

Photocyclization Mechanism of Halopyridinium Salt Tethered to Arene: Flash Photolysis Observation of a Pyridinium σ , Cyclohexadienyl Radicals, and a Dihalide Radical Anion in Aqueous Solution

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Abstract: The photocyclization reactions of 2-halopyridinium salt tethered to arene have been studied. The photocyclization of 2-halophenethylpyridinium salts produced a six-membered heterocyclic product, pyrido[2,1-*a*]-3*H*,4*H*-isoquinolinium salt. The 2-halopyridinium salts tethered to phenyl group with methylene linkage (**1** and **2a**) are more reactive than the 2-halopyridinium salts with an ethylene group (**3** and **4a**). As expected, the 2-bromopyridinium salt linked to the phenyl group with ethylene linkage (**4a**) is more reactive than the 2-chloropyridinium salt with the ethylene group (**3**), which is different from the 2-halopyridinium salt with the methylene linkage. The transient intermediates such as pyridinium salt σ , 2,3-dihydrocyclohexadienyl radicals, and a dibromide radical anion are detected with laser flash photolysis facility. The maximum absorption wavelengths of the pyridinium salt σ , 2,3-dihydrocyclohexadienyl radicals, and dibromide radical anion are 250, 310, and 360 nm, respectively. The lifetimes of the pyridinium salt σ , 2,3-dihydrocyclohexadienyl radicals, and dibromide radical anion are 0.93 ms, 0.84 ms, and 25 μ s, respectively. Thus, a photohomolytic radical mechanism is proposed for the cyclization reaction. The excited singlet state is mainly involved in the photocyclization of 2-halopyridinium salts tethered to phenyl group with ethylene linkage (**3** and **4a**), while both the singlet and triplet states are involved in the photocyclization of the 2-halopyridinium salts with methylene linkage (**1** and **2a**).

Introduction

The photoreactions of haloarenes are diverse depending upon reaction conditions. Generally three photochemical reactions are known for the haloarene: in aromatic solvent, arylation reaction is major, while in solvents able to donate hydrogen atoms, reduction reaction is dominant; under certain conditions, a nucleophilic substitution reaction can occur. The work in the field of haloarene photochemistry has been reviewed extensively.^{1–3} The photochemical reaction of haloarene is considerably important, in that the reaction is not only valuable in organic synthesis but also related to the degradation of the environmental pollutants (halogenated arene). Particularly, the photocyclization of haloarene tethered to arene or heteroarene is simple and valuable for homo- and heterocyclic ring formation.^{4,5} Five- and six-membered heterocyclic ring systems can be readily formed by the photocyclization of haloarene linked

to heteroarene.^{6,7} Therefore, it is important to know the mechanistic aspect of the photocyclization.

Only a few mechanistic studies on the intermolecular photoarylation and intramolecular photocyclization (or photoarylation) have been described,^{4a,8–10} although several studies on the mechanistic aspect and transient species involved in the photoreduction of haloarene have been reported.^{11,12} Pedersen and Lohse⁸ reported that 1,4-dibromobenzene underwent photoarylation in benzene to give 4-bromobiphenyl and *p*-terphenyl *via* transient cyclohexadienyl radical. The transient radical was characterized as follows: it decayed in the second order process with a half-life 0.7 ms. Grimshaw and de Silva reported a photohomolysis of the carbon–halogen bond assisted by radical complexation on the photocyclization of 1,3-diphenyl-5-(2'-halogenophenyl)pyrazoles^{4a} and 2-chlorobenzanilide.^{4b} Grimshaw and Trecha-Grimshaw⁹ detected a transient intermediate, a cyclohexadienyl radical, in the photocyclization of 1,3-diphenyl-5-(2'-halogenophenyl)pyrazoles, supporting the mechanism of homolytic carbon–halogen bond fission assisted by radical complexation. Obviously, a direct observation of a transient intermediate such as a cyclohexadienyl radical involved in the photoreaction is strong evidence for supporting the proposed mechanism.

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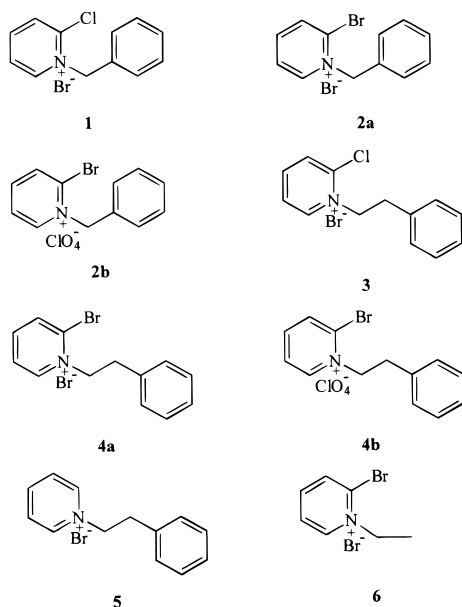
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Chart 1



Recently, we observed the transient intermediates such as a phenyl σ , 2,3-dihydrocyclohexadienyl radicals (a conjugated radical), and a dihalide radical anion¹³ in the photolysis of the aqueous *N*-(2-halobenzyl)pyridinium salts (**1** and **2a** in Chart 1).¹⁰ Thus, it was proposed that the photoreaction proceeds to cyclized product pyrido[2,1-*a*]isoindolium salt *via* a photohomolytic cleavage of the pyridinium ring-halogen bond, followed by arylation of the phenyl σ radical to the neighboring phenyl group and hydrogen atom ejection of the conjugated radical.

