Intramolecular Photocyclization of *N*-[(2-Haloaryl)methyl]pyridinium and *N*-(Arylmethyl)-2-halopyridinium Salts

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Various *N*-[(2-haloaryl)methyl]pyridinium, *N*-(arylmethyl)-2-halopyridinium and *N*-(2-halobenzyl)isoquinolinium salts have been synthesized and their intramolecular photocyclization reactions studied. Upon irradiation the aqueous solution of *N*-[(2-haloaryl)methyl]pyridinium, and *N*-arylmethyl-2-halopyridinium salts **1**, **2** were cyclized to give isoindolium salts. In contrast to the pyridinium salts **1**, **2**, the aqueous solution of *N*-(2-halobenzyl)isoquinolinium salts **3** appear not to undergo photocyclization. *N*-Benzyl-2-chloropyridinium salts **1c** is more reactive than *N*-(2-chlorobenzyl)pyridinium salt **1a** in the photocyclization. *N*-(2-Chlorobenzyl)-2-chloropyridinium salt **1d** is three times more reactive than **1c**. A mechanism of π-complex formation of the halogen moiety of the pyridinium ring with the phenyl ring is suggested for the reactive pyridinium salt. The triplet energy of the isoquinolinium salts **3** is tool low to photocyclize.

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Introduction.

The intramolecular photocyclization of iodostilbene [1], iodobenzyltetrahydroisoquinoline [1], 2-iododibenzylamine derivatives [2] and aryl halides [3] are useful for aromatic ring formation.

Fozard and Bradsher described that aqueous solution of 2-bromo-*N*-benzylpyridinium salt was photocyclized intramolecularly to give pyrido[2,1-*a*]isoindolium salts [4]. The isoindolium salt, on treatment with sodium carbonate afforded the pyrido[2,1-*a*]isoindole of the pseudo-aromatic system. The isoindolium salts were condensated with aryl aldehydes to afford benzylidene derivatives [4]. Lyle and his collaborators [5] reported that the 1-(2-chlorobenzyl)-pyridinium salt were photocyclized, but that 1-(2-halo-3-quinolylmethyl)pyridinium salt was not. They suggested that photocyclodehydrohalogenations between aromatic rings were not successful when both rings were electron-deficient heterocycles.

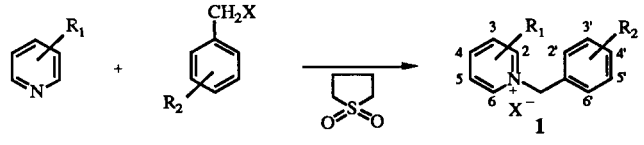
However, the photocyclization reaction of the pyridinium salts have not been studied extensively. Here we report the syntheses, intramolecular photocyclizations, and photo cyclization mechanism of *N*-[(2-haloaryl)-methyl]pyridinium and *N*-arylmethyl-2-halopyridinium salts.

Results and Discussion.

Syntheses.

N-(2-Chlorobenzyl)pyridinium chloride (**1a**, see Scheme 1) was prepared by reaction of 2-chlorobenzyl chloride with pyridine in sulfolane. Observation of a singlet peak in the ^{1}H nmr spectra (δ 6.0 in deuteriotrifluoroacetic acid) indicates the methylene protons of the pyridinium salt. Two α,β-protons of the pyridinium ring occurred at low

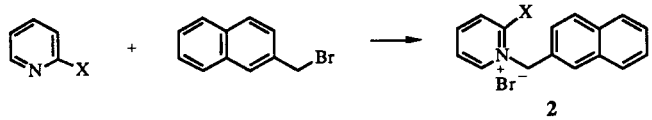
Scheme 1



1

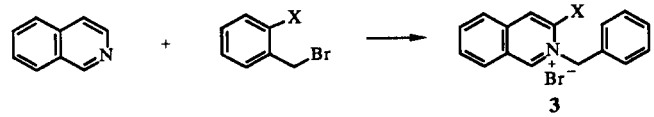
Compound No.	R_1	R_2	X	Compound No.	R_1	R_2	X
1a	2-H,	2'-Cl,	Cl	**1g**	2-H,	2'-Br,	Br
1b	2-H,	2'-Cl,	Br	**1h**	2-Br,	2'-H,	Br
1c	2-Cl,	2'-H,	Br	**1i**	2-Br,	2'-Br,	Br
1d	2-Cl,	2'-Cl,	Br	**1j**	4-CH_3,	2'-Br,	Br
1e	4-CH_3,	2'-Cl,	Cl	**1k**	2,4-Di-CH_3,	2'-Br,	Br
1f	2,4-Di-CH_3,	2'-Cl,	Cl				

Scheme 2



2

X	
2a	Cl
2b	Br

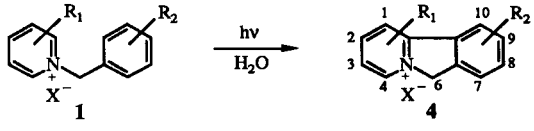


3

X	
3a	Cl
3b	Br

field, a doublet centered at δ, 8.8. A multiplet for γ-proton and a triplet for β-protons of pyridinium ring appeared at δ 8.6 and 8.1, respectively. The resonance of four phenyl protons occurred further upfield as a multiplet centered at δ 7.5. The pyridinium salts **1a** showed a molecular ion peak in the mass spectra. The synthetic reactions and structures of *N*-benzylpyridinium salt derivatives are shown in Scheme 1. *N*-(Arylmethyl)pyridinium and isoquinolinium salts **2** and **3** were prepared by reaction of appropriate substituted benzyl halides or naphthylmethyl halides with substituted pyridines or isoquinoline (see Scheme 2). The identification of new pyridinium and isoquinolinium salts are described in experimental section.

