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The Photolysis of α-Haloketones. II. The Intramolecular Reactions of 9-α-Bromopropionylanthracene

Tamotsu MATSUMOTO, Masanori SATO, and Satoshi HIRAYAMA[1]

Faculty of Textile Science, Kyoto Technical University, Matsugasaki, Sakyo-ku, Kyoto 606

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Synopsis. The main photolysis products of 9-α-bromopropionylanthracene were identified as 2-methyl-1-aceanthrenone and 9-vinylanthryl ketone. The yield of 9-bromoanthracene was very small. A significant solvent and temperature dependence was noted on the yields of these products. The photolysis at −196 °C resulted in the formation of almost 100% of 9-vinylanthryl ketone.

In a previous paper,[2] we reported that 9-ω-bromoacetylanthracene (I) undergoes new intramolecular photochemical reactions, yielding mainly 1-aceanthrenone (II) and 9-bromoanthracene (III). In this note, we will describe an extension of these photochemical reactions to 9-α-bromopropionylanthracene (IV), an analogue of I. Besides the three features noted for the photochemistry of I,[2] several new facts, including a photoelimination reaction peculiar to IV, were found and will be reported herewith.

Experimental

According to the method of May and Mosettig,[3] IV was synthesized by brominating 9-propionylanthracene and was recrystallized from ligroin. For spectroscopic measurements, it was purified further by sublimation *in vacuo*. (UV: (ethanol), $\lambda_{\max}$ ($\varepsilon \times 10^{-3}$), 350 nm (4.36), 366 (6.20), 384 (6.03).)

The fluorescence spectra were recorded on a Shimadzu Spectrofluorophotometer Model RF 502, and the absorption spectra were taken with a Hitachi Spectrophotometer Model 124.

To analyze the photo-products, an ethanol solution of IV (*ca.* 200 mg/250 ml) was irradiated for 2 hr in a reaction vessel previously described.[2] The reaction vessel was kept cooled to dry ice-ethanol temperatures during irradiation. The photo-products thus obtained were separated by column chromatography on silica gel. Elution with benzene gave III, unreacted IV, 9-vinylanthryl ketone (V), 2-methyl-1-aceanthrenone (VI), and anthraquinone. V, NMR: 5.63—7.10 ppm (m, ABX type, 3H), 7.27—8.03 (m, aromatic, 8H), 8.40 (s, aromatic meso-H, 1H). Found: C, 87.44; H, 5.36%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%. IR: 1663 cm^{-1} (C=O). UV: (ethanol), $\lambda_{\max}$ ($\varepsilon \times 10^{-3}$), 329 nm (2.65), 345 (4.72), 362 (6.53), 381 (5.92). VI, mp 88—89 °C. NMR: 1.46 ppm (d, **CH_3**-CH, 3H, J=7.5 Hz), 3.25 (q, CH_3-**CH**, 1H), 7.11—7.91 (m, aromatic, 6H), 8.31 (s, aromatic meso-H, 1H), 8.93 (m, aromatic α-H, 1H). Found: C, 88.00; H, 5.14%. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21%. IR: 1703 cm^{-1} (C=O). UV: (cyclohexane), $\lambda_{\max}$ ($\varepsilon \times 10^{-3}$), 349 nm (3.86), 368 (7.83), 390 (9.71), 413 (9.97); (ethanol), $\lambda_{\max}$ ($\varepsilon \times 10^{-3}$), 351 nm (3.71), 369 (6.80), 397 (7.67), 418 (7.16).

The irradiation source and filters used for the spectrophotometric studies of the photochemical reactions have also been described previously.[2] The product yields were, unless otherwise stated, always determined in the photolysis of dilute solutions (*ca.* 10^{-4} M) by the use of the molar extinction coefficients reported here.

Results and Discussion

The main photolysis products of IV were identified as V and VI. Dissolved oxygen was ascertained to have no significant effect on the qualitative nature of the photochemical reactions of IV.

