BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(2), 358—363 (1974)

New Photochemical Reactions of 9-ω-Bromoacetylanthracene. I

Tamotsu Matsumoto, Masanori Sato, and Satoshi Hirayama
Faculty of Textile Science, Kyoto Technical University, Matsugasaki, Sakyo-ku, Kyoto 606

(Received April 9, 1973)

New photochemical reactions were found on 9-ω-bromoacetylanthracene. The main photo-products were 1-aceanthrenone and 9-bromoanthracene. Their formation was not appreciably affected by the presence of oxygen. Other products such as anthracene, 9-acetylanthracene and anthraquinone were also detected and their yields greatly depended on the reaction conditions. From the low temperature experiments, it was made clear that 9-bromoanthracene and 1-aceanthrenone were formed *via* different mechanisms. A rather stable intermediate, which was not a radical but presumably an intramolecular adduct, was detected spectroscopically. 1-Aceanthrenone was formed from the intermediate both photochemically and thermally with liberation of hydrogen bromide. In the absence of oxygen both the thermal and photochemical reactions of the intermediate yielded almost the same amount of 1-aceanthrenone. The reaction mechanisms were considered in reference to the photochemical reactions of 9-nitroanthracene and sodium 9-anthroate. The relation between these reactions and the radiationless transition processes of carbonyl derivatives of anthracene was also discussed.

Anthracene and its derivatives which have been studied extensively are known to undergo a wide variety of photochemical reactions.[1—4] In most cases, however, they are simple and detailed investigations have been made into their primary photochemical and photophysical processes. It has been made clear that with the anthracene derivatives the radiationless transition processes which sometimes profoundly affect primary photochemical processes are entirely different from those of other organic compounds. The difference is believed to originate from the fairly large energy gap between the lowest excited singlet and the lowest triplet states of these compounds.[5,6]

Recently the substituent effect on the radiationless transition processes has been investigated, valuable results being obtained.[7,8] A detailed investigation we have made of the carbonyl derivatives of anthracene has revealed the existence of interesting relations between the position of a substituent, photochemical reactivity, fluorescent property and the life-times of their triplet state.[9] As regards the fluorescent property, these derivatives are unusual. A typical compound is 9-acetylanthracene (9-CH_3CO-A),[9,10] which is non-fluorescent in various solvents and becomes fluorescent only at temperatures near 77 K. This phenomenon was interpreted in terms of the temperature effect on the intersystem crossing process of $S_{\pi\pi^*} \rightsquigarrow T_{n\pi^*}$.[9,10]

The intersystem crossing process of 9-CH_3CO-A is expected to be perturbed by certain substituents.[11] In order to see what occurs when a hydrogen atom of the acetyl group of 9-CH_3CO-A is substituted by a bromine atom, 9-ω-bromoacetylanthracene (9-CH_2BrCO-A) was synthesized. In contrast to 9-CH_3CO-A, 9-CH_2BrCO-A underwent quite remarkable intramolecular reactions. These new photochemical reactions seem to be useful for clarifying the intramolecular energy dissipation processes of carbonyl derivatives of anthracene and are reported herewith.

Experimental

9-CH_2BrCO-A was synthesized from 9-CH_3CO-A.[13] Commercial solvents of guaranteed grade were used for photochemical reactions without further purification. For spectroscopic measurements, solvents of spectrograde supplied by Nakarai Chemical Co. Ltd. were used.

Absorption spectra were recorded on a Hitachi Spectrophotometer Model 124. The relative yields of the photoproducts were determined spectrophotometrically. Fluorescence and excitation spectra were recorded on a Shimadzu Corrected Recording Spectrofluorophotometer Model RF 502. Fluorescence spectra at low temperature were measured with a modified Beckmann type spectrophotometer equipped with an EMI 9558 QB photomultiplier.

An Ushio 500 W high-pressure mercury-arc lamp was used as an irradiation source. To isolate suitable excitation lines Toshiba glass filter UV-DIB (isolated lines: 313, 334 and 366 nm) or UV-39 (isolated lines: 366 nm and longer ones) was used with a solution filter containing distilled water. A reaction cell was either an ordinary optical cell of 1×1 cm or a cylindrical cell of 3 cm diameter and 3 cm length, each of which was made of quartz and had a side arm for evacuation. Solutions were degassed by repeating freeze-pump-thaw cycles with an oil diffusion pump. When degassing was not necessary, an ordinary optical rectangular cell of 1×1 cm with a ground-glass joint was used.