An electron transfer between haloarene and arene or halide ion followed by halide ion expelling, arylation of the resulting phenyl radical with the neighboring phenyl ring cation, and proton ejection may be assumed, since photochemically induced electron transfer between haloarene and amine, diene, or haloarene itself for the photoreduction is well documented.^{14–16} However, the electron transfer mechanism has not yet been proposed for the photocyclization of haloarene linked to arene. In other words, the photocyclization mechanism of haloarene has not been clarified, albeit limited studies on the photocyclization of haloarene tethered to arene support the photohomolytic mechanism.

In this paper, our objective has been to clarify the detailed mechanism for the photocyclization of halopyridinium salt tethered to arene. To this end, we have studied not only for the reactivities of the steady-state photoreaction of 2-halopyridinium salt tethered to phenyl ring (**1**, **2a**, **3**, and **4a**, Chart 1) but also for the detection and characterization of the transient species involved in the laser flash photolysis of the halopyridinium salts (**3** and **4a**).

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Experimental Section

Material and General. Benzylbromide, phenethylbromide, pyridine, 2-chloropyridine, 2-bromopyridine, and acetonitrile (Aldrich) were used as received. Water distilled triply was used.

UV/visible spectra were recorded on a Shimadzu UV 265 spectrophotometer. NMR spectra were recorded on a Varian Unity Plus spectrometer operating at 300 MHz for proton. The ¹H NMR spectra are referenced with respect to water proton of solvent D₂O. Infrared spectra were recorded on an FT-IR (Mattson Galax Series 7020) spectrophotometer on KBr crystal.

Synthesis of the Pyridinium Salts. *N*-Benzyl-2-chloropyridinium and *N*-benzyl-2-bromopyridinium bromides are prepared as described in ref 7a.

N-Benzyl-2-bromopyridinium perchlorate, **2b**, was prepared by an ion exchange reaction of **2a** with perchloric acid: When excess perchloric acid (60% perchloric acid 0.5 mL, 4.5 mmol) was added slowly into ethanolic solution of **2a** (500 mg, 1.5 mmol), a white crystal appeared: the crystal was filtered and recrystallized from ethanol, yield 50%, mp 97–98 °C.

2-Chloro-*N*-phenethylpyridinium bromide (**3**) was prepared by reaction of phenethyl bromide with 2-chloropyridine in acetonitrile, yield 30%. Recrystallization (acetonitrile) gave the pyridinium salt, **3**, as a white crystal (mp 179–180 °C).

2-Bromo-*N*-phenethylpyridinium bromide (**4a**) was prepared by reaction of phenethyl bromide with 2-bromopyridine in acetonitrile, yield 14%. Recrystallization (acetonitrile) gave the pyridinium salt **4a** as a white crystal (mp 150 °C).

2-Bromo-*N*-phenethylpyridinium perchlorate (**4b**) was prepared by ion exchange reaction of **4a** with perchloric acid: The method was the same as **2b** except the dissolved solvent methanol used. The pyridinium salt **4b** was recrystallized from methanol, yield 80%, mp 184–185 °C.

N-Phenethylpyridinium bromide (**5**) was prepared by reaction of phenethyl bromide with pyridine in acetonitrile, yield 60%. Recrystallization (acetonitrile) gave the pyridinium salt **5** as a white crystal (mp 125–126 °C).

2-Bromo-*N*-ethylpyridinium bromide (**6**) was prepared by reaction of ethyl bromide with 2-bromopyridine, yield 50%. Recrystallization (acetonitrile) gave the pyridinium salt **6** as a white crystal (mp 194–195 °C).

Steady-State Photoreaction. The aqueous solution of the halopyridinium salts **3**, **4a**, or **4b** (2.0×10^{-4} M) in UV cuvette (path length 1 cm, 3 mL) was irradiated with a monochromatic light (278 nm) and the UV/visible absorption change was measured for every 10 min, Figure 1. The new peaks at about 313 and 260 nm refer to a cyclized product, pyrido[2,1-*a*]isoquinolinium bromide (*vide infra*).

An aqueous solution of 2-chloro-*N*-phenethylpyridinium bromide (**3**, 500 mg, H₂O 300 mL) was introduced into an immersion quartz photovessel and then irradiated with a Hg-lamp for 7 h. The reaction was followed by UV absorption change at about 313 nm. The reaction mixture was dried by evaporation, and the residue was dissolved in 10 mL methanol. By adding 50 mL of acetone into the above methanolic solution, the appearing flocculent material was filtered out. After the solvent was dried, when 5 mL of ethanol was introduced, followed by addition of 0.1 mL of perchloric acid, pyrido[2,1-*a*]3*H*,4*H*-isoquinolinium perchlorate (white crystal, **8**) appeared, with a yield 30%. In fact, the yield of the cyclized product **7** before the workup with perchloric acid was 35% in HPLC. The retention times of the product and reactant of reaction mixture were 4.8 and 7.1, respectively (Rainin Instrument; C-18 column, 4.6 × 250 mm; mobile phase, methanol/water (3/1); flow rate, 0.5 mL/min). Recrystallization (ethanol) gave the pyridinium salt **8** as a white crystal (mp 142–143 °C).

