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Flash Photolysis Observation of Aryl, 2,3-Dihydrocyclohexadienyl, and Halogen Anion Radicals in Aqueous Solution: Photohomolytic Radical Cyclization of Aryl Halide[1]

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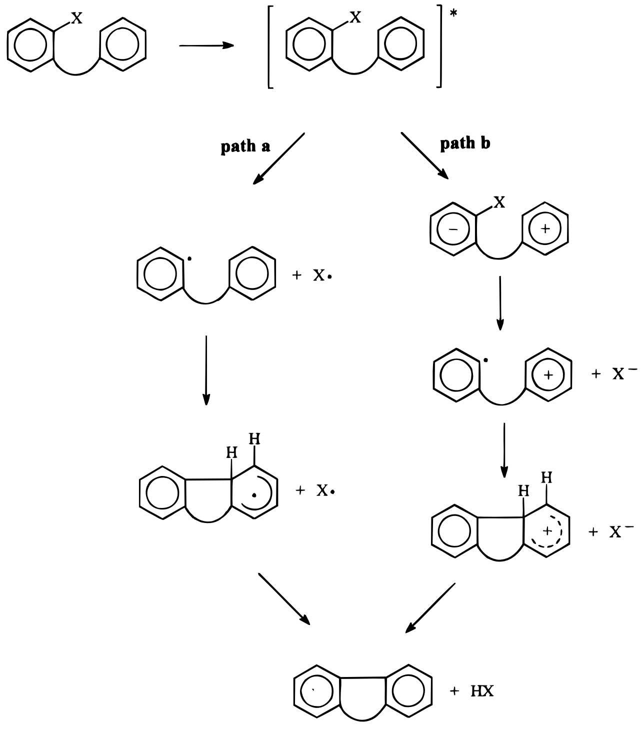
Abstract: A thorough investigation of the transient species from the laser flash photolysis of haloarene tethered arenes has been performed. Some transient species in the laser photolysis of *N*-benzyl-2-halopyridinium and *N*-(2-halobenzyl)pyridinium bromides have been investigated as an effort to understand the photocyclized reaction mechanism as well as to know the properties of the transients themselves. Pyridinium σ, 2,3-dihydrocyclohexadienyl π, and halogen anion radicals are detected in the photolysis of a *N*-benzyl-2-halopyridinium salt (**1** or **2**) in water: the absorption maxima are 250, 310, and 355 ($Br-Cl^{\bullet-}$) nm, respectively. The lifetimes of 2-pyridinium σ radical, 2,3-dihydrocyclohexadienyl π, and bromine chloride (in the case of **1**) anion radicals are 0.72 ms, 1.2 ms, and 9.3 μs, respectively. Phenyl σ, 2,3-dihydropyridinium π, and halogen anion radicals are also detected in the laser photolysis of an aqueous solution of a *N*-(2-halobenzyl)pyridinium salt (**3** or **4**): the absorption maxima are 250, 310, and 360 nm ($Br_2^{\bullet-}$, in the case of **4**), respectively. The lifetimes of the transient intermediates are 1.4 ms, 1.2 ms, and 10 μs, respectively. On the basis of the observation of these intermediates, their properties, and the reactant reactivities, a mechanism of the photohomolytic bond cleavage of carbon−halogen followed by radical arylation and hydrogen ejection is proposed for the intramolecular photocyclization of haloarene tethered arenes in water.

Introduction

The photocyclization reaction of aryl halides is one of the most useful processes in organic synthesis and has attracted numerous synthetic investigations.[2,3] The intramolecular photocyclization of haloarene tethered arenes is particularly useful for a new ring formation.[4,5] It is of interest that a new heterocyclic ring system has been formed from halogenated heteroarenes via the photocyclization reaction.[6,7] Consequently, it is important to understand the reaction mechanism for the photocyclization of haloarene linked arenes. However, few mechanistic studies on this type of reaction have been carried out. Two possible mechanisms have been postulated for the photocyclization reaction as shown in Scheme 1. One is a mechanism involving photohomolytic bond cleavage followed by radical arylation and hydrogen ejection (path a). The other is to involve photoinduced charge transfer followed by radical anion decomposition, radical arylation, and proton ejection (path b).

Scheme 1



Grimshaw *et al.*[4a] reported that, in the photocyclization of

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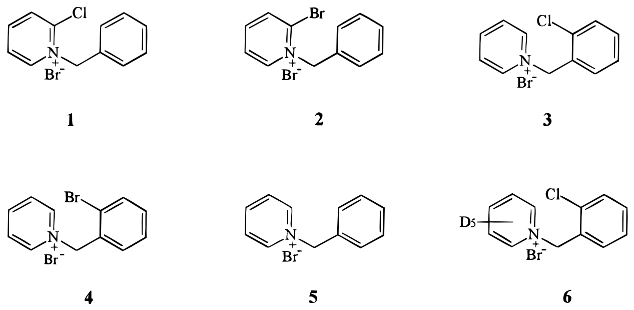
Chart 1



5-(2-chlorophenyl)-1,3-diphenylpyrazoles, a mechanism of homolytic carbon−halogen fission assisted by radical complexation was appropriate to explain their results adequately, thereby supporting the path a. They also detected a cyclohexadienyl radical intermediate involved in the reaction.[8]

In our previous studies,[9] the photocyclization of *N*-benzyl-2-halopyridinium and *N*-(2-halobenzyl)pyridinium salts (**1**−**4** in Chart 1) to produce isoindolium salts was described to pass through a 2,3-dihydrocyclohexadienyl or 2,3-dihydropyridinium salt radical which was formed via a tight or loose π-complex.

