Photochemical Reactions of α-Bromoacetylarenes Studied by Product Analysis and Laser Flash Photolysis

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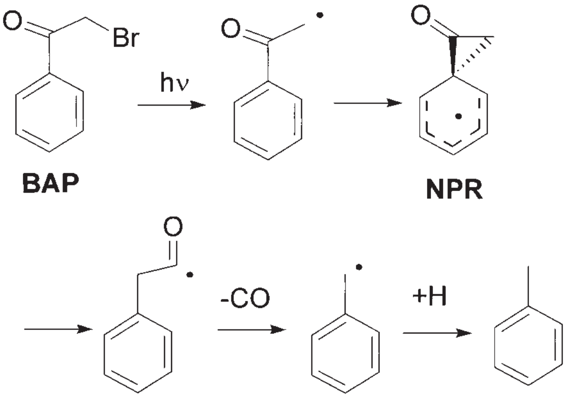
The hydrogen abstraction reaction and rearrangement reaction of aroylmethyl radicals were studied by product analyses and transient absorption spectroscopies. The α-bromoacetylarenes examined in this study gave aroylmethyl radicals by C–Br bond cleavage upon photoirradiation. According to the results of the product analysis, the rearrangement reaction takes place in the aroylmethyl radicals produced on irradiation of 1-bromoacetylnaphthalene (**1-BAN**) and 9-bromoacetylanthracene (**9-BAA**). The rate constants of the rearrangement reaction resulting in an arylmethyl radical and the hydrogen abstraction reaction resulting in an acetylarene for aroylmethyl radicals were estimated based on the results of laser flash photolysis and product analysis.

A photocleavage reaction of aromatic compounds having a halogen atom can be used to generate a radical species to study their dynamic behavior.[1–5] A radical generated by a photochemical reaction can undergo hydrogen abstraction, addition, elimination, or rearrangement reactions.

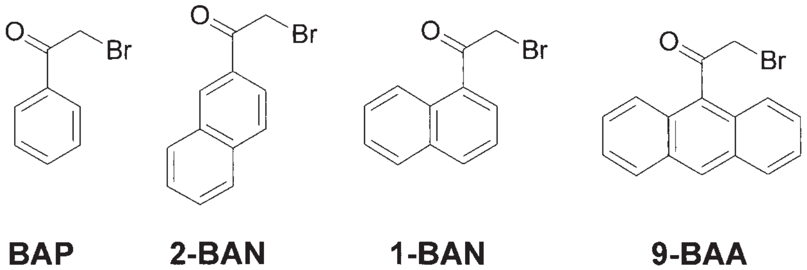
The generation of a radical by C–Br bond cleavage upon photoirradiation of α-bromoacetophenone (**BAP**; $ArCOCH_2Br$) and its derivatives has already been reported by some authors.[6–11] Scaiano et al. reported that **BAP** underwent a photocleavage reaction to give a benzoylmethyl radical followed by rearrangement and decarbonylation[12,13] to give a benzyl radical ($ArCH_2$•), as shown in Scheme 1.[6] In addition, McGimpsey et al. reported that the transient absorption spectra of an arylmethyl radical ($ArCH_2$•) was observed in benzene upon photoirradiation of 2-(α-bromoacetyl)naphthalene (**2-BAN**) and 9-(α-bromoacetyl)anthracene (**9-BAA**).[7] Contrary to these results, we have observed a naphthoylmethyl radical ($ArCOCH_2$•) in the time resolved EPR spectra from the photoreaction of 1-(α-bromoacetyl)naphthalene (**1-BAN**) and **2-BAN**, but we have not observed a naphthylmethyl radical ($ArCH_2$•).[15]



Scheme 1. Scheme of rearrangement reaction for **BAP**.

In previous studies, a quantitative product analysis was not performed on the photocleavage reaction of **BAP** and **BAN**, and **9-BAA**.[6,7] Scaiano et al. reported the production of toluene from the photocleavage reaction of **BAP** in benzene in the presence of thiophenol as a hydrogen donor. However, they did not give any quantitative data. McGimpsey et al. discussed the reaction of naphthyl and anthryl derivatives by transient absorption spectroscopy only. Therefore, it is necessary to determine the yield of final products, and identify products by transient absorption spectra to reveal the reaction mechanism of aroylmethyl radicals.

In this study, transient absorption spectroscopies and product analyses on **2-BAN**, **1-BAN**, and **9-BAA** were performed (Scheme 2). Since these compounds were reported to undergo the C–Br bond cleavage only in the singlet excited state, direct irradiation was used to investigate the reaction dynamics of an aroylmethyl radical, especially to determine whether the rear-



Scheme 2. Structures of α-bromoacetylarenes investigated in this study.

