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Three thieno-fused analogues of benzo[*a*]quinolizinium (1), thieno[3,2-*a*]- and thieno[2,3-*a*]quinolizinium 4 and 5 and thiazolo[2,3-*a*]isoquinolinium (6), were synthesized by photocyclization of 1-(2-thienylvinyl)pyridinium salts 9a and 9b and 3-styrylthiazolium salt 9c, respectively. The nitration of the compounds 4, 5, and 6 occurred predominantly at positions 2, 3, and 7, respectively, while the nitro group was introduced into the 8- and 10-positions of 1 in the ratio of 68:32. The nmr and uv spectral properties and reduction potentials of 4-6 were also compared with those of the parent compound 1.

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Introduction.

The fused heterocyclic systems comprised of a π -excessive and a π -deficient rings have attracted considerable interest in view of their theoretical and pharmacological aspects [1a-d]. The quinolizinium salts fused with a π -excessive ring like pyrrole and thiophene would exhibit interesting properties. The indolo[2,3-*a*]quinolizinium ring systems are found in alkaloids, such as sempervirine and flavopereirine, possessing antitumour activity [2]. The pyrido[1,2-*a*]pyrrolo[2,1-*c*]pyrazin-7-ium salts show an intramolecular charge transfer from the pyrrole to the pyridinium ring [3]. On the other hand, of the nine theoretically possible thienoquinolizinium salts, only the two linearly fused thieno[*b*]quinolizinium salts have been synthesized and found to show the biological activities [4]. However, very little is known about their physical and chemical properties. Furthermore, no attempts on the synthesis on the other isomers have been reported.

In contrast, a number of benzologues of quinolizinium salts have been synthesized [5]. In comparison with a wealth of information on their reactivity toward nucleophiles [6], the electrophilic substitution reactions have been little explored. Of three simple benzologues of the quinolizinium salts 1-3, the nitration and sulfonation of benzo[*b*]- and benzo[*c*]quinolizinium salts 2 and 3 have been examined [7]. The electrophilic attack occurred predominantly at the 10-position of 2 and 3. On the basis of those results, electrophiles would attack the position 8 of benzo[*a*]quinolizinium salt (1), however, it has not been tested to date [8].

In this paper we will report the synthesis of previously unknown angularly thieno-fused quinolizinium salts, namely, thieno[3,2-*a*]quinolizinium salt (4) and thieno[2,3-*a*]quinolizinium salt (5) by oxidative photocyclization [9]. Their physical properties and reactivities of a typical electrophilic substitution, nitration, will be examined and compared with those of the benzo-fused

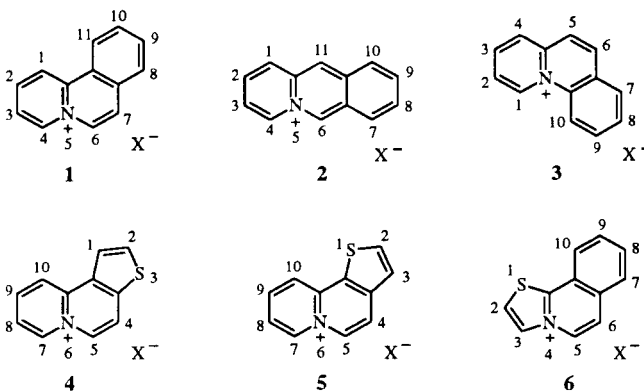
system 1. As the related angularly fused tricyclic system containing a bridgehead quarternary nitrogen atom and a sulfur atom, thiazolo[2,3-*a*]isoquinolinium salt (6) will also be prepared by photocyclization and those properties will be examined. Compound 6 was already synthesized by Bradsher and his co-workers [10] by using the acid-catalyzed cyclization of a keto-sulfide, but its properties have not been described. Although Gronowitz *et al.* [11] studied the synthesis of the aza derivatives of benzo- and thieno[*a*]quinolizinium salts by the procedure involving Pd(0)-catalyzed cross-coupling reaction, the reactivities particularly towards electrophile have not been reported.

Results and Discussion.

a) Synthesis.

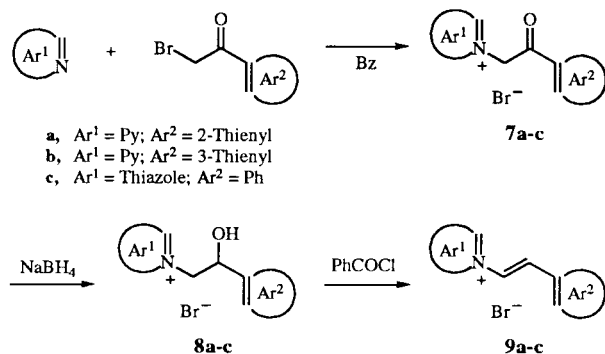
As a continuation of our studies on the construction of azonia aromatic compounds by photochemical methods [12], we applied the oxidative photocyclization method to the synthesis of 4, 5, and 6.

Scheme 1



The two isomers of 1-(2-thienylvinyl)pyridinium salts 9a and 9b and 3-styrylthiazolium salt 9c were prepared in three-steps process according to the method described by McFarland *et al.* [13] (Scheme 2). The reaction of pyridine with bromoacetylthiophenes or of thiazole with phenacyl

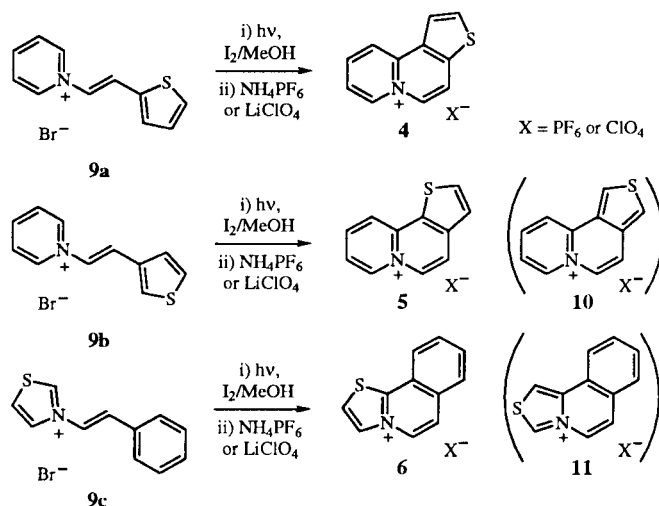
Scheme 2



bromide gave pyridinium or thiazolium salts **7a-c** (42-67% yield). Salts **7a-c** were reduced with sodium borohydride in water to afford the alcohols **8a-c** (76-83% yield). Dehydration of the alcohols **8a-c** with benzoyl chloride gave the olefins **9a-c** (62-73% yield).

