Synthesis and Reactions of Methylbenzo[*c*]quinolizinium Salts [1]

Sadao Arai*, Hitoshi Arai, Kunihisa Tabuchi,
Takamichi Yamagishi and Mitsuhiko Hida*

Department of Industrial Chemistry, Faculty of Technology,
Tokyo Metropolitan University, 1-1 Minami-Osawa,
Hachioji, Tokyo 192-03, Japan

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Six isomers of the methylbenzo[*c*]quinolizinium salt **3** including four new monomethyl derivatives were synthesized by thermal-intramolecular quaternization of the *cis*-methyl-substituted 2-[2-(2-chlorophenyl)-vinyl]pyridines **4** or by the irradiation of *trans*-**4** with selected wavelengths ($290 < \lambda < 340$ nm and $\lambda > 400$ nm) in acetonitrile. Among the regioisomeric monomethyl derivatives **3**, the 1-, 3-, and 6-methyl derivatives **3b**, **3d**, and **3g** reacted with *p*-methoxybenzaldehyde in the presence of bis(1-piperidino)-(*p*-methoxyphenyl)-methane **7** to yield *trans*-(*p*-methoxystyryl)benzo[*c*]quinolizinium salts **6**. The reactivity of **3** and methylbenzo[*a*]quinolizinium salts **1** was discussed on the basis of their π-electron energy.

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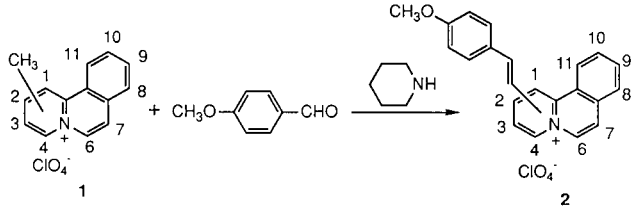
In our previous paper [2], we reported the synthesis of all isomers of (monomethyl)benzo[*a*]quinolizinium salts **1** and examined their reactivity on the aldol-type condensation in order to study the electron-attracting character of the quaternary nitrogen of azonia aromatic compounds. Among the ten regioisomeric monomethyl derivatives, only the 2- and 4-methyl derivatives **1c** and **1e** reacted with *p*-methoxybenzaldehyde in the presence of piperidine to yield *trans*-(*p*-methoxystyryl)benzo[*a*]quinolizinium salts **2** (Scheme 1). Thus, the methyl group was activated at the 2- and 4-positions, located *para* or *ortho* to the azonia ring nitrogen, respectively; however, it was unreactive at the 6-position located at another *ortho* position. The base-catalyzed aldol-type condensation of **1c** was successfully applied to the synthesis of new solvatochromic cyanine-type dyes [3]. These results prompted us to extend our study to (monomethyl)benzo[*c*]quinolizinium salts **3**, which are the structural isomers of compounds **1**. Among the ten possible monomethyl derivatives **3**, however, only two compounds **3e** and **3f** have been described [4], and the methyl derivatives **3b**, **3d**, and **3g**, which contain a methyl group located *ortho* or *para* to the azonia ring nitrogen, have not yet been reported. In this paper we will describe the details of the synthesis of **3**. The reactivity of methylbenzoquinolizinium salts **1** and **3** in the base-catalyzed aldol-type condensation will be also discussed on the basis of π-electron energy and frontier electron density.

Scheme 1

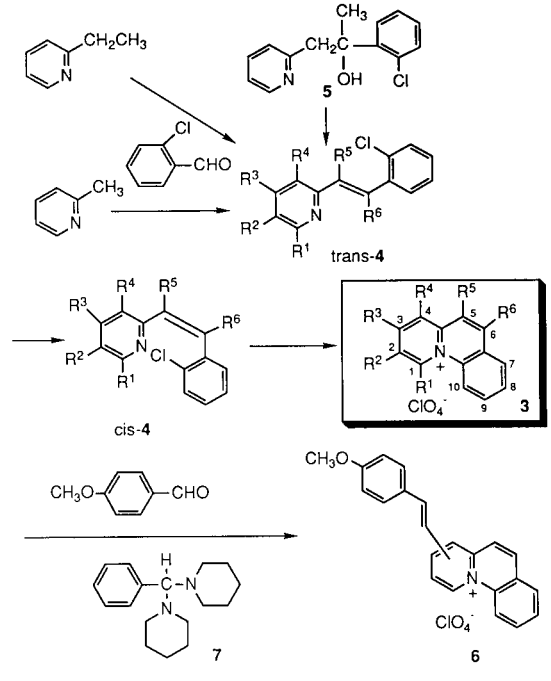


1 or 2	b	c	d	e	f	g	h	i	j	k
Position of Substituent	1	2	3	4	6	7	8	9	10	11

Synthesis of Methylbenzo[*c*]quinolizinium Salts.

Fozard and Bradsher reported the synthesis of benzo[*c*]-quinolizinium salts **3a**, **3e**, and **3f** *via* intramolecular cyclization (Scheme 2) [4]. In order to apply Scheme 2 to the synthesis of the new monomethyl derivatives **3b**, **3c**, **3d**, and **3g**, we first examined the preparation of **3a** in detail.