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Table 1. Product Yield in Photolysis of **1-BAN**, **2-BAN**, and **9-BAA** upon Irradiation of 308 nm Laser Pulse

Solvent		Product yield (mol/mol precursor)		
		Ar–$COCH_3$	Ar–CH_3	Ar–CH_2Br
1-BAN	PhH	31%	6%	7%
	CH_3CN	19%	none	16%
2-BAN	PhH	35%	<1%	<1%
	CH_3CN	19%	none	none
9-BAA	PhH	22%	<1%	46%
	CH_3CN	27%	none	30%

rangement and decarbonylation reactions occurred efficiently or not.

Experimental

Materials. α-Bromoacetophenone (**BAP**; $ArCOCH_2Br$; Kanto Chem. Co. Inc.) was used after recrystallization from methanol. 1-(α-Bromoacetyl)naphthalene (**1-BAN**; $ArCOCH_2Br$) and 2-(α-bromoacetyl)naphthalene (**2-BAN**; $ArCH_2Br$) were prepared from 1-acetylnaphthalene (**2-AN**; $ArCOCH_3$) and 2-acetylnaphthalene (**2AN**), respectively, by direct bromination with bromine.[14] 9-(α-Bromoacetyl)anthracene (**9-BAA**; $ArCOCH_2Br$) was prepared from 9-acetylanthracene (**9-AA**; $ArCOCH_3$) by bromination with triphenylammonium tribromide, as described in detail elsewhere.[7] Toluene, 1-methylnaphthalene (**1-MN**; $ArCH_3$), 2-methylnaphthalene (**2-MN**; $ArCH_3$) and 9-methylanthracene (**9-MN**; $ArCH_3$), which were used as authentic samples for product analysis, were used as received. Benzyl bromide and 2-bromomethylnaphthalene (**2-BMN**; $ArCH_2Br$), which were used as authentic samples, were used as received. 1-Bromomethylnaphthalene (**1-BMN**; $ArCH_2Br$) and 9-bromomethylanthracene (**9-BMA**; $ArCH_2Br$), which were used as authentic samples in product analysis, were prepared from 1-methylnaphthalene (**1-MN**; $ArCH_3$) and 9-methylanthracene (**9-MA**; $ArCH_3$), respectively by bromination with *N*-bromosuccinimide, as described in detail elsewhere.[7,15] 1,3-Cyclohexadiene, which was used as a radical scavenger, was used as received.

Benzene (for spectroscopy, Kanto Chem. Co. Inc.) and acetonitrile (for spectroscopy, Kanto Chem. Co. Inc.) were used as received.

Measurement. Product Analysis of the Photoreaction: An excimer laser (XeCl 308 nm, pulse width ∼20 ns, Lambda physics LEXtra 100) was used for excitation of the sample solution in a 1 cm × 1 cm quartz cell in benzene and acetonitrile. The concentrations of all samples were adjusted to 1.0×10^{-2} M. The experiments were performed under argon atmosphere. Product analysis of the photoreaction of bromoacetylarene was carried out by gas chromatography (Shimadzu GC-14A) and GC–MS (Shimadzu GCMS-QP1100EX). A typical irradiation time was 10–20 min, corresponding to 10–20% conversion of the starting materials. The products increased in proportion to the reaction time at the initial stage. Secondary reactions, which occurred by irradiation of the products, was neglected. The reaction yield of this photoreaction was determined by gas chromatography. The GC peak areas for these products were quantified by use of external standards (naphthalene and 2,5-diacetylpyrazine) and authentic samples.

Transient Absorption Spectroscopy: An excimer laser (XeCl 308 nm, pulse width ∼20 ns, Lambda physics LPX 100) was used for excitation of the sample in a 1 cm × 1 cm quartz cell. A pulsed xenon arc lamp (USHIO UXL-159) was used as a monitoring light source. The monitoring light passed through a monochromator (JASCO CT-25), was detected by a photomultiplier (Hamamatsu Photonics, R 928), and was stored in a storage scope (Iwatsu TS-8123) and the signals were transferred to a personal computer (NEC PC-9801VM). Concentrations of **BAP**, **1-BAN**, **2-BAN**, and **9-BAA** were adjusted to an absorbance of 1.0 at 308 nm. The experiments were performed under argon or oxygen atmospheres.

Results and Discussion

Products on Photoirradiation. The quantitative analyses of the products were performed by gas chromatography (GC) and GC–MS for **1-BAN**, **2-BAN**, and **9-BAA**. The concentrations of the precursor and final products were determined by using naphthalene or 2,5-diacetylpyrazine as external standards. The sample solution (1.0×10^{-2} M, 3.0 mL) was irradiated using 308 nm laser pulses of 40 mJ pulse^{-1} with a repetition of 4 Hz. The results are summarized in Table 1.

