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The Mechanism of the Photocyclization of N-(2-Haloarylmethyl) pyridinium and N-(arylmethyl)-2-Halopyridinium Salts

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The photochemical and photophysical properties of N-(2-haloarylmethyl)pyridinium, N-(arylmethyl)-2-halopyridinium, N-(2-haloarylmethyl)-2-halopyridinium salts and N-(2-halobenzyl)-isoquinolinium salt are studied. The pyridinium salts phototocyclize to afford isoindolium salts, while the isoquinolium salts do not. In thc photocyclization of N-(2-chlorobenzyl)-2-chloropyridinium salts, pyrido[2,1-a]-4-chloroisoindolium salt is formed by the cleavage of chlorine of pyridinium ring. This indicates that the excited moiety is not the phenyl ring, but the pyridinium ring. The triplet states of the pyridinium salts are believed to be largely involved in the photocyclization, since oxygen retards most of the reaction. Some assistance of a π-complex between the excited chlorine moiety of the salt and phenyl plane of the same molecule is required to explain the reactivity of the salts. N-(Benzyl)-2-chloro-pyridinium salt is two times more reactive than N-(2-chloro-benzyl)pyridinium salt. N-(Benzyl)-2-chloropyridinium salt can form π-complex effectively because of the electron-rich phenyl group. The π-complex affords an intermediate, phenyl radical by cleaving the chlorine atom. The photocyclized product, isoindolium salt is obtained by losing the hydrogen atom from the phenyl radical. The reactive pyridinium salts **1a**, **2a** and **3a** have a low fluorescence quantum yield (Φ_F<0.01) and a higher triplet energy (E_T>68 kcal/mole) than the unreactive quinolinium salt. The unreactivity of isoquinolinium salt can be understood in relation to its high fluorescence quantum yield and its low triplet energy (E_T= 61 kcal/mole).

Introduction

Photocyclization of 1-styrylpyridinium salts,[1] N-benzyl-(2-halobenzyl)amines,[2] and 2-chlorobenzanilides[3,4] are useful and convenient method for syntheses of N-heterocyclic compounds. We have been interested in the intramolecular photocyclization of N-arylmethyl-2-chloropyridinium salts[5] and N-(2-haloarylmethyl)-2-halopyridinium salts because the reaction can be used for heterocyclic compound syntheses. Only a little work has been done in this field.

Forzard and Bradsher[6] reported that an aqueous solution of 2-bromo-N-benzylpyridinium salt and N-(2-bromobenzyl) pyridinium salt, on irradiation with ultraviolet, cyclize intramolecularly to afford pyrido [2,1-a]isoindolium salt. Lyle and his collaborators[7] reported that an aqueous solution of N-(2-halobenzyl)-pyridinium salt could be photocyclized, while 1-(2-halogeno-3-quinolylmethyl)pyridinium salt which is electron-deficient in both aromatic rings could not. However, no mechanistic study of these salts has been done.

Here we report the photocyclizations of N-(2-halobenzyl)-2-halopyridinium salts, their reaction mechanisms, and the photophysical properties of the salts.

Results and Discussion

Preparative Photocyclization. When an aqueous solution of N-(2-chlorobenzyl) pyridinium bromide (0.013 M, **2a**) was irradiated with a high pressure Hg lamp, the intramolecular photocyclized product, isoindolium salt (**1b**) was obtained. The reaction was followed by the increasing absorption peak at 312 nm (see Figure 1, 2). It seems that the photocyclization is only reaction because of being observed the isosbestic point in UV absorption change of **2a** in water by monochromatic light (260± 5 nm). In methanol or ethanol, photocyclization of the salt fails. The aqueous solution of salt, **1a**, affords **1b** using the above condition.[5]

In order to study the relative reactivity of halogen atoms on both aromatic rings of the pyridinium salts, N-(2-chlorobenzyl)-2-chloropyridinium salt (**3a**) and N-(2-bromobenzyl)-2-bromopyridinium salt (**4a**) were prepared. In the photochemical reaction of the salt **3a** or **4a**, two possible products, **3b** and **3c** or **4b** and **4c** could be formed depending on which halogen atom is eliminated. Only pyrido [2,1-a]-4-chloroisoindolium bromide (**3b**), which chlorine atom of pyridinium ring is cleaved, was formed when the aqueous solution of