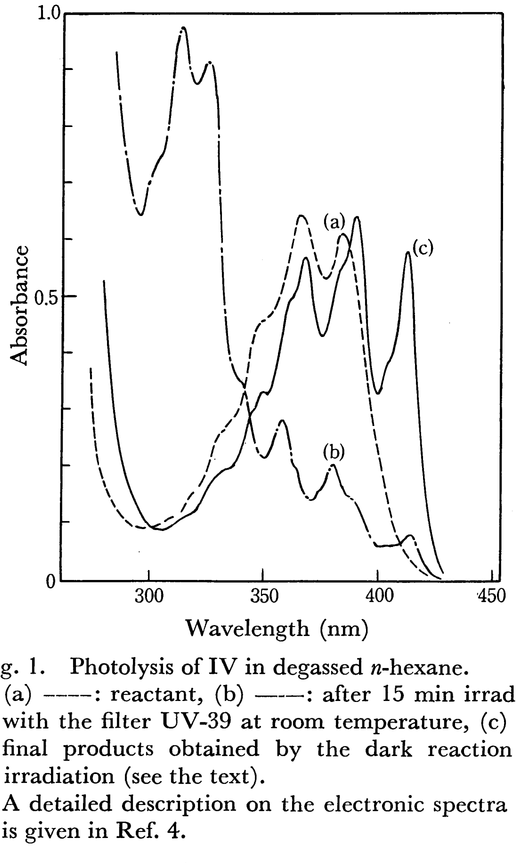


Fig. 1. Photolysis of IV in degassed *n*-hexane.
(a) ----: reactant, (b) ——: after 15 min irradiation with the filter UV-39 at room temperature, (c) ——: final products obtained by the dark reaction after irradiation (see the text).
A detailed description on the electronic spectra of VI is given in Ref. 4.

Figure 1 shows the absorption spectra of IV in degassed *n*-hexane before and after illumination. After about 15 min irradiation at room temperature through the UV-39 filter, which absorbs all light below 344 nm from a high-pressure mercury-arc lamp, a stable intermediate with the absorption band with a peak at 314 nm (Curve b) appeared. A very similar absorption band of the intermediate has been observed in the photolysis of I, indicating the formation of an analogous intermediate.[2] The intermediate gradually underwent a thermal reaction to yield VI and finally gave the absorption spectrum represented by Curve c (two days later). When the intermediate was irradiated through the UV-DIB filter, which transmits light of 313, 334, and 366 nm, VI was formed immediately.

In ethanol the intermediate was not stable at room temperature. It was confirmed, however, that the intermediate could exist stably at dry ice-ethanol temperatures, as is shown in Fig. 2. The absorptions (Curve b) at around 314 nm and in the 340—400 nm region are due to the intermediate and to V respectively;

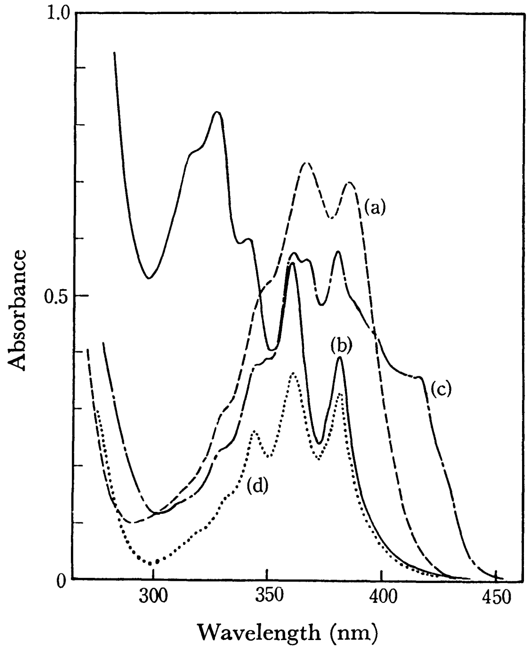
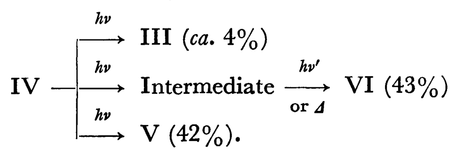