A photoinduced intramolecular charge-transfer mechanism in connection with the photocyclization of haloarenes has not yet been reported, but an intermolecular photoinduced charge-transfer mechanism has been suggested in the photoreduction of bromobiphenyl[10] and 1-chloronaphthalene.[11]

There have been several attempts to detect the transient species in the laser flash photolysis and/or pulse radiolysis of simple aryl halides, albeit not those of the haloarene tethered arenes. Prevetali and Ebbesen[12,13] observed the triplet state absorption (λ_{max} = 305 nm) and the solvated electron (λ_{max} = 650 nm) in the photolysis of chlorobenzene in various solvents. The triplet state lifetime of chlorobenzene ranged from 70 ns (in water) to 1.6 μs (in cyclohexane). Since chlorine anion radical was observed in the photolysis of chlorobenzene in the presence of lithium chloride, the photohomolytic cleavage of the C−Cl bond in the singlet and triplet excited states has been proposed for the photoreduction. Cercek *et al.*[14,15] reported that phenyl and 1,2-dihydrocyclohexadienyl derivative radicals were produced in the pulse radiolysis of aryl iodides. The absorption maxima of phenyl (**7**) and 1,2-dihydro-6-hydroxycyclohexadienyl (**9**) radicals are 260 and 312 nm, respectively (Chart 2).

The objective of this study is to elucidate the mechanism concerning the photocyclization reaction of haloarene tethered arenes. It is important to detect transient intermediates in the photocyclization of the pyridinium salts in order to clarify the reaction mechanism, as well as to obtain information on their properties in water. Thus, *N*-benzyl-2-halopyridinium salts (**1**, **2**) and *N*-(2-halobenzyl)pyridinium salts (**3**, **4**) were prepared, and their photoreactions were studied by using the laser flash photolysis facility.

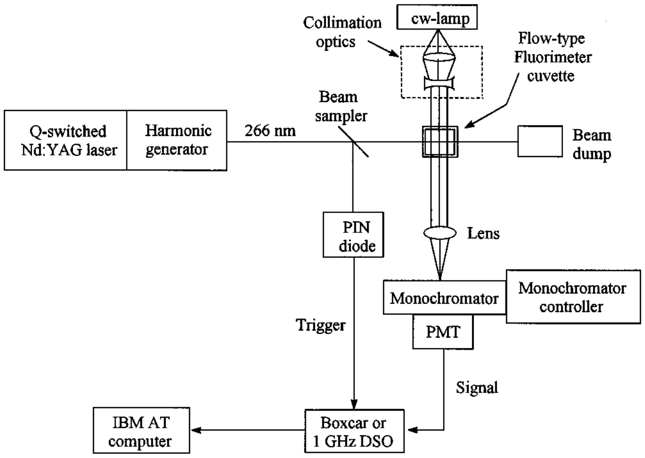
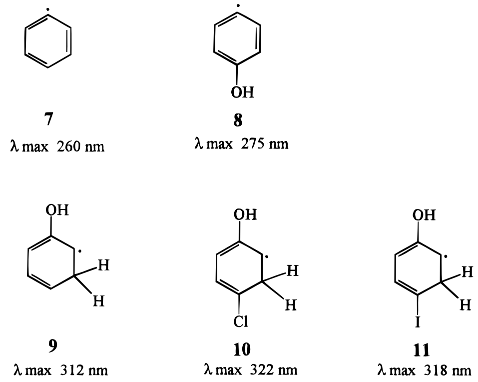


Figure 1. Schematic diagram of laser flash photolysis facility.

Chart 2



Here, we, for the first time, describe the direct observation and lifetime measurement of the reaction intermediates in the photocyclization of halopyridinium salts in aqueous solution by laser flash photolysis. On the basis of such observation and the properties of the transient intermediates as well as the reactant reactivities, a mechanism of photohomolytic bond cleavage followed by radical arylation and hydrogen ejection is proposed.

Experimental Section

Materials. *N*-Benzyl-2-chloropyridinium and *N*-benzyl-2-bromopyridinium bromides (**1**, **2**), *N*-(2-chlorobenzyl)pyridinium and *N*-(2-bromobenzyl)pyridinium bromides (**3**, **4**), and *N*-benzylpyridinium bromide (**5**) were prepared by the methods of Park *et al.*[9] (Chart 1). Two recrystallizations from acetonitrile yielded white crystals with uncorrected melting points of 143, 160, 167, 171, and 110 °C, respectively. The aqueous solution UV of **1**, **2**, **3**, and **4** gave λ_{max} at 275 (ϵ, 7.7 $\times$ 10^3), 278 (ϵ, 6.8 $\times$ 10^3), 260 (ϵ, 4.2 $\times$ 10^3), and 260 (ϵ, 4.0 $\times$ 10^3) nm, respectively.

N-(2-Chlorobenzyl)pentadeuteriopyridinium bromide (**6**) was prepared by reacting 2-chlorobenzyl bromide with pentadeuteriopyridine in sulfolane (Chart 1). Two recrystallizations from acetonitrile yielded white crystals with an uncorrected melting point of 80 °C. All other reagents were commercially available and were used as received. Triple distilled water was used as the solvent.

Laser Flash Photolysis. A schematic diagram of the laser flash photolysis system is shown in Figure 1. 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 the transient absorption measurement.