An aerated methanol solution of 1-[2-(2-thienyl)vinyl]pyridinium bromide (**9a**) was irradiated with a high-pressure mercury lamp through a Pyrex-filter in the presence of iodine to yield the cyclized product **4** ($\text{X} = \text{Br}$) (Scheme 3). Counterion exchange with aqueous lithium perchlorate gave the perchlorate salt **4** ($\text{X} = \text{ClO}_4$) in 74% yield. The structural confirmation of **4** was established by spectral data and elemental analysis. The ^1H nmr spectrum of **4** exhibits two doublets with relatively small $^3J_{\text{HH}}$ (5.4 Hz) at δ 8.45 and 8.61 ppm corresponding to thiophenic α,β -coupling constant (4.9-6.2 Hz). The H-H COSY spectrum of **4** showed characteristic long-range couplings ($^5J_{\text{HH}}$) between H1 and H4, and H5 and H10. These results also confirmed the structure.

Scheme 3



Isomers **9b** and **9c** were subjected to photolysis under similar conditions used for **9a** (Scheme 3). Photocyclization of 1-[2-(3thienyl)vinyl]pyridinium bromide (**9b**) would yield the two isomers, **5** and thieno[3,4-*a*]-quinolizinium salt (**10**), by ring closure at the 2-position and the 4-position of the 3-substituted thiophene ring, respectively. The ^1H nmr spectrum of the product isolated in 69% yield showed two doublets whose coupling constants were similar to thiophene moiety of **4** (see Table II). This result strongly supports that the photo-product is **5** ($\text{X} = \text{ClO}_4$), because the ^1H nmr spectrum of **10** will show two singlets corresponding to the two α -protons of thiophene moiety.

Similarly, irradiation of 3-styrylthiazolium bromide (**9c**) produced only the **6** ($\text{X} = \text{ClO}_4$) in 27% yield with

Table I

^1H NMR Chemical Shifts (δ) of Compounds **1** and **4-6** in DMSO- d_6 [a]

Compounds	1H	2H	3H	4H	5H	6H	7H	8H	9H	10H	11H
1	9.53	8.69	8.28	9.50		9.03	8.39	8.29	8.16	8.09	9.17
4	8.61	8.45		8.76	9.15		9.44	8.13	8.54	9.15	
5		8.64	7.95	8.48	9.14		9.42	8.09	8.47	8.82	
6		8.56	9.01		9.12	8.32	8.33	8.16	8.64	8.74	

[a] The numbering is given in Scheme 1.

Table II

^1H NMR Coupling Constants (*J*, Hz) of Compounds **1** and **4-6** in DMSO- d_6 [a]

Compounds	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$	$J_{8,9}$	$J_{9,10}$	$J_{10,11}$	$J_{1,3}$	$J_{2,4}$	$J_{7,9}$	$J_{8,10}$	$J_{9,11}$
1	8.9	7.3	7.6			7.3		7.3	7.3	8.3	1.3	1.3		1.3	1.3
4	5.4			7.3			6.6	7.3	8.9				1.0	1.0	
5		5.3		7.1			6.6	7.4	8.9				1.0	1.3	
6		3.4			7.3		7.9	7.3	8.3				1.2	1.0	

[a] The numbering is given in Scheme 1.

Table III
¹³C NMR Chemical Shifts (δ) of Compounds **1** and **4-6** in DMSO-*d*₆ [a]

Compounds	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C3a	C6a	C7a	C10a	C10b	C11a	C11b
1	123.1	140.2	124.3	139.6		131.2	123.0	128.2	134.0	130.9	125.7			131.3			124.6	142.8
4	123.3	134.2		118.7	130.7		137.7	122.8	138.3	123.6		143.9			139.3	132.5		
5		138.6	125.4	118.8	132.4		138.0	123.3	138.5	127.7		142.1			139.2	133.7		
6		123.3	132.4		129.1	121.5	128.5	134.5	131.1	126.1			131.1		123.8	156.8		

[a] The numbering is given in Scheme 1.

no detectable thiazolo[4,3-*a*]isoquinolinium salt (**11**) being formed. The ¹H nmr spectrum of **6** shows two two-spin systems and one four-spin system which were unambiguously assigned from the COSY spectrum (Table I). The similar regio-selectivity was reported in the photolysis of 1-styrylimidazole [14], which cyclized only at the 2-position of imidazole to give imidazo-[2,1-*a*]isoquinoline.

The hexafluorophosphate salts **4**, **5**, and **6** (X = PF₆) were also obtained in 67%, 58%, and 33% yields by counterion exchange of the photo-products (X = Br) with aqueous ammonium hexafluorophosphate, respectively. All ¹H and ¹³C nmr assignments of the photo-products **4-6** and **1** were performed on the basis of homo- and hetero-nuclear 2D nmr techniques. Details of the ¹H and ¹³C nmr data of the photo-products are presented in Tables I, II, and III.

b) Physical Properties.