As mentioned in the introduction, it was reported that a naphthylmethyl radical ($ArCH_2^\bullet$) was observed in the transient absorption spectra of **2-BAN** in benzene and in acetonitrile.[7] However, our product analyses showed that a main product in the photochemical reaction was 2-acetylnaphthalene (**2-AN**; $ArCOCH_3$) and the product yield of 2-methylnaphthalene (**2-MN**; $ArCH_3$) and 2-bromomethylnaphthalene (**2-MN**; $ArCH_2Br$) was less than 1% in benzene.

On the other hand, **1-BAN** and **9-BAA** gave products ($ArCH_3$ and $ArCH_2Br$) produced from an arylmethyl radical ($ArCH_2^\bullet$) as shown in Table 1. As a typical example, the time development of the concentrations of the initial compound and the products was observed, the results for **1-BAN** in benzene is shown in Fig. 1. The concentration of **1-BAN** decreased in approximate proportion to the irradiation time at the initial stage with a concomitant increase in the concentration of 1-acetylnaphthalene (**1-AN**; $ArCOCH_3$) and 1-bromomethylnaphthalene (**1-BMN**; $ArCH_2Br$). When the irradiation time was longer than 10 min, **1-BAN** disappeared probably due to a secondary photocleavage reaction. Therefore, ratios within 30% conversion of the initial compound were used for the determination of the product yields. The quantum yield of the photocleavage reaction was determined in benzene as 0.3 for **1-BAN** (Table 2).[7]

The difference in reactivity of an addition reaction in a naphthalene ring between the 1 position and the 2 position is generally explained by molecular orbital calculations of a transition state and an electron density of a frontier molecular orbital. For example, the nitration of a naphthalene ring occurs at the 1 position much faster than at the 2 position.[16] When an electrophilic substitution reaction occurs in an aromatic ring, the reaction

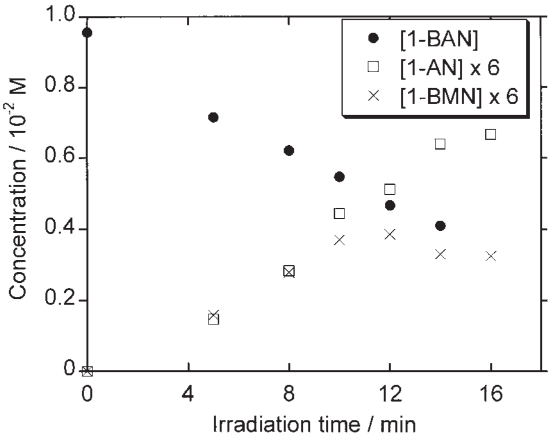

Fig. 1. Time profile of the ratio of the compounds determined by GC in photoreaction of **1-BAN** in benzene.

Table 2. Reaction Rate Constants and Quantum Yields of Photoreaction of Bromoacetylarene in Benzene

	Φ	$\tau_{\rm r}/\mu$s	$k_{\rm r}/10^4$ s^{-1}	$k_{\rm a}/10^4$ s^{-1}	$k_{\rm rea}/10^4$ s^{-1}
1-BAN	0.30	65	1.5	0.3	0.2
2-BAN	0.34$^{\rm a)}$	51	2.0	0.4	<0.02
9-BAA	0.06$^{\rm a)}$	33	3.0	0.8	0.9

a) From Ref. 7.

proceeds via a sigma complex as a transition state.[6,7] In the case of a naphthalene ring, the electron density at the 1 position is higher than that at the 2 position. Therefore, the rearrangement reaction to produce a neophyl (2-methyl-2-phenylpropyl) like radical (**NPR** in Scheme 1) from a 1-naphthoylmethyl radical should occur faster than that for a 2-naphthoylmethyl radical. Since the conformation of the transition state in the rearrangement reaction is expected to have an orthogonal structure, steric hindrance should play an important role in the rearrangement reaction. Thus, the rearrangement could feasibly occur when the carbonyl group and the aromatic ring in an aroylmethyl radical take a perpendicular conformation. A similar discussion was made in the decarboxylation reaction of benzoyloxyl or naphthoyloxyl radicals.[17–19] Thus, the electron density and the steric effect of the hydrogen atom on the peri position of the aromatic ring accelerates the rearrangement reaction of 1-naphthoylmethyl radical compared with that of 2-naphthoylmethyl radical, as observed in the product analysis.