Scheme 2



3 and 4
a: R^1 - R^6 = H
b: R^1 = CH_3, R^2 - R^6 = H
c: R^2 = CH_3, R^1 = R^3 - R^6 = H
d: R^3 = CH_3, R^1 = R^2 = R^4 - R^6 = H
e: R^4 = CH_3, R^1 - R^3 = R^5 = R^6 = H
f: R^5 = CH_3, R^1 - R^4 = R^5 = H
g: R^6 = CH_3, R^1 - R^5 = H

The condensation of 2-methylpyridine with 2-chlorobenzaldehyde afforded *trans*-2-[2-(2-chlorophenyl)vinyl]pyri-

dine **4a**. A benzene solution of *trans*-**4a** was irradiated with a 300W high-pressure Hg lamp through a Pyrex-filter ($\lambda > 280$ nm) to give the *cis-trans* mixture. The *cis*-derivative **4a** in the mixture underwent intramolecular quaternization at 170° for 1 hour to afford benzo[*c*]quinolizinium salt **3a** in 47% yield from *trans*-**4a**. The salt **3a** was obtained only in a trace amount by heating *cis*-**4a** in refluxing acetonitrile or in sulfolane at 80°, while heating at 170° in sulfolane gave a higher yield (66%) (Table 1).

Table 1
Thermal Cyclization of **4a** [a]

Solvent	Temp (°C)	Time (h)	Yield (%) of **3a**
None	170	1	47
Ethanol	78	10	0
Acetonitrile	82	10	trace
Sulfolane	80	7	trace
Sulfolane	170	0.5	66

[a] After *trans*-**4a** in benzene was irradiated for 10 hours, the *trans-cis* mixture was heated.

Although the irradiation with a Pyrex filtered-light of *trans*-**4a** in benzene gave only *cis*-**4a**, compound **3a** was obtained by irradiation of *trans*-**4a** in acetonitrile. Figure 1 shows the time course of the photocyclization of **4a** in

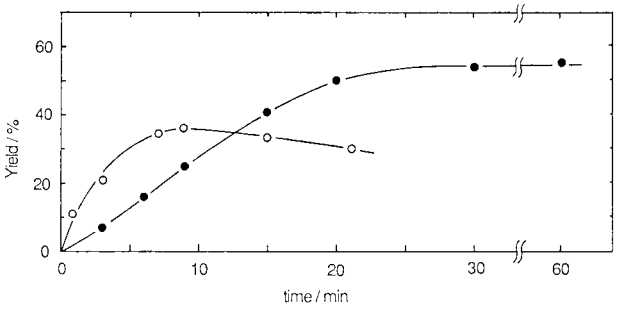


Fig. 1 Time course of the Photocyclization of **4a** [a]

[a] The acetonitrile solution of trans-**4a** (6×10^{-5} mol dm^{-3}) was irradiated. Yields were obtained spectrophotometrically.
○: The solution was irradiated with a Pyrex-filtered light ($\lambda > 280$ nm).
●: The solution was irradiated with a selected wavelength ($290 < \lambda < 340$ nm and $\lambda > 400$ nm) using aqueous potassium chromate solution filter.

acetonitrile. By the use of a Pyrex-filtered light ($\lambda > 280$ nm), the yield reached a maximum (34%) after 9 minutes and then decreased. This result suggested the photo-decomposition of the product **3a** under irradiation. When *trans*-**4a** was irradiated with a selected wavelength ($290 < \lambda < 340$ nm and $\lambda > 400$ nm) using an aqueous potassium chromate solution filter, the yield gradually increased and remained unchanged at a maximum value (54%). Figure 1 indicates that the maximum yield obtained by the irradiation with the selected wavelength ($290 < \lambda < 340$ nm and $\lambda > 400$ nm) was better than that obtained by a Pyrex-filtered light ($\lambda > 280$ nm) irradiation. Table 2 shows that the highest yield was obtained in acetonitrile.

Table 2
Yield (%) of **3a** on Photocyclization of *trans*-**4a** [a]

Solvent	Reaction Conditions [b]	[c]
Benzene	0	0
Acetonitrile	34	54
Ethanol	[d]	8
Sulfolane	[d]	36
Formamide	[d]	9

[a] The compound *trans*-**4a** ($\sim 6 \times 10^{-5}$ mol dm^{-3}) was irradiated. Yields were obtained spectrophotometrically. [b] The solution was irradiated with a Pyrex-filtered light ($\lambda > 280$ nm). [c] The solution was irradiated with a selected wavelengh ($290 < \lambda < 340$ nm and $\lambda > 400$ nm) using aqueous potassium chromate solution filter. [d] The reactions were not attempted.

