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Photocyclization of *N*-Arylmethyl-2-chloropyridinium Salts

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We are interested in the photocyclization of *N*-Arylmethyl-2-chloropyridinium salts because of the possibility of a useful way for alkaloid synthesis. Only a little work has been done in this field.

Forzard and Bradsher[1] reported that when aqueous solution of 2-bromo-*N*-benzylpyridinium salt or *N*-(2-bromobenzyl)pyridinium salt was irradiated, photocyclized product, pyrido[2,1-a]isoindolium salt was formed. Portlock and his collaborators[2] reported that aqueous solution of *N*-(2-chlorobenzyl)pyridinium salt could be photocyclized, while 1-(2-halogeno-3-quinolylmethyl) pyridinium salt could not.

Here we report the photocylization of *N-benzyl-2-chloropyridinium bromide*(**1**) and *N*-(β-naphthylmethyl)-2-chloropyridinium bromide(**2**) in water.

N-benzyl-2-chloropyridinium bromide (**1**) was prepared by reaction of benzyl bromide (8.6 g, 0.05 moles) and 2-chloropyridine (6.0 g, 0.05 moles) at room temperature in sulfolane for 3 days (yield 43%, mp. 142-143 °C). Observation of a singlet peak at δ, 6.0 in the NMR spectra taken in CF_3CO_2D (TFA-D) indicates methylene protons of the pyridinium salt **1** (see Table 1). *N*-(β-naphthylmethyl)-2-chloropyridinium bromide (**2**) was obtained when a mixture of 15 m*l* of sulfolane, 11 g of 2-bromomethylnaphthalene (0.05 mole), and 6 g of 2-chloropyridine (0.05 mole) was heated at 45-50 °C for 2 days (yield 39%, mp 138-140 °C). The pyridinium salt **2** also showed the methylene protons at δ, 6.20 ppm in ^{1}H NMR spectra. The compounds of **1** and **2** have been characterized by the spectral data as shown in Table 1.

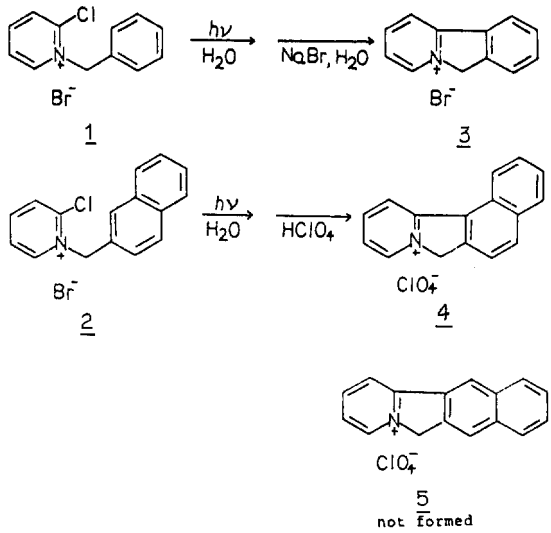


Figure 1. Photocyclization reactions of pyridinium salts in water.

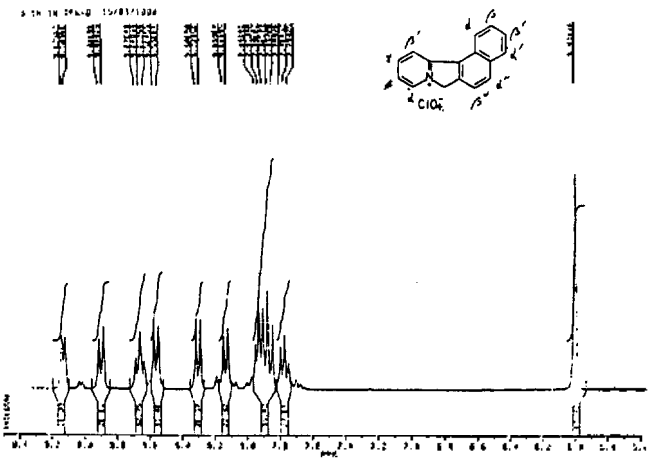
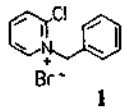
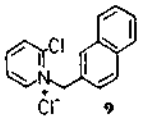
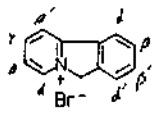
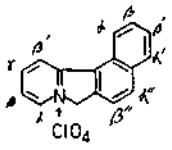


Figure 2. Proton NMR spectrum, at 300 MHz in TFA-D, of isoindolium salt **4**.

When the aqueous solution of *N*-benzyl-2-chloropyridinium bromide (**1**, 3 g, in 450 m*l* of water) was irradiated with a high pressure Hg arc lamp (Hanovia, 450 W), photocyclized product, pyrido[2,1-a]isoindolium bromide (**3**) (after treatment with NaBr for anion exchange) was obtained (see Figure 1): yield 28%, mp: 207-209 °C (lit 207.5-209.5 °C)[2]. *N*-(β-naphthylmethyl)-2-chloropyridinium bromide (**2**) photocyclized to give benzo[g]pyrido[2,1-a]isoindolium perchlorate (**4**) (after treatment with $HClO_4$ for anion exchange, 18% yield) (see Figure 1). This reaction is useful for the syntheses of polybenzo-fused pyridinium salts.