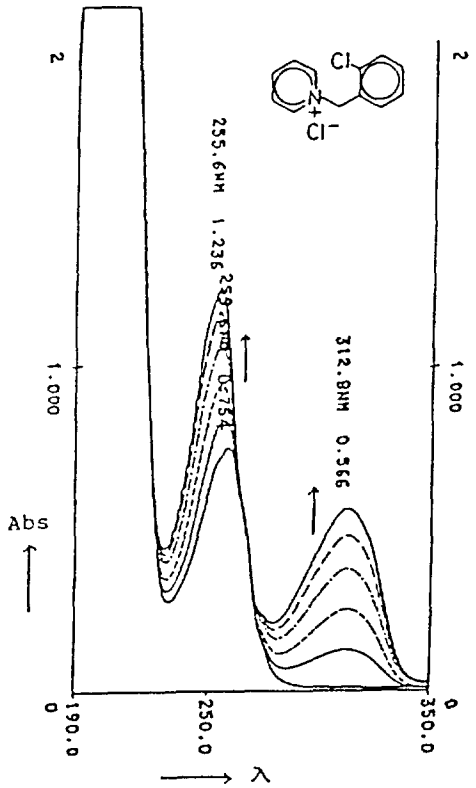


Figure 1. UV absorption change of N-(2-chlorobenzyl)-pyridinium salt, **2a** in water by monochromatic light (260± 5 nm) irradiation.

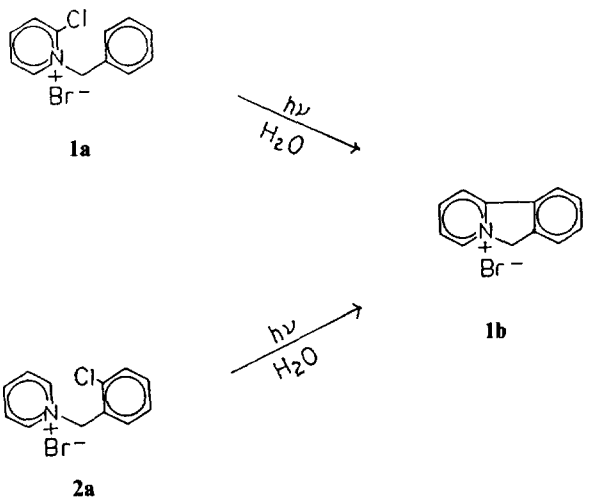


Figure 2. Intramolecular photocyclization N-(benzyl)-2-chloropyridinium(**1a**) and N-(2-chlorobenzyl)pyridinium salts(**2a**).

the salts **3a** was irradiated using the above condition (Figure 3).

The proton resonance at δ 9.40 (d, J=6 Hz, 1H) indicates that the product has the structure **3b** and not **3c** (Figure 3 and 4). The splitting pattern and coupling constant at δ, 8.57 (t, J=9 Hz, 1H) and at δ, 8.43 (d, J=9 Hz, 1H) indicate 7-proton and 6-proton respectively. The doublet of doublet peaks at δ, 8.08 (dd, $J_{1,2}$=6.0 Hz, $J_{1,3}$=1.4 Hz, 1H) are assigned to the proton on C-1 and a triplet at δ, 7.97 (t, J=6 Hz, 1H) is assigned to the proton on C-2. A triplet at δ,

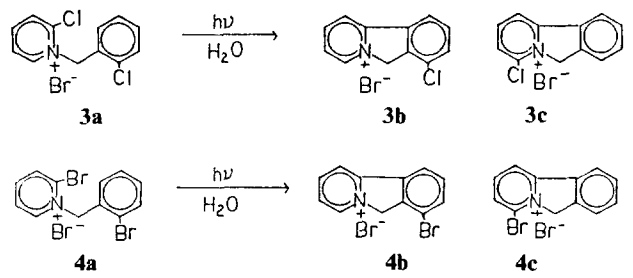


Figure 3. Intramolecular photocyclization of N-(2-halobenzyl)-2-halopyridinium salts (**3a** and **4a**).

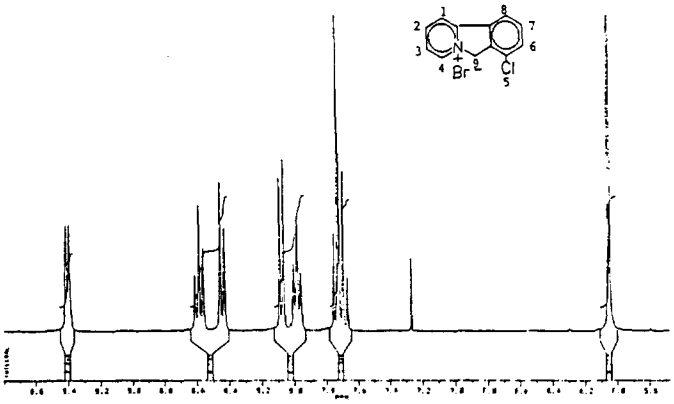


Figure 4. Proton NMR spectrum, at 300 MHz, in TFA−D+ $CDCl_3$, of isoindolium salt, **3b**.