Transient Absorption Spectra and the Assignment of Radicals. It was reported that naphthylmethyl radical was observed in the transient absorption spectra after laser excitation of **2-BAN**.[7] If naphthylmethyl radical is observed in the transient absorption spectra, 2-methylnaphthalene or 2-(α-bromomethyl)naphthalene should be detected by the GC analysis. However, in the product analysis, we did not detect these products. Therefore, the previously reported transient species for **2-BAN** was not likely to be a naphthymethyl radical. On the other hand, 1-methylnaphthalene and 1-(α-bromomethyl)naphthalene were detected by the GC analysis for the photoreaction of **1-BAN**, as shown in Table 1. This means that a naphthylmethyl radical could be observed on laser excitation of **1-BAN**. Therefore, the transient absorption spectra of **1-BAN** were studied using a quenching experiment.

Figure 2 shows the transient absorption spectra of **1-BAN** in benzene and acetonitrile upon excitation with a laser pulse at 308 nm under argon. The maximum wavelength shifted to a longer wavelength with the delay time, from 510 nm to 550 nm at 0.47 µs and 3.59 µs, respectively, after the laser pulse. Oxygen affected the transient spectra (Fig. 3). The decay curve at 540 nm fits the two component analysis with a time constants of 1.5 µs and 2 µs under an argon atmosphere (Fig. 4). The decay curve gave two components of 100 ns and 2 µs under an oxygen atmosphere (Fig. 4a). Thus, the quenching rate constant of the shorter lived component by oxygen was estimated to be 1.5×10^9 M^{-1} s^{-1}. Therefore, the shorter lived component as-

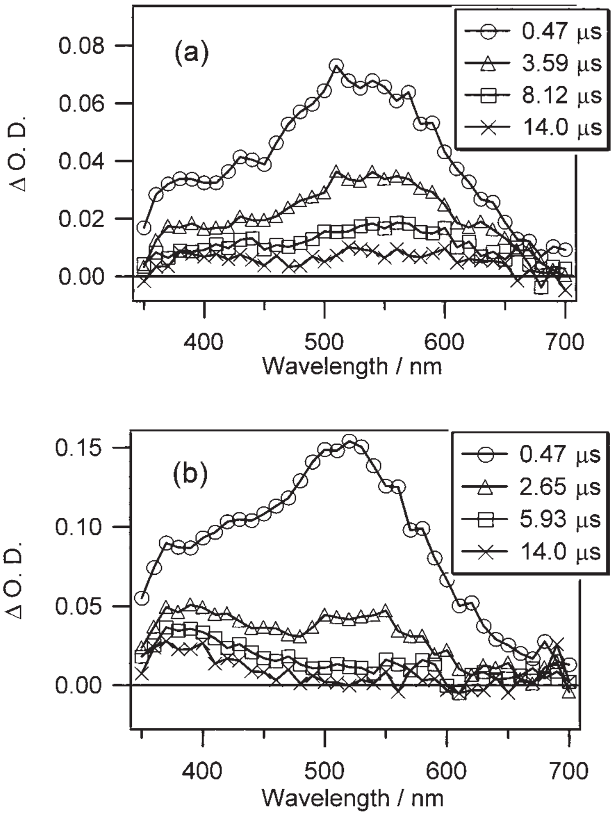

Fig. 2. Transient absorption spectra of **1-BAN** in benzene (a) and in acetonitrile (b) under argon.

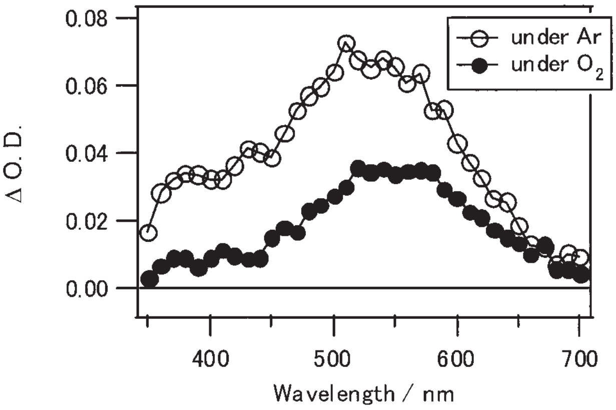

Fig. 3. Transient absorption spectra of **1-BAN** in benzene at 400 ns after laser excitation.