Scheme 3



Reactant No.	Product No.	R_1	R_2	X
1a	**4a**	4-H,	7-H,	Cl
1b	**4b**	4-H,	7-H,	Br
1c	**4b**			
1d	**4d**	4-H,	7-Cl,	Br
1e	**4e**	2-CH_3,	7-H,	Cl
1f	**4f**	2,4-Di-CH_3	7-H,	Cl
1g	**4b**			
1h	**4b**			
1i	**4i**	4-H,	7-Br,	Br
1j	**4j**	2-CH_3,	7-H,	Br [a]
1k	**4k**	no reaction		

[a] The product was not isolated in the preparative photochemical reaction, but the absorption spectra of the product could be observed.

Preparative Photocyclization.

When the aqueous solutions of *N*-(2-chlorobenzyl)pyridinium chloride (**1a**) were irradiated with a high pressure Hg lamp (the reaction was followed by the increasing absorption peak at 312 nm), an intramolecular photocyclized product, isoindolium chloride (**4a**, Scheme 3) was obtained. The ^{1}H nmr singlet peak (300 MHz) at δ 5.96 (2H) indicates the methylene protons; multiplet (3H) at δ 7.88 phenyl protons (7, 8, 9-H), triplet (J = 6.3 Hz, 1H) at δ 7.93, 3-H, doublet (J = 7.7 Hz, 1H) and δ 8.20 phenyl H (10-H), doublet (J = 8.3 Hz, 1H) at δ 8.46 pyridinium H(1-H), triplet (J = 7.8 Hz, 1H), at δ 8.60 pyridinium H (2-H), doublet (J = 6.2 Hz, 1H), at δ 9.05 pyridinium α-H (see Figure 1). Although the intramolecular photocyclized product seems to be the only product in the reaction with monochromatic light, the isolated yield of the preparative reaction with broad light spectrum (29%) was moderately low. The maximum conditions for the photocyclization were not studied further. However the reaction is a simple and useful was for aromatic ring formation. In methanol or ethanol photocyclizations of the pyridinium salts failed.

In order to study the relative reactivity of chlorine atoms on both aromatic rings of the pyridinium salt, *N*-(2-chlorobenzyl)-2-chloropyridinium salt **1d** was prepared. In the photochemical reaction of the salt two possible products could be formed according to which chlorine atom is cleaved. 4-Chloropyrido[2,1-*a*]isoindolium bromide, in which chlorine was cleaved from the pyridinium ring, was formed. The chemical shift of the product at δ 9.40 indicates the structure of **4d**, not **4d'** (δ-chloropyrido[2,1-*a*]-isoindolium salt). Furthermore, the splitting pattern and coupling constant at δ 8.60 and 8.44 ppm indicate the

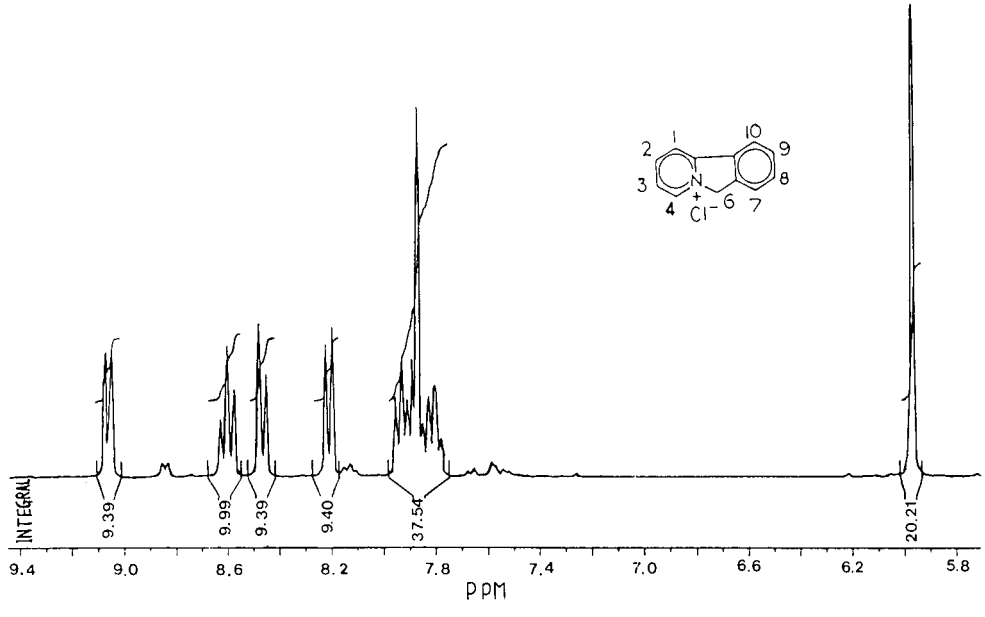


Figure 1. Nmr spectra of pyrido[2,1-*a*]isoindolium chloride.

9-proton and 8-proton of **4d**, respectively. Intramolecular photocyclization reactions of several *N*-(2-halobenzyl)pyridinium and *N*-(benzyl)-2-halopyridinium salts were studied and are shown in Scheme 3. The photocyclization of the pyridinium salt **1i** gave **4i** as **1d**. Both pyridinium salts **1g** and **1h** afforded also **4b**. *N*-β-Napthylmethyl)-2-chloropyridinium salt **2** 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 conditions. However, *N*-(2-chlorobenzyl) or *N*-(2-bromobenzylisoquinolinium salts **3a** and **3b** were unreactive (see Scheme 4). The starting salts were recovered from the reaction mixture.