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The probe light was collimated onto the reaction cell at a right angle with respect to the laser beam. The probe light after the reaction cell was focused into the entrance slit of a 320-mm monochromator (Jovin-Yvon HR320). The slit width of the monochromator was adjusted to obtain the spectral resolution of *ca* 1 nm in the 200~800-nm range. A photomultiplier tube (PMT, Hamamatsu R955) was attached to the exit slit of the monochromator for the signal detection. Linearity of the output signal was light intensity was checked by measuring the absorbance of neutral density filters.

The output signal from the PMT was amplified by using a 300-MHz fast preamplifier (Stanford Research System SR445). A boxcar signal averager (Stanford Research System SR250) was used for the sampling of amplified signal with 600-ns gate width at predetermined delay times. Typically, signals from 100~150 shots of the laser pulses were averaged. The absorbance at 50-ms delay after the laser pulse was subtracted from the transient absorption at 3~300-μs delay times to remove the product absorption which induces a permanent absorption.

The temporal profile of the transient absorption signal was monitored by using a 500-MHz digital storage oscilloscope (DSO, Hewlett Packard HP54503A). Averaged output from boxcar or DSO was digitized and stored in a personal computer by using a GPIB interface board.

A PIN photodiode (Hamamatsu Model S1190-13) with a fast rise time ($\leq$1 ns) was employed to provide a trigger signal for the boxcar or DSO. Thus the zero time of excitation was set by the trigger pulse electronically. This allows a time resolution down to 10 ns.

All the sample solutions were prepared by dissolving the reactants in triply distilled water. The concentration of the solution was adjusted to give 0.8~1.5 in optical density at 266 nm. The 2.5-L sample solution was circulated through a quartz cuvette with a 10-nm pathlength (Helma QS1.0) to reduce incidental effects caused by an accumulation of the reaction product. UV−visible spectra were recorded by a Shimadzu UV-265 spectrophotometer.

Quenching Study. The appropriate concentrations of pyridinium salt (**1**, **3**, or **6**, 1.0×10^{-4} M) with and without a triplet quencher, methylviologen (0, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0×10^{-5} M), in water were prepared, and the solution (3 mL) was transferred into a 10-mm-path UV cuvette. The solution was deaerated by introducing argon for 20 min and then was irradiated with a 450-W cw Xe lamp light via a filter (Action Research Corp. Serial #170-3-18B) for 30 s. The absorption change around 312 nm, at which the isoindolium salt (product) absorbed, was monitored. The light intensity was measured to be 2.0×10^{-6} einstein/(s·cm^2) with ferrioxalate actinometry. The Stern−Volmer plot was obtained from the calculated quantum yield.

Results and Discussion

For detecting transient intermediates in the photocyclization of the halopyridinium salts (**1**, **2**, **3**, **4**, **5**, or **6**), the laser flash photolysis of the pyridinium salts in water was studied. When the argon-saturated aqueous solution of **1** in 10-mm-path UV cuvette, which circulated within a 2.5-L bottle (76.3 mg of **1** in 2.5 L of water), was irradiated by a 266-nm laser pulse, a transient absorption spectra was obtained (Figure 2). At a 3-μs delay after the laser pulse, three transient absorption bands appeared at about 250 (strong), 315 (strong), and 355 (strong) nm whereas only two peaks at about 250- and 310-nm transients remained at 300 μs delay.

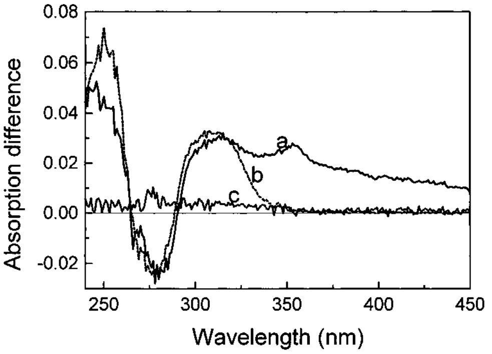

Figure 2. Transient absorption spectra: curve a (solid line), measured 3 μs after the laser pulse for *N*-benzyl-2-chloropyridinium bromide (**1**, 1.1×10^{-4} M) in water under argon; curve b (dash line), obtained 300 μs after the laser pulse for the same solution; curve c (dotted line), measured 5 μs after the laser pulse for *N*-benzylpyridinium bromide (**5**, 1.1×10^{-4} M) in water under argon.

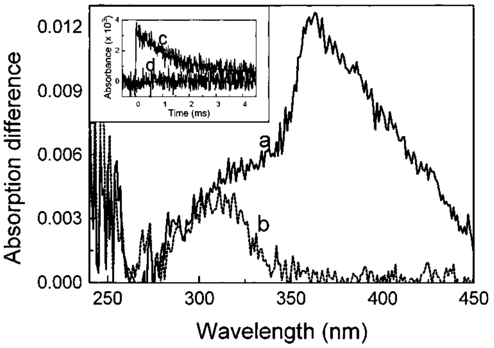

Figure 3. Transient absorption spectra: curve a (solid line), measured 3 μs after the laser pulse for *N*-(2-bromobenzyl)pyridinium bromide (**4**, 2.0×10^{-4} M) in water under Ar; curve b (dash line), obtained 300 μs after the pulse for the same solution under the same condition. Inset: effect of the phenylnitrone on the temporal profile of the 250-nm transient; curve c, 250-nm transient absorption−time curve; curve d, the same curve in the presence of the phenylnitrone (1.1×10^{-4} M).

