SYNTHESIS OF 6-METHYLISOQUINOLINO[7,8-*a*]QUINOLIZINIUM SALT: EFFICIENT SYNTHESIS OF 2-(2-ARYLVINYL)QUINOLIZINIUM SALTS BY KNOEVENAGEL CONDENSATION USING ACETONITRILE AS A SOLVENT AND THE PHOTOCYCLIZATION#

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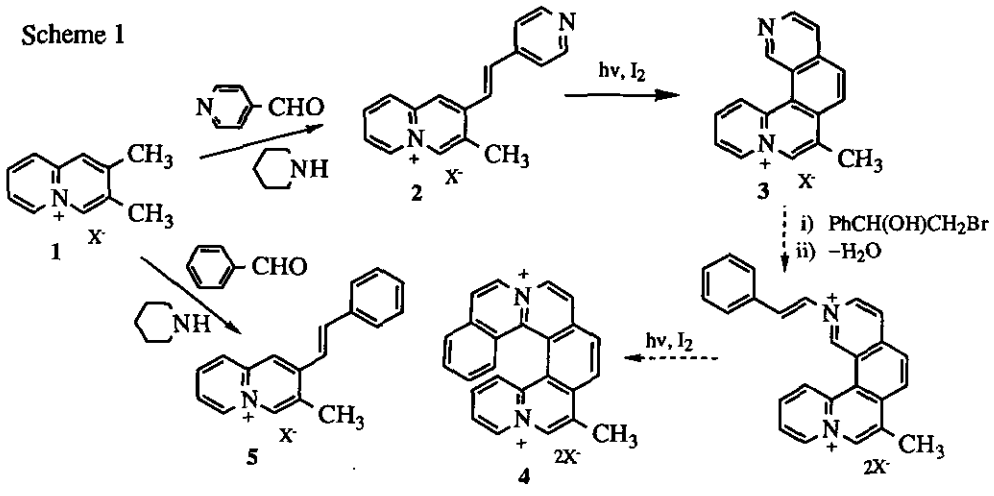
Abstract - In the Knoevenagel condensation of 2,3-dimethylquinolizinium salt with a wide variety of aromatic aldehydes in the presence of piperidine, the use of acetonitrile as a solvent gave excellent yields (77-100 %) of 2-(2-arylvinyl)-quinolizinium salts. In the condensation using methanol the yields were low because active bis(1-piperidino)arylmethane derived from aldehyde and piperidine changed to inactive aryl(methoxy)-1-piperidinomethane. The photocyclization of 2-[2-(4-pyridyl)vinyl]quinolizinium salt led to 6-methylisoquinolino[7,8-*a*]quinolizinium salt.

We have developed a convenient synthesis of polycyclic azonia aromatic compounds[1] such as azoniahexahelicene and azoniabenzocoronene by photocyclodehydrogenation reaction.[2,3] During our quest for the synthesis of novel diazoniahelicenes we needed a convenient access to 3-methyl-2-[2-(4-pyridyl)vinyl]quinolizinium salt (**2**). As shown in Scheme 1 the photocyclization of the olefin (**2**) would give 6-methylisoquinolino[7,8-*a*]quinolizinium salt (**3**), which was surmised to be a starting compound to construct new diazoniahelicene (**4**). We have reported previously that the Knoevenagel condensation of methylbenzoquinolizinium salts with benzaldehyde derivatives in the presence of piperidine yielded the corresponding styrylbenzoquinolizinium salts,[4] while the reaction of 2,3-dimethylquinolizinium salt[5] (**1**) with 4-pyridinecarbaldehyde gave the olefin (**2**) only in a moderate yield (*vide infra*). Thus the reaction conditions for an efficient synthesis of 2-(2-arylvinyl)quinolizinium salts were devised and are herein reported. The photocyclization of the olefin (**2**) will be also described.