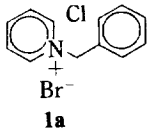
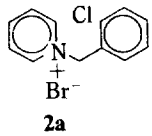
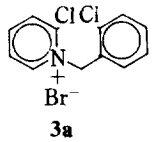
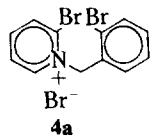
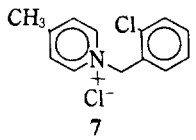
7.66 (t, J=6 Hz, 1H), a somewhat high field, indicates the proton on C-3, while double doublets at δ, 7.74 (dd, $J_{7,8}$=9 Hz, $J_{7,9}$=1.4 Hz, 1H) indicate the proton on C-8. Molecular ion peaks at m/e, 203 (M^+ −1, ^{37}Cl, 33%), and 201 (M^+ −1, ^{35}Cl, 100%) in mass spectra indicate the structure of **3b**.

This result indciates that the excited moiety is not the phenyl ring, but the pyridinium ring. Pyrido [2,1-a]-4-bromoisoindolium bromide **4b** was obtained in the photochemical reaction of **4a** (Figure 3, see experimental section for the identification). N-(β-naphthylmethyl)-2-chloropyridinium salt[5] was photocyclized to give benzo [g]-pyrido [2,1-a] isoindolium perchlorate but not benzo [f] pyrido [2,1-a] isoindolium perchlorate using the above condition. However, N-(2-chlorobenzyl) isoquinolinium salts were unreactive using the above condition.

Mechanistic Study. To study the excited state of intramolecular photocyclization of N-(halobenzyl) pyridinium and N-(benzyl)-2-halopyridinium salt, the effect of oxygen on the reaction was examined. In the presence of oxygen, the quantum yield of the photocyclization formation of the isoindolium salts was much lower than in the absence of oxygen. Since oxygen is a triplet quencher, the triplet excited states of the haloarylmethylpyridinium and arylmethyl-1-halopyridinium salts seem to be largely involved in the photocyclization (see Table 1). Some photocyclizations proceed even in the presence of oxygen. Probably the photocyclization reaction can not be quenched completely.

To study the effect of substituents of both aromatic rings of the salts, the relative rate of the photocyclization of several pyridinium salts were measured and shown in Table 1.

Table 1. Quantum Yield of Intramolecular Photocyclization of Several Pyridinium Salts in the Presence of Oxygen and in the Absence of Oxygen. Relative rate of the Photocyclization of the Pyridinium Salts in Water

Reactants	Φ without O_2	Φ with O_2	Relative rate
 **1a**	0.22	0.066	2.2
 **2a**	0.10	0.066	1.0
 **3a**	0.60	0.03	6.1
 **4a**	0.98	0.10	10.0
 **7**	0.13	0.07	1.3

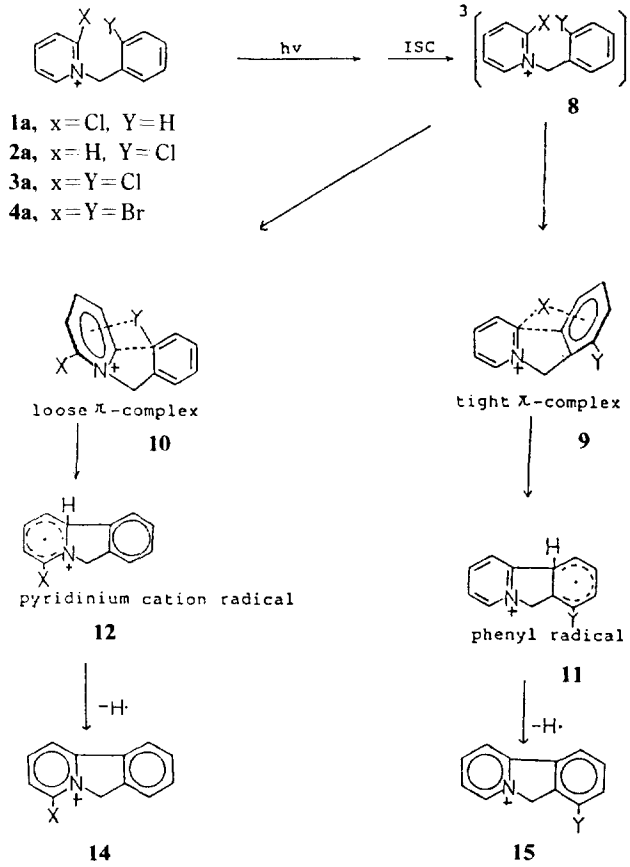


Figure 5. Mechanistic pathway of intramolecular photocyclization of N-(2-haloarylmethyl) pyridinium and N-(benzyl)-2-halo-pyridinium salts.

