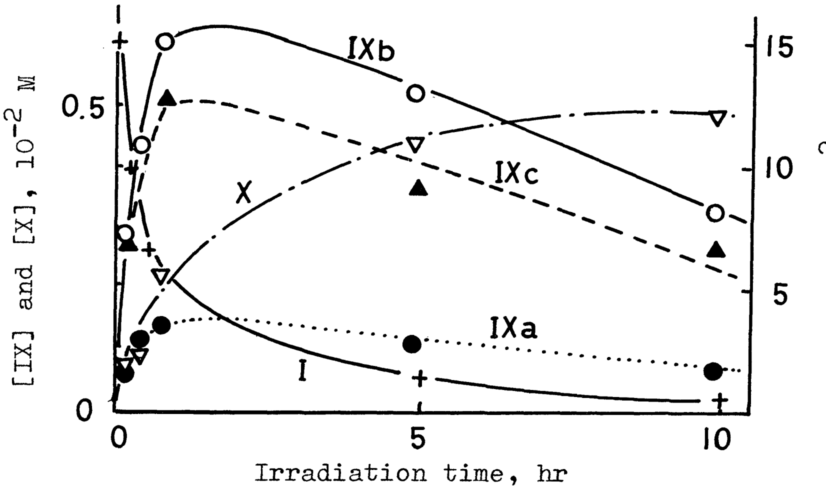


Fig. 1. The growth and decay of relevant species during the irradiation of dibromomaleic anhydride (154 mg) in toluene (5 ml) with a high-pressure mercury lamp.

is the same as that of IX or not. We found also that an appreciable amount of benzyl bromide and bibenzyl was formed, which strongly suggests that at least a part of the reaction proceeds via free radical mechanism. Bibenzyl and benzyl bromide were detected again, when purified sample of α-(p-methoxyphenyl)-α'-bromomaleic anhydride was irradiated in toluene. Hence, it is quite likely that the second step of the reaction is initiated by the photolysis of C-Br bond in α-aryl-α'-bromomaleic anhydride which leads to the formation of a bromine atom.

Table 1. Physical characteristics of the relevant reaction products

Compound	mp, °C	IR*, cm^{-1}	$\lambda_{max}^{CH_3CN}$,nm,(log ε)	NMR, ppm
II	above 300	1842, 1773 1186, 1156	359 (4.0)	7.6 (m, 4H), 8.5 (m, 4H) in DMSO (140 °C)
III	77.5-78.1	1825, 1760, 1240	326 (4.2)	7.6 (m, 3H), 8.0 (m, 2H) in CCl_4
VII	177.5-178.5	1855, 1780, 1240	368 (4.0)	3.65 (s, 3H), 3.4 (s, 3H), 7.0-7.7 (m, 8H) in acetone
VIIIa	111.4-112.3	1855, 1770- 1750, 1240	370 (4.7)	3.92 (s, 3H), 7.1 (d, 2H), 8.2 (d, 2H) in CCl_4
VIIIb	61.0-62.0	1860, 1785, 1230 in CCl_4	360 (3.5)	3.8 (s, 3H), 6.9-7.6 (m, 4H) in CCl_4
IXa	liquid	1850, 1775, 1240, neat	319	2.3 (s, 3H), 7.2-7.4 (m, 4H) in CCl_4
IXb	80.0-81.0	1960, 1770, 1240	325 (3.9)	2.4 (s, 3H), 7.3-7.7 (m, 4H) in CCl_4
IXc	60.0-61.0	1845, 1765, 1230	345 (4.4)	2.4 (s, 3H), 7.3 (d, 2H), 8.0 (d, 2H) in CCl_4
X	liquid	1858, 1776 1240, neat	268	3.8 (s, 2H), 7.2 (s, 5H) in CCl_4

* The value for KBr disk unless otherwise specified.

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