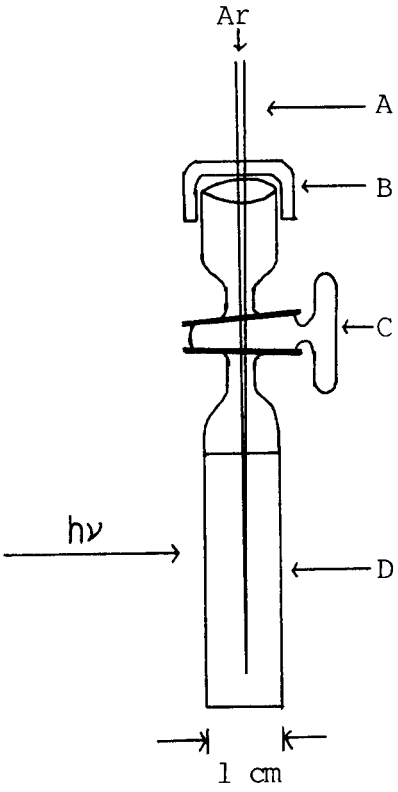


Figure 2. Reaction cuvette. (A) needle for deaeration, (B) rubber stopper, (C) cock, (D) quartz uv-cuvette.

Relative Rates of Photocyclization.

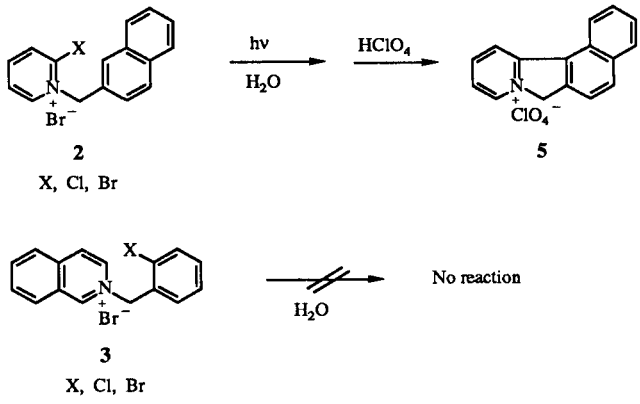
An appropriate concentration of the pyridinium salts in the uv cuvette (Figure 2) was made and the absorption spectra were measured. The absorption change of *N*-(2-chlorobenzyl)pyridinium salt by monochromatic light irradiation indicates that the isoindolium salt is the only product, because of the appearance of an isobestic point. The isoindolium salt product absorbs at a longer wavelength than pyridinium salt reactant. This seems to be a general pattern for all reactions of *N*-(2-halobenzyl)-pyridinium and *N*-(arylmethyl)-2-halopyridinium salts.

Table 1
Irradiation wavelength (λ max), Light Intensity of the Irradiation Wavelength and Relative rate of Photocyclization of the Pyridinium Salts

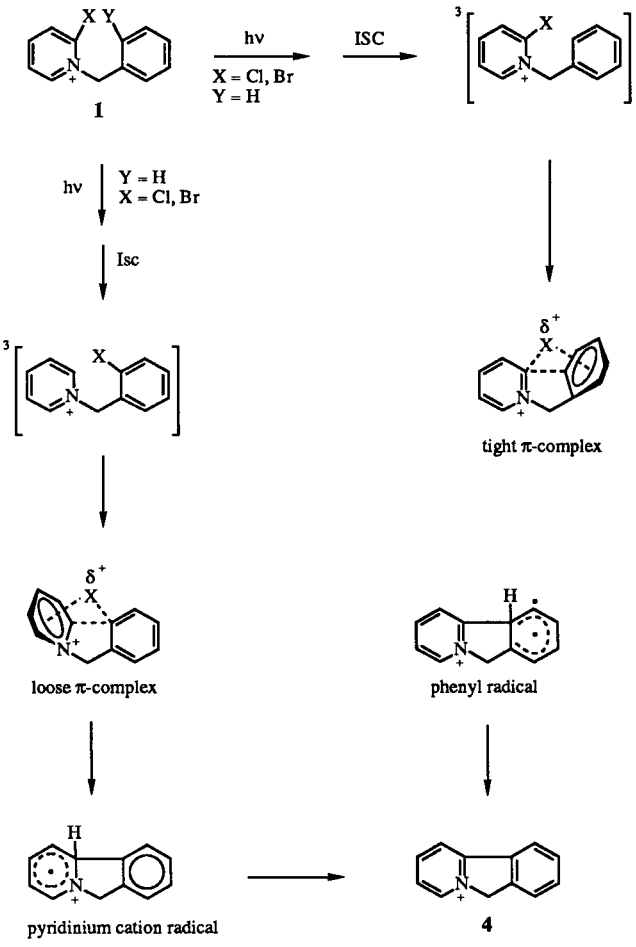
Reactant No.	Irradiation wavelength (λ max, nm)	Light Intensity (ein/sec) x 10^7	Concentration Change (M/20 min) x 10^6	Relative rate
1a	260	2.9	3.4	1.0
1b	260	2.9	3.7	1.1
1c	276	3.2	8.2	2.2
1d	275	3.2	23.0	6.1
1e	256	2.7	4.0	1.3
1f	263	2.1	3.5	1.4
1g	260	2.9	0.84	0.25
1h	278	3.7	9.0	2.1
1i	278	3.7	42.8	10.0
1j	256	2.3	0.78	0.30