#Dedicated to Professor Alan R. Katritzky on the occasion of his 65th birthday

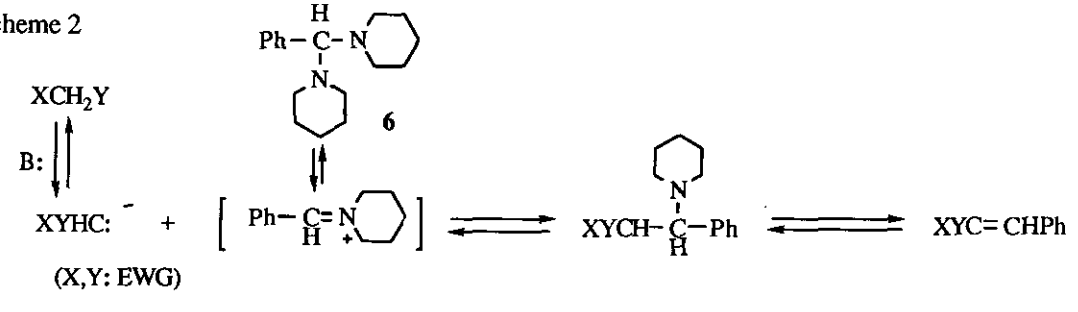
Scheme 1

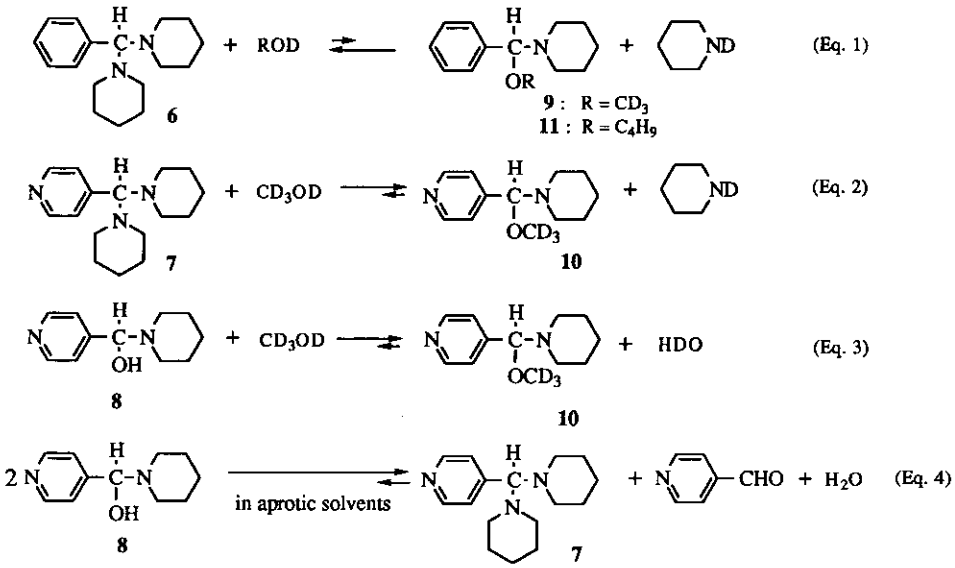


RESULTS AND DISCUSSION

The reaction of **1** (1 mmol) with benzaldehyde and with 4-pyridinecarbaldehyde (5 mmol) in the presence of piperidine (2 mmol) in methanol (5 ml) at refluxing temperature for 50 h afforded the corresponding *trans*-2-(2-arylvinyl)quinolizinium salts (**5**) and (**2**) in 31 % and 51 % yields, respectively (Table 1, Entries 1 and 5). It has been reported that the iminium ion formed from bis(1-piperidino)phenylmethane (**6**) is a reactive species in the Knoevenagel condensation of active methylene compounds with benzaldehyde as shown in Scheme 2.[6,7] The diamine (**6**) was obtained easily on standing a mixture of benzaldehyde and piperidine overnight at room temperature, whereas 4-pyridinecarbaldehyde reacted rapidly with piperidine at room temperature to give unexpected 1-piperidino-4-pyridylmethanol (**8**) instead of bis(1-piperidino)(4-pyridyl)-methane (**7**). The diamine (**7**) was obtained in a good yield upon heating 4-pyridinecarbaldehyde with a large excess of piperidine at refluxing temperature. By using the diamine (**6**) the yield of the olefin (**5**) slightly increased (Entry 2). Unexpectedly the yield of the olefin (**2**) decreased to 30 % by using the diamine (**7**) (Entry 6). The reaction with the alcohol (**8**) gave less satisfactory result (Entry 7). These results indicate that the reactivities of the diamine (**7**) and the alcohol (**8**) differ from that of the diamine (**6**) under these reaction conditions.