The photochemical behavior of **4a** or **4b** is the same as that of **3**: The identical product is obtained in the photoreaction of **4a** or **4b**.

To measure the quantum yield of the photocyclization of the pyridinium salts (**1**, **2a**, **2b**, **3**, **4a**, or **4b**), the following procedure was performed. The intensity of the monochromatic light was measured by using standard ferrioxalate actinometry; the intensity at 278 nm was 1.02×10^{-6} ein/s. The aqueous solution of the pyridinium salt in UV cuvette (1 cm path, 3 mL) under argon or oxygen was irradiated with the above monochromatic light. The absorption change at 312 nm was monitored. The molar absorptivities of the photocyclized products,

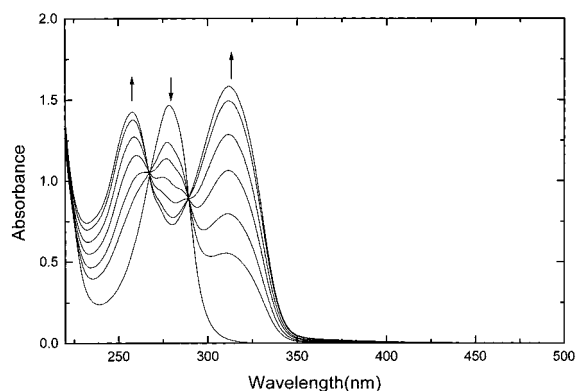


Figure 1. The UV absorption change of an aqueous solution of **4a** (2.0×10^{-4} M) under argon *vs* irradiation time (each interval 10 min).

pyrido[2,1-*a*]isoindolium bromide and pyrido[2,1-*a*]isoquinolinium perchlorate, are 1.0×10^4 and 1.3×10^4 $\text{M}^{-1} \text{cm}^{-1}$, respectively, and were used for the determination of the concentration change corresponding to the absorption change.

For the Stern–Volmer plot, the following procedure was performed: the aqueous solutions of the pyridinium salts (**3** or **4**, 2.0×10^{-4} M) with and without methylviologen ($0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 \times 10^{-5}$ M) under argon were irradiated with monochromatic light (278 nm, 450W Xe-lamp, Shimadzu monochromator). The absorption change at 313 nm was monitored to measure the quantum yield of the cyclized product.

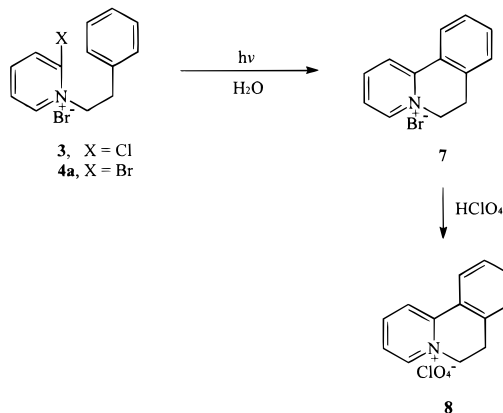
Laser Flash Photolysis. A detailed description of the experimental setup can be found elsewhere.¹⁰ The fourth harmonic (266 nm) output from a Q-switched Nd:YAG laser (Spectron SL803G) was used as an excitation source. The time duration of the excitation pulse was *ca.* 5 ns, and the pulse energy was typically 55 mJ. A cw Xe-arc lamp (Atago Bussan Co. XC-150) was used as a probe light source for transient absorption measurement. The spectral resolution was obtained by using 320 nm monochromator (Jobin-Yvon HR320) after the probe light passed through the sample solution. A boxcar signal averager (Stanford Research Sys. SR250) was used in recording the transient signals. The temporal profile of the transient absorption signal was monitored by a 500 MHz digital storage oscilloscope (Hewlett Packard HP54503A). Sample solutions were prepared by dissolving the reagents in triply distilled water, and the concentration of the solution was adjusted to be 0.8–1.5 in absorbance at 266 nm. The sample solution was circulated from a Teflon bottle (2.5 L in volume) to the fluorometer quartz cuvette of 10 mm in path length (flow type, Helma QS1.0) to reduce the effect by the accumulation of the reaction product and dilution of the reactant in the photolysis cell.

Results and Discussion

Steady-State Photoreaction. When the aqueous solution of 2-bromo-*N*-phenethylpyridinium bromide (**4a**, 2.0×10^{-4} M, 3 mL) in UV-cuvette (path length 1 cm) was irradiated with monochromatic light (278 nm, 450W Xe-lamp) under argon, the UV absorption change *vs* irradiation time (interval 10 min) was measured and is shown in Figure 1. The absorption band at about 278 nm corresponding to the absorption of the starting pyridinium salt decreased meanwhile those at about 313 and 260 nm corresponding to a product increased. For chloropyridinium salt **3**, a parallel spectrum change was obtained (not shown). The 313-nm absorbing product from **3** or **4a** is readily identified as a cyclized product because the absorbing wavelength is similar to the photocyclized product of halopyridinium salt **1** or **2a**. The clear isosbestic points are seen at about 292 and 268 nm, indicating that only one product is formed.

