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CHARGE-TRANSFER EXCITATION IN PHOTOREACTION OF THE TROPONOID SYSTEM (1)

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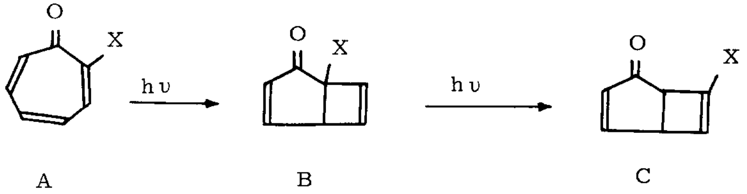
A variety of substituents located in the tropone ring affects remarkably the mode of photoreaction of the troponoid system. For example, the irradiation of tropone and 2-chlorotropone (A: X=H and Cl) afforded photo-dimers (2), whereas most derivatives such as tropolones and their methyl ethers (A: X=OH, OCH_3) produced easily photo-valence isomers, bicyclo[3.2.0]hepta-3,6-dien-2-ones (B) and (C) (3). However, 2-aminotropone (IA) which has an isoelectronic structure with tropolone, upon irradiation, was very stable and gave no single photo-product (4). There has been no report to elucidate the difference in photo-behavior between tropolone and 2-aminotropone. We found out that acylation or arylation of 2-aminotropone (IA) brought the photo-cyclization from A to B. In addition, a remarkable solvent effect was observed in the photo-valence isomerization of 2-acetylaminotropone (IIA), 2-benzoylaminotropone (IIIA) and 2-arylaminotropones. These photochemical transformations are expected to form an excellent system for studying the relationship between reactivity and excited state.



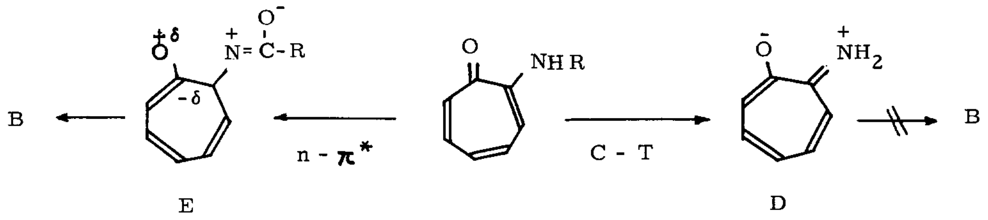
When a solution of IA in benzene or ethanol was externally irradiated in a Pyrex vessel with a high pressure mercury lamp (Toshiba H-400p), IA was almost completely recovered with the formation of a small amount of polymer. However, irradiation of IIA or IIIA under the same conditions afforded 1-acetylamino-(IIB), m.p. 158°, 7-acetylaminobicyclo[3.2.0]hepta-3,6-dien-2-one

(IIC), m.p. 183° (5), 1-benzoylamino-(IIIB), m.p. 170°, and 7-benzoylamino-bicyclo[3.2.0]hepta-3,6-dien-2-one (IIIC), m.p. 180°,(after irradiation for a few hours in benzene 87, 10 and 65 and 5% yields and in ethanol 71, 29, and 90 and 10% yields were obtained respectively). Since IIC and IIIC were obtained by irradiation of IIB and IIIB, they were secondary photo-products of IIA and IIIA (6). It was also discovered that the photoreaction of IIA and IIIA in aprotic solvents proceeded more rapidly than in protic solvents. As an example, depletion of IIIA and formation of IIIB and IIIC during the irradiation of IIIA are shown in Fig. 1. Quantum yield of disappearance of IIA and IIIA by irradiation at 365 nm light are listed as follow: 0.035 and 0.031 in cyclohexane; 0.016 and 0.018 in methanol respectively.

2-Anilinotropone (IVA), upon irradiation in an aprotic solvent such as cyclohexane, afforded 1-anilinobicyclo[3.2.0]hepta-3,6-dien-2-one (IVB), m.p. 105-106°, in 37% yield, while it was recovered quantitatively in a protic solvent like ethanol. If electron-donating substituents such as methyl and methoxyl groups are introduced in p-position of the phenyl group in IVA; in the resulting arylaminotropones the photo-cyclization from A to B does not take place in both protic and aprotic solvents. On the other hand, the introduction of electron-withdrawing groups such as chlorine, bromine, acetyl or methoxycarbonyl group in the p-position of the phenyl group of IVA causes the photocyclization of 2-arylaminotropones to occur in aprotic solvents, but not in protic solvents.

In the ultraviolet spectrum of IA as shown in Fig. 2, the absorption band at the longest wave-length region exhibits a red shift in a protic solvent. Contrarily IIA shows a blue shift in aprotic solvent as shown in Fig. 3. These facts seem to prove that the lowest lying level of IA is a charge-transfer state (D), which does not lead to the formation of the bicycloheptadienone (B). On the other hand, an excited state of IIA or IIIA is assumed to be a n-π^* transition (7) and this state (E) can lead to the cyclization as in B. The solvent effect observed above may support this interpretation.