Scheme 2





6 7 8 9 10 11

^{1}H Nmr experiments in methanol-d_4 showed that the spectral changes were observed in the case of the diamine (**7**) and the alcohol (**8**), while the diamine (**6**) afforded no spectral change even at 60 °C. The spectrum of the diamine (**7**) in methanol-d_4 at 25 °C showed two singlets at δ = 3.65 and 4.84. The signal intensity at δ = 4.84 increased rapidly with a decrease of that at δ = 3.65 and the signals corresponding to free piperidine were also observed (Figure 1). In the case of the alcohol (**8**) in methanol-d_4 at 25 °C a singlet at δ = 5.54 assigned to the methine diminished and a new singlet was observed at δ = 4.84, which was identical with the new signal in the case of the diamine (**7**) in methanol-d_4 (Figure 2). These results might suggest that the diamine (**7**) and the alcohol (**8**) reacted with methanol-d_4 to give the ether (**10**) (Eqs. 2 and 3). Two singlets at δ = 3.65 and 4.84 of the diamine (**7**) could be assigned to the methines of (**7**) and (**10**), respectively. Stewart and Hauser reported that refluxing a mixture of the diamine (**6**) and benzaldehyde in the presence of anhydrous potassium carbonate in butanol gave the butyl ether (**11**), which was too unstable to regenerate the diamine (**6**) on standing overnight.[8] These results indicate that the equilibrium exists between the diamine (**6**) and the ether (**9**) and it is shifted toward the diamine (**6**) even at 60 °C (Eq. 1) contrary to the cases of the diamine (**7**) and the alcohol (**8**), in which the ether (**10**) was *predominant* (Eqs. 2 and 3). On the other hand the diamines (**6**) and (**7**) were stable in aprotic solvents such as acetonitrile-d_3 and dimethyl sulfoxide-d_6. However, the alcohol (**8**) was converted in aprotic solvents to the diamine (**7**), 4-pyridinecarbaldehyde, and water at 25 °C as shown in Figure 3. This fact shows that the equilibrium lies in favor of the formation of the diamine (**7**) *in aprotic solvents* (Eq. 4).

These findings suggest that difficulties in the condensation could be overcome by changing the solvent from methanol to acetonitrile. Table 1 shows that the condensation was dramatically activated by using acetonitrile

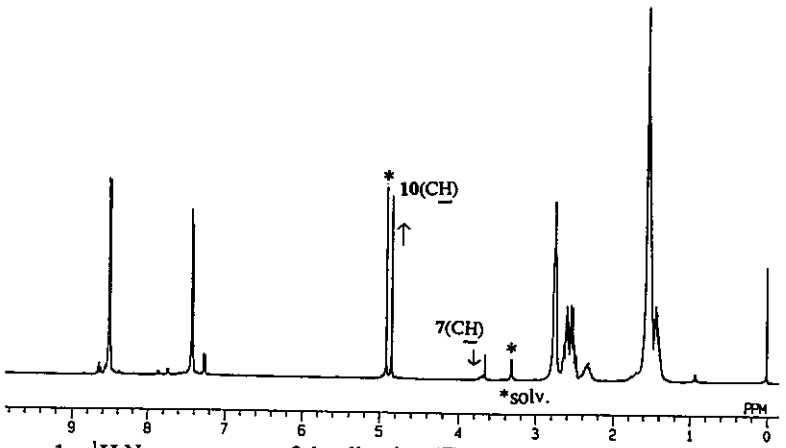


Figure 1 ^{1}H Nmr spectrum of the diamine (**7**) in CD_3OD (Eq. 2)

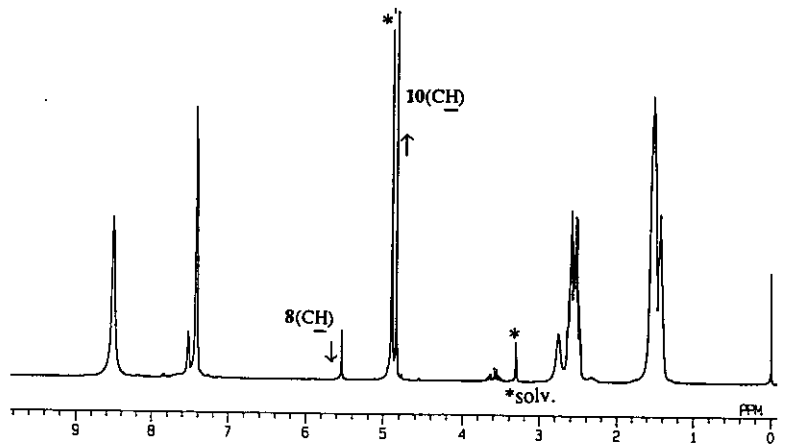


Figure 2 ^{1}H Nmr spectrum of the alcohol (**8**) in CD_3OD (Eq. 3)