To study the effect of substituents of both aromatic rings of the arylmethylpyridinium salts on the reactivity, the relative rates of intramolecular photocyclization of several pyridinium salts were measured and are shown in Table 1. Comparing **1a** and **1b**, anions (Cl^- and Br^-) have no effect on the rate of photocyclization. Comparing *N*-(2-chlorobenzyl)pyridinium salt **1a** and *N*-benzyl-2-chloropyridinium salt **1c**, **1c** is more reactive than **1a**. This result is consistent with the preparative photocyclization of *N*-(2-chlorobenzyl)-2-chloropyridinium salt **1d**. Compound **1d** gave the photocyclized product by cleavage of the chlorine atom from the pyridinium ring. Two explanations are possible for the relative reactivity: the easier the triplet is formed through intersystem crossing for **1c** because of the chlorine atom effect, the more reactive the reactant is; the other is that the excited state of **1c** can form π-complex of the chlorine atom of the pyridinium ring with the phenyl ring easier than **1a** because of the electron-rich phenyl group which is more reactive (see Scheme 5). The triplet energy of the pyridinium salt **1a** or **1c** (80 and 78 Kcal/mole, respectively) [6a] is not sufficient to overcome the bond dissociation energy (96 kcal/mole for

Scheme 4



Scheme 5



aromatic chloride) [6b]. π-Complex formation between the excited chlorine moiety of the salts and the aromatic ring assists the cleavage of the chlorine atom from aromatic ring. A similar explanation was given for the photocyclization of 2-chlorobenzanilide by Grimshaw [3b]. *N*-(2-Chlorobenzyl)-2-chloropyridinium salt **1d** is three times more reactive than **1c**. The chlorine group on the phenyl ring assists the intramolecular 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 chlorine group, and in turn, assists the cleavage of the chlorine atom from the pyridine ring. The methyl group on the pyridinium salt assists the photocyclization somewhat (compare **1a**, **1e**, and **1f**). (*N*-(2-Bromobenzyl)pyridinium salt **1g** is less reactive for the photocyclization. The excited bromine moiety of the benzyl ring could not form a π-complex with the pyridinium plate effectively because of the bulky bromine atom. Thus, the mechanism of the photocyclization of *N*-(2-halobenzyl)pyridinium and *N*-benzyl-2-halopyridinium salts is proposed in Scheme 5. The triplet excited state of the pyridinium salt [6a] is populated *via* intersystem crossing of the singlet excited state. Depending upon the electron availability, a tight or loose complex is formed. The tight π-complex can produce the cyclized product **4** easily *via* a conjugated phenyl radical. The loose π-complex can produce the cyclized product **4** with difficulty *via* a conjugated pyridinium cation radical. The phenyl radical or the pyridinium cation affords the isoindolium salts by losing hydrogen atom.

EXPERIMENTAL

General method.

All melting points were determined on an Electrothermal Melting Point Apparatus and are uncorrected. Nuclear magnetic resonance (nmr) spectra were measured in deuteriotrifluoroacetic acid and deuteriochloroform on Brucker-80 MHz or Brucker-300 MHz spectrometers. Chemical shifts are reported in parts per million (δ) downfield from TMS as an internal standard. Mass spectra were determined on Kratos MS 25 RFA at 50 or 70 ev. Infrared spectra were obtained from sampled in potassium bromide, on a Jasco, IR A_3. Elemental analyses were performed with Carlo Erba Strum, DP 200.

Preparative photochemical reactions were carried out in a water-cooled quartz immersion well apparatus with circulating nitrogen using a 200 W Hg lamp (Hanovia, high pressure). Measurement of relative rates of intramolecular photocyclization of the pyridinium salts was accomplished in a quartz uv cuvette (see Figure 2) using 5 nm band pass monochromatic light from a Schimadzu Bausch and Lomb Monochrometer, Grating 1200 equipped with Xe-lamp (500 W). 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 [7].

General Procedure for the Syntheses of the Pyridinium Salts **1a-1k**.

When a mixture of 4 ml of pyridine (0.05 mole), 8.8 g of 2-chlorobenzyl chloride (0.05 mole) and 10 ml of sulfolane was stirred at room temperature in a round-bottom flask for 3 days, white crystals developed. The crystals were washed with ethyl ether. Recrystallization from acetonitrile gave 8.8 g (74%) of white crystalline product.

N-(2-Chlorobenzyl)pyridinium Chloride (**1a**).

This compound was obtained as white crystals (acetonitrile), mp, 83-84°; uv (water): λ max 259.6 nm (log 3.59); ir (potassium bromide): ν aromatic CH 3100, 3040, 2920, aromatic C=C 1620, 1582, 1480 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 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); ms: (m/z) 206 (M^++2), 204 (M^+, 7%), 127 ($C_7H_6{}^{37}Cl^+$, 30%), 125 ($C_7H_6{}^{35}Cl^+$, 100%).

Anal. Calcd. for $C_{12}H_{11}NCl_2$: C, 60.02; H, 4.62; N, 5.83. Found: C, 59.88; H, 4.35; N, 5.90.

N-(2-Chlorobenzyl)pyridinium Bromide (**1b**).