Fig. 2. Photolysis of IV in aerated ethanol.
(a) ——: reactant, (b) ——: after 30 min irradiation with the filter UV-39 at dry ice–ethanol temperatures, (c) ——: final products obtained immediately after warming the solution in the dark (Curve b) to room temperature, (d) ······: the absorption spectrum of V.

no absorption due to VI is seen. On the other hand, the formation of III could easily be revealed by observing the fluorescence spectrum of the solution with the absorption spectrum b.⁵⁾ When this solution was allowed to warm to room temperature in the dark, the absorption of the intermediate disappeared rapidly and the absorption due to VI built up, as is shown by Curve c. Thus, it is evident that the process to form the intermediate and those to form III and V are different and that only VI is formed from the intermediate. In this respect, the photochemistry of IV is closely similar to that of I. Thus, the reaction scheme to give III, V, and VI can be summarized as follows;



Different pathways are given for the formation of III and V, because the yields of these two products show a very different temperature dependence, as will be shown below. The yields obtained in an aerated ethanol solution at dry-ice–ethanol temperatures are shown in parentheses. The value for III was determined by fluorometric measurements. In contrast to the case of the photolysis of I, the yield of III is very small.

Photolysis at Low Temperatures. The ratio of the yield of VI to that of V was found to depend significantly on the solvent and the temperature. As the temperature decreased, the ratio decreased from 4.0, 2.6, and 1.2 at 0 °C to zero at −196 °C in isopentane, EPA, and ethanol respectively.⁶⁾ The yield of V reached almost 100% at −196 °C in all these solvents. It was also confirmed by fluorometric measurements that the yield of III decreased to zero when the temperature was lowered. The retardation of the photochemical reaction of IV to give III by lowering the temperature was evidenced even more clearly by the temperature effect on the photochemical reactions of I, where the yield of III is of the order of 30% at dry ice–ethanol temperatures.²⁾ At first the amount of III increased against that of II as the temperature decreased (*ca.* 72% in ethanol at −145 °C), since the reaction to give II was more rapidly retarded. However, as the temperature was decreased further, the irradiation time needed to complete the reaction of I became logner and longer, and at last no photochemical reaction could be observed at −196 °C. Thus, the retardation of the reaction by lowering the temperature can be said to increase in the order of the reactions to give V, III, and VI (or II). The occurrence of the photolysis of IV at −196 °C is one of the most prominent differences in behavior between I and IV.⁷⁾

Cause of the Great Decrease in the Yield of III. The IR absorption spectrum of a streching mode of the carbonyl group of I shows a clear splitting (1729 and 1700 cm^{-1}) characteristic of α-haloketones; this indicates the existence of two distinct conformations of the bromine atom to the carbonyl group. On the other hand, the corresponding IR absorption spectrum of IV shows no splitting (1703 cm^{-1}), suggesting that there are not two distinguishable conformations.

Since the IR and UV spectra of I and IV reveal that the plane of the carbonyl group is almost perpendicular to the anthracene ring, in one of the two conformations of I the bromine atom is expected to take a position where non-bonding electrons of the bromine atom lie just above the *p*-orbital of 9-carbon atom. If the photorearrangement mechanism proposed for 9-nitroanthracene is referred to,⁸⁾ such a conformation can be expected to be suitable for the formation of III. On the other hand, in the photolysis of IV the yield of III greatly decreased. This may, therefore, reflect either the circumstance that the allowed conformation of IV is unfavorable for such an interaction between the bromine atom and 9-carbon atom or the fact that the reaction rates to give V and VI are faster than that to give III.

References

1) To whom correspondence should be addressed.

2) T. Matsumoto, M. Sato, and S. Hirayama, This Bulletin, **47**, 358 (1974).

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

4) S. Hirayama, This Bulletin, **43**, 1127 (1975).

5) The solution was immediately cooled to −196 °C in order to quench a dark reaction and to enhance the fluorescence intensity. The observed fluorescence was almost entirely due to III. Compound V is practically non-fluorescent.

6) T. Matsumoto, M. Sato, and S. Hirayama, *Chem. Phys., Lett.*, **27**, 237 (1974).

7) It is interesting to note that I comes to fluoresce near −196 °C, while IV is non-fluorescent even at −196 °C and undergoes photo-elimination at this temperature.

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