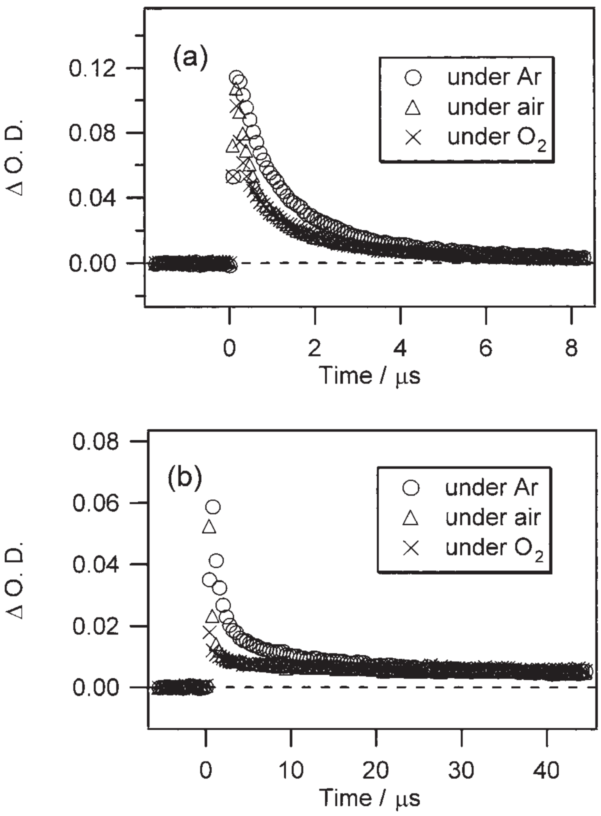

Fig. 4. Decay profiles of transient absorption monitored at 540 nm (a) and 400 nm (b) after the laser photolysis of **1-BAN** in benzene.

signed to the triplet state had fully disappeared at 400 ns after the laser pulse in the presence of oxygen (Fig. 3). In analogy with the previous reports, the longer lived component with $\lambda_{\max} = 540$ nm is assigned to the π-complex between bromine atom and benzene. Thus, the broad band at 510 nm in Figs. 2 and 3 under argon consists of the triplet state of **1-BAN** ($\lambda_{\max} = 510$ nm) and the π-complex between the bromine atom and benzene ($\lambda_{\max} = 550$ nm). The decay curve at 400 nm also fits the two component analysis, giving 1.5 μs and 65 μs (Fig. 4b). The former component was assigned to the triplet state, because it was quenched by oxygen. The latter component was not affected by oxygen and was asigned to a radical. The absorbance of the π-complex oberved under oxygen is the same as that observed under argon, indicating that the C–Br bond cleavage occurred in the singlet excited state.

In acetonitrile, the π-complex was not observed, as shown in Fig. 2. The transient absprption observed at 520 nm with a lifetime of 1.5 μs under argon was quenched by oxygen with a rate constant of 1.3×10^9 $\mathrm{M^{-1}\,s^{-1}}$, and was assigned to the triplet state. However, the longer-lived transient absorption was not quenched by oxygen and was assigned to a radical. In the mean time, the lifetime of 1-naphthylmethyl radical ($\mathrm{ArCH_2^\bullet}$) generated from **1-BMN** (1-bromomethylnaphthalene; $\mathrm{ArCH_2Br}$), which exhibited a transient absorption spectra around 380 nm, was quenched by oxygen with a rate constant of 3.2×10^6 $\mathrm{M^{-1}\,s^{-1}}$ (Fig. 5). In addition, the radical produced from **1-BAN** was quenched by 1,3-cyclohexadiene, which is a radical quencher, with a rate constant of 4.9×10^6 $\mathrm{M^{-1}\,s^{-1}}$.

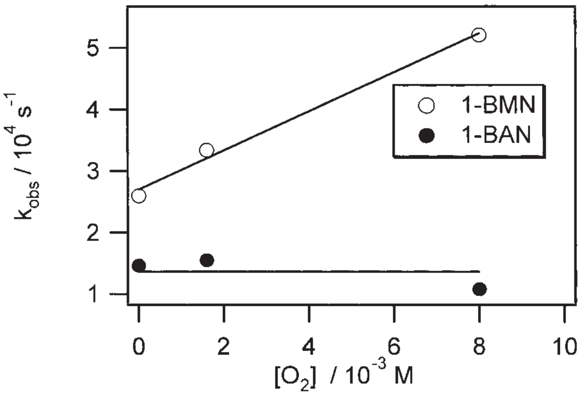

Fig. 5. Stern–Volmer plot of the radical quenching experiment observed by photolysis of **1-BAN** and **1-BMN** by oxygen in acetonitrile.