This compound was obtained as white plates (acetonitrile), yield 60%, mp 171°; uv (water): λ max 259.6 nm (3.62); ir (potassium bromide): ν aromatic C-H 3120, 3075, 3050, C-H 2930, aromatic C=C 1630, 1590, 1470 cm^{-1}; ^1H nmr (deuteriotrifluoro-

acetic acid and deuteriochloroform): δ 6.3 (s, 2H, CH_2), 7.4 (m, 3H, phenyl), 8.1 (d, J = 3 Hz, 1H, 3'-H on phenyl), 8.2 (t, J = 6.3 Hz, 2H, β-H on pyridinium ring), 8.7 (t, J = 6.3 Hz, 2H, γ-H on pyridinium ring), 9.4 (d, J = 6.3 Hz, 2H, α-H on pyridinium ring); ms: (m/z) 208 ($C_7H_6ClBr^+$, 5%), 206 ($C_7H_6ClBr^+$, 20%), 204 ($C_7H_6ClBr^+$, 17%), 127 ($C_7H_6{}^{37}Cl^+$, 33%), 125 ($C_7H_6{}^{35}Cl^+$, 100%).

Anal. Calcd. for $C_{12}H_{11}NClBr$: C, 50.65; H, 3.90; N, 4.92. Found: C, 50.25; H, 3.88; N, 4.97.

N-Benzyl-2-chloropyridinium Bromide (**1c**).

This compound was obtained as white needles (acetonitrile and ethyl ether), yield 43%, mp 142-143°; uv (water): λ max 275.0 (3.89); ir (potassium bromide): ν aromatic C-H 3078, 3035, C-H 2970, aromatic C=C 1612, 1570, 1465 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 6.0 (s, 2H, CH_2), 7.3-7.6 (m, 5H, Ar), 8.1-8.4 (m, 3H), 8.9 (m, 1H, α-H); ms: (m/z) 115 ($C_5H_4N^{37}Cl^+$, 17%), 113 ($C_5H_4N^{35}Cl^+$, 50%), 91 ($C_7H_7^+$, 100%).

Anal. Calcd. for $C_{12}H_{11}NClBr$: C, 50.65; H, 3.90; N, 4.92. Found: C, 50.57; H, 3.80; N, 5.02.

N-(2-Chlorobenzyl)-2-chloropyridinium Bromide (**1d**).

This compound was obtained as white plates (acetonitrile and ethyl ether), yield 41%, mp 132-133°; uv (water): λ max 275.0 (3.85); ir (potassium bromide): ν aromatic C-H 3110, 3050, 3000, CH 2950, aromatic 1610 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 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); ms: (m/z) 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%).

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-Chlorobenzyl)-4-methylpyridinium Chloride (**1e**).

This compound was obtained as white crystals (acetonitrile and ethyl ether), yield 71%, mp 208-209° (lit 208-209.5°) [5]; uv (water): λ max 255.8 nm (3.59); ir (potassium bromide): ν aromatic CH 3059, 3012, 2997, 2943, aromatic 1639, 1593 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 2.8 (s, 3H, CH_2), 5.9 (s, 2H, CH_2), 7.6 (m, 4H, Ar), 7.9 (d, J = 6.3 Hz, 2H, β-H), 8.6 (d, J = 6.3 Hz, 2H, α-proton on pyridinium ring); ms: (m/z) 219 (M^+ -1, 3%), 217 (M^+-H, 10%), 125 ($C_7H_6Cl^+$, 91%), 93 ($C_6H_7N^+$, 45%).

N-(2-Chlorobenzyl)-2,4-dimethylpyridinium Chloride (**1f**).

This compound was obtained as light pink crystals (acetonitrile and ethyl ether), yield 39%, mp 209° (lit 210-211° [5]); uv (water): λ max 262.6 nm (3.72); ir (potassium bromide): ν aromatic 3050, 2990, aromatic C=C 1575 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 2.6 (s, 3H, γ-CH_3), 2.8 (s, 3H, α-CH_3), 5.8 (s, 2H, CH_2), 7.0-7.8 (m, 6H, Ar), 8.3 (d, J = 6.3 Hz, 1H, α-H); ms: (m/z) 233 (M^++2, 10%), 231 (M^+, 30%), 125 ($C_7H_6Cl^+$, 73%), 107 ($C_7H_9N^+$, 50%).

N-(2-Bromobenzyl)pyridinium Bromide (**1g**).

This compound was obtained as white plates (ethanol and ethyl acetate), yield 91%, mp 165-167°; uv (water): λ max 259.8 (3.60); ir (potassium bromide): ν aromatic CH 3078, 3051, 2939, aromatic C=C 1628, 1570 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 6.0 (s, 2H, CH), 7.4-7.8 (m, 4H, Ar), 8.1 (t, J = 6.3 Hz, 2H), 8.6 (t, J = 6.3 Hz, 2H), 8.9 (d, J = 6.3 Hz, 2H); ms: (m/z) 251 (M^+-1, 3%), 250 (M^+, 5%), 249 (M^+-H, 3%), 171 ($C_7H_6Br^+$, 60%), 169 ($C_7H_6Br^+$, 60%).

Anal. Calcd. for $C_{12}H_{11}NBr_2$: C, 43.81; H, 3.37; N, 4.26. Found: C, 43.62; H, 3.19; N, 4.38.

N-Benzyl-2-bromopyridinium Bromide (**1h**).