The methodology in Scheme 2 was applied to the synthesis of the methyl derivatives **3b-3g**. The condensation of 2,3- and 2,5-dimethylpyridines with *o*-chlorobenzaldehyde in refluxing acetic anhydride gave only the *trans*-2-styryl derivatives **4e** (68%) and **4c** (44%), respectively. On the other hand, the reaction of 2,4- and 2,6-dimethylpyridines afforded the *trans*-2-styrylpyridines **4d** (59%) and **4b** (20%) along with the distyryl derivatives, respectively. The olefin *trans*-**4f** was obtained by the condensation of 2-ethylpyridine with *o*-chlorobenzaldehyde. The synthesis of **4g** was attempted by the dehydration of 2-(2-chlorophenyl)-1-(2-pyridyl)-2-propanol **5**, which was prepared by the reaction of the carbanion of 2-methylpyridine with 2-chloroacetophenone in 27% yield. The dehydration of the alcohol **5** with thionyl chloride in pyridine gave *E*- and *Z*-**4g** mixtures in 15% and 38% yields, respectively. The configuration of *E*- and *Z*-**4g** was determined as follows. The ^{1}H nmr spectrum of *E*-**4g** revealed the methyl proton which appeared as doublet ($J = 1.46$ Hz) at lower field ($\delta = 2.46$) than that of *Z*-**4g** ($\delta = 2.23$) with doublet ($J = 1.54$ Hz). Hence the signal at δ 2.46 can reasonably be assigned to a methyl group *cis* to a pyridyl group. The uv spectra showed that the absorption maximum of *Z*-**4g** was shifted to shorter wavelength than that of *E*-**4g**. This assignment was also confirmed by the finding that only *Z*-**4g** was thermally cyclized to afford **3g** (*vide infra*). On dehydration of the alcohol **5** with refluxing acetic anhydride and acetic acid, cyclization product **3g** was unexpectedly obtained in 19% yield with *E*-**4g** (16%) and *Z*-**4g** (24%). This result showed that the resulting *Z*-**4g** was thermally cyclized to give **3g** under these conditions. Table 3 shows that the monomethyl derivatives **3c-3g** were obtained by thermal cyclization of *cis*-**4c-4g** at 170°. The thermal cyclization of *cis*-**4b** at 170°, however, failed and

trans-**4b** was recovered (82%). This result may be due to the steric hindrance in *cis*-**4b**. The desired **3b** was successfully obtained by the irradiation of *trans*-**4b** in acetonitrile. Table 3 shows that the photocyclization under selected wavelength ($290 < \lambda < 340$ nm and $\lambda > 400$ nm) was effective for the synthesis of **3** irrespective of the position of a methyl group.

Table 3

Yield (%) of **3** on Thermal Cyclization and Photocyclization of **4**

Starting Compound	Reaction condition [a]	[b]	[c]
4a	47	34	54
4b	0	18	56
4c	45	41	71
4d	37	14	46
4e	45	47	75
4f	48	10	20
Z-**4g**	35 [d]	27	40
E-**4g**	0 [d]	25	32

[a] After *trans*-**4** in benzene was irradiated for 10 hours, the *trans*-*cis* mixtures were heated at 170° for 1 hour. [b] The acetonitrile solution of *trans*-**4** ($\sim 6 \times 10^{-5}$ mol dm^{-3}) was irradiated with a Pyrex-filtered light ($\lambda > 280$ nm). Yields were obtained spectrophotometrically. [c] The solution was irradiated with a selected wavelength ($290 < \lambda < 340$ nm and $\lambda > 400$ nm) using aqueous potassium chromate solution filter. Yields were obtained spectrophotometrically. [d] The compound *Z*- or *E*-**4g** was heated at 170° for 1 hour.

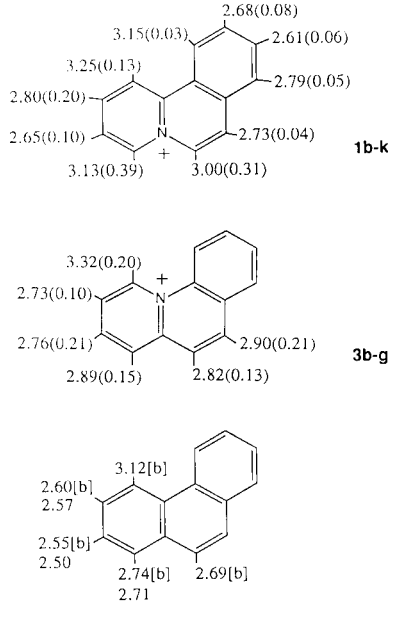


Fig. 2 ^{1}H nmr Chemical Shift of Methyl Group of **1b-k**, **3b-g**, and Methylphenanthrene in DMSO-d_6[a]

[a] The differences of the chemical shifts between methylbenzoquinolizinium salt in DMSO-d_6 and the corresponding methylphenanthrene in CCl_4 are shown in parentheses.
[b] Chemical shifts in CCl_4(K. D. Bartle and J. A. S. Smith, Spectrochim. Acta, **23A**, 1689(1967).

The ^{1}H nmr chemical shifts of the methyl group of the monomethyl derivatives **3b-3g** are shown in Figure 2, together with those of the compounds **1** and (monomethyl)-phenanthrenes. All the methyl proton signals of methylbenzoquinolizinium salts **1b-1k** and **3b-3g** were shifted downfield compared with those of the corresponding methylphenanthrenes. The downfield shift of methyl proton signals of compounds **1b-1k** and **3b-3g** was especially large at *ortho* and *para* positions to the azonia ring nitrogen as designated in parentheses in Figure 2.

Reactivity of Monomethylbenzoquinolizinium Salts.