The uv-spectral data of compounds **1** and **4-6** are collected in Table IV. The spectra of the two thieno-fused systems **4** and **5** show considerable similarity to that of benzo-fused system **1**; the thienoquinolizinium salts have three main absorption bands, at *ca.* 350-300, 280-270, and 240-230 nm (log ε_{max} values *ca.* 4.2, 4.4, and 4.0, respectively), which indicate small hypsochromic shifts compared with the spectrum of **1** [15]. These features are similar to the relation between the spectrum of

phenanthrene and those of naphthothiophenes [16]. There is no evidence of intramolecular charge-transfer between quinolizinium and thiophene moieties. The spectrum of thiazoloisoquinolinium system **6** also resembled those of **5**.

A similar tendency was observed for the reduction potentials of **1** and **4-6**, which were obtained from cyclic voltammeteries in acetonitrile solution. All of the reduction waves were irreversible and the values of peak potential (at scan rate of 0.1V/s) of the thiophene derivatives **4** (-1.575 V), **5** (-1.555 V), and **6** (-1.530 V vs Ag/Ag⁺) are more negative than that of benzologue **1** (-1.435 V vs Ag/Ag⁺). This result can be explained by the effect of the annelation of π-excessive heterocyclic ring.

c) Electrophilic Substitution (Nitration).

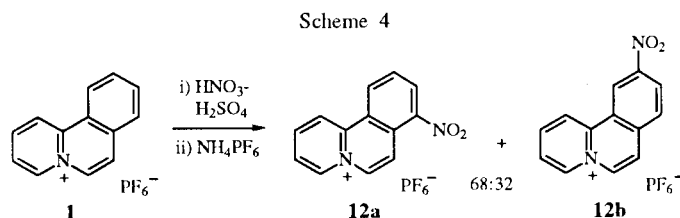
Nitration of **1** (X = PF₆) occurred almost quantitatively (94%) in a mixture of concentrated nitric and sulfuric acids at 100° for 2 hours. No further nitrated and unreacted starting materials were detected by mass-spectrum. The ¹H nmr spectrum of the product indicated that the mono-nitration occurred at two positions in the ratio of 68:32. Identification of the two isomeric nitro compounds was accomplished by 2D nmr technique, which proved that the substitution took place at the 8- and 10-positions in the fused benzene ring (Scheme 4). This assignment

Table IV
 UV-Absorption Bands of Compounds **1** and **4-6**

Compound	Solvent	λ max/nm (log ε)
1	EtOH [a]	354 (4.14) 337 (4.01) 323 (3.70) 278 (4.28) 269 (4.23) 256 sh (4.08) 237 (4.26) 222 (4.32) 217 (4.29)
4	MeCN	342 (4.14) 329 (3.96) 313 sh (3.67) 272 (4.41) 233 sh (4.13)
5	MeCN	345 (4.22) 330 (4.12) 316 (3.98) 303 sh (3.89) 279 (4.34) 241 (3.67)
6 [b]	MeCN	346 (3.94) 330 (3.88) 307 (3.96) 297 sh (3.91) 264 (4.44) 255 (4.43)

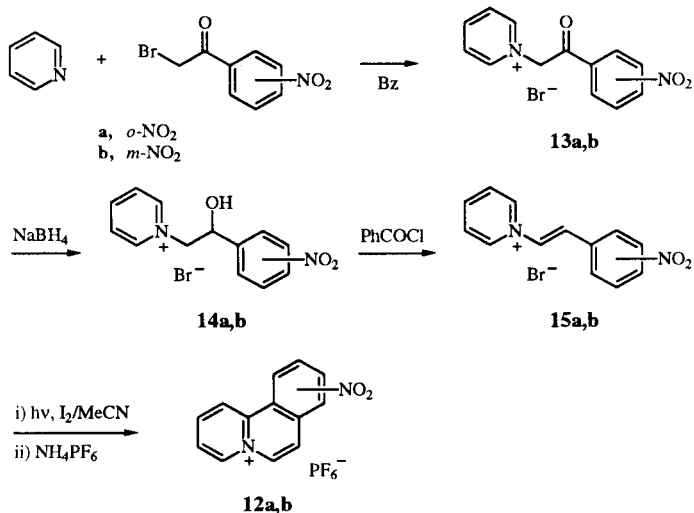
[a] Data from reference [15].

[b] The uv data were not reported in ref [10].



was also confirmed by the direct comparison with independently prepared samples (Scheme 5). The nitro-substituted styrylpyridinium salts **15a** and **15b** [13] were prepared from 2'- and 4'-nitro-2-bromoacetophenones in three steps, respectively. The photoirradiation of an acetonitrile solution of 1-(4'-nitrostyryl)pyridinium bromide (**15b**) in the presence of iodine gave 10-nitrobenzo[*a*]quinolizinium salt (**12b**) in 33% yield. Its ¹H nmr spectrum was identical with that of the minor product obtained

Scheme 5

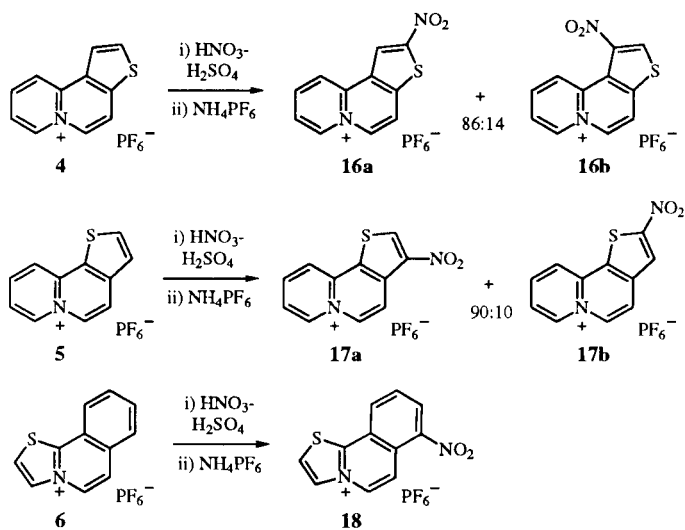


by the nitration reaction of **1**. The irradiation of 1-(2'-nitrostyryl)pyridinium bromide (**15a**) in acetonitrile also led to 8-nitrobenzo[*a*]quinolizinium salt (**12a**) in 5.8% yield, whose spectral properties were identical with those of the major product.