When an aqueous solution of 2-chloro-*N*-phenethylpyridinium bromide (**3**, 0.5 g, H_2O 300 mL, quartz photovessel) was irradiated with a high pressure mercury lamp for 7 h and worked up with perchloric acid, a cyclized product, pyrido[2,1-*a*]3*H*,4*H*-isoquinolinium salt (**8**), was obtained in 30% yield (Scheme

Scheme 1



Scheme 2

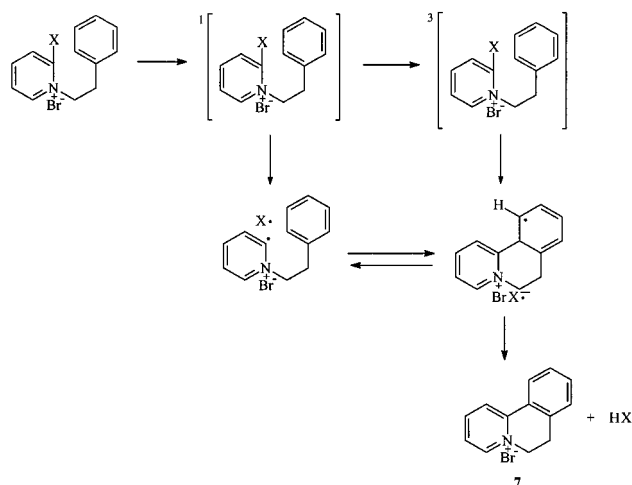


Table 1. The Quantum Yield of the Photocyclized Product of the Aqueous Pyridinium Salts

reactant	Φ		reactant	Φ	
	under Ar	under O_2		under Ar	under O_2
1	0.22	0.07	3	0.03	0.02
2a	0.20	0.08	4a	0.06	0.05
2b	0.21	0.09	4b	0.06	0.04

1). The yield of the cyclized product **7** before the workup with perchloric acid was 35% in HPLC. The identical product was also obtained from the bromopyridinium salt **4a**. For six-membered heterocyclic ring formation, this reaction is a simple and convenient method.

In order to study the effect of the counter ion of the pyridinium salts, 2-bromo-*N*-phenethylpyridinium perchlorate (**2b**) and 2-bromo-*N*-phenethylpyridinium perchlorate (**4b**) having nonoxidizable counter anion were prepared and studied in steady-state photoreaction and laser flash photolysis. The identical photocyclized product (**8**) was obtained from the steady-state photoreaction of **4b**.

The quantum yields of the photocyclized product of the pyridinium salts (**1**, **2a**, **2b**, **3**, **4a**, and **4b**) were measured and are shown in Table 1. The quantum yield of **1** or **2a**, in which the halopyridinium ring is connected to phenyl group by methylene group, is 3–10 times as great as that of **3** or **4a**, in which the halopyridinium ring is linked to phenyl by ethylene group, under argon. This result is understandable in consideration of the conformation of the pyridinium salts: the pyridinium salts with ethylene connector (**3** and **4a**) mainly have a staggered conformation because of the different propensity of both the

pyridinium and phenyl rings toward the solvent, water; the pyridinium salts with methylene connector (**1** and **2a**) have only a close conformation of both the pyridinium and phenyl rings whatever the properties of the rings toward the water are. Thus, it is indicative that the interacting pyridinium ring with phenyl ring should be brought into a sufficiently close proximity for cyclization to take place effectively.

Quantum yield of *N*-benzyl-2-chloropyridinium salt **1** is higher than that of *N*-benzyl-2-bromopyridinium salt, **2a**, although the bond energy of phenyl-chlorine (96 kcal/mol) is higher than that of phenyl-bromine (81 kcal/mol).¹⁷ This result is in line with that of 2-halobenzanilide^{4b} and 2-phenethyl-1-halobenzene.^{5b} However, for halopyridinium salts **3** and **4a**, in which the halopyridinium ring is connected with the ethylene group, this is not the case; chloropyridinium salt **3** is less reactive than bromopyridinium salt **4a**. Probably, some assistance of chlorine moiety of the excited pyridinium ring in the photocyclization of the pyridinium salt with methylene connector **1** may exist for phenyl-chlorine bond cleavage and/or for bringing into close proximity of the pyridinium and phenyl moieties. The argument is not applicable to the pyridinium salt with longer-chain connector, ethylene group, probably because of difficulty of accessible conformation of close proximity of the pyridinium and phenyl rings.

The quantum yield of **1** or **2a** is reduced to one-third in the presence of oxygen, while that of **3** or **4a** is not reduced effectively. This means that at least two-thirds of the photocyclization of **1** or **2a** originate from the triplet state and the photocyclization of **3** or **4a** occur mainly from the singlet state, albeit ineffective.

The quantum yields of **2b** and **4b** having a nonoxidizable counter anion under argon or oxygen are the same as **2a** and **4a**, respectively. These results imply that the counter anion has no effect on the reaction and in turn the electron transfer to excited pyridinium ring from anion can be excluded.