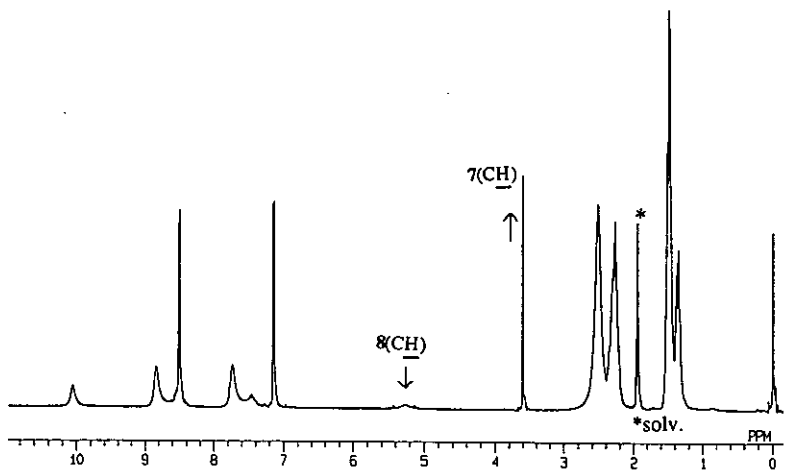


Figure 3 ^{1}H Nmr spectrum of the alcohol (**8**) in CD_3CN (Eq. 4)

Table 1. Reaction of **1** with benzaldehyde and with 4-pyridinecarbaldehyde[a]

Entry	Aldehydes (mmol)	Amines (mmol)	solvents	time/h	yield/ %
1	 CHO (5)	piperidine (2)	CH_3OH	50	31
2	 CHO (4)	**6** (1)	CH_3OH	40	38
3	 CHO (5)	piperidine (2)	CH_3CN	1.5	91
4	 CHO (4)	**6** (1)	CH_3CN	1.5	95
5	 CHO (5)	piperidine (2)	CH_3OH	50	51
6	 CHO (4)	**7** (1)	CH_3OH	50	30[b]
7	 CHO (3)	**8** (2)	CH_3OH	50	20[b]
8	 CHO (5)	piperidine (2)	CH_3CN	9	100
9	 CHO (4)	**7** (1)	CH_3CN	5	99
10	 CHO (3)	**8** (2)	CH_3CN	8	97

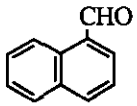
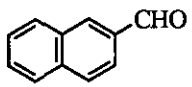
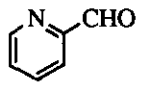
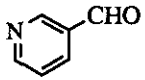
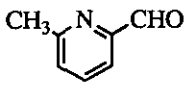
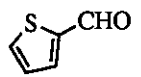
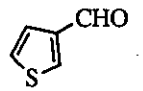
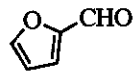
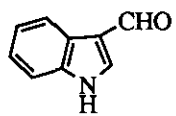
a: **1** (1 mmol), solvent (5 ml)
b: determined by uv and visible spectroscopy

as a solvent. An acetonitrile (5 ml) solution of **1** (1 mmol) and the diamine (**7**) (1 mmol) or the alcohol (**8**) (2 mmol) in the presence of excess 4-pyridinecarbaldehyde (3-4 mmol) was heated at refluxing temperature for 5 or 8 h to give the olefin (**2**) quantitatively (Table 1, Entries 9 and 10). It was also found that by using acetonitrile as a solvent the reaction with piperidine afforded the olefins (**5**) and (**2**) in excellent yields (Entries 3 and 8). These results clearly indicate that the diamines (**6**) and (**7**) are reactive in the Knoevenagel condensation, while the ether (**10**) is much less reactive.