Irradiation at dry ice-ethanol temperatures (−74—−80 °C) was carried out in a Pyrex cylindrical cell of 1.2 cm diameter, which was dipped into a transparent Dewar vessel containing dry ice-ethanol mixture.

Preparative photolysis was carried out in an Ushio photochemical reaction vessel Model UM 103B. A 100 W medium-pressure mercury-arc lamp was immersed in a water-cooled jacket made of Pyrex glass, the outside of which was surrounded by a window glass pipe of 1 mm thickness. Cyclohexane solution of 9-CH_2BrCO-A (*ca.* 1 g/300 ml) was irradiated at 7—10 °C[14] for about 4 hr by bubbling nitrogen gas gently through the solution. After the reaction the solvent was evaporated with a rotary evaporator. The residue was then dissolved in an appropriate amount of ethanol and was allowed to stand for a while to complete the reaction. The solvent was again evaporated and the residue was separated by column chromatography on silica gel. Elution with benzene gave 9-bromoanthracene (9-Br-A) and *ca.* 300 mg of crude 1-aceanthrenone as main photo-products. The latter was identified by means of IR, NMR, mass spectra and elemental analysis. The UV absorption spectrum of photochemically synthesized 1-aceanthrenone agreed with that of the authentic sample synthesized chemically.[15] Recrystallization from acetone and then twice from benzene gave pure 1-aceanthrenone, for which the molar extinction coefficient was determined.

Electric conductivity measurements were made on a Yanagimoto Conductivity Outfit Model MY-7.

Result

The UV absorption spectrum of 9-CH_2BrCO-A is similar to that of 9-CH_3CO-A, but shifts to the red *ca.* 2 nm and is slightly broader. As regards fluorescence, 9-CH_2BrCO-A also resembles 9-CH_3CO-A,[10)] which is non-fluorescent at room temperature and becomes fluorescent at temperatures near 77 K. In spite of these similarities, both compounds differ completely in their photo-reactivity. Only 9-CH_2-BrCO-A undergoes photochemical intramolecular reactions, yielding mainly 1-aceanthrenone and 9-Br-A.

Irradiation at Room Temperature. The change in absorption spectra when the aerated cyclohexane solution of 9-CH_2BrCO-A was irradiated at room temperature through the filter UV-39 for about 20 min is shown in Fig. 1. The absorption band assignable to the p-band of anthracene disappears with irradiation and a large new band appears at about 315 nm (curve b). This band is attributed to the intermediate, which reacts both thermally and photochemically to give 1-aceanthrenone. At least two separate reactions seemed to proceed at different rates in cyclohexane so that no isosbestic point was observed.[16)] The absorption spectrum (curve c) was observed after standing the solution showing the absorption spectrum b for about 40 hr without irradiation at room temperature. The absorption spectrum with a band maximum at 414 nm is due to 1-aceanthrenone.

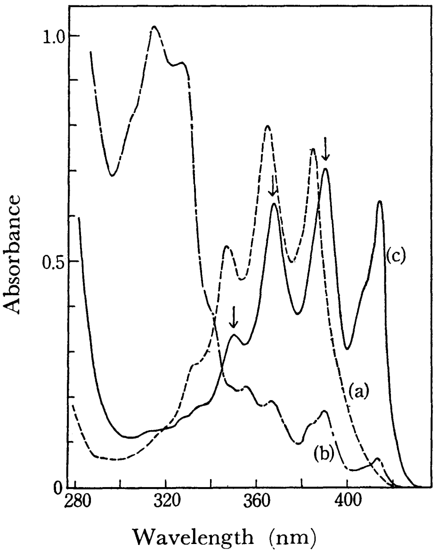

Fig. 1. Change in the absorption spectra of the aerated cyclohexane solution of 9-CH_2BrCO-A caused by irradiation.

(a) ----: 9-CH_2BrCO-A (1.0×10^{-4} M)

(b) — —: the spectrum of the intermediate obtained after 20 min irradiation through the filter UV-39.

(c) ——: final products obtained by the dark reaction of the intermediate (see the text).

The arrows indicate that the absorptions at these wavelength are partly due to 9-Br-A.