The reason of low regio-selectivity in benzo[*a*]quinolizinium ion (**1**) compared with other two benzologues **2** [7a] and **3** [7c] is unknown, but the reactivity of the 8-position, which was predicted by Bradsher [8] on the basis of the results in **2** and **3**, was two fold larger than that of the 10-position.

The thieno analogues **4** and **5** were nitrated under similar reaction conditions to benzo analogue **1**. The results are compared in Scheme 6. In both cases mononitro isomers **16a,b** and **17a,b** were produced with high positional selectivities, respectively. The structural determination of

Scheme 6



the four isomers was carried out by homo- and hetero-nuclear 2D nmr measurements.

The H-H COSY spectrum of the major nitrated product from **4** showed the presence of the characteristic two long-range couplings ⁵J_{5,10} and ⁵J_{1,4}. This fact indicates that the two protons in the bay-region of **4** still remained intact after the substitution and the nitro group was consequently introduced in the 2-position. In contrast, the lack of the long-range coupling of ⁵J_{1,4} in the spectrum of the minor product from **4** suggested that the substitution took place at the 1-position. By the introduction of a nitro group, the protons *ortho* to the nitro group of **16a** and **16b** were shifted downfield by 1.11 and 0.94 ppm in comparison with the corresponding protons of **4**, respectively. On the other hand, both major and minor nitrated products from **5** show one singlet proton belonging to the thiophene ring in the ¹H nmr spectra, and the chemical shifts of each protons were 9.74 and 8.88 ppm, respectively. By comparing with the values of the corresponding protons of the thiophene ring of **5**, which were 8.64 (at H-2) and 7.95 (at H-3) ppm, the major and minor isomers were identified as the 3-nitro and 2-nitro derivatives **17a** and **17b**, respectively.

The nitration of **6** required much reaction time (3.5 hours) compared with **4** and **5**. In contrast with the results of **1**, **4**, and **5**, the sole mononitro product, 7-nitro derivative **18**, was obtained in 43% yield.

The ¹H and ¹³C nmr data of the nitro derivatives **12** and **16-18** are summarized in Tables V, VI and VII.

It should be pointed out that no isomers substituted at the quinolizinium or thiazolopyridinium moiety have been obtained by nitration of **4**, **5**, and **6**. These results support Bradsher's prediction [8] that electrophilic attack occurs in fused rings. Although naphtho[2,1-*b*]thiophene (**19**) was exclusively nitrated at the 2-position [17a], the nitration of naphtho[1,2-*b*]thiophene (**20**) gave 87% of the 5-isomer and 13% of the 2-isomer [17b]. The replacement of a bridgehead carbon atom of **19** by a quaternary nitrogen atom, *i.e.* **4**, leads to the no-change of the regio-selectivity of the electrophilic nitration, while in the azonia-derivatives of **20**, *i.e.* **5** and **6** the substitution occurred on the fused ring at the 3- and 7-positions with high regio-selectivity, respectively.

Scheme 7

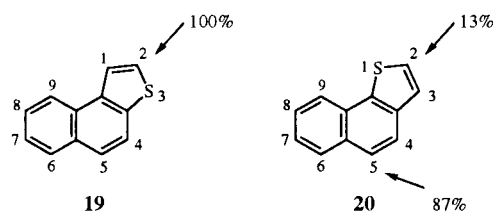


Table V
¹H NMR Chemical Shifts (δ) of Compounds **12**, **16**, **17** and **18** in DMSO-d₆ [a]

Compounds	1H	2H	3H	4H	5H	6H	7H	8H	9H	10H	11H
12a	9.65	8.81	8.40	9.62		9.19	8.66		8.83	8.27	9.56
12b	9.84	8.80	8.40	9.58		9.19	8.52	8.52	8.85		9.96
16a	9.72			8.75	9.31		9.51	8.25	8.69	9.34	
16b		9.39		8.82	9.29		9.55	8.25	8.60	8.78	
17a		9.74		8.82	9.34		9.58	8.25	8.62	9.06	
17b			8.88	8.49	9.23		9.58	8.29	8.65	9.09	
18		8.67	9.13		9.29	8.65		8.85	8.21	9.17	

[a] The numbering is given in Scheme 1.

Table VI
¹H NMR Coupling Constants (J, Hz) of Compounds **12**, **16**, **17** and **18** in DMSO-d₆ [a]

Compounds	J _{1,2}	J _{2,3}	J _{3,4}	J _{4,5}	J _{5,6}	J _{6,7}	J _{7,8}	J _{8,9}	J _{9,10}	J _{10,11}	J _{1,3}	J _{2,4}	J _{7,9}	J _{8,10}	J _{9,11}
12a	8.1	7.3	6.6			7.9			7.9	8.3	[b]	[b]			[b]
12b	8.1	7.3	6.6			7.9			7.9	8.3	1.0	1.0			2.0
16a				7.3			6.9	7.3	8.9				1.0	1.2	
16b				7.3			6.6	7.3	9.2				1.3	1.2	
17a				7.3			6.9	7.4	8.6				1.2	1.0	
17b				7.1			6.6	7.3	8.6				[b]	[b]	
18		4.0			7.6			7.9	8.3					[b]	

[a] The numbering is given in Scheme 1. [b] First-order analysis were not performed.