The improved reaction conditions were applied to the condensation with a wide variety of aromatic aldehydes including π-excessive heteroaromatic aldehydes. Table 2 shows that the reaction in the presence of piperidine in acetonitrile gave the corresponding *trans*-2-(2-arylvinyl)quinolizinium salts (**12a-i**) in excellent yields (77-100 %).

Our reaction conditions were also effective for the condensation of 1,4-dimethylpyridinium iodide with 2-naphthaldehyde to afford 1-methyl-4-[2-(2-naphthyl)vinyl]pyridinium iodide (**13**) in 97 % yield. However, 4-methylpyridine *N*-oxide and 4-methylpyridine were much less reactive than the methylpyridinium salts under our conditions and no reactions occurred.

Table 2. Reaction of **1** with Aromatic Aldehydes[a]

	Aromatic Aldehydes	Time h	Yield %	mp °C	Formula	Ms *m/z* (M-ClO_4)	Analysis/ % Calcd	Found	Ir[b] $\bar{\nu}$ / cm^{-1}	Uv/λ_{max}[c] nm (log ε)
12a		4	80	>300	$C_{22}H_{18}NClO_4$	296	C: 66.75 H: 4.58 N: 3.54	66.86 4.59 3.65	1090, 1613	385 (4.39)
12b		4	97	>300	$C_{22}H_{18}NClO_4$	296	C: 66.75 H: 4.58 N: 3.54	66.86 4.54 3.53	968, 1086, 1613	381 (4.56)
12c		4	92	275-276(decomp.)	$C_{17}H_{15}N_2ClO_4$	247	C: 58.88 H: 4.36 N: 8.08	58.88 4.25 8.13	978, 1094, 1622	363 (4.46)
12d		4	100	281-282(decomp.)	$C_{17}H_{15}N_2ClO_4$	247	C: 58.88 H: 4.36 N: 8.08	58.87 4.30 8.18	970, 1084, 1620	363 (4.44)
12e		1	81	255-256(decomp.)	$C_{18}H_{17}N_2ClO_4$	261	C: 59.92 H: 4.75 N: 7.76	60.16 4.80 7.81	980, 1094, 1618	366 (4.48)
12f		1.5	90	280-284(decomp.)	$C_{16}H_{14}NSClO_4$	252	C: 54.63 H: 4.01 N: 3.98	54.59 3.87 3.92	961, 1098, 1605	388 (4.52)
12g		2	91	246(decomp.)	$C_{16}H_{14}NSClO_4$	252	C: 54.63 H: 4.01 N: 3.98	54.64 4.02 4.26	966, 1098, 1611	374 (4.49)
12h		4.5	97	256(decomp.)	$C_{16}H_{14}NClO_5$	236	C: 57.24 H: 4.20 N: 4.17	57.47 4.19 4.27	961, 1090, 1615	390 (4.55)
12i		3.5	77	>300	$C_{20}H_{17}N_2ClO_4$	285	C: 62.42 H: 4.45 N: 7.28	62.64 4.42 7.30	1094, 1597, 3302	434 (4.55)

a: **1** (2 mmol), ArCHO (8 mmol), piperidine (2 mmol), CH_3CN (10 ml). b: the selected bands c: the first absorption band in CH_3CN

In general, the Knoevenagel condensation of pyridinium type of compounds was performed under conditions using a catalytic amount of piperidine and alcohol as a solvent.[6,9] The present procedure using acetonitrile as a solvent provides a simple and high-yield reaction conditions for the condensation with a wide variety of aromatic aldehydes. It is also noted that our reaction conditions require neither dry solvent nor inert atmosphere and acetonitrile could be replaced by dimethyl sulfoxide or dimethylformamide.

Finally the photocyclization of the olefin (**2**) was achieved by the irradiation of air-saturated dilute acetonitrile solution of **2** containing iodine with a Pyrex-filtered light to afford desired 6-methylisoquinolino[7,8-*a*]-quinolizinium perchlorate (**3**) in 93 % yield. Thus, the compound (**3**) was synthesized from **1** in two steps in a quantitative yield.

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 JEOL JNM-EX270 (270 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 or FT/IR-5300 spectrophotometer. The uv and visible spectra were obtained with a Hitachi 220A spectrophotometer. The fast-atom bombardment (fab) mass spectra were recorded with a JEOL JMS-DX 300 spectrometer with *m*-nitrobenzyl alcohol as matrix. Microanalyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer.