Use of 300 MHz spectroscopy allowed analysis of the structure of **4** and all signals were assigned in a straightforward way on the basis of chemical shift, multiplicity and coupling constant. No singlet peak of aromatic protons in the ^{1}H NMR (300 MHz) indicated that the salt is not the benzo [f]-pyrido[2,1-a]isoindolium salt (**5**) which could be formed theoretically. Observation of a singlet peak at δ, 6.00 (TFA-D) indicated the methylene protons of isoindolium salt

Table 1. Spectroscopic Properties of *N*-Arylmethyl-2-chloropyridinium and Substituted Isoindolium Salts

Compound	^{1}H NMR (80 MHz) (TFA-D, *vs.* TMS, in ppm)	Ms (*m/e*, intensity)	UV (λ_{max}, log ε H_2O)	IR (KBr, cm^{-1})
 1	6.02(s, 2H, CH_2)	115(17%, $C_5H_4N^{37}Cl^+$)	275.8 nm	3078
	7.42–7.80(m, 5H, ArH)	113(50%, $C_5H_4N^{35}Cl^+$)	(3.89)	3035
	8.00–8.70(m, 3H, PyH)	91(100%, $C_7H_7^+$)		2970
	8.90(d, J = 6.0 Hz, 1H, α-PyH)			1612
				1570
 2	6.20(s, 2H, CH_2)	141(36%, $C_{11}H_9^+$)	274.0 nm	3078
	7.40–8.50(m, 10H, Ar)	115(10%, $C_5H_4N^{37}Cl^+$)	(4.04)	3055
	9.80(d, J = 6.3 Hz, 1H, Pyr. α-H)	113(30%, $C_5H_4N^{35}Cl^+$)		2970
				2935
				1612
 3	6.00(s, 2H, CH_2)*	168(10%, M$^+$–Anion)	255.0 nm	3020
	7.80(m, 1H, β-pyrH)	167(100%, M$^+$–1,	(4.11)	2943
	7.83(m, 2H, β'-pyrH + β'ArH)	Pseudo Aromatic)	312.4 nm	2893
	7.95(t, J = 6.0 Hz, 1H, γ-pyrH)		(4.01)	1632
	8.22(d, J = 9.0 Hz, 1H, α'-ArH)			1562
	8.47(d, J = 9.0 Hz, 1H, α-ArH)			
	8.60(t, J = 9.0 Hz, 1H, β-ArH)			
	9.11(d, J = 6.0 Hz, 1H, α-pyrH)			
 4	6.00(s, 2H, CH_2)*	218(20%, M$^+$–Anion)	253.8 nm	3086
	7.76(m, 1H, β-pyrH)	217(100%, M$^+$–1,	(4.16)	3070
	7.91(t, J = 6.0 Hz, 1H, γ-pyrH)	Pseudo Aromatic)	326.8 nm	3051
	7.88(m, 2H, β'-pyrH + α''-ArH)		(3.70)	2928
	8.12(m, 1H, β'-ArH)			1628
	8.30(d, J = 9.0 Hz, 1H, β''-ArH)			1589
	8.56(d, J = 9.0 Hz, 1H, α'-ArH)			
	8.64(t, J = 9.0 Hz, 1H, β-ArH)			
	8.88(d, J = 9.0 Hz, 1H, α-ArH)			
	9.11(d, J = 6.0 Hz, 1H, α-pyrH)			

*: 300 MHz ^{1}H NMR.

(4) (see Figure 2 and Table 1). A doublet peak for α-proton of pyridinium ring appeared in the low field (at δ, 9.11, J = 6.0 Hz) and a multiplet peak for β-proton of pyridinium ring appeared in high field somehow (at δ, 7.76). A triplet peak for γ-proton of pyridinium ring appeared at high field (at δ, 7.91) with J equal 6.0 Hz. The remaining three doublet peaks at δ, 8.88, 8.56 and 8.30 indicated α-, α'- and β''-proton of naphthyl ring respectively (all J = 9.0 Hz). A triplet peak at δ, 8.64 coupled with α-proton of naphthyl ring indicated β-proton of naphthyl ring. Two multiplet peaks at δ, 8.12 (1H) and 7.88 (2H) appeared for β'- and α''-proton of naphthyl ring and β'-proton of pyridinium ring respectively. The molecular cation constitution was also confirmed by mass determination of the molecular ion at m/e 218 which revealed the composition of $C_{16}H_{12}N$ (218.275).

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Synthesis of a Novel 3-(1'-Chloroethenyl)-cephem

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Since the introduction of cefixime[1] as an orally absorbable cephalosporin in 1983, the preparation of cefixime analogs has been reported in the literature.[2] In this laboratory we were interested in the modification of C-10 position in vinyl group by substitution with chlorine atom. To our best knowledge, the preparation of 3-(1-chloroethenyl)cephem has not yet been reported in the literature.[3] Here we wish to report a synthesis of 7-[(Z)-2-amino-4-thiazole)-2-[(1-carboxy-1-methyl)ethoxyimino]acetamido]-3-(1'-chloroethenyl)-3-