Stern-Volmer plot of photocyclization of **4a** with triplet quencher methylviologen has been performed. The $k_Q\tau$ value is $3.8 \times 10^3 \text{ M}^{-1}$ which is one-tenth of **1** or **2a**,¹⁰ indicating that the triplet state is less significantly involved, compared with that of **1** or **2a**. This result is consistent with that of the forgoing quantum yield measurement. If k_Q is assumed as the diffusion control rate ($k_Q = 6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in water),¹⁸ the lifetime of the triplet state of **4a** is 0.6 μs (lower limit). For the chloropyridinium salt, **3**, the $k_Q\tau$ and lifetime are $5.9 \times 10^3 \text{ M}^{-1}$ and 0.9 μs (lower limit), respectively.

Laser Flash Photolysis. Transient absorption spectra were obtained from the laser flash photolysis of 2-chloro-*N*-phenethylpyridinium bromide (**3**) in argon-saturated water as shown in Figure 2. There are three major transient absorption peaks at about 250, 310, and 380 nm at 3 μs delay after laser flash. At 300 μs delay after the laser flash, the absorption bands at about 250 and 310 nm remain, and that around 380 nm diminishes. A similar spectra were obtained for 2-bromo-*N*-phenethylpyridinium salt **4a**, as shown in Figure 3. At 3 μs delay, three bands around 250, 310, and 350–420 nm appear. At 300 μs delay, both peaks around 250 and 310 nm remain, while the band at around 350–420 weakens significantly. Both spectra from **3** and **4a** are similar to those of *N*-benzyl-2-halopyridinium salts (**1** and **2a**)¹⁰ except that the broad band in the region of 350–420 nm of **3** and **4a** is weaker and broader than that of **1** and **2a**.

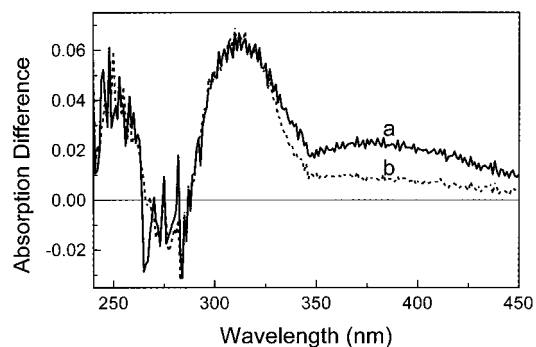


Figure 2. Transient absorption spectra obtained upon 266-nm excitation of **3** in aqueous solution under argon (—) 3 μs after laser pulse and (---) after 300 μs .

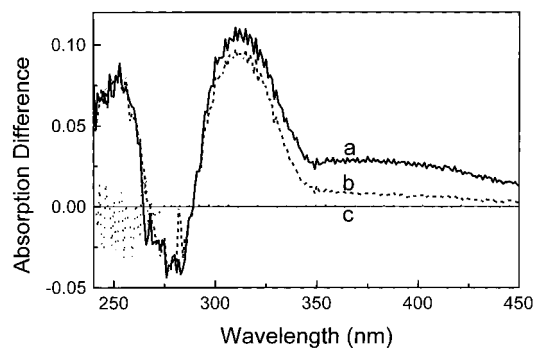


Figure 3. Transient absorption spectra obtained upon 266-nm excitation of **4a** and **5** (dashed line) in aqueous solution under argon (—) 3 μs after laser pulse and (---) after 300 μs .

In order to identify which bonds of the pyridinium salts are ruptured to give the transient species, the transient absorption spectra of 2-bromo-*N*-phenethylpyridinium salt (**4a**) and *N*-phenethylpyridinium salt (**5**, Chart 1) were obtained under argon and are compared in Figure 3. For pyridinium salt **5** without halogen substituent, no transient species was detected under our experimental condition. These results imply that the transient species of the 2-halopyridinium salts **3** or **4a** originate from the aryl-halogen bond cleavage, not from the benzyl-hydrogen bond cleavage of the pyridinium salt (side chain of the pyridinium salt).

Faria and Steenken¹⁹ reported that a benzyl radical and solvated electron (measured at 650 nm, λ_{max} 720 nm) were generated by the laser photolysis of triphenylmethane and diphenylmethane in several solvents. The reaction was described in terms of a biphotonic process based on the quadratic dependence of the benzyl-type radical yield on the laser light intensity. The structure of the pyridinium system here is quite similar to that of Faria and Steenken's diphenylmethane. Therefore, the possibility of the photoionization of the side chain of the pyridinium salts **3** or **4a** was examined by using DSO (500 MHz). For the pyridinium salts **3**, **4a**, or **5**, no sign of the presence of hydrated electron has been detected in the region of 400–750 nm. Consequently, based upon this and the forgoing results, we suggest that photoionization of the benzyl-hydrogen bond of (or side chain of) the pyridinium salts does not occur.