Table VII
¹³C NMR Chemical Shifts (δ) of Compounds **12a**, **12b**, **16a**, **17a** and **18** in DMSO-d₆ [a]

Compounds	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C3a	C6a	C7a	C10a	C10b	C11a	C11b
12a	123.8	141.6	125.5	140.1		133.9	117.1	145.9	130.0	130.4	131.5			123.8			126.1	142.0
12b	124.1	141.5	125.5	140.4		134.2	122.1	130.3	127.4	148.2	121.7			134.9			125.1	142.7
16a	125.3	154.5		118.6	134.8		139.0	124.0	140.2	123.8		144.5			140.5	129.9		
17a		141.8	141.8	117.1	134.8		138.6	124.2	139.8	123.3		133.0			138.8	133.4		
18		124.9	132.7		131.6	116.2	145.8	130.8	130.7	132.3			123.6		125.1	157.1		

[a] The numbering is given in Scheme 1.

EXPERIMENTAL

General.

Melting points were determined on a Yamato melting point apparatus MP-21 and are uncorrected. The ¹H and ¹³C nmr spectra were obtained using a JEOL JNM-EX270 (270 MHz and 67.5 MHz) spectrometer, respectively. Chemical shifts are reported in ppm from tetramethylsilane as 0.0 ppm and DMSO-d₆ as 39.5 ppm, respectively. The ir spectra were recorded with a JASCO FT/IR-5300 spectrometer. The uv and visible spectra were obtained with a Hitachi 220A spectrophotometer. The fast-atom bombardment mass spectra were recorded with a JEOL LX1000 spectrometer with *m*-nitrobenzyl alcohol as the matrix. Microanalyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer.

Reduction potentials were determined by cyclic voltammetry at the scan rate of 0.1V/s by the use of a Hokuto-Denko HA-501 potentiostat and a HB-104 function generator, and a Riken-Denshi X-Y recorder Model F-35. A Pt working electrode was

used in conjunction with a Pt counter electrode and a Ag/0.01M AgNO₃ (acetonitrile) reference electrode. All potential measurements were made against a Ag/Ag⁺. All perchlorate salts investigated were dissolved in dry acetonitrile (1 mM), and tetrabutylammonium perchlorate (0.1 M) was used as supporting electrolyte. Solutions were purged thoroughly with dry nitrogen prior to electrolysis.

Benzo[a]quinolizinium Salts (**1**, X = ClO₄, PF₆) were prepared by photocyclization of 1-styrylpyridinium bromide according to the literature [12a]. 2-(1-Pyridinium)-1-(2-thienyl)ethanone bromide (**7a**), 1-(2-hydroxy-2-thienylethyl)pyridinium bromide (**8a**), (*E*)-1-[2-(2-thienyl)vinyl]pyridinium bromide (**9a**), 2-(1-pyridinium)-1-(2'-nitrophenyl)ethanone bromide (**13a**), 2-(1-pyridinium)-1-(4'-nitrophenyl)ethanone bromide (**13b**), 1-(2-hydroxy-4'-nitrophenylethyl)pyridinium bromide (**14b**), and (*E*)-1-(4'-nitrostyryl)pyridinium bromide (**15b**) were prepared according to the literature [13] with some modifications as described below.

General Procedure for the Preparation of the 1-(2-Arylvinyl)-pyridinium Salts **9a,b** and **15a,b** and 3-Styrylthiazolium Salt (**9c**).

To a benzene solution (50 ml) of 2-bromoacetyl derivatives (50 mmoles), which were obtained by bromination of acetylthiophene and acetophenone derivatives with copper(II) bromide [18] and used without isolation, pyridine or thiazole (60 mmoles) was added. The mixture was refluxed for 3-4 hours. The resulting solid was filtered, washed with benzene and acetone, and recrystallized from ethanol to afford 1-(aroyl-methyl)pyridinium salts **7a,b** and **13a,b** and 3-phenacylthiazolium salt **7c**.

To a solution of 18 mmoles of the pyridinium salt or thiazolium salt in water (100 ml), a solution of 0.2 g (5.5 mmoles) of sodium borohydride in water (10 ml) was added portionwise at room temperature. After hydrolysis with hydrobromic acid (48%), the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to give 1-(2-aryl-2-hydroxyethyl)pyridinium bromides (**8a,b** and **14a,b**) or 3-(2-phenyl-2-hydroxyethyl)thiazolium bromide (**8c**).

A solution of the alcohol (10 mmoles) **8a-c** and **14a,b** in benzoyl chloride (10 ml) was heated at 190-200° for several hours. After the reaction mixture was cooled to room temperature, the excess benzoyl chloride was removed under reduced pressure. The residue was recrystallized from ethanol-ethyl acetate to yield (*E*)-1-(2-arylvinyl)pyridinium salts **9a,b** and **15a,b** and (*E*)-3-styrylthiazolium salt (**9c**).

2-(1-Pyridinium)-1-(3-thienyl)ethanone Bromide (**7b**).

This compound was obtained as pale-brown needles (54%), mp 177.5-178.5° dec; ir (potassium bromide): ν 3080, 3030 (CH), 1674 (C=O), 1634 (C=N), 1491, 1415, 1395, 1231, 1175, 882, 810, 737, 677 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 6.42 (s, 2H, CH_2), 7.62 (dd, $J = 1.4$ and 5.4 Hz, 1H, thienyl-4), 7.80 (dd, $J = 2.6$ and 5.4 Hz, 1H, thienyl-5), 8.28 (dd, $J = 6.1$ and 7.8 Hz, 2H, pyridyl-3,5), 8.74 (dd, $J = 1.0$ and 7.8 Hz, 1H, pyridyl-4), 8.80 (dd, $J = 1.4$ and 2.6 Hz, 1H, thienyl-2), 9.05 (dd, $J = 1.0$ and 6.1 Hz, 2H, pyridyl-2,6); ms: m/z 204 (M-Br^+).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{NOSBr}$: C, 46.49; H, 3.55; N, 4.93. Found: C, 46.26; H, 3.40; N, 4.71.