The pyridinium salt **1a** has a higher reaction rate then **2a**. Comparing **2a** and **3a**, **3a** is 6 times more reactive then **2a**. These results are consistent with the observation of the product of preparative photocyclization of **3a**. The pyridium salt **4a** is more reactive than **3a** in the photocyclization.

Two explanations are possible for the relative reaction rate. The easier the triplet is formed through intersystem crossing in photoexcited **3a** and **4a**, because of halogen atom effect, the more reactive the reactants are. However, the triplet energy of **2a** and **4a**(80 and 76 kcal/mole respectively, see below) is not enough to cleave a halogen atom form an aromatic ring (97 and 82 kcal/mole) for bond energy of Ar-Cl and Ar-Br respectively).

Thus some assistance of π-complexation of the halogen moiety of the aromatic ring with another aromatic ring for the halogen cleavage is necessary. Similar explanation of π-complex formation for the photocylcization of 2-chlorobenzanilides was given by Grimshaw and de Silva.[9] The excited state of **1a**(or **3a**) can form a tighter π-complex between the chlorine of the pyridinium ring with the phenyl ring than **2a** in which the chlorine of phenyl ring should form π-complex with electron poor pyridinium ring. A possible mechanism of the photocyclization is shown in Figure 5. The triplet state of the salt is populated *via* intersystem crossing. The triplet state **8** can form a tight of loose π-complex **9** or **10** depending on the electron availability. The tight π-complex **9** loses the halogen to give a phenyl radical **11**, while the loose π-complex **10** loses halogen to give a pyridinium radical cation **12**. Both the intermediates can afford isoindolium salts **13** and **14** by losing the hydrogen atoms. The salts **3a** and **4a** can form π-complex effectively and in turn are more reactive. The chlorine group on the phenyl ring assists the photocyclization. Probably the chlorine group on the phenyl ring assists the formation of the π-complex between the excited chlorine moiety of the pyridinium ring and the phenyl plane with the chlorine group, and in turn, assists the detachment of the chlorine atom from the pyridinium ring. The introduction of a methyl group on the phenyl ring of **2a** enhances the reactivity because of the electron donation of the methyl group for π-complex formation (see, **7** in Table 1). According to Portlock and his collaborators,[7] electron-deficient 1-(2-halo-3-quinolylmethyl) pyridinium salt could not photocyclize. However, N-(2-chlobenzyl)-2-chloropyridinium salt **3a**, which is electron-deficient, is three times more reactive than **1a**. Unreactive behavior of 1-(2-halo-3-quinolymethyl) pyridinium salt[7] for the photocyclization could be explained by intramolecular quenching of the excited state by the quinolylmethyl moiety. We observed that N-(2-chlorobenzyl) isoquinolinium salt can not undergo photocyclization and it is believed that the triplet energy state is too low to cleave the chlorine atom from the phenyl goup (see below).

Photophysical Properties. The UV absorption spectra of several pyridinium salts and isoquinolinium salt in water

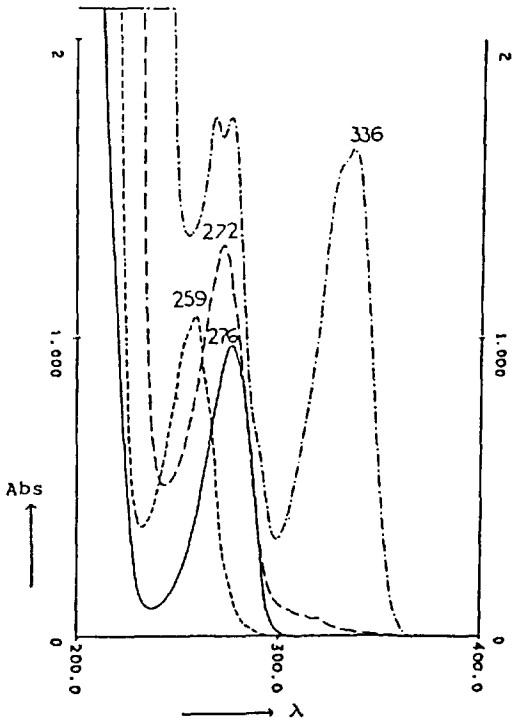


Figure 6. The absorption spectra of N-(2-haloarylmethyl)-pyridinium, N-arylmethyl-2-halopyridinium salts and N-(2-haloarylmethyl) isoquinolinium salt in wter. **1a**; ——, **2a**; ---------, **5a**; — — —, **6**; — · — · —.