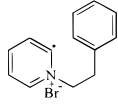
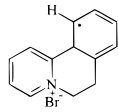
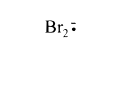
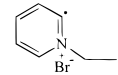
***o*-Pyridinium σ Radical.** The temporal profile of the transient species at about 250 nm from the photolysis of **4a** is shown in Figure 4. The species decays in a first order process, and its lifetime and rise times are 0.93 and 0.40 ns, respectively, Table 2. The absorption wavelength is the same as that from

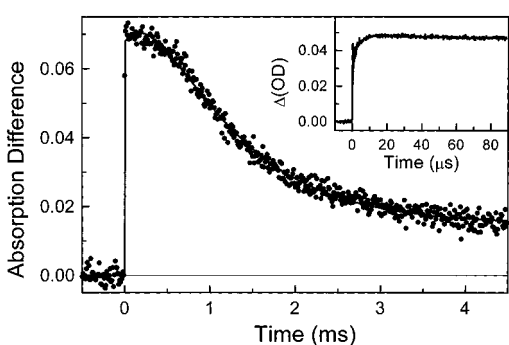
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Table 2. The λ_{\max} and Lifetimes of the Transient Intermediates

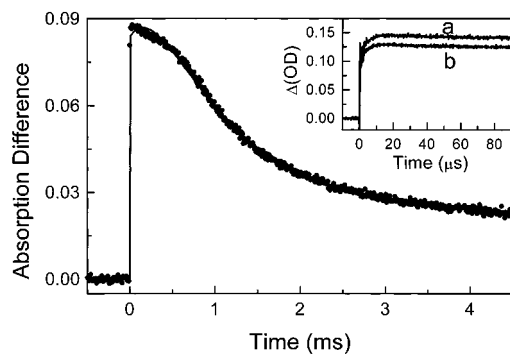
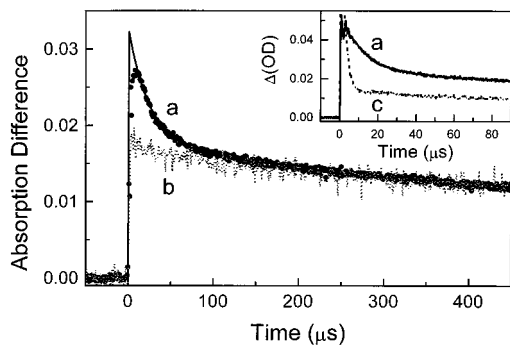
Transient	λ_{\max} (nm)	Lifetime	Reactant
	250	0.93ms	3 or 4a
	310	0.84ms	3 or 4a
	350-380	25 μ s	4a
$\text{Br}_2^{\cdot-}$	360 ¹⁰	10 μ s ¹⁰	
	360	14 μ s	6
	250	1.4ms	6

**Figure 4.** Temporal profile of 250-nm transient from laser flash photolysis of 2-bromo-*N*-phenethylpyridinium bromide (**4a**) under argon. Inset: same as above at μ s time scale.

1 or **2a**, and the lifetime is a little longer than that from **1** or **2a** (0.7 ms). The 250-nm transient diminishes by the presence of *N*-*tert*-butylphenylnitron, radical scavenger. Thus, the 250-nm transient is assigned unequivocally to *o*-pyridinium σ radical formed from the photohomolytic cleavage of the aryl–bromine bond. It is understandable that the lifetime of pyridinium σ radical from **4a** is longer than that from **1** or **2a**, since the photocyclization quantum yield of **4a** is much lower than that of **1** or **2a**.

It is unusual to observe another short rise time (10 μ s) for the formation of the 250-nm transient (inset in Figure 4). One possible explanation is that the short one is the rise time for formation of *o*-pyridinium σ radical from the singlet state and the long one is that from the triplet state. Another possible explanation is that the short one is the rise time for formation of *o*-pyridinium σ radical from the excited pyridinium salt and the long one (400 μ s) is that from the conjugated radical, 2,3-dihydro-cyclohexadienyl radical (vide infra). We prefer the latter explanation over the first one because the lower-limit triplet lifetime is in the range of 0.6 μ s.

2,3-Dihydrocyclohexadienyl Radical. The temporal profile of a transient species at about 310 nm from **4a** is shown in Figure 5. The transient decays in a first order process, and its lifetime and rise time are 0.84 and 0.33 ms, respectively. The absorption wavelength is the same as that of a 2,3-dihydro-cyclohexadienyl radical from **1** or **2a** reported¹⁰ and that of a cyclohexadienyl radical ($\lambda_{\max} = 310$ nm) produced upon γ -irradiation of benzene in methanol at 77 K.²⁰ This lifetime of 310 nm transient from **4a** is similar to the corresponding cyclohexadienyl radical from **1** or **2**¹⁰ and to that from, 1,4-

**Figure 5.** Temporal profile of 310-nm transient from laser flash photolysis of **4a** under argon. Inset: same as above at μ s time scale under argon (a) and oxygen (b).**Figure 6.** Temporal profile of 360-nm transient (s) from laser flash photolysis of **4a** (curve a) and **4b** (curve b) under argon. Inset: Effect of addition of ferrous ion on 360 nm transient formed from **4a** under argon (curve a $\xrightarrow{\text{Fe}^{2+}}$ curve c).

dibromobenzene.⁸ Hence, the 310-nm transient is identified as a conjugated radical, 2,3-dihydrocyclohexadienyl radical, Table 2.

To confirm the assignment, the transient species from a half-moiety model of the pyridinium salt **6**, which cannot form 2,3-dihydrocyclohexadienyl radical, were examined. Laser flash photolysis of the pyridinium salt **6** in water under argon produced 250- and 360-nm transients, but a 310-nm transient at 300 μ s delay after laser flash, supporting the above assignment (vide infra).