This compound was obtained as white plates (ethanol and ethylacetate), yield 57%, mp 159-160° (lit 156-157° [4a]); uv (water): λ max 277.8 (3.83); ir (potassium bromide): ν aromatic CH 3104, 3075, 3029, 2970, aromatic C=C 1645, 1454 cm^{-1}, ^1H nmr (deuteriotrifluoroacetic acid): δ 6.0 (s, 2H, CH_2), 7.3-7.6 (m, 5H, Ar), 8.1 (t, J = 6.3 Hz, 1H, γ-H), 8.4 (d, J = 6.3 Hz, 2H, β-H), 8.9 (d, J = 6.3 Hz, 1H, α-H), ms: (m/z) 159 ($C_5H_4NBr^+$, 58%), 157 ($C_5H_4NBr^+$, 59%), 91 ($C_7H_7^+$, 100%), 78 ($C_5H_4N^+$, 93%).

Anal. Calcd. for $C_{12}H_{11}NBr_2$: C, 43.80; H, 3.37; N, 4.26. Found: C, 43.68; H, 3.21; N, 4.47.

N-(2-Bromobenzyl)-2-bromopyridinium Bromide (**1i**).

This compound was obtained as white crystals (ethanol and ethyl acetate), yield 58%, mp 144-145°; uv (water): λ max 277.8 (3.99); ir (potassium bromide): ν aromatic CH 3113, 3074, 3028, 2931, aromatic C=C 1631 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 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), ms: (m/z) 329 (M^+-H, ^{81}Br, 15%), 328 (M^+, 40%), 327 (M^+-H, ^{79}Br, 15%), 171 ($C_7H_6Br^+$, 100%), 169 ($C_7H_6Br^+$, 100%), 159 ($C_5H_4Br^+$, 60%), 157 ($C_7H_4Br^+$, 60%).

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, 3.3l.

N-(2-Bromobenzyl)-4-methylpyridinium Bromide (**1j**).

This compound was obtained as light pink crystals (acetonitrile and ethyl ether), yield 74%, mp 158-159°; uv (water): λ max 255.6 (3.61); ir (potassium bromide): ν aromatic CH 3124, 3092, aromatic C=C 1639, 1589 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 2.7 (s, 3H, CH_2), 5.9 (s, 2H, CH_2), 7.3-7.8 (m, 4H, Ar), 7.9 (d, J = 6.3 Hz, 2H, Py-β-H), 8.6 (d, J = 6.3 Hz, 2H, py-α-H); ms: (m/z) 171 ($C_7H_6Br^+$, 33%), 169 ($C_7H_6Br^+$, 34%), 93 ($C_6H_7N^+$, 28%).

Anal. Calcd. for $C_{13}H_{13}NBr_2$: C, 45.51; H, 3.82; N, 4.08. Found: C, 45.40; H, 3.60; N, 4.19.

N-(2-Bromobenzyl)-2,4-dimethylpyridinium Bromide (**1k**).

This compound was obtained as light pink crystals (acetonitrile and ethyl ether), yield 46%, mp 152-153°; uv (water): λ max 264.0 (3.66); ir (potassium bromide): ν aromatic CH 3089, 3059, 2998, aromatic C=C 1635, 1562 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 2.7 (s, 3H, γ-methyl), 2.9 (s, 3H, α-methyl), 5.8 (s, 2H, CH_2), 7.1-7.9 (m, 6H, Ar), 8.3 (d, J = 6.3 Hz, 1H, α-pyr-H); ms: (m/z) 171 ($C_7H_6Br^+$, 36%), 169 ($C_7H_9Br^+$, 37%), 107 ($C_7H_9N^+$, 28%), 83 (100%).

Anal. Calcd. for $C_{14}H_{15}NBr_2$: C, 47.09; H, 4.23; N, 3.92. Found: C, 47.01; H, 4.20; N, 3.80.

General Procedure of the Syntheses of the Pyridinium Salts **2**.

N-(β-Naphthylmethyl)-2-chloropyridinium Bromide (**2a**).

A mixture of 15 ml of sulfolane, 11 g (0.05 *M*) of 2-bromomethylnaphthalene and 6 g (0.05*M*) of 2-chloropyridine was heated at 45-50° for 2 days. Diethyl ether was introduced into the reaction mixture to precipitate the desired salt. Recrystallization from ethanol afforded white solid, yield 39%, mp 138-140°; uv (water): λ max 274.0 nm (4.04); ir (potassium bromide): ν aromatic CH 3078, 3055, 3032, 2970, 2935, aromatic C=C 1612 cm^{-1}; ^1H nmr (deuteriotrifluoroacetc acid): δ 6.2 (s, 2H, CH_2), 7.4-8.5 (m, 10H, Ar), 8.9 (d, J = 6.3 Hz, 1H, pyridine-α-H); ms: (m/z) 141 ($C_{11}H_9^+$, 36%), 115 ($C_5H_4NCl^+$, 10%), 113 ($C_5H_4NCl^+$, 30%).

Anal. Calcd. for $C_{16}H_{13}NClBr$: C, 57.43; H, 3.92; H, 4.19. Found: C, 57.49; H, 3.82; N, 4.27.

N-(β-Naphthylmethyl)-2-bromopyridinium Bromide (**2b**).

This compound was obtained as white needle crystals (ethanol), yield 69%, mp 159-160°; uv (water): λ max 277.3 nm (4.30); ir (potassium bromide): ν aromatic CH 3070, 3055, 3032, 2970, aromatic C=C 1613 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 6.2 (s, 2H, CH_2), 7.4-8.1 (m, 8H), 8.4 (t, J = 6.0 Hz, 1H, γ-H on pyridinium ring), 8.5 (d, J = 6.0 Hz, 1H, H adj Br), 9.0 (d, J = 6.0 Hz, 1H, α-H on pyridinium ring); ms: (m/z) 159 ($C_5H_4{}^{81}Br^+$, 40%), 157 ($C_5H_4N^{79}Br^+$, 40%), 141 ($C_{11}H_9^+$, 65%), 91 (100%).