The rate of decrease of the intermediate and that of increase of 1-aceanthrenone were obtained by measuring the changes in the optical densities at 315 nm and 414 nm, respectively. Both rates were found to follow the same first order equation with the opposite sign. This means that the intermediate at 315 nm turns unimolecularly into 1-aceanthrenone. It was also ascertained that the rate of the reaction was accelerated as temperature increased. The half life of the intermediate was of the order of several hours in cyclohexane.

Similar experiments were carried out in the deaerated solutions. Almost the same results as those in the presence of oxygen were obtained.

These photochemical reactions did not show any appreciable concentration dependence in the range $5\times10^{-6}-2\times10^{-4}$ M in cyclohexane, proceeding likewise in various solvents. Thus the main photochemical reactions of 9-CH_2BrCO-A are considered to be intramolecular.

The stable intermediate observed in cyclohexane could not be detected in alcoholic solutions at 30—35 °C because of its instability. The result obtained in the ethanol solution by irradiation through the filter UV-39 is shown in Fig. 2. There is no absorption attributable to the intermediate. Instead, the isosbestic points are seen at 322 nm and 392 nm, indicating that the final products are formed simultaneously with irradiation.[16)]

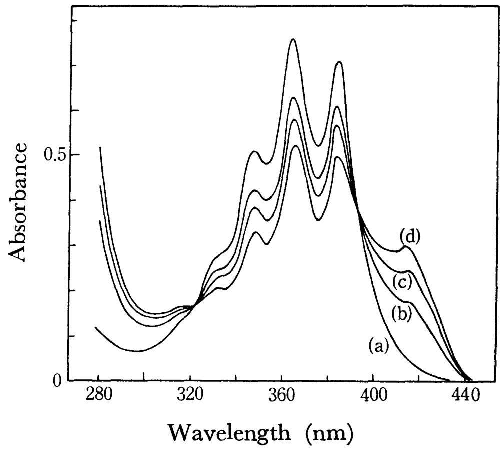

Fig. 2. Change in the absorption spectra of the aerated ethanol solution of 9-CH_2BrCO-A caused by irradiation.
(a) reactant, (b) after 5 min, (c) after 10 min, (d) after 25 min (final products).
The solution was irradiated through the filter UV-39 at 30–35 °C. No absorption attributable to the intermediate is observable and the isosbestic points are seen at 322 nm and 392 nm.

The absorption spectra of 1-aceanthrenone in cyclohexane and in ethanol are shown in Fig. 3. A comparison of the absorption spectrum in cyclohexane with that given in Fig. 1 shows that the increment of the absorption indicated by the arrows is due to 9-Br-A. The yield of each compound can thus be easily calculated from its molar extinction coefficient. The values obtained in this way are given in Table 1.

TABLE 1. YIELDS OF PHOTO PRODUCTS

Reaction conditions[a]			Yield (%)		Other products[b]
Solvent	Temperature	Presence of oxygen	1-Aceanthrenone	9-Br-A	
Cyclohexane	Room temp.	Yes	71	9	anthraquinone (UV) (425 nm)
Cyclohexane	Room temp.	No	77	11	9-CH_3CO-A (UV, IR) anthracene (Fl, Ex)
Ethanol	Room temp.	Yes	52	14	9,10 di-Br-A (UV) anthraquinone (UV)[c] (387 nm, 425 nm)
Ethanol	Dry ice-ethanol temp.	Yes	58	32	anthraquinone (UV)
Ethanol	Dry ice-ethanol temp.	No	59	36	9-CH_3CO-A (UV) anthracene (Fl, Ex)

a) The yields were obtained in the reactions of dilute solutions (*ca.* 10^{-4} M).

b) Method of detection is given in parentheses in abbreviated form; Fl: fluorescence spectrum, Ex: excitation spectrum. The longest wavelengths of the absorption spectra observed in cyclohexane after separation by column chromatography are also given in parentheses.

c) Prolonged irradiation of a more concentrated solution gave anthraquinone and 9,10-di-Br-A in high yields.