1-(2-Hydroxy-3-thienylethyl)pyridinium Bromide (**8b**).

This compound was obtained as white powders (83%), mp 180-182° dec; ir (potassium bromide): ν 3225 (OH), 3059 (CH), 1634 (C=N), 1489, 1306, 1177, 1078 (OH), 777, 677 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 4.71 (dd, $J = 8.9$ and 12.9 Hz, 1H, CH_2), 5.01 (dd, $J = 3.0$ and 12.9 Hz, 1H, CH_2), 5.18 (dd, $J = 3.0$ and 8.9 Hz, 1H, CH), 6.09 (broad s, 1H, OH), 7.24 (dd, $J = 1.3$ and 5.0 Hz, 1H, thienyl-4), 7.44 (dd, $J = 1.3$ and 3.0 Hz, 1H, thienyl-2), 7.60 (dd, $J = 3.0$ and 5.0 Hz, 1H, thienyl-5), 8.18 (dd, $J = 6.3$ and 7.6 Hz, 2H, pyridyl-3,5), 8.65 (dd, $J = 1.0$ and 7.6 Hz, 1H, pyridyl-4), 9.05 (dd, $J = 1.0$ and 6.3 Hz, 2H, pyridyl-2,6); ms: m/z 206 (M-Br^+).

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{NOSBr}$: C, 46.16; H, 4.04; N, 4.76. Found: C, 45.83; H, 4.04; N, 4.76.

(*E*)-1-[2-(3-Thienyl)vinyl]pyridinium Bromide (**9b**).

This compound was obtained as yellowish green powders (73%), mp 160-162.5° dec; ir (potassium bromide): ν 3056 (CH), 1653 (CH=CH), 1620 (C=N), 1478, 1260, 1208, 1152, 949 (CH=CH), 797, 667 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 7.57 (dd, $J = 1.0$ and 5.0 Hz, 1H, thienyl-4), 7.74 (dd, $J = 2.9$ and 5.0 Hz, 1H, thienyl-5), 7.84 (d, $J = 14.2$ Hz, 1H, CH=CH), 7.92 (dd, $J = 1.0$ and 2.9 Hz, 1H, thienyl-2), 8.25 (dd, $J = 6.4$ and 7.8 Hz, 2H, pyridyl-3,5), 8.36 (d, $J = 14.2$ Hz, 1H, CH=CH), 8.65 (dd, $J =$

1.0 and 7.8 Hz, 1H, pyridyl-4), 9.36 (dd, $J = 1.0$ and 6.4 Hz, 2H, pyridyl-2,6); ms: m/z 188 (M-Br^+).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{NSBr}$: C, 49.27; H, 3.76; N, 5.22. Found: C, 49.38; H, 3.67; N, 4.95.

2-(3-Thiazolium)-1-phenylethanone Bromide (**7c**) [19].

This compound was obtained as colorless prisms (42%), mp 224-225° dec (ref 227-229° [19]).

3-(2-Hydroxy-2-phenylethyl)thiazolium Bromide (**8c**).

This compound was obtained as white micro crystals (76%), mp 153.5-155°; ir (potassium bromide): ν 3355 (OH), 3048 (CH), 1618 (C=N), 1553, 1453, 1424, 1279, 1196, 1096, 1067 (OH), 922, 768, 694 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 4.68 (dd, $J = 9.1$ and 13.0 Hz, 1H, CH_2), 4.85 (dd, $J = 3.0$ and 13.0 Hz, 1H, CH_2), 5.09 (dd, $J = 3.0$ and 9.1 Hz, 1H, CH), 6.07 (broad s, 1H, OH), 7.30-7.48 (m, 5H, phenyl), 8.36 (d, $J = 3.6$ Hz, 1H, thiazolyl-5), 8.60 (d, $J = 3.6$ Hz, 1H, thiazolyl-4), 10.17 (s, 1H, thiazolyl-2); ms: m/z 206 (M-Br^+).

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{NOSBr}$: C, 46.16; H, 4.23; N, 4.90. Found: C, 46.39; H, 4.20; N, 4.82.

(*E*)-3-Styrylthiazolium Bromide (**9c**).

This compound was obtained as white powders (73%), mp 202.5-204.0° dec; ir (potassium bromide): ν 3015 (CH), 1628 (C=N), 1541 (CH=CH), 1431, 1277, 1225, 1169, 949 (CH=CH), 748, 689 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 7.43 (dd, $J = 1.3$ and 7.1 Hz, 1H, phenyl-4), 7.50 (dd, $J = 7.1$ and 7.6 Hz, 2H, pyridyl-3,5), 9.36 (dd, $J = 1.3$ and 7.6 Hz, 2H, phenyl-2,6), 7.84 (d, $J = 14.7$ Hz, 1H, CH=CH), 8.51 (d, $J = 14.7$ Hz, 1H, CH=CH), 8.52 (d, $J = 4.0$ Hz, 1H, thiazolyl-5), 9.13 (d, $J = 4.0$ Hz, 1H, thiazolyl-4), 10.51 (s, 1H, thiazolyl-2); ms: m/z 188 (M-Br^+).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{NSBr}$: C, 49.27; H, 3.76; N, 5.22. Found: C, 48.89; H, 3.69; N, 5.10.

1-(2-Hydroxy-2'-nitrophenylethyl)pyridinium Bromide (**14a**) [20].

This compound was obtained as pale brown micro crystals (77%), mp 218-221° dec (ref 208° [20]).

(*E*)-1-(2'-Nitrostyryl)pyridinium Bromide (**15a**).