There are also two different rise times for the 2,3-dihydro-cyclohexadienyl radical: one is 10 μ s (inset in Figure 5) and the other is 327 μ s under argon. The possible explanation is that the short one is the rise time for the formation of the conjugated radical from the excited pyridinium salt and the long one is that from the pyridinium salt σ radical. The rise time of the conjugated radical is not the same as the decay time of the pyridinium σ radical. The reverse is also true. They are understandable since either of the transients does not come from only one source. The presence of oxygen diminished a little amount of the transient (10%) at 300 μ s delay, indicating the fact that about 10% of the conjugated radical originates from the triplet state. The 310-nm transient of the inset of Figure 5 is also reduced to only 11% in the presence of oxygen. In other words, about 90% of the radical is generated from the singlet state. This result is consistent with the lack of oxygen effect on the quantum yield of the steady-state photoreaction.

Dihalide Radical Anion. The region of 350–420 nm from **4a** in Figure 3 exhibits a complicated spectral feature. The temporal profile of 360-nm transient shown in Figure 6 (curve a) showed two component decays for the peaks: the short-lived transient is 25 μ s and the long-lived one is 780 μ s. It has been reported that the absorption of dichloride radical anion ($\text{Cl}_2^{\cdot-}$)

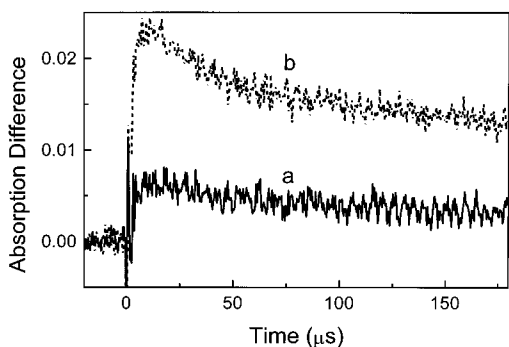


Figure 7. Temporal profile on a transient at 400 nm formed from **4a** under argon.

was suppressed by addition of potassium hexacyanoferrate(II) in the pulse radiolysis of aqueous sodium chloride.^{21,22} The presence of ferrous ion diminishes the intensity of the short-lived transient at 360 nm (Inset in Figure 6). Therefore, the short-lived transient at 360 nm is dibromide radical anion, Table 2. The lifetime is somehow a little longer than that reported.¹⁰ The long-lived component ($\tau = 780 \mu\text{s}$) is not identified yet.

In order to clarify the role of counter anion, the property of a transient at 360 nm was examined with **4b** or **2b** having a nonoxidizable anion. The temporal profile of 360-nm transient from the laser flash photolysis of **4b** is shown in curve b in Figure 6. Surprisingly, the transient absorption at 360 nm ($\text{Br}_2^{\bullet-}$) from **4b** is seen, even though it is very weak compared with that of **4a** (curve a). This is probably formed from the reaction of bromine radical produced in the cleavage of C–Br bond with HBr produced as product. This explanation is supported by the following observation: At the initial stage of illumination of **2b** (within 2 min) the transient at 360 nm was hardly seen, while at the latter stage of illumination (within 10 min) the transient was obviously seen (not shown). These observations support again the assignment of the short component of the transient at 360 nm to $\text{Br}^{\bullet-}$ in the reaction of **4a**.

The temporal profile of the transient species at 400 nm was examined with old and new batches of the pyridinium salt **4a** (Figure 7): this transient could be observed only in the old batch which was illuminated for long period time, but not in the new batch, which is illuminated in a very short period of time, indicating that the transients are formed from product, pyrido[2,1-*a*]-3,4-dihydroisoquinolinium salt. It is possible that a photochemical transient formation from photocyclized product occurs probably because of the open structure of the product for hydrogen abstraction of the benzylic hydrogen or of the rigid structure of the product in which the energy cascade is not efficient. The transient from the product will not be discussed further here.

Transients from 2-Bromo-*N*-ethylpyridinium Salt (6). In order to identify the transient species from **3** or **4a**, the transient absorption spectra of a structurally halopyridinium salt **6** were measured and are shown in Figure 8. At $3 \mu\text{s}$ delay after laser flash, the spectral features consist of three absorption peaks at about 250, 300, and 360 nm. At $300 \mu\text{s}$ delay, 250- and 290-nm transients remain, and 305- and 360-nm transients disappear, while the bleaching at 277 nm is less. The 360-nm transient is unequivocally recognized as the dibromide radical anion as expected because of its properties (lifetime $14 \mu\text{s}$, λ_{max} 360 nm, and diminished by the presence of ferrous ion).

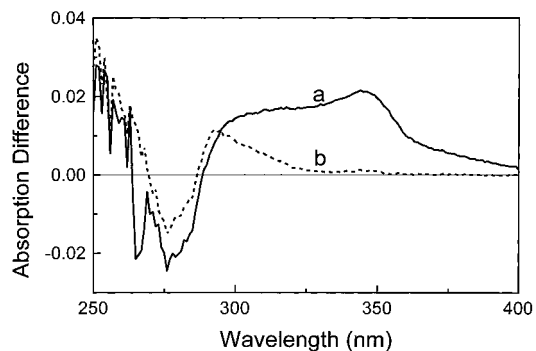


Figure 8. A transient absorption spectra acquired from laser flash photolysis of 2-bromo-*N*-ethylpyridinium bromide (**6**) under argon. Solid line, at $3 \mu\text{s}$ delay and dotted line, at $300 \mu\text{s}$ delay after laser flash.