Anal. Calcd. for $C_{16}H_{13}NBr_2$: C, 50.70; H, 3.46; N, 3.69. Found: C, 50.40; H, 3.15; N, 3.80.

General Procedure for the Syntheses of the Isoquinolinium Salts **3**.

A mixture of 10 ml of ethanol, 4 g (0.03 mole) of isoquinoline and 6 g of 2-chlorobenzyl bromide (0.03 mole) was heated at reflux for 6 hours. The salt was crystallized by addition of acetone to the reaction mixture.

N-(2-Chlorobenzyl)isoquinolinium Bromide (**3a**).

This compound was obtained as yellow crystals (ethanol), yield 60%, mp 125-127°; uv (water): λ max 269.0 (3.85), 276 (3.85), 326.2 nm (3.84); ir (potassium bromide): ν aromatic C-H 3093, 3078, 3028, 2993, 2972, aromatic CH 1647, 1624, cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.5 (s, 2H, CH_2), 7.4 (m, 4H, phenyl), 8.5 (m, 5H, isoquinoline), 8.7 (m, 2H, α-H on isoquinoline), ms: (m/z) 129 ($C_9H_7N^+$, 55%), 127 ($C_7H_7{}^{37}Cl^+$, 23%), 125 ($C_7H_7{}^{35}Cl^+$, 59%).

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-Bromobenzyl)isoquinolinium Bromide (**3b**).

This compound was obtained as white crystals (ethanol), yield 63%, mp 183-185°; uv (water): λ max 269.3 (3.75), 277.6 (3.74), 337.2 nm (3.72); ir (potassium bromide): ν aromatic CH 3063, 3028, 3009, 2978, 2939, aromatic C=C 1643, 1604 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 6.1 (s, 2H, CH_2), 7.6 (m, 4H, phenyl), 8.4 (m, 6H, isoquinoline), 9.6 (s, 1H, α-proton on isoquinoline); ms: (m/z) 171 ($C_7H_6{}^{81}Br^+$, 74%), 169 ($C_7H_6{}^{79}Br^+$, 75%), 129 ($C_9H_7N^+$).

Anal. Calcd. for $C_{16}H_{13}NBr_2$: C, 50.70; H, 3.46; N, 3.69. Found: C, 50.46; H, 3.38; N, 3.79.

3.5-General Procedure for the Preparative Photocyclization: Syntheses of Pyrido[2,1-*a*]isoindolium Salts **4a-4i** and **5a**.

Into a 500 ml water-cooled quartz immersion well apparatus were introduced 3 g (0.013*M*) of **1a**, and 450 ml of triple distilled water. The mixture was irradiated for 6 hours with an Hg-lamp (Havovia 200 W, high pressure) under nitrogen. The reaction was followed by the increase of a new absorption peak at 312 nm. The mixture was evaporated to about 10 ml, decolorized by the addition of active carbon, and then recrystallized in ethanol by addition of ethyl acetate.

Pyrido[2,1-*a*]isoindolium Chloride (**4a**).

This compound was obtained as white needles, yield 20%, mp 139-140°; uv (water): λ max 258.0 (4.10), 312 nm (4.01); ir (potassium bromide): ν aromatic CH 3128, 3113, 3074, 3047, 2974, 2943, aromatic C=C 1627, 1593 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ, 5.96 (s, 2H, CH_2), 7.88 (m, 3H, phenyl 7, 8, 9-H), 7.93 (t, J = 6.3 Hz, 1H, 3-H), 8.20 (d, J = 7.7 Hz, 1H, 10-H), 8.46 (d, J = 8.3 Hz, 1H, 1-H), 8.60 (t, J = 7.8 Hz, 1H, 2-H), 9.05 (d, J = 6.2 Hz, 1H, pyr α-H); ms: (m/z) 168 (M^+, 10%), 167 (M^+-H, 100%).

Anal. Calcd. for $C_{12}H_{10}NCl$: C, 70.77; H, 4.95; N, 6.88. Found: C, 70.70; H, 4.98; N, 6.59.

Pyrido[2,1-*a*]isoindolium Bromide (**4b**).

This compound was obtained as light brown crystals (ethanol by addition of ethyl acetate), yield 18%, mp 207-209° (lit 207.5 209.5° [4a]); uv (water): λ max 255.0 (4.11), 312.4 nm (4.01); ir (potassium bromide): ν aromatic CH 3020, 2943, 2893, aromatic C=C 1632, 1562 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid): δ 6.0 (s, 2H, CH_2), 7.8 (m, 4H, phenyl). 8.2 (two d, 1H), 8.5 (two triplet, 2H), 9.1 (d, 1H); ms: (m/z) 168 (M^+, 10%), 167 (M^+-H, 100%).

4-Chloropyrido[2,1-*a*]isoindolinium Bromide (**4d**).