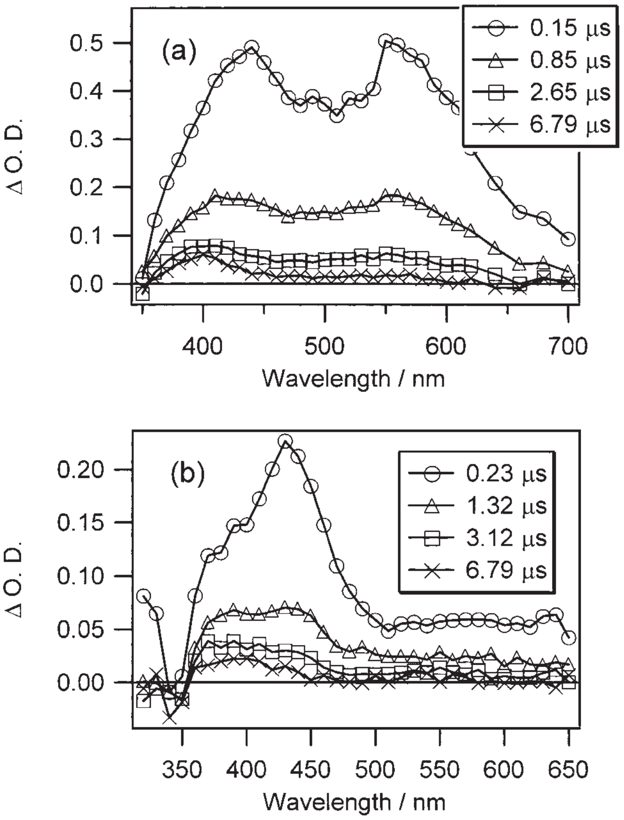

Fig. 6. Transient absorption spectra of **2-BAN** in benzene (a) and in acetonitrile (b) under argon.

These results indicate that the radical generated from **1-BAN** upon irradiation with a transient absorption at ~400 nm in benzene and acetonitrile should be assigned not to a naphthylmethyl radical ($\mathrm{ArCH_2^\bullet}$), but to a naphthoylmethyl radical ($\mathrm{ArCOCH_2^\bullet}$). These results are consistent with the results of time resolved CIDEP experiment.[14]

The transient absorption spectra of **2-BAN** under argon and oxygen in benzene and acetonitrile are showen in Fig. 6. The transient absorption with a maximum at 440 nm and a lifetime of 1.5 μs under argon was assigned to the excited triplet state, which was quenched by oxygen with a quenching rate constant of 1.9×10^9 $\mathrm{M^{-1}\,s^{-1}}$. The transient absorption at 550 nm was observed only in benzene, and the lifetime was not quenched by oxygen. Therefore, the peaks at 440 nm and 550 nm were assigned to the triplet state and the π-complex between bromine atom and benzene, respectively. In addition, the transient species at 380 nm with a lifetime of 51 µs was not quenched by oxygen, and therefore, was assigned not to a 2-naphthylmethyl radical, but to a 2-naphthoylmethyl radical. The initial absorbance of the radical produced upon 308 nm laser excitation of **2-BAN** was not affected by oxygen, indicating that the C–Br bond cleavage occurred in the singlet excited state. The assignment of the radical was also consistent with the results of the time resolved CIDEP experiment.[14]

9-BAA gave a transient absorption spectra in the wavelength region from 300 nm to 600 nm, with a maximum wavelength at 420 nm upon excitation with a 308 nm laser pulse under argon in benzene (Fig. 7). The transient species at 420 nm was quenched by oxygen, and was assigned to the triplet excited state. The transient absorption bands at 300–350 nm ($\lambda_{\max} =$ 340 nm) and 500–600 nm were not quenched by oxygen, and were assigned to be a radical and π-complex, respectively. The reduction of the transient absorption spectra (360–390 nm) in Figs. 6 and 7 is due to the decomposition of **9-BAA**. Because the quantum yield of the C–Br bond cleavage of **9-BAA** was 0.06,[7] the absorbance at 550 nm due to the π-complex between bromine atom and benzene was much smaller than that of **1-BAN** ($\Phi = 0.30$) and **2-BAN** ($\Phi = 0.34$). As mentioned above, the lifetime of the radical species observed at 340 nm ($\tau = 33$ µs) was not affected by oxygen. Taking into account the effect of oxygen on a napththylmethyl radical and a naphthoylmethyl radical, the radical species produced by the photocleavage of **9-BAA** could be assigned to a 9-anthroylmethyl radical.