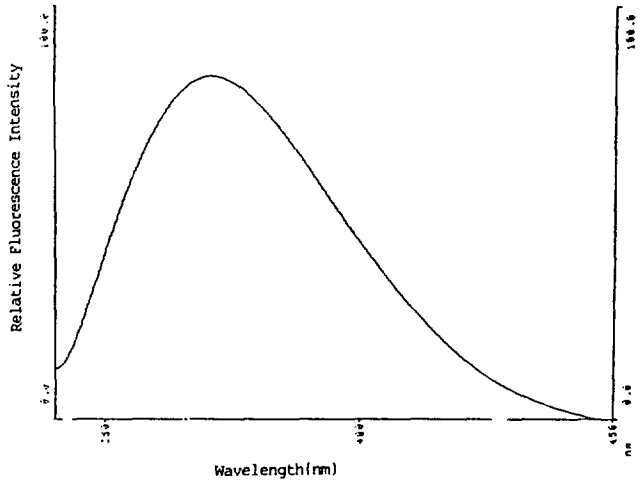
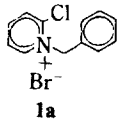
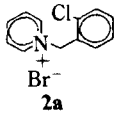
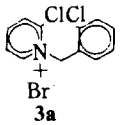
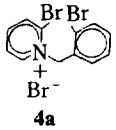
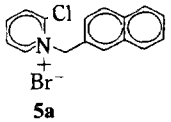
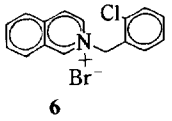


Figure 7. Fluroescence emission spectra of N-(2-chlorobenzyl)-pyridinium salt (0.1 mM) in water. The excitaion wavelength was 260 nm. The optical density was 0.39 at 260 nm.

are shown in Figure 6. The maximum absorption of **1a**, **2a**, **3a**, **4a**, **5a** and **6** are 275.8, 259.6, 275.0, 277.8, 274.0 and 337.0 nm, respectively. The salt, **1a** absorbs a rather longer wavelength light than **2a** (see Table 2).

Fluorescence emission spectra of **1a**, **2a**, **3a**, **4a** and **6** could be observed in solution, but not for compound **5a** (detection limit $\Phi_F < 10^{-5}$). The very low quantum yield of fluorescence for the pyridinium salt, **4a** (2×10^{-4}) is understandable in term of the heavy atom effect of bromine. An example is shown in Figure 7. The maximum fluorescence emission and

Table 2. Photophysical Properties of N-(2-Haloarylmethyl)pyridinium, N-(arylmethyl)-2-Halopyridinium, N-(2-Haloarylmethyl)-2-Halopyridinium and N-(2-Haloarylmethyl)isoquinolinium Salts

Compound structure (number)	Absorption max (nm, log) in H_2O	Fluorescence max(nm) in H_2O	Φ_F in H_2O	E_T kcal/mole	τ_p msec at 77 K in ETOH
 **1a**	*275.8 (3.89)	372	0.01	78	1.4
 **2a**	259.6 (3.59)	371	0.01	80	3.0
 **3a**	275.0 (3.85)	364	0.01	75	2.1
 **4a**	277.8 (3.99)	378	2×10^{-4}	76	2.3
 **5a**	274.0 (4.04)	unable to measure	unable to measure	68	1.4
 **6**	337.0 (3.57)	383	0.4	61	1.1

*in acetone .