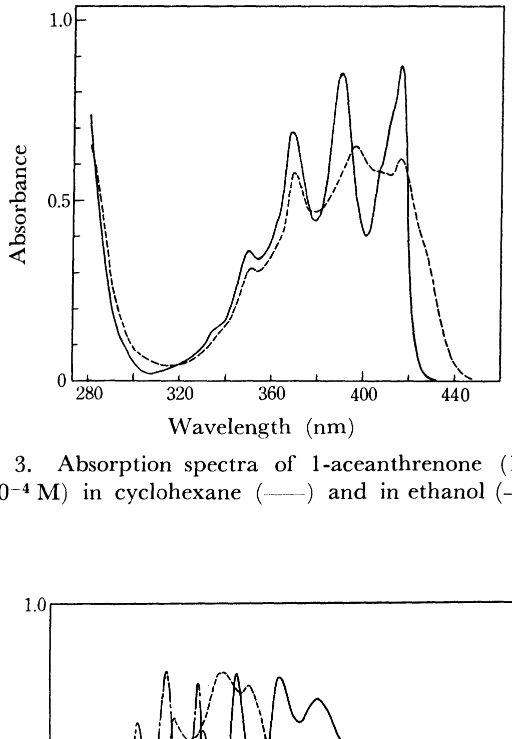

Fig. 3. Absorption spectra of 1-aceanthrenone (1.0×10^{-4} M) in cyclohexane (——) and in ethanol (----).

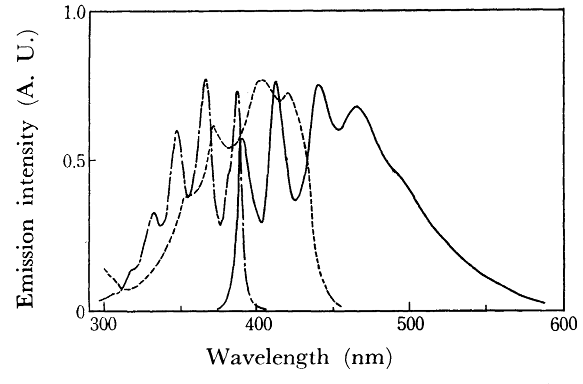

Fig. 4. Fluorescence and excitation spectra of the photoproducts in ethanol. The solution shows the absorption spectrum represented by Fig. 2d.
——: fluorescence spectrum,
-·-: excitation spectrum observed at 412 nm,
----: excitation spectrum observed at 500 nm.
The emission at the shorter wavelength region is not due to 9-Br-A.[17]

The fluorescence and excitation spectra of the solution having the absorption spectrum shown in Fig. 2d are given in Fig. 4. The emission band at the longer wavelength is due to 1-aceanthrenone, judging from the excitation spectrum. The component at the shorter wavelength is not assignable to 9-Br-A and is due to some other unidentified product.[17] The absorption spectrum of this compound overlaps that of 9-Br-A. The yields were thus determined spectrophotometrically after separation by column chromatography.

Irradiation at Dry Ice-Ethanol Temperatures. When the degassed *n*-hexane solution of 9-CH_2BrCO-A was irradiated through the filter UV-39 at dry ice-ethanol temperatures, the absorption spectrum given by curve a in Fig. 5 was obtained. *n*-Hexane was used because of high freezing point of cyclohexane. At these temperatures the reaction of the intermediate to form 1-aceanthrenone is completely retarded. Thus no absorption can be seen at 414 nm (curve a, Fig. 5). There is a small absorption peak at 388 nm where 9-Br-A shows absorption. After temperature was raised to room temperature and the reaction was completed, the yield of 9-Br-A was determined from the difference of the absorbances at 388 nm and at 414 nm. The yield of 9-Br-A obtained in this way agreed well with that gained before temperature was raised. This fact makes it clear that 9-Br-A is not formed by a thermal reaction after irradiation and that only 1-aceanthrenone is formed from the intermediate.

When the solution at the state shown by curve a (Fig. 5) was irradiated further through the filter UV-DIB, photochemical reactions occurred as indicated by curves b-f, the final state being shown by curve f. As seen from the absorption spectrum, 1-aceanthrenone was produced. In the absence of oxygen, the yields obtained by the photochemical and thermal reactions of the intermediate were almost the same. In the presence of oxygen, however, the yield for the former procedure was lower than that for the latter by about 60%. The irradiation of the intermediate seems to produce other compounds than 1-aceanthrenone.