To understand the effect of a halogen substituent on **1**−**4**, the transient absorption spectra of *N*-benzylpyridinium bromide (**5**) under the same condition of **1** was taken and compared with that of **1** in Figure 2. No transient species were observed 5 or 300 μs after the laser pulse. This implies that all transient intermediates observed from **1**, **2**, **3**, **4**, or **6** (vide intra) originate from the aryl−halogen bond cleavage, not from benzyl−hydrogen bond cleavage of the pyridinium salts.

For an argon-saturated aqueous solution of **4**, the transient spectra taken 3 μs after laser pulse showed that three peaks at about 250 (medium), 310 (strong), and 360 (strong) nm appeared and two peaks at about 250 and 310 nm remained at 300 μs after the laser pulse (Figure 3).

Halogen Anion Radicals. The 355-nm transient from laser photolysis of **1** decays in a first-order process, and its lifetime is 9.3 μs (curve a of Figure 4). The 355-nm transient is assigned as bromine chloride anion radical ($Br-Cl^{\bullet-}$) since the absorption region and the lifetime are similar to those of $Cl_2^{\bullet-}$ ($\lambda_{max} = 340$ nm, $\tau = 10$ μs) and $Br_2^{\bullet-}$ ($\lambda_{max} = 360$ nm) reported.[16−19]

It has been reported that the absorption of chlorine anion radical ($Cl_2^{\bullet-}$) was suppressed by addition of potassium hexacyanoferrate(II) in the pulse radiolysis of aqueous sodium chloride.[16,17] As expected, the bromine chloride anion radical

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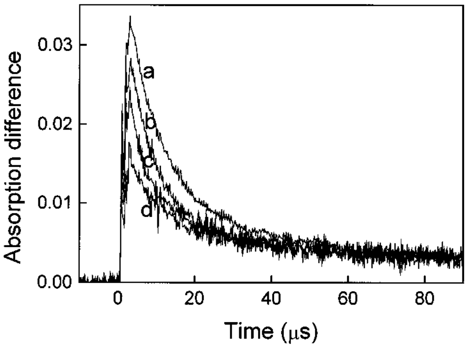
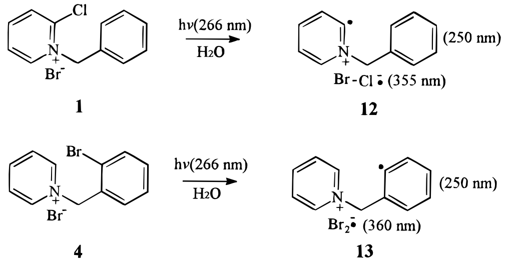


Figure 4. Transient absorption−time curve from the laser flash photolysis of **1** (1.4×10^{-4} M) in water under argon: curve a, the transient was monitored at 355 nm; curves b, c, and d monitored same way as above, but in the presence of 3.2×10^{-6}, 6.4×10^{-6}, and 6.4×10^{-5} M of potassium hexacyanoferrate(II), respectively.

Scheme 2



is suppressed in the presence of potassium hexacyanoferrate(II) (Figure 4). The same bromine chloride anion radical is also detected from the photolysis of **3** in aqueous solution. The behavior of the 360-nm transient from the photolysis of **2** or **4** is the same as the bromine chloride anion radical, and their lifetimes are shown in Table 1. The lifetimes of both bromine and bromine chloride anion radicals ranged from 9.3 to 10 μs.

Faria and Steenken[20] reported that an arylmethyl radical (benzyl type) and solvated electron (measured at 650 nm, $\lambda_{\max}$ 720 nm) were formed by laser photolysis of triphenylmethane and diphenylmethane in several solvents including aqueous acetonitrile. The reaction was described as a biphotonic process because of the quadratic dependence of the diarylmethyl radical yield on laser light intensity. The possibility of the photoionization of the pyridinium salts (**1**−**5**) was examined by DSO (500 MHz). No sign of the presence of hydrated electron has been detected in the 400−750-nm region. Therefore, the observation of halogen anion radicals and no sign of the photoionization imply that the primary process in the photolysis of the halopyridinium salts in the photohomolytic cleavage of aryl−halogen to give an aryl and halogen anion radicals (Scheme 2). The results of our studies on the pyridinium salts are different from those of Faria and Steenken, probably because the reaction conditions such as the wavelengths of lasers, electron affinities of reactants, solubilities of reactants, and solvents are different each from other.

Although the decay rate of the bromine chloride anion radical is independent of oxygen, its formation level taken 3 μs after laser pulse is a little lower in the presence of oxygen. This behavior could be attributable to the fact that the triplet state of **1** was quenched by oxygen.[21] Thus, it is suggestive that bromine chloride anion and aryl radicals are formed from both singlet and triplet states of **1**. The analogous oxygen effects for bromine anion radical formations from **2**, **3**, or **4** were also observed.

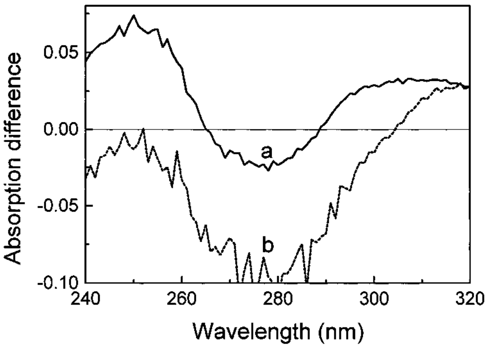


Figure 5. Effect of phenylnitrone addition on the transient absorption at 250 nm in the photolysis of the aqueous solution of **1** (1.2×10^{-4} M): (a) 300-μs delayed spectrum of **1** under argon, (b) the same spectrum as in a in the presence of *N*-*tert*-butyl-α-phenylnitrone (1.3×10^{-4} M).