In order to study the reactivity of compounds **3b-3g** for electrophilic reagents, the reaction with *p*-methoxybenzaldehyde was attempted. We reported previously that in the aldol-type condensation of compounds **1c** and **1e** the yield was increased by using an adduct, bis(1-piperidino)-(*p*-methoxyphenyl)methane **7** [2]. In the presence of the adduct **7**, the reaction of the monomethyl derivatives **3b**, **3d**, and **3g** gave *trans*-*p*-methoxystyrylbenzo[*c*]quinolizinium perchlorates **6** in 86, 91, and 93% yields, respectively. The reaction of the monomethyl derivatives **3c**, **3e**, and **3f**, however, did not yield the compounds **6** (Table 4). Thus the methyl group which is located *ortho* or *para* to the azonia ring nitrogen was reactive in the aldol-type condensation.

Table 4

Yields of the Reaction of **1b-k** and **3b-k** with *p*-Methoxybenzaldehyde and the Difference of Total π-Electron Energy ($\Delta E\pi/\beta$) between $AzCH_3$ and $Az\bar{C}H_2$

Compound	Yield (%) [a]	$\Delta E\pi/\beta$	Compound	Yield (%) [a]	$\Delta E\pi/\beta$
1b	0	1.2307	**3b**	86	1.3480
1c	99	1.3272	**3c**	0	1.2047
1d	0	1.1876	**3d**	91	1.3220
1e	46	1.3527	**3e**	0	1.2498
1f	0	1.2829	**3f**	0	1.2593
1g	0	1.2603	**3g**	93	1.3686
1h	0	1.2492	**3h**	[b]	1.2842
1i	0	1.2280	**3i**	[b]	1.1862
1j	0	1.2043	**3j**	[b]	1.2444
1k	0	1.2664	**3k**	[b]	1.2303

[a] Ref [2]. [b] The reactions were not attempted.

These results were understood by the assumption that the reactivity of the methyl group depends on its acidity. The acidity of (monomethyl)benzoquinolizinium salts ($AzCH_3$) can be correlated with the difference in total π-electron energy ($\Delta E\pi/\beta$) between $AzCH_3$ and the carbanion ($Az\bar{C}H_2$) [5].

$\Delta E\pi/\beta = \{E\pi(Az\bar{C}H_2) - E\pi(AzCH_3)\}/\beta$, where β is the resonance integral. The value $\Delta E\pi/\beta$ is the larger, the acidity of the methyl group is larger. Table 4 lists the values $\Delta E\pi/\beta$ of compounds **1b-g** and **3b-g**. The values

$\Delta E\pi/\beta$ of the derivatives whose methyl group is located at *ortho* or *para* position to azonia ring nitrogen are larger than those of the others. In the base-catalyzed aldol-type condensation, compounds **1c, 1e, 3b, 3d,** and **3g** afforded the corresponding styryl derivatives (Table 4). These results will indicate that the threshold of $\Delta E\pi/\beta$ for the reaction of compounds **1b-k** and **3b-k** with the aldehyde is about 1.30.

The frontier electron densities $\{f_r^{(N)} = 2\ (LUMO)^2\}$ of the parent compounds, **1a** and **3a**, are also shown in Table 5. A methyl group connected at the position of large $f_r^{(N)}$ is expected to be acidic, because the hyperconjugation of the methyl group can be estimated approximately by the interaction between the pseudo-pi orbitals of the methyl group and the frontier orbitals of the aromatics. Table 5 shows that $f_r^{(N)}$ at the 2 and 4 positions of **1a** and the 3 and 6 positions of **3a** are larger than those of the others indicating a good correlation to the results obtained.

Table 5
The Frontier Electron Density ($f_r^{(N)}$) of **1a** and **3a** [a]

Postition in **1a**	$f_r^{(N)}$	Postition in **3a**	$f_r^{(N)}$
1	0.030	1	0.137
2	0.415	2	0.082
3	0.019	3	0.246
4	0.333	4	0.005
6	0.010	5	0.082
7	0.217	6	0.426
8	0.144	7	0.202
9	0.097	8	0.040
10	0.052	9	0.130
11	0.178	10	0.129

[a] See Schemes 1 and 2 for numbering.

EXPERIMENTAL

Melting points were determined on a Yamato melting point apparatus MP-21 and were uncorrected. The ^{1}H nmr spectra were obtained using a Hitachi R-24 (60 MHz) or JEOL FX90Q (90 MHz) spectrometer. Chemical shifts are reported in ppm from TMS as an internal standard and given in δ units. The ir spectra were recorded with a JASCO IRA-1 spectrometer. The uv and visible spectra were obtained with a Hitachi 220A spectrometer. The fast-atom bombardment (FAB) mass spectra were recorded with a JEOL JMS-DX 300 spectrometer with *m*-nitrobenzyl alcohol as matrix. Elemental analyses were performed by Mr. Hirokatsu Suzuki at Department of Chemistry, Tokyo Metropolitan University. An Eikosha 300 W high-pressure mercury lamp was used as the irradiation source. All MO calculations were carried out by Huckel MO using the parameters suggested by Streitwieser, Jr. [6].

Procedure for the Preparation of *trans*-2-[2-(2-Chlorophenyl)-vinyl]pyridines (**4**), *e.g.* Compound (**4a**).

trans-2-[2-(2-Chlorophenyl)vinyl]pyridine (**4a**).