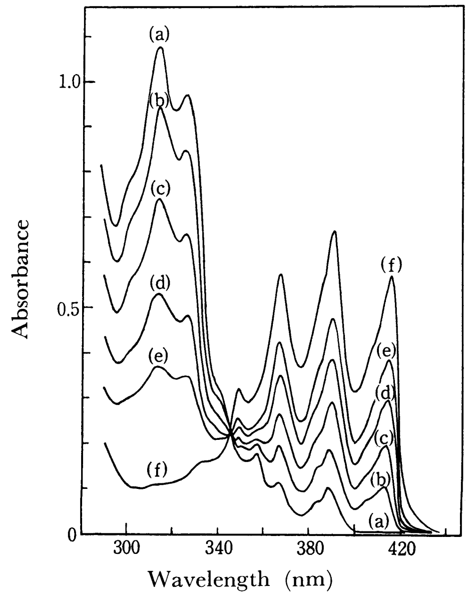

Fig. 5. Photochemical reactions of the intermediate in the degassed *n*-hexane solution.
(a) before the second irradiation, (b) after 30 s (c) after 90 s, (d) after 180 s, (e) after 300 s, (f) final products
Curve a was observed after 30 min irradiation through the filter UV-39 at dry ice-ethanol temperatures. The second irradiation was carried out through the filter UV-DIB at room temperature. The absorption spectrum f did not change by further irradiation.

Their compositions are not identified.

Even in ethanol it was confirmed that the intermediate could exist stably at temperatures as low as dry ice-ethanol temperature in the following way. After sufficient irradiation of the ethanol solution of 9-CH_2BrCO-A at dry ice-ethanol temperatures through the filter UV-39, the reaction cell was dipped into a transparent Dewar vessel containing liquid nitrogen and the fluorescence spectra were measured. The only emissive species was 9-Br-A. When temperature was raised to room temperature, a new fluorescence band due to 1-aceanthrenone appeared. This indicates that the intermediate can exist stably at low temperatures and only 1-aceanthrenone is formed from the intermediate.

Miscellaneous. Measurements of electric conductivity enabled us to elucidate the intermediate. The cyclohexane solution of 9-CH_2BrCO-A (*ca.* 10^{-3} M) which had been irradiated through the filter UV-39 and enriched with the intermediate was shaken well with distilled water. This operation did not appreciably affect the stability of the intermediate. The water layer was separated and its electric conductivity was measured. After this, the aqueous solution was again combined with the cyclohexane layer. The above operation was repeated several times at certain time intervals. The electric conductivity of the water layer was found to increase as the intermediate decreased by the thermal reaction. This shows that the reaction of the intermediate to form 1-aceanthrenone is accompanied by the elimination of a certain molecule which can dissociate into ions. Hydrogen bromide is the most probable candidate, judging from the structures of the reactant and the product and from the reaction mechanisms.

On the irradiation of a completely degassed solution of 9-CH_2BrCO-A, an appreciable amount of 9-CH_3CO-A and a small amount of anthracene were formed as minor photo-products. In an aerated solution, anthraquinone was formed instead of these two compounds. The formation of other minor photo-products depends on reaction conditions. A detailed description is given in Table 1.

1-Aceanthrenone was rather photo-stable in cyclohexane, but in ethanol its absorption spectrum gradually changed with irradiation. The products in this reaction were not identified.

Heating an *o*-dichlorobenzene solution of 9-CH_2BrCO-A to *ca.* 135 °C for 2 hr was unsuccessful to produce 9-Br-A or 1-aceanthrenone, for no UV absorption change was observed.

A preliminary experiment on 9-ω-chloroacetylanthracene showed that it underwent photochemical reactions analogous to those of 9-CH_2BrCO-A.

Discussion

If we neglect the photodimerization of 9-CH_2BrCO-A in the low concentration range $5\times10^{-6}-2\times10^{-4}$ M, the photochemical reaction mechanisms of 9-CH_2BrCO-A can be given as shown in Fig. 6. The reactions are noteworthy particularly as regards the following three points: (i) The main photochemical reactions proceed in various solvents in the presence or in the absence of oxygen, *i. e.*, paths (1), (2) and (3) do not seem to be affected greatly by the presence of oxygen. In contrast, oxygen completely suppresses path (4). (ii) With an appropriate choice of excitation wavelength and reaction temperature, the reaction intermediate can be produced stably and can be detected by its UV absorption spectrum. The intermediate gives 1-aceanthrenone by either the dark reaction or the photochemical reaction. (iii) It can be shown that 9-Br-A and 1-aceanthrenone are produced *via* two different processes.