This compound was obtained as yellow powders (47%), mp 228.5-229.5°; ir (potassium bromide): ν 2990 (CH), 1618 (C=N), 1572 (CH=CH), 1520 (NO_2), 1473, 1340 (NO_2), 1213, 1165, 965 (CH=CH), 862, 797, 735, 681 cm^{-1} ; ^1H nmr (DMSO- d_6): δ 7.76 (ddd, $J = 1.7$, 7.3, and 8.3 Hz, 1H, phenyl-4), 7.92 (ddd, $J = 1.3$, 7.3, and 7.9 Hz, 1H, phenyl-5), 7.97 (dd, $J = 1.7$ and 7.9 Hz, 1H, phenyl-6), 8.06 (d, $J = 14.2$ Hz, 1H, CH=CH), 8.18 (dd, $J = 1.3$ and 8.3 Hz, 1H, phenyl-3), 8.31 (dd, $J = 6.6$ and 7.8 Hz, 2H, pyridyl-3,5), 8.37 (d, $J = 14.2$ Hz, 1H, CH=CH), 8.75 (dd, $J = 1.0$ and 7.8 Hz, 1H, pyridyl-4), 9.39 (dd, $J = 1.0$ and 6.6 Hz, 2H, pyridyl-2,6); ms: m/z 227 (M-Br^+).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_2\text{Br}$: C, 50.84; H, 3.61; N, 9.12. Found: C, 51.07; H, 3.44; N, 8.84.

General Procedure for the Photocyclization of 1-(2-Arylvinyl)pyridinium Salts **9a,b** and 3-Styrylthiazolium Salt (**9c**).

A methanol solution (1000 ml) of **9** (400 mg, 1.5 mmoles) and iodine (80 mg) in a Pyrex vessel was irradiated with a 450W high-pressure mercury lamp (Ushio UM-452) at room temperature. After the irradiation was complete, the solution was concentrated and the residue was dissolved in hot water (50 ml). An insoluble brown solid was filtered off and a saturated aqueous

solution of ammonium hexafluorophosphate was added to the filtrate. The precipitate was filtered, washed with cold water, and recrystallized from acetonitrile-ethanol to afford **4-6** ($X = PF_6$) as needles.

The perchlorate salts **4-6** ($X = ClO_4$) were also obtained by addition of a saturated aqueous lithium perchlorate to the filtrate, and recrystallized from acetonitrile-ethanol.

Thieno[3,2-*a*]quinolizinium Hexafluorophosphate (**4**, $X = PF_6$).

This compound was obtained as colorless micro needles (acetonitrile-ethanol), yield 67%, mp 220.5–222.0°; ir (potassium bromide): 3121 (CH), 1624 (C=N), 1462, 1375, 1200, 839 (PF), 735 cm^{-1} ; ms: m/z 186 (M- PF_6)⁺.

Anal. Calcd. for $C_{11}H_8NSPF_6$: C, 39.89; H, 2.43; N, 4.23. Found: C, 40.08; H, 2.23; N, 4.17.

Thieno[3,2-*a*]quinolizinium Perchlorate (**4**, $X = ClO_4$).

This compound was obtained as pale yellow needles (acetonitrile-ethanol), yield 74%, mp 213–214°; ir (potassium bromide): 3106 (CH), 1638, 1620 (C=N), 1460, 1373, 1200, 1088 (ClO), 822, 739 cm^{-1} ; ms: m/z 186 (M- ClO_4)⁺.

Anal. Calcd. for $C_{11}H_8NSClO_4$: C, 46.24; H, 2.82; N, 4.90. Found: C, 46.14; H, 2.57; N, 4.86.

Thieno[2,3-*a*]quinolizinium Hexafluorophosphate (**5**, $X = PF_6$).

This compound was obtained as white micro crystals (acetonitrile-ethanol), yield 58%, mp 251–252°; ir (potassium bromide): 3123 (CH), 1642 (C=N), 1483, 1462, 1433, 1408, 1360, 1175, 837 (PF) cm^{-1} ; ms: m/z 186 (M- PF_6)⁺.

Anal. Calcd. for $C_{11}H_8NSPF_6$: C, 39.89; H, 2.43; N, 4.23. Found: C, 39.95; H, 2.13; N, 4.21.

Thieno[2,3-*a*]quinolizinium Perchlorate (**5**, $X = ClO_4$).

This compound was obtained as pale green needles (acetonitrile-ethanol), yield 69%, mp 197–198°; ir (potassium bromide): 3094 (CH), 1636 (C=N), 1483, 1460, 1435, 1406, 1360, 1175, 1090 (ClO) cm^{-1} ; ms: m/z 186 (M- ClO_4)⁺.

Anal. Calcd. for $C_{11}H_8NSClO_4$: C, 46.24; H, 2.82; N, 4.90. Found: C, 46.05; H, 2.63; N, 4.91.

Thiazolo[2,3-*a*]isoquinolinium Hexafluorophosphate (**6**, $X = PF_6$).

This compound was obtained as colorless micro crystals (acetonitrile-ethanol), yield 33%, mp 241–243°; ir (potassium bromide): 3150 (CH), 1632 (C=N), 1495, 1391, 1372, 1310, 1275, 837 (PF) cm^{-1} ; ms: m/z 186 (M- PF_6)⁺.

Anal. Calcd. for $C_{11}H_8NSPF_6$: C, 39.89; H, 2.43; N, 4.23. Found: C, 40.03; H, 2.19; N, 4.26.

Thiazolo[2,3-*a*]isoquinolinium Perchlorate (**6**, $X = ClO_4$).

This compound was obtained as colorless micro crystals (acetonitrile-ethanol), yield 27%, mp 235–235.5° (ref 233.5–235° [10]); ir (potassium bromide): 3106 (CH), 1630 (C=N), 1491, 1389, 1372, 1310, 1273, 1084 (ClO), 824 cm^{-1} ; ms: m/z 186 (M- ClO_4)⁺.

Anal. Calcd. for $C_{11}H_8NSClO_4$: C, 46.24; H, 2.82; N, 4.90. Found: C, 46.05; H, 2.60; N, 4.91.