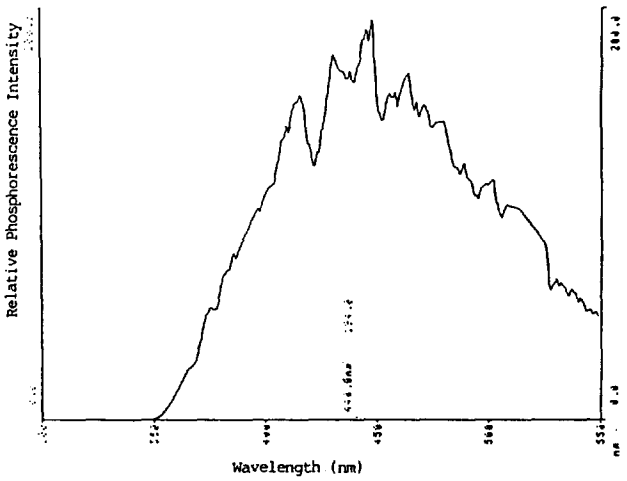
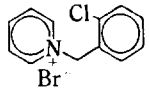
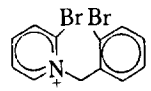


Figure 8. Phosphorescence emission spectra of N-(2-chlorobenzyl)-pyridinium salt (0.5 mM) in ethanol at 77 °K. The exciting wavelength was 270 nm. The optical density was 0.8 at 270 nm.

the quantum yield of **1a**, **2a**, **3a**, **4a**, **5a** and **6** are shown in Table 2. The reactants prone to intramolecular photocycli-

Table 3. Spctroscopic Properties of Pyridinium Salts and Isoquinolinium Salt

Compound	^{1}H-NMR	MS	UV	IR
	TFA-D *vs* TMS in ppm	M/e, intensity	λ_{max} logε	KBr, cm^{-1}
 **2a** mp. 83-84℃	6.0(s, 2H, CH_2) 7.5(m, 4H, Ar) 8.1(t, J=6.3 Hz, 2H, β-H) 8.6(m, 1H, γ-H) 8.8(d, J=6.3 Hz, 2H, δ, α-H)	206(M^++2) 204(M^+, 7%) 127($C_7H_6{}^{37}Cl^+$, 30%) 125($C_7H_6{}^{35}Cl^+$, 100%)	259.6 (3.59)	3100 3040 2920 1620 1582 1480 750 680
 **3a** mp. 131-133℃	6.3(s, 2H, CH_2) 7.3-7.6(m, 4H, Ar) 8.1(t, J=6.3 Hz, 1H) 8.3(d, J=6.3 Hz, 1H) 8.7(t, J=6.3 Hz, 1H) 9.3(m, 1H)	208($C_7H_6ClBr^+$, 3%) 206($C_7H_6ClBr^+$, 13%) 204($C_7H_6ClBr^+$, 10%) 127($C_7H_6{}^{37}Cl^+$, 33%) 125($C_7H_6{}^{35}Cl^+$, 100%)	275.0 (3.85)	3110 3050 3000 2950 1610 1560 1450 795 750
 **4a** mp. 143-145℃	6.1(s, 2H, CH_2) 7.4-7.8(m, 4H, Ar) 8.1(t, J=6.3 Hz, 1H, γ-H) 8.4(d, J=6.3 Hz, 2H, β-H) 8.6(d, J=6.3 Hz, 1H, α-H)	329(M^+-H^{81}Br, 15%) 328(M^+, 40%) 327(M^+-H^{79}Br, 15%) 171($C_7H_6{}^{81}Br^+$, 100%) 169($C_7H_6{}^{79}Br^+$, 100%)	277.8 (3.99)	3113 3074 3028 2931 1631 1608 1566 1492 1465 1442 775 667
 **6** mp. 125-127℃	6.5(s, 2H, CH_2) 7.4(m, 4H, phenyl) 8.5(m, 5H, isoquinoline H) 8.7(m, 2H, α-H on isoquinoline)	129($C_9H_7N^+$, 55%) 127($C_7H_7{}^{37}Cl^+$, 23%) 125($C_7H_7{}^{35}Cl^+$, 59%)	269.0 (3.85)	3093 3078 3028 2993 2972 1647 1624 1473 829 763

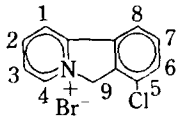
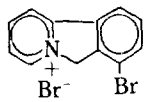
zation [**1a**, **2a**, **3a**, **4a**, **5a**] show little or no fluorescence emission, while nonreactive salt **6** shows strong fluorescence emission.

Phosphorescence emission spectra of **1a**, **2a**, **3a**, **4a**, **5a** and **6** at 77 °K in ethanol were obtained and an example is shown in Figure 8. The triplet energy was calculated from the spectra and is shown in Table 2. The triplet energy of the reactive salts for the photocyclization are relatively higher (more than 68 kcal/mole) than that of the nonreactive salt **6**. The absence of photocyclization of isoquinolinium salt **6** could be understood in relation to high fluorescence emission quantum yield (loss of excited state energy) and low triplet energy (61 kcal/mole). The triplet life time of **1a**, **2a**, **3a**, **4a**, **5a** and **6** at 77 °K in ethanol were also measured and shown in Table 2. The triplet life times of the salts are similar.