2,3-Dimethylquinolizinium Perchlorate (**1**: X = ClO_4). The bromide (**1**: X=Br) prepared according to the method of Westphal[5] was converted to the perchlorate by metathesis with 70 % $HClO_4$ and recrystallized from ethanol: mp 176 °C; λ_{max} (CH_3CN) 264 (log ε 3.35), 274 (3.42), 288 (3.50), 300 (3.78), 313 (4.13), ca. 320 (sh. 4.03), and 327 nm (4.34); ir (KBr) 1088 and 1649 cm^{-1}; ^{1}H nmr (DMSO-d_6) δ = 2.50 (3H, s, 3-CH_3), 2.59 (3H, s, 2-CH_3), 7.97 (1H, dd, J = 7.3, 6.9 Hz, 7-H), 8.25 (1H, dd, J = 8.4, 7.3 Hz, 8-H), 8.36 (1H, s, 1-H), 8.37 (1H, d, J = 8.4, 9-H), 9.11 (1H, d, J = 6.9 Hz, 6-H), and 9.18 (1H, s, 1-H). Fab ms *m/z* 158 (M-ClO_4)$^+$. Anal. Calcd for $C_{11}H_{12}NO_4Cl$: C, 51.27; H,4.69; N, 5.44. Found: C, 51.30; H, 4.60; N, 5.27.

Bis(1-piperidino)phenylmethane (**6**). To 2.18 g (20.6 mmol) of benzaldehyde, 3.50 g (41.1 mmol) of piperidine was added. The mixture was stirred overnight at room temperature. Recrystallization from acetonitrile or sublimation at 80 °C (266 Pa) gave **6** (3.60 g; 68 %) as colorless prisms: mp 80.0 °C (lit.,[7] mp 80.0 °C).

Bis(1-piperidino)(4-pyridyl)methane (**7**). A mixture of 4-pyridinecarbaldehyde (1.25 g; 11.7 mmol) and piperidine (7.96 g; 93.5 mmol) was refluxed for 3.5 h. Then the excess piperidine and water were removed *in vacuo* to give **7** (2.88 g; 96 %) as pale yellow viscous oil: ir (neat) 765, 795, 1075, 1420, 1455, 1465, 1480, 1610, 2830, and 2970 cm^{-1}; ^{1}H nmr (CD_3CN) δ = 1.39 - 1.54 (12H, m, piperidino 3-, 4-, and 5-H), 2.25 - 2.52 (8H, m, piperidino 2- and 6-H), 3.61 (1H, s, -CH), 7.15 (2H, dd, J = 4.6, 1.5 Hz, pyridyl 3- and 5-H), and 8.51 (2H, dd, J = 4.6, 1.5 Hz, pyridyl 2- and 6-H).

1-Piperidino-4-pyridylmethanol (**8**). To 1.13 g (10.6 mmol) of 4-pyridinecarbaldehyde, 0.96 g (11.2 mmol) of piperidine was added. The mixture immediately solidified and was allowed to stand overnight at room temperature. The pale yellow solid was triturated with ether/hexane (2:1; 20 ml), filtered off, and dried *in vacuo* for 1 h to afford **8** (1.65 g: 81 %) as colorless powder: mp 65 °C; ir (nujol) 650, 775, 800, 985, 1055, 1405, 1595, and 3120 cm^{-1}; ^1H nmr (CD_3OD) δ = 1.59 (6H, m, piperidino 3-, 4-, and 5-H), 2.76 (4H, m, piperidino 2- and 6-H), 5.54 (1H, s, -CH), 7.53 (2H, d, J = 5.3 Hz, pyridyl 3- and 5-H), and 8.52 (2H, d, J = 5.3 Hz, pyridyl 2- and 6-H). Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.53; H, 8.69; N, 14.49.