Pyridinium Salt σ Radical (12). A strong 250-nm transient measured 3 or 300 μs after laser pulse for an aqueous solution of **1** was observed with its lifetime of 0.72 ms (Figure 2).

To confirm that the 250-nm transient is a radical species, the effect of *N*-*tert*-butyl-α-phenylnitrone, a spin trapping agent,[22] on the transient species was examined. The transient absorption spectra taken 300 μs after laser pulse for the aqueous solution of **1** under argon are shown in Figure 5. The phenylnitrone eliminates the species at 250 nm, indicating that the transient is a radical.

The absorption maxima of phenyl and hydroxyphenyl radicals have been reported to be 260 nm (**7**, $\epsilon = 630$ M^{-1} cm^{-1}) and 275 nm (**8**, $\epsilon = 1950$ M^{-1} cm^{-1}), respectively, in the pulse radiolysis of iodobenzene and bromophenol[15] (Chart 2).

Therefore, the 250-nm transient is assigned an *o*-pyridinium salt σ radical (**12**) from *N*-benzyl-2-chloropyridinium salt (**1**) (Scheme 2). As expected, the pyridinium salt σ radical disappears completely by saturation with nitrous oxide.[23] The 250-nm transient produced from the laser flash photolysis of **2** shows the identical properties as a pyridinium salt σ radical (**12**).

Phenyl Radical (13). A weak 250-nm transient taken 3 or 300 μs after laser pulse for the photolysis of aqueous solution of **4** is observed (Figure 3). The transient decays in a first-order process, and its lifetime is 1.4 ms (Table 1). In a preminary communication a very weak 283-nm transient was assigned for a phenyl radical.[1] The 283-nm transient absorption is a tail of a transient of the 240∼283-nm region because their lifetimes are identical. Photobleaching of the reactant ($\lambda_{\max} =$ 260 nm) interferes with the observation of the genuine phenyl σ radical.

Curve d in the inset of Figure 3 demonstrates the lack of the 250-nm transient absorption signal in the presence of the phenylnitrone. On the basis of the absorption wavelength and radical property, the 250-nm transient could be assigned as a *o*-phenyl σ radical (**13**) in Scheme 2 through the photohomolytic cleavage of the aryl−bromide of *N*-(2-bromobenzyl)pyridinium salt **4**. As expected, the phenyl σ radical was also eliminated by addition of nitrous oxide. The same transient absorption at 250 nm, phenyl radical, was also observed in the photolysis of an aqueous solution of **3**.

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(20) Faria, J. L.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 1924−1930.

(21) Since the fluorescence lifetime is too short to measure with nanosecond laser pulse excitation (*ca*. 6-ns pulse), it is not the singlet excited state that is influenced by the addition of oxygen in the system.

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(23) Unpublished result: the presence of nitrous oxide eliminates a phenyl radical-mediated reaction.

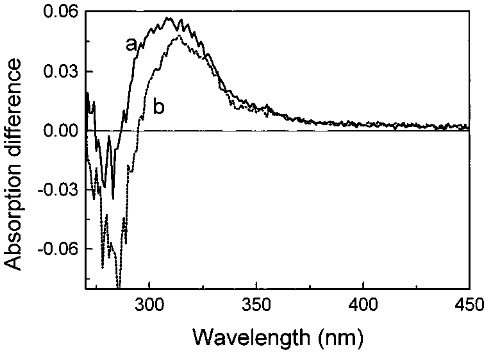


Figure 6. Transient absorption spectra: curve a (solid line), measured 300 μs after laser pulse for an aqueous solution of **2** (1.3×10^{-4} M) in water under argon; curve b (dash line), same as above but in the presence of *N*-*tert*-butyl-α-phenylnitrone (5.6×10^{-5} M).

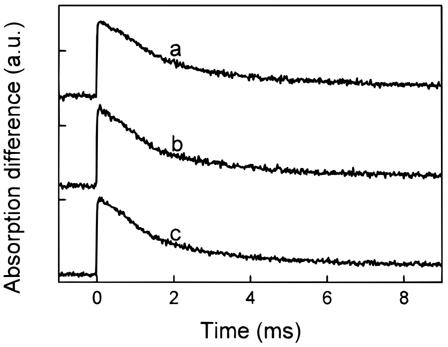


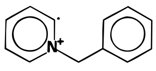
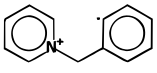
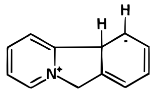
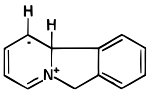
Figure 7. Temporal profile of a transient at 310 nm from the photolysis of **1** (1.5×10^{-3} M): curve a, under argon; curve b, under oxygen; curve c, under argon in the presence of cupric chloride (1.4×10^{-3} M).

A 2,3-Dihydrocyclohexadienyl Radical (14, Conjugated Radical). The 310-nm transient absorption signal from **2** was reduced by addition of the phenyl nitrone (Figure 6). The temporal profile of the 310-nm transient in the photolysis of **1** is shown in Figure 7. This transient shows the first-order decay with a lifetime of 1.2 ms (curve a in Figure 7). The lifetime was not much affected by the addition of oxygen or cupric ion, which are known as triplet quenchers.