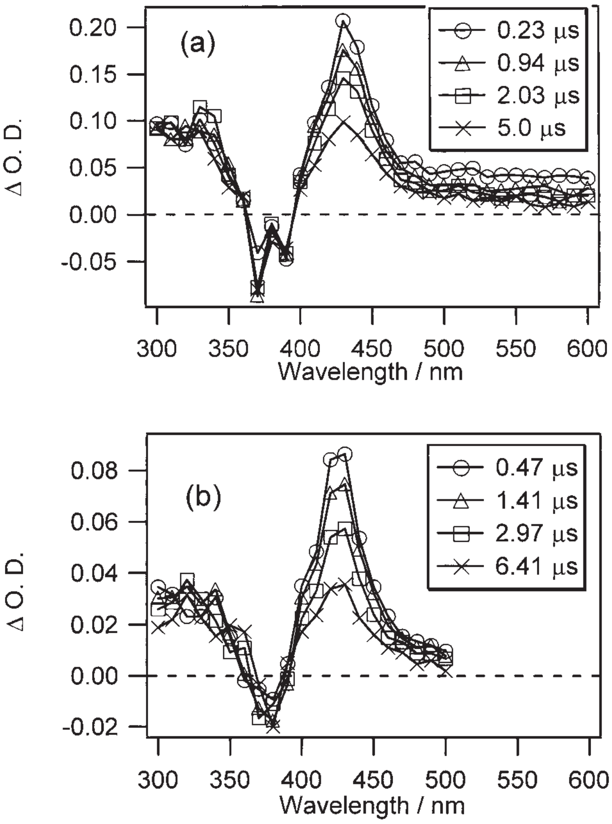

Fig. 7. Transient absorption spectra of **9-BAA** in benzene (a) and in acetonitrile (b) under argon.

Although the yield of 9-bromomethylanthracene was high (Table 1), 9-anthrylmethyl radical ($ArCH_2^\bullet$) was not observed upon laser excitation. This result indicates that the rate constant of the rearreangement reaction should be lower than the other prosesses.

Reaction Mechanism. On the basis of these results, we can suggest the reaction dynamics of an aroylmethyl radical rearranging to give an arylmethyl radical. A typical reaction scheme for **1-BAN** is shown in Fig. 8. **1-BAN**, **2-BAN**, and **9-BAA** gave a radical in the singlet state, which is enough to bring about C–Br bond cleavage (266 kJ mol^{-1}).[22,23] While the product analysis indicates the production of an arylmethyl radical in **1-BAN** and **9-BAA**, the arylmethyl radical was not detected in the transient absorption spectra or the time resolved CIDEP experiment. The rate constant for the rearrangement and decarbonylation reaction seems to be smaller than the sum of that of the hydrogen abstraction of an aroylmethyl radical ($ArCOCH_2^\bullet$) to give $ArCOCH_3$ and other processes. One can estimate the rate constants of the hydrogen abstraction reaction (k_a) and the rearangement reaction (k_{rea}) from the lifetime of the radical ($\tau_r = 1/k_r$) and product ratio, as summarized in Table 2. The rate constant for the rearrangement reaction decreased in the order of **9-BAA**, **1-BAN**, **2-BAN**, and is in accord with the steric effect of the hydrogen atom at the peri position of the aromatic ring. Therefore, the steric effect may play an important role in the rearrangement assuming the transition state of the rearrangement reaction has an orthogonal structure.

Conclusion

We have studied the behavior of aroylmethyl radicals quantitatively by the determination of the product yields as well as by the transient absorption spectroscopies. The rearrangement and decarbonylation reactions depended on the aryl substituent and substitution positions. The rate constant for the rearrangement reaction decreased in the order of **9-BAA**, **1-BAN**, and **2-BAN**, and is in accord with the steric effect of the hydrogen atom at the peri position of the aromatic ring. Therefore, the steric effect may play an important role in the rearrangement assuming the transition state of the rearrangement reaction has an orthogonal structure. Although the production of arylmethyl radicals upon photoirradiation of **1-BAA** and **9-BAA** was estimated by the product analysis, arylmethyl radicals were not observed in the transient absorption spectra. This means that the rate constant of the rearreangement should be lower than the other process. The observation of only the aroylmethyl radical in the present laser flash photolysis is consistent with the results of the time resolved CIDEP experiment. The product analyses gave important information about the reaction mechanism of the aroylmethyl radicals.