A mixture of α-picoline (6.0 g, 64 mmoles) and 2-chlorobenzaldehyde (9.3 g, 66 mmoles) in acetic anhydride (12 ml) was heated under reflux for 16 hours under a nitrogen atmosphere. After the solvent was evaporated under reduced pressure, benzene (200 ml) was added to the residue, washed with 5% aqueous sodium bisulfite and water. The organic layer was chromatographed through a column (neutral alumina) using benzene as eluent. Concentrated hydrochloric acid (30 ml) and water (100 ml) were added to the benzene solution and the aqueous layer was separated, then aqueous sodium hydroxide (1 *N*) was added to the water layer. The aqueous layer was extracted with benzene, then the extract was washed with water and evaporated to dryness. Recrystallization from hexane afforded **4a** as pale yellow crystals (5.36 g, 39%), mp 75.9-76.4° (lit [3] 75-76.5°); ir (potassium bromide): 1580, 1467, and 983 cm^{-1}; ^{1}H nmr (60 MHz, deuteriochloroform): δ 6.8-7.8 (m, 8H, ArH and CH=), 7.9 (d, J = 16 Hz, 1H, CH=), and 8.57 (d, J = 5 Hz, 1H, pyridine 6-H).

Anal. Calcd. for $C_{13}H_{10}NCl$: C, 72.38; H, 4.67; N, 6.49. Found: C, 72.56; H, 4.52; N, 6.34.

trans-2-[2-(2-Chlorophenyl)vinyl]-6-methylpyridine (**4b**).

The reaction of 2,6-lutidine (4.73 g, 44 mmoles) and 2-chlorobenzaldehyde (6.30 g, 44.8 mmoles) in acetic anhydride (10 ml) under reflux for 12.5 hours gave **4b** (2.03 g, 20%) as white crystals, mp 52.2-52.9° (lit [3] 154°/1 mm Hg); ir (potassium bromide): 1580, 1448, 967, and 790 cm^{-1}; ^{1}H nmr (90 MHz, deuteriochloroform): δ 2.57 (s, 3H, CH_3), 6.9-8.1 (m, 9H, ArH and CH=CH).

Anal. Calcd. for $C_{14}H_{12}NCl$: C, 73.20; H, 5.27; N, 6.10. Found: C, 73.29; H, 5.14; N, 6.29.

trans-2-[2-(2-Chlorophenyl)vinyl]-5-methylpyridine (**4c**).

The reaction of 2,5-lutidine (10.5 g, 98 mmoles) and 2-chlorobenzaldehyde (14.6 g, 0.10 mole) in acetic anhydride (15 ml) under reflux for 17 hours gave **4c** (9.89 g, 44%) as pale yellow crystals, mp 64.8-66.4°; ir (potassium bromide): 1484, 970, and 768 cm^{-1}; ^{1}H nmr (60 MHz, deuteriochloroform): δ 2.26 (s, 3H, CH_3), 7.0-7.85 (m, 7H, ArH and CH=), 8.03 (d, J = 16 Hz, 1H, CH=), and 8.50 (s, 1H, pyridine-6H).

Anal. Calcd. for $C_{14}H_{12}NCl$: C, 73.20; H, 5.27; N, 6.10. Found: C, 73.45; H, 5.12; N, 6.33.

trans-2-[2-(2-Chlorophenyl)vinyl]-4-methylpyridine (**4d**).

A mixture of 2,4-lutidine (Aldrich, 29.2 g, 0.272 mole) and 2-chlorobenzaldehyde (38.2 g, 0.272 mole) in acetic anhydride (15 ml) was heated under reflux for 3.5 hours under nitrogen atmosphere. The distillation using Kugelrohr distillation apparatus at 165-167° (oven temperature)/1 mm Hg afforded the title compound **4d** as pale yellow oil (36.9 g, 59%); ir (sodium chloride): 1598, 1470, 965, and 752 cm^{-1}; ^{1}H nmr (60 MHz, deuteriochloroform): δ 2.26 (s, 3H, CH_3), 6.8-7.7 (m, 7H, ArH and CH=), 7.92 (d, J = 16 Hz, 1H, CH=), and 8.37 (d, J = 5 Hz, 1H, pyridine-6H).

Anal. Calcd. for $C_{14}H_{12}NCl$: C, 73.20; H, 5.27; N, 6.10. Found: C, 73.03; H, 5.33; N, 6.14.

The residue was recrystallized from hexane to afford 2,4-bis[2-(2-chlorophenyl)vinyl]pyridine as white crystals (4.4 g, 4.6%), mp 104.1-105.5°; ir (potassium bromide): 1592, 1465, 1045, 970, and 758 cm^{-1}; ^{1}H nmr (60 MHz, deuteriochloroform): δ 6.8-8.6 (m, 15H, ArH and CH=CH).

Anal. Calcd. for $C_{21}H_{15}NCl_2$: C, 71.60; H, 4.26; N, 3.98. Found: C, 71.63; H, 4.11; N, 3.70.

trans-2-[2-(2-Chlorophenyl)vinyl]-3-methylpyridine (**4e**).

The reaction of 2,3-dimethylpyridine (8.57 g, 80 mmoles) and

o-chlorobenzaldehyde (11.3 g, 80 mmoles) gave **4e** (12.4 g, 68%) as white crystals, mp 100.8-102.4° (lit [3] 100-102°); ir (potassium bromide): 1577, 1464, 972, 778, and 763 cm^{-1}; ^1H nmr (60 MHz, deuteriochloroform): δ 2.36 (s, 3H, CH_3), 6.97-7.87 (m, 7H, ArH and CH=), 8.30 (d, J = 16 Hz, 1H, CH=), and 8.57 (d, J = 5 Hz, 1H, pyridine-5H).