The 250-nm transient decays in a first order process, and the lifetime and rise time are 1.4 ms and $364 \mu\text{s}$, respectively, Table 2. The lifetime and rise time of 290-nm transient are the same as those of 250-nm transient. Thus the 290-nm species belong to a part of 250-nm transient. As expected, the 250-nm transient is unambiguously recognized as pyridinium σ radical, because of the above properties and diminishing effect of the transient spectra by the addition of radical scavenger, *N*-*tert*-butylphenylnitrene.

The broad band around 305 nm has a lifetime of $59 \mu\text{s}$. The transient diminishes in the presence of oxygen, while the bleaching at 277 nm is less. The most interesting observation is that the 305-nm transient disappeared at $300 \mu\text{s}$ delay, while the bleaching at 277 nm weakened, indicating that the 305-nm species is due to the excited state of **6**. As expected, that 305-nm transient from **6** is obviously different from the 310-nm transient in the photolysis **3** or **4a**. Previtali and Ebbesen^{11c} reported that the triplet–triplet absorption of chlorobenzene appeared at 305 nm. The 305-nm transient from **6** is probably the triplet–triplet absorption of the pyridinium salt **6**. In other words, the assignments of transients from **3** or **4a** are supported by experiments showing that the flash photolysis of 2-bromo-*N*-ethylpyridinium salt **6** produced a phenyl σ radical and bromine anion radical but not a 2,3-dihydrocyclohexadienyl radical.

Mechanism. A mechanism of an electron transfer to the pyridinium ring from the counter anion or phenyl ring is excluded based on the following observations: (1) photocyclized product is only observed in the steady-state photoreaction; (2) no photoreduced product was observed; (3) quantum yield of **2b** or **4b** having nonoxidizable anion is the same as **2a** and **4a**, respectively. Since the transients such as pyridinium salt σ , 2,3-dihydrocyclohexadienyl radicals, and dihalide radical anion are detected in laser flash photolysis, a photohomolytic radical mechanism for the photocyclization of **3** or **4a** is proposed as in the photoreaction of *N*-benzyl-2-halopyridinium salt,¹⁰ Scheme 2. The excited singlet state populated by the light absorption of the pyridinium salt ground state undergoes either homolytic cleavage of an aryl–hydrogen bond to give a pyridinium salt σ radical or an intersystem crossing to give the triplet state. Both the pyridinium salt σ radical and triplet state proceed to the conjugated radical, 2,3-dihydrocyclohexadienyl radical, by the cyclization reaction. The conjugated radical in turn proceeds ultimately to the cyclized product, pyrido[2,1-*a*]-3,4-dihydroisoquinolinium salt, by ejecting hydrogen atom.

Conclusion

Five- and six-membered heterocyclic ring systems can be readily formed by photocyclization of 2-halopyridinium salts

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linked to phenyl rings with methylene (**1** and **2a**) and ethylene groups (**3** and **4a**). Photocyclization of halopyridinium salts with an ethylene connector is less effective than a halopyridinium salt with a methylene group, probably because the halopyridinium salts with an ethylene group take a staggered conformation freely while the halopyridinium salts with a methylene group take only an "eclipsed" conformation of their pyridinium and phenyl rings. For the pyridinium salts with a methylene group, the photocyclization reaction of chloropyridinium salt predominates over a bromopyridinium salt with a methylene group, whereas for the pyridinium salt with an ethylene group, this is not the case. Probably, for the chloropyridinium salt with a methylene group, some assistance of the excited chlorine moiety can hold the neighboring phenyl ring for cyclization to take place, but for a chloropyridinium salt with an ethylene group, the assistance cannot overcome the eclipsed conformation energy for the cyclization. Thereby, the bromopyridinium salt with an ethylene group is more reactive than a chloropyridinium salt with an ethylene group, as expected.

The transient intermediates such as pyridinium salt σ (λ_{\max} 250 nm), 2,3-dihydrocyclohexadienyl radicals (λ_{\max} 310 nm), and dibromide radical anion (λ_{\max} 360 nm) were detected and characterized by using the nanosecond laser flash photolysis technique. The lifetime of pyridinium salt σ , 2,3-dihydro-

cyclohexadienyl radicals, and dibromide radical anion in argon-saturated water are 0.93 ms, 0.84 ms, and 25 μ s, respectively. Thus a photohomolytic radical mechanism involving the intermediates is proposed. For a halopyridinium salt with an ethylene group, the photocyclization originates mainly from the singlet state along the minor triplet-state path, albeit ineffective. For a halopyridinium salt with a methylene group, both singlet and triplet states are involved for the photocyclization. A photonic ionization of the side chain of 2-halopyridinium salt linked to arene in water does not occur, although the photoionization possibility of the side chain of the photocyclized product may not be excluded.

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Supporting Information Available: UV, IR, NMR, and element analysis data for **2a**, **3**, **4a**, **4b**, **5**, **6**, and **8** (2 pages). See any current masthead page for ordering and Internet access instruction.

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