This compound was obtained as light brown crystals ethanol by addition of ethyl acetate), yield 25%, mp 250° dec; uv (water): λ max 251.4 (4.08), 256.6 (4.07), 308.8 (4.09); ir (potassium bromide): ν aromatic CH 3075, 3045, 2900, 2873, aromatic C=C 1623, 1603, 1450, 765 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid and deuteriochloroform): δ, 6.04 (s, 2H, CH_2), 7.68 (t, J = 6.0 Hz, 1H, 3-H), 7.74 (d, J = 9.0 Hz, 1H, 10-H), 7.97 (t, J = 6.0 Hz, 1H, 2-H), 8.08 (d, J = 6.0 Hz, 1H, 1-H), 8.44 (d, J = 9.0 Hz, 1H, 8-H), 8.60 (t, J = 9.0 Hz, 1H, 9-H), 9.40 (d, J = 6.0 Hz, 1H, 4-H), ms: (m/z) 203 (M^+-1, ^{37}Cl, 33%), 201 (M^+-1, ^{35}Cl, 100%).

Anal. Calcd. for $C_{12}H_9$ NClBr: C, 51.01; H, 3.21; N, 4.96. Found: C, 50.98; H, 3.02; N, 5.01.

4-Methylpyrido[2,1-*a*]isoindolium Chloride (**4e**).

This compound was obtained as white crystals (ethanol and ethyl acetate), yield 25%, mp 246° dec (lit mp 246° dec [5]); ir and ^1H nmr of **4e** are the same as those in ref [5].

4,6-Dimethylpyrido[2,1-*a*]isoindolium Chloride (**4f**).

This compound was obtained as light brown crystals (ethanol and ethyl acetate), yield 30%, mp 290° dec; uv (water): λ max 258.4 (4.15), 313.2 nm (4.08); ir (potassium bromide): ν aromatic CH 3050, 2920, aromatic C=C 1639, 1617 cm^{-1}; ^1H nmr (deuteriotrifluoroacetic acid and deuteriochloroform): δ 2.70 (s, 3H, methyl), 2.85 (s, 3H, methyl), 5.62 (s, 2H, methylene), 7.48 (s, 1H), 7.71 (m, 1H), 7.76 (m, 2H), 7.98 (s, 1H), 8.05 (d, J = 6.0 Hz, 1H); ms: (m/z) 196 (M^+, 20%), 195 (M^+-1, 100%).

Anal. Calcd. for $C_{14}H_{14}NCl$: C, 72.57; H, 6.09; N, 6.04. Found: C, 72.40; H, 6.21; N, 5.91.

4-Bromopyrido[2,1-*a*]isoindolium Bromide (**4i**).

This compound was obtained as light brown crystals (ethanol and ethyl acetate), yield 17%, mp 250° dec; uv (water): λ max 257.6 (3.96), 309.2 nm (3.97); ir (potassium bromide): ν aromatic CH 3043, 2874, aromatic C=C 1628, 1570, 1492, 1450, 772 cm^{-1}, ^1H nmr (deuteriotrifluoroacetic acid and deuteriochloroform): δ 5.98 (s, 2H, CH_2), 7.63 (t, 1H, J = 7.5 Hz), 7.89 (d, J = 7.5 Hz, 1H), 7.63 (t, 1H, J = 7.5 Hz), 8.41 (m, 2H), 8.58 (m, 1H), 9.40 (m, 1H); ms: (m/z) 245 (M^+-H, ^{79}Br, 100%), 247 (M^+-H, ^{81}Br, 95%), 166 (80%).

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.

Benzo[*g*]pyrido[2,1-*a*]isoindolium Perchlorate (**5a**).

This compound was obtained as light brown needles (ethanol and ethyl acetate), yield 7.5%, mp 258-260°; uv (water): λ max 212.6 (4.46), 253.8 (4.16), 326.8 (3.70); ir (potassium bromide): ν aromatic CH 3086, 3070, 3051, 2928, aromatic C=C 1628 cm^{-1}, ^1H nmr (deuteriotrifluoroacetic acid): δ 5.95 (s, 2H, CH_2), 7.69 (m, 1H, naphthyl), 7.84 (m, 3H, naphthyl), 8.10 (d, 1H, J = 8.5 Hz, γ-H on naphthyl), 8.23 (1H, d, J = 8.5 Hz, α-H on naphthyl), 8.50 (m, 2H, β,γ-H on pyridinium ring), 8.95 (1H, d, J = 8.5 Hz, β-H on pyr), 9.08 (1H, d, J = 6.3 Hz, α-H on pyr); ms: (m/z) 218 (M^+, 20%), 217 (M^+-H, 100%).

Anal. Calcd. for $C_{16}H_{12}NClO_4$: C, 60.48; H, 3.81; N, 4.41. Found: C, 60.19; H, 3.92; N, 4.38.

Photochemistry of Isoquinolinium Salts **3a** and **3b**.

When a mixture of **3a** or **3b** (1 g) and water (450 ml) in a 500 ml photochemical cell was irradiated for 30 hours, no uv absorption change at λ max 337 nm was observed. Only the reactants were recovered.

Relative Rates of Photocyclization.

An appropriate concentration of the aqueous pyridinium salt (which absorbance is more than 1.5) was made and the solution (2.7 ml) transferred into 1 cm-path uv cuvette (Figure 2). The solution was deaerated by introducting nitrogen for 10 minutes. Before irradiation, the exact concentration was checked by the absorption spectra. The solution was irradiated with monochromatic light which wavelength is corresponding to the absorption λ max of the pyridinium salt. The aborption change around 315 nm was measured on several time interval. Before and after irradiation, the light intensity was measured with Ferrioxaiate actionometry. The irradiation wavelength, light intensity (average value before and after irradiation), concentration change of the pyridinium salt upon irradiation for 20 minutes and the relative rates of the photocyclization are shown in Table 1.

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