Anal. Calcd. for $C_{14}H_{12}NCl$: C, 73.20; H, 5.27; N, 6.10. Found: C, 73.01; H, 5.30; N, 6.19.

trans-2-[1-Methyl-2-(2-chlorophenyl)ethenyl]pyridine (**4f**).

The reaction of 2-ethylpyridine (11.1 g, 0.104 mole) and 2-chlorobenzaldehyde (15.4 g, 0.110 mole) gave **4f** (17.1 g, 72%) as a pale yellow oil; ir (potassium bromide): 1584, 1470, 1433, 1059, 1039, 780, and 755 cm^{-1}; ^1H nmr (60 MHz, deuteriochloroform): δ 2.24 (d, J = 1 Hz, 3H, CH_3), 7.1-7.8 (m, 8H, ArH and CH=), and 8.75 (d, J = 6 Hz, 1H, pyridine-6H).

Anal. Calcd. for $C_{14}H_{12}NCl$: C, 73.20; H, 5.27; N, 6.10. Found: C, 73.34; H, 5.20; N, 6.04.

2-(2-Chlorophenyl)-1-(2-pyridyl)-2-propanol (**5**).

To phenyllithium solution [from bromobenzene (15.7 g, 0.1 mole) and lithium (1.39 g, 0.2 mole) in diethyl ether (10 ml)] was added at room temperature, a diethyl ether (10 ml) solution of 2-methylpyridine (0.32 g, 0.1 mole). After stirring the mixture for 30 minutes, diethyl ether (10 ml) solution of 2-chloroacetophenone (15.5 g, 0.1 mole) was added and stirred at room temperature for overnight. The mixture was added to ice-water. The ether layer was separated and washed with water. After drying (magnesium sulfate) and concentration of the organic layer, the residue was recrystallized from methanol-hexane twice to afford the title compound **5** (6.66 g, 27%) as pale brown solid, mp 87.5-88.2°; ir (potassium bromide): 3300, 1595, 1441, 1420, 1030, and 764 cm^{-1}; ^1H nmr (60 MHz, deuteriochloroform): δ 1.72 (s, 3H, CH_3), 3.61 (ABq, 2H, CH_2), and 6.8-8.4 (m, 8H, ArH).

Anal. Calcd. for $C_{14}H_{14}NOCl$: C, 67.88; H, 5.70; N, 5.66. Found: C, 68.02; H, 5.81; N, 5.83.

The Dehydration of the Alcohol **5**.

Method A.

To a stirred solution of alcohol **5** (300 mg, 1.2 mmoles) and pyridine (0.5 ml) in ethyl ether (5 ml) was added dropwise a chloroform solution (1 ml) of thionyl chloride (0.09 ml, 1.2 mmoles) at 0°. The solution was stirred at 0° for 3 hours and then at room temperature overnight. After having removed the solvent the residue was extracted with benzene. The organic phase was washed with water, and dried (anhydrous magnesium sulfate). The residue after removing the solvent was chromatographed on plc (Merck Kieselgel 60 F_{254}) eluting with benzene to give compounds *E*-**4g** (42 mg, 15%) and *Z*-**4g** (106 mg, 38%).

E-2-[2-Methyl-2-(2-chlorophenyl)vinyl]pyridine (**4g**).

This compound was obtained as a pale yellow oil; uv (acetonitrile): λ max 250 (log ε 4.24) and 280 nm (4.14); ir (sodium chloride): 3060, 3010, 1640, 1585, 1470, 1425, 1042, 758, and 695 cm^{-1}; ^1H nmr (90 MHz, deuteriochloroform): δ 2.46 (d, J = 1.46 Hz, 3H, CH_3), 6.50 (d, J = 1.46 Hz, 1H, olefin), 7.0-7.8 (m, 6H, ArH), and 8.65 (d, J = 4.1 Hz, 1H, pyridine-6H); ms: (FAB) 230 (M + 1).

Anal. Calcd. for $C_{14}H_{12}NCl$: C, 73.20; H, 5.27; N, 6.10. Found: C, 73.07; H, 5.12; N, 6.02.

Z-2-[2-Methyl-2-(2-chlorophenyl)vinyl]pyridine (**4g**).

This compound was obtained as a pale yellow oil; uv (acetnitrile): λ max 243 nm (log ε 3.85); ir (sodium chloride): 3060, 2985, 1642, 1585, 1478, 1462, 1435, 1045, 753, and 672 cm^{-1}; ^1H nmr (90 MHz, deuteriochloroform): δ 2.23 (d, J = 1.54 Hz, 3H, CH_3), 6.55 (d, J = 7.91 Hz, 1H, phenyl-6H), 6.74 (d, J = 1.54 Hz, 1H, olefin), 6.8-7.5 (m, 6H, ArH), and 8.46 (d, J = 4.8 Hz, 1H, pyridine-6H); ms: (FAB) 230 (M + 1).

Anal. Calcd. for $C_{14}H_{12}NOCl$: C, 73.20; H, 5.27; N, 6.10. Found: C, 73.32; H, 5.25; N, 6.18.

Method B.