The cyclohexadienyl radicals were observed in the reaction of monosubstituted benzene with an OH radical by the pulse radiolysis.[14] The reported absorption maxima of hydroxy-2,3-dihydrocyclohexadienyl (**9**), hydroxy-4-chloro-2,3-dihydrocyclohexadienyl (**10**), and hydroxy-4-iodo-2,3-dihydrocyclohexadienyl (**11**) radicals are 312, 322, and 318 nm, respectively (Chart 2). The reaction rate of 2-hydroxy-5-iodo-1,2-dihydrocyclohexadienyl radical (**11**) with oxygen is reported to be very slow (7×10^{6} M^{-1} s^{-1}).[15] This intermediate from **1** is less sensitive to the presence of oxygen than the previously reported radical **11**. Thus, the long-lived 310-nm transient from **1** is assigned as a 2,3-dihydrocyclohexadienyl radical (**14**) of pyrido[2,1-*a*]isoindolium salt. The 310-nm transient produced from **2** showed properties identical with that from **1** (Table 1).

Figure 8 shows the dependence of the 310-nm transient species on the photolysis laser pulse energy. The slope of the log−log plot for the transient absorption vs laser pulse energy was obtained to be 1.01. This result indicates that the 310-nm transient was formed by a single photon process and eliminates the possibility of the benzyl cation production by two-photon process.[20]

Table 1. Lifetime of Transient Intermediates

transient intermediates	λ_{max}/nm	lifetime	reactant
 **12**	250	0.72 ms	**1** **2**
 **13**	250	1.4 ms	**3** **4**
 **14**	310	1.2 ms	**1** **2**
 **15**	310	3.3 ms	**3** **4**
$Br{-}Cl^{\bullet -}$	355	9.3 μs	**1** **3**
$Br{-}Br^{\bullet -}$	360	10 μs	**2** **4**

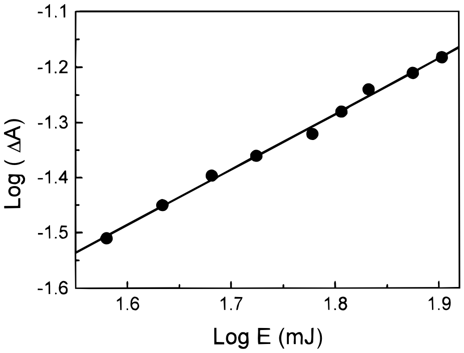


Figure 8. Dependence of the 310-nm transient concentration on the laser pulse energy in the photolysis of aqueous solution of **1** (1.2×10^{-4} M) under argon; the slope in the log−log plot is 1.01, indicating the monophotonic process of the 310-nm transient formation.

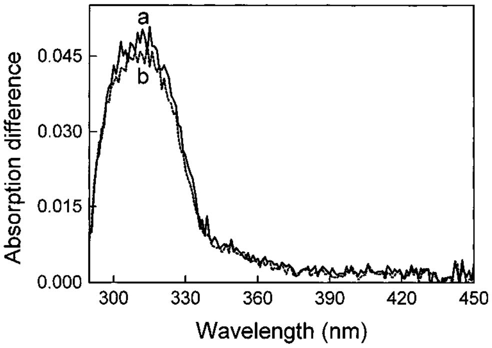


Figure 9. Oxygen effect on transient absorption at 310 nm: curve a, measured 300 μs after laser pulse for the aqueous solution (1.0×10^{-4} M) of **1** under argon; curve b, measured 300 μs after laser pulse for the same solution, but under oxygen.

The 310-nm transient absorption signal was decreased by the presence of oxygen (Figure 9). The quantum yield of the product (**16**) formation under argon was much higher than that under oxygen.[9] These observations imply that the precursor for the conjugated radical is partially quenched by oxygen dissolved in solution, and in turn, the radical is produced from both the singlet and triplet states of **1**.

A 2,3-Dihydropyridinium Salt π Radical (15). The transient absorption produced from **4** is shown in Figure 3. The 310-nm transient decays in first-order process with a lifetime of 3.3 ms (curve a in Figure 10). We believe that the 310-nm

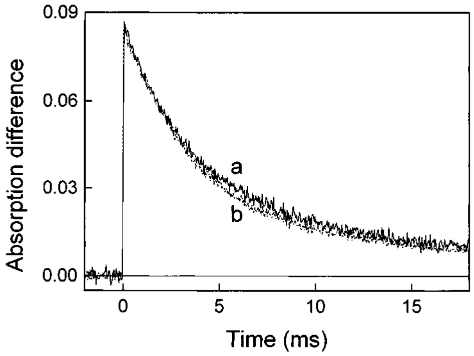


Figure 10. Temporal profile of the transient absorption at 310 nm in the photolysis of **4** and **6** under argon: (a) aqueous solution of **4** (1.5×10^{-4} M), (b) aqueous solution of **6** (1.3×10^{-4} M).