The structure of the intermediate (Fig. 6) has been

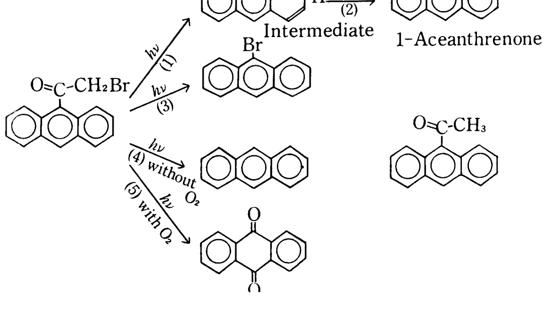

Fig. 6. Mechanisms of the photochemical reactions of 9-CH_2BrCO-A. Only the identified products are shown. For further detailed descriptions on the other products, see Table 1.

proposed on the basis of the following: The intermediate eliminates a hydrogen bromide in path (2). The absorption spectrum of the intermediate can be most reasonably interpreted by assigning it to a derivative of naphthalene. The intermediate has a long half life at room temperature in cyclohexane and shows no ESR signal. Thus it is probably not a free radical. The solvent itself is not involved in the formation of the intermediate.

The thermal and photochemical reaction mechanisms of the intermediate could be reconciled by considering the photochemical reaction of the intermediate to occur at vibrationally excited states, *i. e.*, vibrational excess energy supplied by direct photoexcitation or by a succeeding radiationless transition process would facilitate the liberation of a hydrogen bromide molecule. The structure of the intermediate we proposed seems to be pertinent to this interpretation.

The primary process of the photochemical reactions of 9-nitroanthracene (9-NO_2-A) and sodium 9-anthroate (9-COONa-A) to produce anthraquinone in the presence of oxygen is analogous to that of 9-CH_2BrCO-A. For 9-NO_2-A and 9-COONa-A, the most relevant primary process is considered to be not the dissociation and recombination of the substituent but the intramolecular rearrangement at the $n\pi^*$ states.[18-20] In the ground states of these compounds the plane containing the three atoms of each substituent makes almost a right angle to the anthracene ring[21,22] owing to the steric hindrance by *peri* hydrogen atoms. Thus, in the $n\pi^*$ excited state populated either by direct photo-excitation or by intersystem crossing process, an unpaired electron in the n-orbital of the oxygen atom can just interact attractively with an electron in the p-orbital of the carbon atom at 9-position. As a result, the intramolecular photochemical reactions take place. Experimental evidence for the above supposition, however, has not yet been obtained.

If we take into account the structure of 9-CH_3CO-A, the substituent of 9-CH_2BrCO-A can be considered to be perpendicular to the anthracene ring[9] in the ground state. Although we have no experimental evidence at present with regard to the nature of reactive excited states, a change in the electronic state of the anthracene ring or the carbonyl group on photo-excitation seems to make the lone pair of electrons of the bromine atom interact with a p-orbital electron of the carbon atom at 9- or 2-position. As a result, 9-Br-A or the intermediate will be formed. In the case of 9-NO_2-A and 9-COONa-A, rotation of the substituents on excitation is not taken into account. An unpaired n-orbital electron of these compounds interacts with a p-orbital electron solely at 9-position. In this respect 9-CH_2BrCO-A differs from these compounds. Considering its reaction products, the interactions both at 9- and 2-positions should exist. This leads to the occurrence of rotation of the substituent on photo-excitation.

A change in interaction between a substituent and an anthracene ring caused by photo-excitation has been proposed by Werner and Hercules[23,24] in the case of 9-anthroic acid. They attributed its abnormally large Stokes shift of the fluorescence to the conformational change in the excited state, where the carbonyl group rotates into a co-planar configuration, forming a hydrogen bond with a hydrogen atom at a *peri* position. The photochemical formation of 1-aceantherenone would verify the existence of such interaction.

Thus it is expected that the relative yield of 9-Br-A and 1-aceanthrenone would be affected by the kind of solvent, viscosity and temperature, which would influence the ease of the rotation of the substituent on photo-excitation. The values cited in Table 1 seem to indicate such a tendency.

It is worthwhile to consider the relation between these new photochemical reactions of 9-CH_2BrCO-A and its relaxation processes of excitation energy.[9,10,12]

With regard to the reactive excited state of 9-CH_2-BrCO-A, one possible candidate is the singlet $\pi\pi^*$ state where the change in the π-electron density at 9- or 2-position causes the attractive interaction between the bromine atom and the carbon atom at 9- or 2-position, leading to the bond formation between them. If this is the case, only the existence of a bromine atom is indispensable for the progress of similar intramolecular photochemical reactions and it may be unnecessary for a substituent to have a carbonyl group.