The 8- and 10-nitrobenzo[a]quinolizinium salts **12a** and **12b** were obtained by irradiation of an acetonitrile solution of 1-(nitrostyryl)pyridinium salts **15a** and **15b** and iodine, respectively.

8-Nitrobenzo[a]quinolizinium Hexafluorophosphate (**12a**).

This compound was obtained as pale yellow micro crystals (acetonitrile-ethanol), yield 5.8%, mp 198.5–199.5°; ir (potassium bromide): 3127 (CH), 1636 (C=N), 1541 (NO₂), 1474, 1356 (NO₂), 1321, 1242, 1202, 1181, 839 (PF) cm^{-1} ; uv (acetonitrile): λ max 264 (log ϵ 4.47), 323 sh (3.69), 341 (4.01), 357 nm (4.08); ms: m/z 225 (M- PF_6)⁺.

Anal. Calcd. for $C_{13}H_9N_2O_2PF_6$: C, 42.18; H, 2.45; N, 7.57. Found: C, 42.22; H, 2.20; N, 7.59.

10-Nitrobenzo[a]quinolizinium Hexafluorophosphate (**12b**).

This compound was obtained as pale yellow micro crystals (acetonitrile-ethanol), yield 33%, mp 248–250°; ir (potassium bromide): 3119 (CH), 1638 (C=N), 1547, 1520 (NO₂), 1474, 1348 (NO₂), 1260, 1173, 1150, 837 (PF) cm^{-1} ; uv (acetonitrile): λ max 227 (log ϵ 4.32), 243 sh (4.29), 284 (4.43), 324 (3.92), 339 (3.99), 356 nm (4.03); ms: m/z 225 (M- PF_6)⁺.

Anal. Calcd. for $C_{13}H_9N_2O_2PF_6$: C, 42.18; H, 2.45; N, 7.57. Found: C, 41.93; H, 2.21; N, 7.47.

General Procedure for Nitration of **1** and **4-6**.

Addition of 200 mg (0.6 nmol) of benzo[a]quinolizinium derivatives to a mixture of equal volumes (0.3 ml) of nitric acid (d 1.38) and sulfuric acid (d 1.84) was followed by heating at 100° for several hours. After the reaction mixture was cooled to room temperature, the mixture was poured into water and a saturated aqueous solution of ammonium hexafluorophosphate was added to give the hexafluorophosphate salts. The structural elucidation of nitration products **12** and **16-18** were carried out as described below.

Nitration of Benzo[a]quinolizinium Salt (**1**).

The resulting precipitate (94%) contained two components (the ratio was 68:32 from the ¹H nmr spectrum). Since the separation of these products was difficult, these were identified as 8-nitro- and 10-nitrobenzo[a]quinolizinium salts **12a** and **12b** by a comparison of the ¹H nmr spectrum with those of photochemically prepared materials.

Nitration of Thieno[3,2-*a*]quinolizinium Salt (**4**).

The resulting precipitate (78%) contained two components (the ratio was 86:14 from the ¹H nmr spectrum). Recrystallization from acetonitrile-ethanol (1:4) gave 2-nitro compound **16a** as pale brown needles (49%), mp 244–246° dec; ir (potassium bromide): 3115 (CH), 1638 (C=N), 1534 (NO₂), 1460, 1343 (NO₂), 1196, 835 (PF) cm^{-1} ; uv (acetonitrile): λ max 241 (log ϵ 4.31), 264 (4.22), 278 sh (4.17), 301 (4.10), 329 (4.09), 349 nm (4.16); ms: m/z 331 (M- PF_6)⁺.

Anal. Calcd. for $C_{11}H_7N_2O_2SPF_6$: C, 35.12; H, 1.88; N, 7.45. Found: C, 35.20; H, 1.65; N, 7.31.

The minor component was identified as 1-nitrothieno[3,2-*a*]quinolizinium salt (**16b**) by ¹H nmr analysis without isolation.

Nitration of Thieno[2,3-*a*]quinolizinium Salt (**5**).

The resulting precipitate (82%) contained two components (the ratio was 90:10 from the ¹H nmr spectrum). Recrystallization from acetonitrile-ethanol (1:4) gave 3-nitro compound **17a** as brown needles (56%), mp 239–240.5° dec; ir (potassium bromide): 3129 (CH), 1642 (C=N), 1539 (NO₂), 1441, 1362, 1339 (NO₂), 1202, 1169, 833 (PF) cm^{-1} ; uv (acetonitrile): λ max 265 (log ϵ 4.53), 299 (4.01), 315 (4.00), 329 (4.18), 344 (4.29), 483 nm (2.75); ms: m/z 331 (M- PF_6)⁺.

Anal. Calcd. for $C_{11}H_7N_2O_2SPF_6$: C, 35.12; H, 1.88; N, 7.45. Found: C, 35.14; H, 1.62; N, 7.38.

The minor component was identified as 2-nitrothieno[2,3-*a*]-quinolinizinium salt (**17b**) by ^1H nmr analysis without isolation.

Nitration of Thiazolo[2,3-*a*]isoquinolinium Salt (**6**).

The resulting precipitate (65%) was identified as 7-nitro-compound **18** by the ^1H nmr spectrum. Recrystallization from acetonitrile-ethanol (1:4) gave pale pink micro crystals (43%), mp 220-222°; ir (potassium bromide): 3135 (CH), 1638 (C=N), 1535 (NO₂), 1487, 1356 (NO₂), 1310, 841 (PF) cm⁻¹; uv (acetonitrile): λ max 224 (log ϵ 4.29), 268 (4.37), 339 (3.84), 354 nm (3.89); ms: m/z 331 (M-PF₆)⁺.

Anal. Calcd. for C₁₁H₇N₂O₂SPF₆: C, 35.12; H, 1.88; N, 7.45. Found: C, 35.16; H, 1.64; N, 7.42.

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