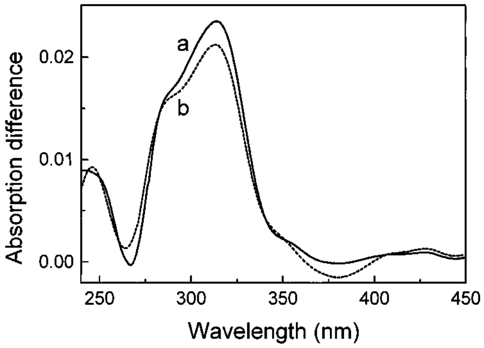


Figure 11. Oxygen effect on the formation of 2,3-dihydropyridinium π radical taken 300 μs after laser pulse for the aqueous solution of **4**: curve a, under argon; curve b, under oxygen.

transient is a 2,3-dihydropyridinium π radical of isoindolium salt because the lifetime is rather longer and the absorption region is same as that of hydroxy-2,3-dihydrocyclohexadienyl radical.

Figure 11 shows that the formation of a 2,3-dihydropyridinium π radical from the photolysis of **4** decreases under oxygen, compared with that under argon. This implies that the formation of the pyridinium π radical is blocked by quenching the triplet state of **3** by oxygen. From this result and the previous study in which product was formed, albeit inefficient, even under oxygen,[9] the 2,3-dihydropyridinium π radical is produced from both triplet and singlet states. The same behavior for the π radical from **3** is also observed.

A triplet quencher, methylviologen, was employed to obtain the Stern–Volmer plot in the steady-state photocyclization. The result is shown in Figure 12 for the pyridinium salt **1**. The decrease of the quantum yield with increased quencher concentration implies that the triplet state is involved in the reaction. If the quenching process is a diffusion-controlled reaction (6.4×10^9 M^{-1} s^{-1} in water[24]), we can calculate the triplet lifetime of **1** to be 5.8 μs from the slope of 3.7×10^4 M^{-1} ($K_Q\tau$). From this method, the lower limits of triplet lifetimes of **3** and **6** were also estimated to be 1.3 and 5.1 μs, respectively.

To see the deuterium isotope effect, a transient absorption spectra measured at 5- and 300-μs delay after laser pulse for the aqueous solution of *N*-(2-chlorobenzyl)perdeuteropyridinium salt (**6**) (1.2-L sample solution) were studied and are shown in Figure 13. At 5-μs delay after laser pulse, three peaks at about 280, 330, and 355 nm appeared, while at 300-μs delay, two peaks at about 280 and 310 nm remained.

The new transient around 330 nm is supposed to be generated from the product, isoindolium salt, by laser pulsing due to a less amount of the sample solution used (1.2-L sample solution). A 330-nm transient could be only seen when an old batch of **3** was excited by 266-nm laser light. Thus this is probably a benzyl-type radical of the photocyclized product, isoindolium salt.

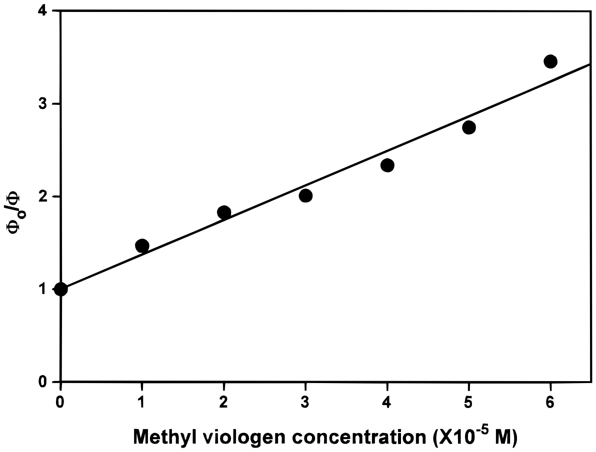


Figure 12. Stern–Volmer plot of the photocyclization of pyridinium salt **1** using the triplet quencher methylviologen.

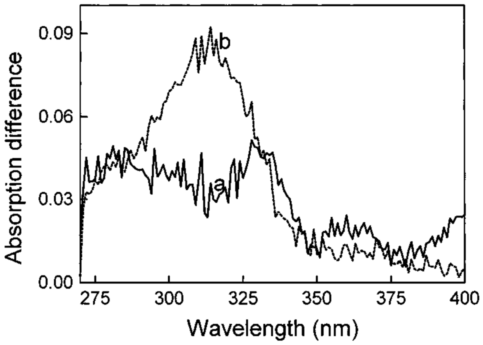


Figure 13. Transient absorption taken at 5 (a) and 300 μs (b) delay after the laser pulse for the aqueous solution of *N*-(2-chlorobenzyl)-perdeuteriopyridinium bromide (**6**) under argon. [The sample solution (1.2 L) is used.]

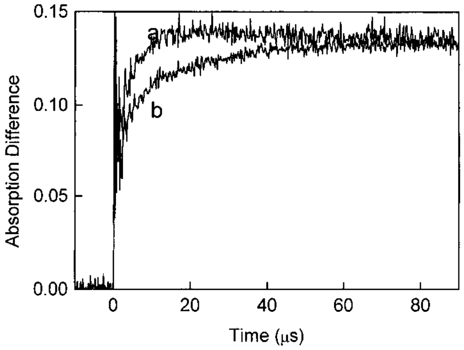


Figure 14. Temporal profile measured at 310 nm in the laser photolysis of **3** (curve a) and **6** (curve b) under argon.