Another possibility is to relate these photochemical reactions to the characteristic radiationless transitions of carbonyl derivatives of anthracene. The nonfluorescent property of the majority of these compounds reflects the existence of the efficient intersystem crossing process of $S_{\ *} \rightsquigarrow T_{n\pi^*}$.[9,10,12] 9-$CH_2BrCO$-A is expected to behave as 9-CH_3CO-A and thus the effective intersystem crossing process of $S_{\pi^*} \rightsquigarrow T_{n\pi^*}$ is thought to be working also in this molecule. If this is the case, photo-excitation will mainly produce the triplet $n\pi^*$ state and some highly vibrationally excited states which are produced from the triplet state by radiationless transitions. In the triplet $n\pi^*$ state, excitation is localized to the carbonyl group, so in the vibrationally excited states formed from that state, the excess vibrational energy would be localized also to the bromoacetyl group. In the triplet $n\pi^*$ state itself or in the vibrationally excited state, the bromoacetyl group is supposed to interact strongly with the anthracene ring, or the excess vibrational energy would aid in breaking the C–C and C–Br bonds. As a result, the photochemical reactions including the C–C and C–Br bond rupture are considered to proceed. In the sense that the occurence of the efficient $S_{\ *} \rightsquigarrow T_{n\pi^*}$ intersystem crossing results in the activation of the bromoacetyl group, the photochemical reactions of 9-CH_2BrCO-A is correlated to non-fluorescent property of carbonyl derivatives of anthracene.

Of the two possibilities, the latter is more interesting, since it takes into consideration the role of the carbonyl group and can interpret more reasonably the production of anthracene and 9-CH_3CO-A. However, neither has experimental evidence at present.

References

1) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag New York Inc. (1968).

2) S. Kusuhara and R. Hardwick, *J. Chem. Phys.*, **41**,

2386 (1964).

3) J. Osugi, S. Kusuhara, and S. Hirayama, *Rev. Phys. Chem. Jap.*, **37**, 94 (1967).

4) I. Fujihara, M. Okushima, S. Hirayama, S. Kusuhara, and J. Osugi, This Bulletin, **44**, 3495 (1971).

5) E. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959).

6) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectry.*, **19**, 412 (1966).

7) B. R. Henry and J. L. Charlton, *J. Amer. Chem. Soc.*, **95**, 2782 (1973).

8) D. S. Klinger and A. C. Albrecht, *J. Chem. Phys.*, **53**, 4059 (1970).

9) S. Hirayama, *Rev. Phys. Chem. Jap.*, **42**, 49 (1972).

10) T. Matsumoto, M. Sato, and S. Hirayama, *Chem. Phys. Lett.*, **13**, 13 (1972).

11) In the case of 9-benzoylanthracene a distinct substituent effect on the intersystem crossing process has been noted.[12]

12) T. Matsumoto, M. Sato, and S. Hirayama, *Chem. Phys. Lett.*, **18**, 563 (1973).

13) E. L. May and E. Mosetting, *J. Amer. Chem. Soc.*, **70**, 686 (1948).

14) Low temperatures which retarded the thermal reaction (Fig. 6) were preferred because of the low absorptivity of the intermediate (Fig. 1) at the excitation wavelength.

15) "Beilsteins Handbuch der Organischen Chemie," E. III 7, p. 2627 (1968).

16) G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **11**, 1072 (1972).

17) Fluorescence of 9-Br-A is rather weak and its o-o band appears at 393 nm.

18) O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. W. Reasoner, *Pur. Appl. Chem.*, **9**, 585 (1964).

19) O. L. Chapamn, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Amer. Chem. Soc.*, **88**, 5550 (1966).

20) A. W. Bradshaw and O. L. Chapman, *ibid.*, **89**, 2372 (1967).

21) J. Trotter, *Acta Cryst.*, **12** 237, 922 (1959).

22) A. S. Cherkasov and K. G. Voldikina, *Izvest. Akad. Nauk SSSR, Ser. Fizicheskaja*, **27**, 628 (1963).

23) T. C. Werner and D. M. Hercules, *J. Phys. Chem.*, **73**, 2005 (1969).

24) T. C. Werner and D. M. Hercules, *ibid.*, **74**, 1030 (1970).