The alcohol **5** (554 mg, 2.24 mmoles) in acetic anhydride (20 ml) and acetic acid (10 ml) was heated under reflux for 7 hours. After removing the solvents, the residue was washed with benzene. The insoluble solid was dissolved in water. The aqueous solution was filtered to remove an insoluble grey solid. The aqueous lithium perchlorate was added to the aqueous solution and the resulting white solid was collected to give 6-methylbenzo[c]quinolizinium perchlorate **3b** (125 mg, 19%) as pale yellow crystals. The organic layer was chromatographed on plc (Merck Kieselgel 60 F_{254}) with benzene as the eluent to afford *E*-**4g** (82 mg, 16%) and *Z*-**4g** (123 mg, 24%).

Typical Procedure for the Preparation of Compounds **3** by Thermal Cyclization of **4**, *e.g.* **3d**.

3-Methylbenzo[c]quinolizinium Perchlorate (**3d**).

A mixture of *trans*-2-[2-(2-chlorophenyl)vinyl]-4-methylpyridine (4.60 g, 20 mmoles) in benzene (1000 ml) was irradiated by a Pyrex-filtered 300 W mercury lamp for 10 hours. After removing the solvent, the residue was heated at 170° for 50 minutes. The reaction mixture was dissolved in water and decolorized by charcoal. After 60% perchloric acid was added to the filtrate, the resulting dark yellow solid was collected and dissolved in water at 50°. The solution was filtered to remove insoluble dark solid. The filtrate was concentrated and recrystallized from methanol twice to afford **3d** (1.70 g, 37%) as pale yellow crystals, mp 212.8-214.4°; uv (ethanol): λ max 228 (log ε 4.20), 253 (4.51), 276 (4.04), 300 (3.66), 329 (3.79), 345 (4.15), 361 nm (4.29); ir (potassium bromide): 1645, 1620, 1489, 1100, 832, and 780 cm^{-1}; ^1H nmr (90 MHz, DMSO-d_6): δ 2.76 (s, 3H, CH_3), 7.9-8.7 (m, 7H, ArH), 9.09 (d, J = 8.8 Hz, 1H, 10-H), and 10.25 (d, J = 7.0 Hz, 1H, 1-H).

Anal. Calcd. for $C_{14}H_{12}NClO_4$: C, 57.24; H, 4.13; N, 4.77. Found: C, 57.39; H, 4.40; N, 4.66.

Typical Procedure for the Preparation of Compounds **3** by Photocyclization of **4**, *e.g.* **3b**.

1-Methylbenzo[c]quinolizinium Perchlorate (**3b**).

The acetonitrile solution (1000 ml) of compound **4b** (27.7 mg, 0.12 mmole) was irradiated with the selected wavelength (290 < λ < 340 nm and λ > 400 nm) using aqueous potassium chromate solution filter. At regular time intervals, an aliquot was taken out and subjected to uv spectral measurements. After the cyclization was judged to be essentially complete, the solution was concentrated. This procedure was repeated ten times. The combined residue was dissolved in water. An insoluble brown solid was filtered and 60% aqueous perchloric acid was added to the filtrate. The resulting white solid was filtered, washed with cold water, and recrystallized from ethanol to afford **3b** (X = ClO_4) (145 mg, 41%) as pale yellow needles, mp 115-116°; uv (acetonitrile): λ max 256 (log ε 4.46), 360 (3.97), and 376 nm (4.07); ir (potassium bromide): 1628, 1610, 1534, 1440, 852, and 764 cm^{-1}; ^1H nmr (90

MHz, DMSO-d_6): δ 3.32 (s, 3H, CH_3) and 7.9-8.9 (m, 9H, ArH).

Anal. Calcd. for $C_{14}H_{12}NClO_4$: C, 57.24; H, 4.13; N, 4.77. Found: C, 57.02; H, 4.36; N, 4.65.

Benzo[*c*]quinolizinium Perchlorate (**3a**).

This compound was obtained as white crystals (methanol), mp 187.5-189.0° (lit [4] 187-189°); uv (ethanol): λ max 365 (log ε 3.80), 348 (3.68), 255 (4.07), and 228 nm (3.85); ir; ^{1}H nmr (90 MHz, DMSO-d_6): δ 7.9-8.8 (m, 8H, ArH), 9.15 (d, J = 8.8 Hz, 1H, 10-H), and 10.39 (d, J = 6.7 Hz, 1H, 1-H).

Anal. Calcd. for $C_{13}H_{10}NClO_4$: C, 55.83; H, 3.60; N, 5.01. Found: C, 55.75; H, 3.61; N, 4.88.

2-Methylbenzo[*c*]quinolizinium Perchlorate (**3c**).

This compound was obtained as white crystals (methanol), mp 219.9-220.8°; uv (ethanol): λ max 230 (log ε 4.20), 256 (4.53), 278 (3.96), 302 (3.68), 335 (3.72), 349 (4.06), and 367 nm (4.17); ir (potassium bromide): 1633, 1520, 1462, 1086, 835, and 772 cm^{-1}; ^{1}H nmr (90 MHz, DMSO-d_6): δ 2.73 (s, 3H, CH_3), 7.9-8.7 (m, 7H, ArH), 9.17 (d, J = 8.5 Hz, 1H, 10-H), and 10.20 (s, 1H, 1-H).

Anal. Calcd. for $C_{14}H_{12}NClO_4$: C, 57.24; H, 4.13; N, 4.77. Found: C, 57.04; H, 4.36; N, 4.61.