It is noteworthy that the transient absorption at about 310 nm from **6** was much less pronounced at a 5-μs delay than that at a 300-μs delay. A similar behavior was also observed in the temporal profile measured at 310 nm for **3** (Figure 14). The rise time of a 2,3-dideuterioperdeuteriopyridinium π radical from **6** is longer than that of the corresponding radical from **3**. It may be due to the fact that the deuteropyridinium π radical originates from the long-lived triplet state as well as the singlet state of **6**. The triplet lifetime of deuteriopyridinium salt **6** (τ = 5.1 μs) was measured to be longer than that of the plain pyridinium salt **3** (τ = 1.3 μs) from the quenching experiment

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[24] Calvert, J. G.; Pitts, J. N. *Photochemistry*; John Wiley and Sons: New York, 1966; pp 627–627.

by using methylviologen. The longer rise time of the 310-nm transient from **6** than that from **3** indicates that the triplet state of the reactant is significantly involved in the generation of 310-nm transient species.

No difference in the lifetime of the 310-nm transient produced from the pyridinium or the perdeuteriopyridinium salts is measured (b curve in Figure 10). This implies that the hydrogen abstraction of 2,3-dihydropyridinium π radical by the chlorine radical or bromine chloride anion radical is so reactive that the abstraction does not differentiate the deuterated π-radical from the plain radical.

The Mechanism. A photohomolytic radical mechanism is obviously involved in the photocyclization of the pyridinium salts, since pyridinium σ, phenyl σ, 2,3-dihydrocyclohexadienyl π, 2,3-dihydropyridinium π, and halogen anion radicals are directly observed. From the consideration of detected intermediates and power dependence of product formation, the mechanism involving electron transfer and radical anion decomposition in the photocyclization[10,11,25] could be discarded. If this mechanism operated, the photoreduced and/or photosubstituted products would be obtained. For the pyridinium salt (**1**−**4**), only photocyclized product is obtained.

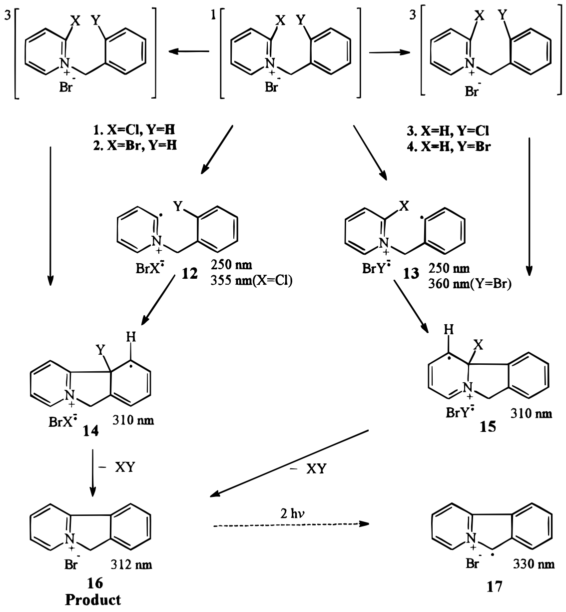
On the basis of detecting the transients involved, a quenching experiment by methylviologen, the effect of oxygen on the product quantum yield,[9] and the deuteration effect, we suggest that both singlet and triplet states are involved in the reaction and propose the following reaction mechanism (Scheme 3).

The singlet state of the pyridinium salts (**1**, **2**, **3**, or **4**) is populated by excitation of laser pulse or steady-state light illumination. The singlet state undergoes either homolytic cleavage of the aryl−halogen bond to give a phenyl or pyridinium σ radical (**12**, **13**, 250 nm) and halogen anion radical, or the triplet state via intersystem crossing. The phenyl or pyridinium σ radicals can be generated from the triplet state (in the cases of **2** and **4**). The aryl radicals proceed to a 2,3-dihydropyridinium or 2,3-dihydrocyclohexadienyl π radical (**14**, **15**) in which hydrogen abstraction by the halogen radical produces the cyclized product, isoindolium salt **16**. The conjugated radical can be directly formed from the triplet state probably via a π-complex in the case of **1** or **3** because the triplet energy is not enough to cleave the aryl−Cl bond. A benzyl-type radical (**17**, 330-nm transient) of the photocyclized product can be generated by a biphotonic process or hydrogen ejection of the product with a radical. The investigation on the formation and the properties of the transient intermediates from products are being studied and will be reported later.

Conclusions

Some transient intermediates, pyridinium σ, 2,3-dihydrocyclohexadienyl, and halogen anion radicals, are detected in the laser flash photolysis of *N*-benzyl-2-halopyridinium bromide (**1** or **2**) in Ar-purged water. The absorption maxima of pyridinium σ, 2,3-dihydrohexadienyl, and bromine chloride anion radicals are 250 (τ = 0.72 ms), 310 (τ = 1.2 ms), and 355 (τ = 9.3 μs) nm, respectively.

Scheme 3



Some transient species, phenyl, 2,3-dihydropyridinium σ, and halogen anion radicals, are observed from the laser flash photolysis of *N*-(2-halobenzyl)pyridinium bromide (**3** or **4**) in Ar-purged water. The absorption maxima of phenyl, 2,3-dihydropyridinium π, and halogen anion radicals are 250 (1.5 ms), 310 (τ = 3.3 ms), and 360 nm (τ = 10 μs) (in the case of $Br_2^{\bullet-}$), respectively.

Direct observations of the radical intermediate generated by laser flash excitation of the haloarene tethered arene (**1**, **2**, **3**, or **4**) in water support the mechanism of photohomolytic bond cleavage followed by radical arylation and hydrogen ejection in the photocyclization reaction.

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(25) Chesta, C. A.; Cosa, J. J.; Previtali, C. M. *J. Photochem.* **1986**, *32*, 203−215.