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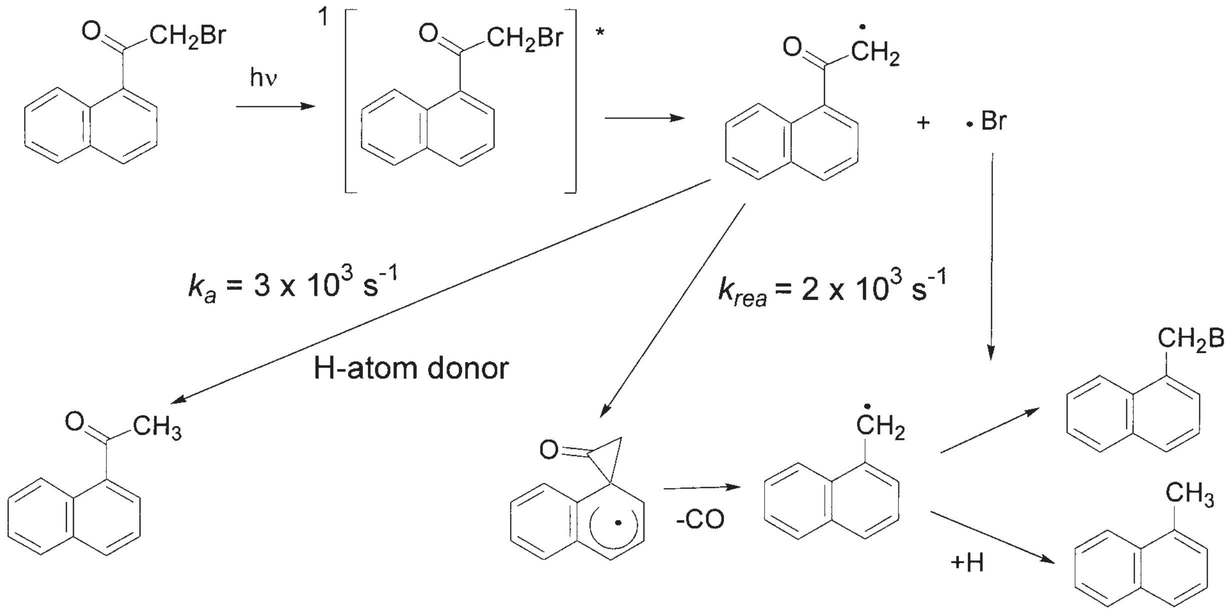

Fig. 8. Reaction scheme of a photochemical reaction of **1-BAN**.

References

1 B. Arnold, L. Donald, A. Jurgens, and J. A. Pincock, *Can. J. Chem.*, **63**, 3140 (1985).

2 L. J. Johnston and J. C. Scaiano, *J. Am. Chem. Soc.*, **107**, 6368 (1985).

3 G. H. Slocum and G. B. Schuster, *J. Org. Chem.*, **49**, 2177 (1984).

4 E. F. Hilinski, D. Huppert, D. F. Kelley, S. V. Milton, and P. M. Rentzepis, *J. Am. Chem. Soc.*, **106**, 1951 (1984).

5 F. Elisei, L. Latterini, G. G. Aloisi, and M. D'Auria, *J. Phys. Chem.*, **99**, 5365 (1995).

6 W. G. McGimpsey and J. C. Scaiano, *Can. J. Chem.*, **66**, 1474 (1988).

7 M. Hall, L. Chen, C. R. Pandit, and W. G. McGimpsey, *J. Photochem. Photobiol. A: Chem.*, **111**, 27 (1997).

8 G. Burnton, H. C. McBay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 4447 (1977).

9 S. V. Jovanovic, J. Rnoaud, A. B. Brinstain, and J. C. Saiano, *Can. J. Chem.*, **73**, 223 (1995).

10 J. Renaud and J. C. Scaiano, *Can. J. Chem.*, **74**, 1724 (1996).

11 J. Renaud and J. C. Scaiano, *Res. Chem. Intermediates*, **21**, 457 (1995).

12 W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944).

13 B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 1224 (1976).

14 T. Suzuki, Y. Kaneko, K. Maeda, T. Arai, K. Akiyama, and S. Tero-Kubota, *Mol. Phys.*, **100**, 1469 (2002).

15 T. L. Fletcher, M. J. Namkung, W. H. Wetzel, and H.-L. Pan, *J. Org. Chem.*, **25**, 1342 (1960).

16 M. Tanaka, E. Muro, H. Ando, Q. Xu, M. Fujiwara, Y. Souma, and Y. Yamaguchi, *J. Org. Chem.*, **65**, 2972 (2000).

17 T. Najiwara, J. Hashimoto, K. Segawa, and H. Sakuragi, *Bull. Chem. Soc. Jpn.*, **76**, 575 (2003).

18 Y. Saitoh, M. Kaneko, K. Segawa, H. Itoh, and H. Sakuragi, *Bull. Chem. Soc. Jpn.*, **75**, 2025 (2002).

19 J. T. Banks and J. C. Scaiano, *J. Phys. Chem.*, **99**, 3527 (1995).

20 R. E. Bühler, *Red. Res. Rev.*, **4**, 233 (1972).

21 J. M. Bossy, R. E. Bühler, and M. Ebert, *J. Am. Chem. Soc.*, **92**, 1099 (1970).

22 X.-M. Zhang, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 2275.

23 J.-P. Cheng and Z. Zheng, *Tetrahedron Lett.*, **37**, 1457 (1996).