Experimental

General Method

Table 4. Spectroscopic Properties of Photocyclized products, Isoindolium Salts

Compound	^{1}H-NMR	MS	UV	IR
	TFA-D *vs* TMS in ppm	M/e, intensity	λ_{max} logε H_2O	KBr, cm^{-1}
	6.04(s, 2H, CH_2)**	203(M^+-H, ^{37}Cl, 33%)	251.4	3075
	7.66(t, J=6.0 Hz, 1H, 3-H)	201(M^+-H, ^{35}Cl, 100%)	(4.08)	3045
	7.74(dd, $J_{7,8}$=9.0 Hz, $J_{6,8}$=1.4 Hz, H, 8-H)		308.8	2900
	7.97(t, J=6.0 Hz, 1H, 2-H)		(4.09)	2873
3b	8.08(dd, $J_{1,2}$=6.0 Hz, $J_{1,3}$=1.4 Hz, 1H, 1-H)			1623
	8.43(d, J=9.0 Hz, 1H, 6-H)			1603
	8.57(t, J=9.0 Hz, 1H, 7-H)			1450
	9.40(d, J=6.0 Hz, 1H, 4-H)			765
	5.91(s, 2H, CH_2)	247(M^+-H, ^{81}Br, 100%)	257.6	3074
	7.65(t, J=7.5 Hz, 1H, 3-H)	245(M^+-H, ^{79}Br, 100%)	(3.96)	3043
	7.93(d, J=8.3 Hz, 1H, 8-H)	166(80%)	309.2	2874
	7.97(t, J=7.5 Hz, 1H, 2-H)		(3.97)	1628
4b	8.13(t, J=7.5 Hz, 1H, 1-H)			1570
	8.43(d, J=8.3 Hz, 1H, 6-H)			1492
	8.62(t, J=8.3 Hz, 1H, 7-H)			1450
	9.14(d, J=6.3 Hz, 1H, 4-H)			772

* 300 MHz ^{1}H-NMR. **TFA-D+$CDCl_3$.

Nuclear magnetic resonance (NMR) spectra were measured in CF_3COOD(TFA-D) and $CDCl_3$ on Bruker-80 MHz or Bruker-300 MHz spectrometers. Mass spectra were determined on Karatos MS 25 RFA at 50 or 70 eV. Infrared spectra were obtained from sample in KBr on Jasco, IR A_3.

Preparative photochemical reaction was carried out in a water-cooled quartz immersion well apparatus with circulating N_2 using 200 W Hg lamp (Hanovia, high pressure). Determination of relative rates of intramolecular photocyclization of the pyridinium salts were accomplished in quartz UV cuvette with long neck (1 cm path) using 5 nm band pass monochromatic light from Shimazu Bausch and Lomb Monochromater Grating 1200 equipped with Xe-lamp (500 W). To see oxygen effect on the relative rate of photocyclization, oxygen or Ar was introduced into the sample in UV cuvette with long neck. The absorption change of the sample in the UV cuvette by irradiation was checked. Light intensities at each excitation wavelength used were determined by actinometry with ferrioxalate actinometry.[8]

Syntheses of Pyridinium Salts

The pyridinium salts were prepared by nucleophilic substitution reaction of substituted aryl halide with appropriate pyridine derivatives by the reference method.[7] In a typical experiment 6.3 g (0.05 mole) of benzyl chloride and one mole equivalent of pyridine were dissolved in 10 m*l* sulfolane and stirred at room temperature for 1 day. Some white crystals typically came out of solution. The crystals were filtered, washed with ether and recrystallized from acetonitrile and ether. The following pyridinium salts were prepared. Their spectroscopic properties are shown in Table 3.

N-benzyl-2-chloropyridinium bromide(1a). This compound was obtained in a yield of 43%, white needle crystal, mp. 142-143℃.

N-(2-chlorobenzyl) pyridinium bromide(2a). This compound was obtained in a yield of 74%, white plate crystal, mp. 83-84℃.

N-(2-chlorobenzyl)-2-chloropyridinium bromide(3a). This compound was obtained in yield of 41%, white plate crystal, mp. 132-133℃.

Anal. Calcd. for $C_{12}H_{10}NCl_2Br$: C, 45.18; H, 3.16; N, 4.39. Found: C, 45.09; H, 3.18; N, 4.27.