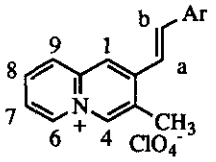
General Procedure for the Preparation of *trans*-2-(2-Arylviny)quinolizinium Salts (**2**, **5**, **12a-i**, and **13**). To a refluxing acetonitrile solution of **1** and aldehyde was added either piperidine or the diamine. The mixture was refluxed under the conditions given in Tables 1 and 2. After the mixture was allowed to cool at room temperature, ether was added. The resulting precipitates were filtered, washed with ether, and dried *in vacuo* to give *trans*-2-(2-arylvinyl)quinolizinium salts. The analytical samples were obtained by recrystallization from acetonitrile or methanol. In the case of indole derivative (**12i**), the crude zwitter ionic product was recrystallized from acidic ($HClO_4$) acetonitrile. The analytical data and physical properties of **12a-i** are given in Tables 2-4.

3-Methyl-2-[2-(4-pyridyl)vinyl]quinolizinium Perchlorate (**2**). mp 284 - 286 °C (decomp.); λ_{max} (CH_3CN) 262 (log ε 4.26), 276 (4.24), ca. 318 (sh), ca. 333 (sh), and 358 nm (4.37); ir (KBr) 1096 and 1624 cm^{-1}; ^1H nmr (DMSO-d_6) δ = 2.68 (3H, s, CH_3), 7.74 (1H, d, J = 16.5 Hz, -CH=CH-), 7.77 (2H, d, J = 4.6 Hz, pyridyl 3- and 5-H), 7.85 (1H, d, J = 16.5 Hz, -CH=CH-), 8.01 (1H, ddd, J = 7.6, 6.9, 1.3 Hz, 7-H), 8.29 (1H, dd, J = 8.6, 7.6 Hz, 8-H), 8.42 (1H, d, J = 8.6 Hz, 9-H), 8.69 (2H, dd, J = 4.6, 1.3 Hz, pyridyl 2- and 6-H), 8.92 (1H, s, 1-H), 9.13 (1H, d, J = 6.9 Hz, 6-H), and 9.24 (1H, s, 4-H). Fab ms *m/z* 247 $(M\text{-}ClO_4)^+$. Anal. Calcd for $C_{17}H_{15}N_2O_4Cl$: C, 58.88; H, 4.36; N, 8.08. Found: C, 58.97; H, 4. 23; N, 8.04

3-Methyl-2-(2-phenylvinyl)quinolizinium Perchlorate (**5**). mp 280 - 282 °C (decomp.); λ_{max} (CH_3OH) 265 (log ε 4.05), ca. 290 (sh), and 369 nm (4.42); ir (KBr) 970, 1096 and 1618 cm^{-1}; ^1H nmr (DMSO-d_6) δ = 2.66 (3H, s, CH_3), 7.44 (1H, t, J = 7.3 Hz, phenyl 4-H), 7.50 (2H, dd, J = 7.3, 6.6 Hz, phenyl 3- and 5-H), 7.57 (1H, d, J = 16.5 Hz, -CH=CH-), 7.82 (1H, d, J = 16.5 Hz, -CH=CH-), 7.83 (2H, d, J = 6.6 Hz, phenyl 2- and 6-H), 7.95 (1H, dd, J = 7.4, 6.9 Hz, 7-H), 8.24 (1H, dd, J = 7.4, 8.6 Hz, 8-H), 8.38 (1H, d, J = 8.6 Hz, 9-H), 8.88 (1H, s, 1-H), 9.08 (1H, d, J = 6.9 Hz, 6-H) and 9.20 (1H, s, 4-H). Fab ms *m/z* 246 $(M\text{-}ClO_4)^+$. Anal. Calcd for $C_{18}H_{16}NO_4Cl$: C, 62.52; H, 4.66; N, 4.05. Found: C, 62.64; H, 4.68; N, 3.99.