Although tropolone, upon irradiation in methanol or water, afforded photoproducts resulted from the bicyclo compound (B) (3); it was not changed in an alkaline solution even after irradiation for a long period of time (8). As



shown in Fig.4, the UV spectrum of tropolone in an alkaline solution is very similar to that of IA, whereas the UV spectrum in methanol or cyclohexane is similar to that of IIA. The nonreactivity of the tropolonate ion towards light may be explained by the fact that the lowest lying level is the charge-transfer

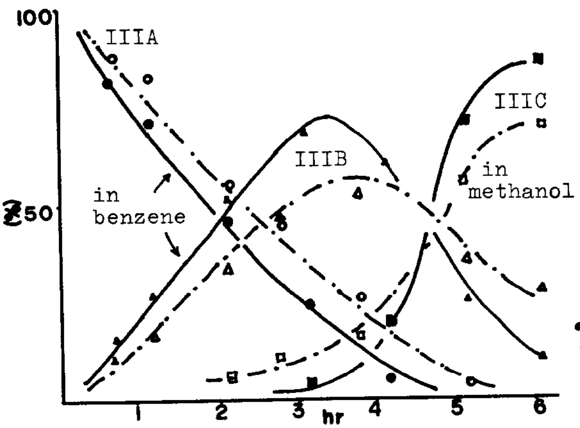


Fig. 1. Depletion of IIIA and formation of IIIB and IIIC during irradiation

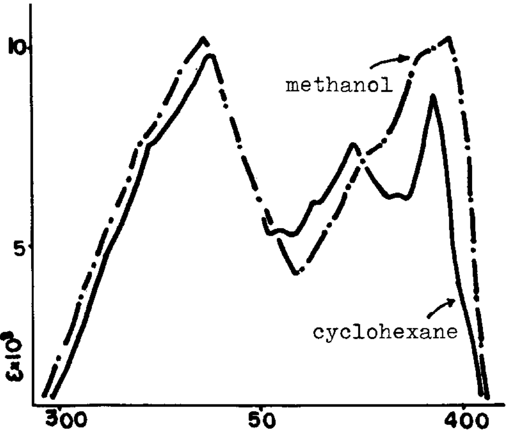


Fig. 2. UV spectrum of IA.

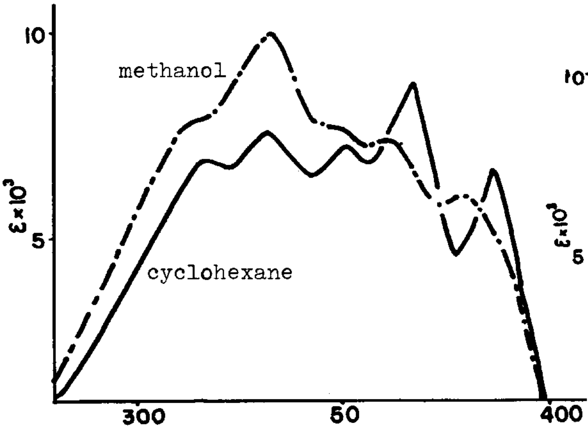


Fig. 3. UV spectrum of IIA

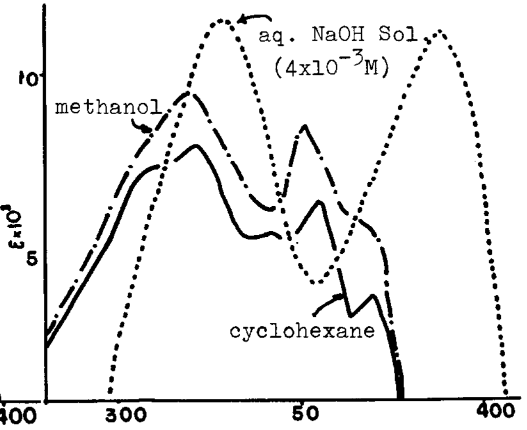


Fig. 4. UV spectrum of Tropolonate ion and Tropolone

state, while that of tropolone in methanol it would be an excited state different from the charge-transfer state (7). In addition, the fact that photocyclization of 5-aminotropolone occurred more readily in an acidic solution rather than in a neutral solution can be explained in the same manner (9).

The photo-cyclization of IIA and IIIA was not retarded in the presence of quenchers such as oxygen, isoprene or ferrocene. Fluorescence was observed in the 2-aminotropone derivatives which showed the photocyclization. These facts indicate that the photo-valence isomerization from A to B proceeds via the singlet state. It should be noted that the photochemistry in the series of the 2-aminotropone derivatives has some similarities to the photo-reduction of 4-aminobenzophenone which was reported by Porter and Suppan (10). The result of our work, as well as the Porter's study, would be of importance as one model in the photochemistry of organic molecules from the viewpoint of the relationship between reactivity and the excited state.

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