N-(2-bromobenzyl)-2-bromopyridinium bromide(4a). This compound was obtained in a yield of 58%, white crystal, mp. 144-145℃.

Anal. Calcd. for $C_{12}H_{10}NBr_3$: C, 35.33; H, 2.47; N, 3.43. Found: C, 35.11; H, 2.50; N, 3.31.

N-(β-naphthylmethyl)-2-chloropyridinium bromide(5a). This compound was obtained in a yield of 39%, white solid, mp. 139-140℃.[5]

N-(2-chlorobenzyl) isoquinolinium bromide(6). This compound was obtained in a yield of 60%, white crystal, mp. 126-127℃.

Anal. Calcd. for $C_{16}H_{13}NClBr$: C, 57.43; H, 3.91; N, 4.19. Found: C, 57.18; H, 3.97; N, 4.08.

N-(2-chlorobenzyl)-4-methylpyridinium chloride(7). This compound was obtained in a yield of 71%, white crystal, mp. 208-209℃ (lit 208-209.5℃).[7]

The spectroscopic properties and melting points of the pyridinium salts (**2a**, **3a**, **4a**) and isoquinolinium salt (**6**) are given in Table 3 and the salts, **1a**, **5a** and **7** were identical those which already were reported.[5]

Photocyclization of The Pyridinium Salts

Into a 500 m*l* water-cooled quartz immersion well apparatus were introduced 3 g (0.013 M) of **2a** and 450 m*l* of triple distilled water. The mixture was irradiated for 6 hrs with Hg-lamp (Hanovia 200 W, High pressure) under nitrogen. The reaction was followed by increasing of a new absorption peak at 312 nm. The mixture was evaporated to about 10

ml, decolorized by addition of active carbon and then recrystallized in ethanol by addition of ethyl acetate. The resulting white needles [Yield, 0.5 g, 20%, mp. 207-209℃[5,7]] were pyrido [2,1-a]isoindolium bromide (**1b**). The other photocyclization reactions have been done using the above condition.

Synthesis of pyrido [2,1-a]-4-chloroisoindolium bromide 3b. Pyrido [2,1-a]-4-chloroisoindolium bromide **3b** was obtained in a yield 25%, light brown crystal, mp. 250℃ decompose.

Anal. Calcd. for $C_{12}H_9NClBr$: C, 51.01; H, 3.21; N, 4.96. Found: C, 50.90; H, 3.23; N, 4.90.

Synthesis of pyrido [2,1-a]-4-bromoisoindolium bromide 4b. Pyrido [2,1-a]-4-bromoisoindolium bromide **4b** was obtained in a yield of 17%, light brown crystal, mp. 250℃.

Anal. Calcd. for $C_{12}H_9NBr_2$: C, 44.07; H, 2.77; N, 4.28. Found: C, 44.05; H, 2.86; N, 3.98.

The spectroscopic properties and mp. of the photocyclized indolium salts are shown in Table 4.

Photophysical Properties

UV spectra were recorded on Shimadzu UV-260. Fluorescence emission spectra were recorded on Hitachi F-3000 Fluorescence Spectrophotometer. The quantum yield, Q_x of the sample x was determined using the following equation.

$$Q_x = \frac{I_x Q_s (1-10^{-As})}{I_s (1-10^{-As})}$$

Where Q_s is quantum yield of the standard, I_x and I_s are the integrated fluorescence intensities in wavenumber of the sample and standard, respectively, and A_x and A_s are the absorbance of each solution at the exciting wavelength. Triptophan quantum yield of 0.2 in water was used as the standard.

For the measurement of phosphorescence emission spectra and decay curves of phosphorescence, Hitachi F-3000 Fluorescence Spectrophotometer with phosphorescence accessories was used. In spectra mode for measuring phosphorescence spectra, the exciting radiation is chopped into a succession of pulses and the phosphorescing component that appears due to excitation is measured through the sampling gate electrically controlled in synchronization with chopper rotation. In decay curve mode, phosphorescence decay is assumed to be identical at each beam chopping. The sequence signifies that different segments of a decay curve are sampled. The measured signals are smoothed to translate the rapid phenomena of phosphorescence decay into a slower form. Thus a decay curve can be plotted on the recorder. A phosphorescence life time means a period of time until the phosphorescence intensity $I_{a.c}$ is reached with respect to an arbitrary point. All measurement of phosphorescence spectra and decay curves were carried out at liguid nitrogen temperature in ethanol.

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