4-Methylbenzo[*c*]quinolizinium Perchlorate (**3e**).

This compound was obtained as white crystals (methanol), mp 193.8-195.0°; uv (ethanol): λ max 228 (log ε 4.12), 254 (4.50), 283 (3.97), 305 (3.67), 337 (3.76), 352 (4.12), and 369 nm (4.25); ir (potassium bromide): 1618, 1604, 1428, 1115, 820, and 758 cm^{-1}; ^{1}H nmr (90 MHz, DMSO-d_6): δ 2.89 (s, 3H, CH_3), 7.9-8.8 (m, 7H, ArH), 9.14 (d, J = 8.5 Hz, 1H, 10-H), and 10.28 (d, J = 6.7 Hz, 1H, 1-H).

Anal. Calcd. for $C_{14}H_{12}NClO_4$: C, 57.24; H, 4.13; N, 4.77. Found: C, 57.37; H, 4.27; N, 4.59.

5-Methylbenzo[*c*]quinolizinium Perchlorate (**3f**).

This compound was obtained as white crystals (methanol), mp 224.8-225.4° (lit [4] 217-218°); uv (ethanol): λ max 254 (log ε 4.46), 281 (4.04), 301 (3.74), 339 (3.49), 355 (4.03), and 372 nm (4.10); ir (potassium bromide): 1625, 1451, 1100, 772, and 752 cm^{-1}; ^{1}H nmr (90 MHz, DMSO-d_6): δ 2.82 (s, 3H, CH_3), 7.9-8.3 (m, 7H, ArH), 9.08 (d, J = 7.6 Hz, 1H, 10-H), and 10.41 (d, J = 7.0 Hz, 1H, 1-H).

Anal. Calcd. for $C_{14}H_{12}NClO_4$: C, 57.24; H, 4.13; N, 4.77. Found: C, 57.10; H, 4.26; N, 4.70.

6-Methylbenzo[*c*]quinolizinium Perchlorate (**3g**).

This compound was obtained as white crystals (methanol), mp 238-240° dec; uv (acetonitrile): λ max 252 (log ε 4.50), 333 (sh), 348 (4.10), and 365 (4.18); ir (potassium bromide): 1642, 1620, 1459, 1100, and 772 cm^{-1}; ^{1}H nmr (90 MHz, DMSO-d_6): δ 2.90 (s, 3H, CH_3), 8.0-8.7 (m, 7H, ArH), 9.14 (d, J = 8.8 Hz, 1H, 10-H), and 10.31 (d, J = 7.0 Hz, 1H, 1-H).

Anal. Calcd. for $C_{14}H_{12}NClO_4$: C, 57.24; H, 4.13; N, 4.77. Found: C, 57.05; H, 4.33; N, 4.59.

The reaction of compounds **3** with *p*-methoxybenzaldehyde in the presence of bis(1-piperidino)-(*p*-methoxyphenyl)methane **7** in methanol was carried out as described in the previous paper [1].

trans-1-(*p*-Methoxystyryl)benzo[*c*]quinolizinium Perchlorate (**6b**).

The reaction of compound **3b** with *p*-methoxybenzaldehyde gave **6b** (86%) (brown crystals from methanol-acetone), mp 209-211°; uv (methanol): λ max 234 (log ε 4.38), 265 (4.45), 345 (4.19), and 434 nm (4.26); ir (potassium bromide): 1628, 1600, 1440, 1255, 1090, 979, and 842 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 3.83 (s, 3H, CH_3) and 7.0-8.8 (m, 15H, ArH and CH=CH).

Anal. Calcd. for $C_{22}H_{18}NClO_5$: C, 64.16; H, 4.40; N, 3.40. Found: C, 64.37; H, 4.59; N, 3.51.

trans-3-(*p*-Methoxystyryl)benzo[*c*]quinolizinium Perchlorate (**6d**).

The reaction of compound **3d** and *p*-methoxybenzaldehyde gave **6d** (91%) (orange crystals from methanol-acetone), mp 240-241°; uv (methanol): λ max 263 (log ε 4.31) and 425 nm (4.68); ir (potassium bromide): 1592, 1515, 1452, 1255, 1090, 978, and 827 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 3.83 (s, 3H, CH_3) and 6.9-10.2 (m, 15H, ArH and CH=CH).

Anal. Calcd. for $C_{22}H_{18}NClO_5$: C, 64.16; H, 4.40; N, 3.40. Found: C, 64.10; H, 4.67; N, 3.58.

trans-6-(*p*-Methoxystyryl)benzo[*c*]quinolizinium Perchlorate (**6g**).

The reaction of compound **3g** with *p*-methoxybenzaldehyde gave **6g** (93%) (yellow crystals from ethanol-ethyl acetate), mp 236-237°; uv (ethanol): λ max 255 (log ε 4.52) and 426 nm (4.46); ir (potassium bromide): 1652, 1599, 1518, 1459, 1178, 1090, 980, 828, and 758 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 3.85 (3H, s, CH_3) and 7.0-10.3 (m, 15H, ArH and CH=CH).

Anal. Calcd. for $C_{22}H_{18}NClO_5$: C, 64.16; H, 4.40; N, 3.40. Found: C, 63.96; H, 4.61; N, 3.55.

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