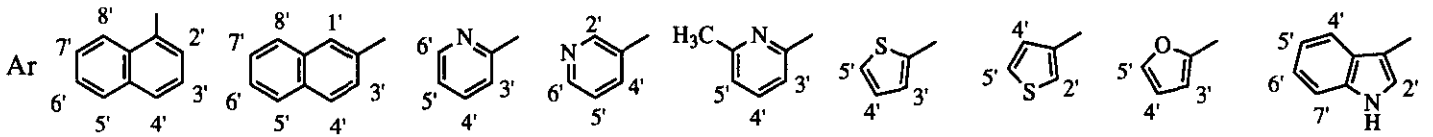
1-Methyl-4-[2-(2-naphthyl)vinyl]pyridinium Iodide (**13**). mp 274 °C; λ_{max} (CH_3OH) *ca.* 270 (sh), 283 (log ε 4.44), 293 (3.84), and 360 nm (4.68); ir (KBr) 972 and 1618 cm^{-1}; ^1H nmr (DMSO-d_6) δ = 4.28 (3H, s, CH_3), 7.58 (1H, dd, J = 9.2, 4.0 Hz, naphthyl 7-H), 7.62 (1H, dd, J = 8.6, 4.0 Hz, naphthyl 6-H), 7.68 (1H, d, J = 16.5 Hz, -CH=CH-), 7.97 (2H, dd, J = 8.6, 8.4 Hz, naphthyl 3- and 5-H), 8.01 (1H, d, J = 9.2 Hz, naphthyl

Table 3. ^{1}H Nmr Spectral Data (δ_H ppm) of Compounds (**12a-i**) in DMSO-d_6



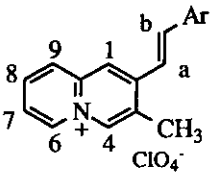
										Ar								
12	3-Me	1	4	6	7	8	9	a	b	1'	2'	3'	4'	5'	6'	7'	8'	
a	2.70	9.21	9.26	9.13	7.98	8.28	8.43	7.65	8.69	–	8.20	7.65	8.05	8.02	7.69	7.62	8.56	
b	2.69	8.98	9.25	9.12	7.96	8.25	8.41	8.01	7.69	8.23	–	8.08	8.02	8.02[a]	7.59[b]	7.57[c]	7.96[d]	
c	2.66	8.96	9.23	9.11	8.00	8.28	8.41	7.84	7.97	–	–	7.77	7.93	7.43	8.71	–	–	
d	2.67	8.89	9.21	9.11	7.98	8.27	8.40	7.83	7.71	–	8.96	–	8.30	7.53	8.61	–	–	
e	2.66	8.97	9.23	9.11	7.99	8.27	8.40	7.80	7.91	–	–	7.61	7.81	7.30	–	–	–	2.56 (6'-Me)
f	2.62	8.84	9.16	9.05	7.92	8.22	8.32	8.03	7.21	–	–	7.57	7.21	7.77	–	–	–	
g	2.63	8.82	9.18	9.06	7.92	8.22	8.35	7.84	7.39	–	7.95	–	7.73	7.70	–	–	–	
h	2.61	8.84	9.16	9.04	7.92	8.21	8.31	7.71	7.21	–	–	6.93	6.71	7.92	–	–	–	
i	2.64	8.78	9.07	8.95	7.80	8.13	8.26	8.13	7.25	11.86	8.03	–	8.06	7.23	7.26	7.51	–	

a: 5' or 8', b: 6' or 7', c: 7' or 6', d: 8' or 5'.



12a **12b** **12c** **12d** **12e** **12f** **12g** **12h** **12i**

Table 4. ^{1}H Nmr Spectral Data (J /Hz) of Compounds (**12a-i**) in DMSO-d_6



	Ar											
12	$J_{6,7}$	$J_{7,8}$	$J_{8,9}$	$J_{a,b}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$	$J_{6',7'}$	$J_{7',8'}$	
a	6.9	7.6	8.6	16.2	–	7.3	7.9	–	7.2	6.6	8.3	
b	6.8	7.3	8.3	16.1	–	–	8.8	–	6.4	5.9	6.4	
c	6.9	7.5	8.3	15.8	–	–	7.7	7.4	4.8	–	–	
d	6.9	7.3	8.3	16.2	–	–	–	8.1	4.8	–	–	1.9 ($J_{2',5'}$)
e	6.6	7.8	8.6	16.2	–	–	7.6	7.6	–	–	–	
f	6.6	7.3	8.3	16.2	–	–	3.3	5.0	–	–	–	
g	6.6	7.3	8.3	16.2	–	–	–	5.0	–	–	–	2.6 ($J_{2',5'}$)
h	6.6	7.3	7.9	15.8	–	–	3.3	1.8	–	–	–	
i	6.6	7.3	8.3	16.2	3.0	–	–	6.6	7.3	8.9	–	

8-H), 8.04 (1H, d, J = 8.4 Hz, naphthyl 4-H), 8.19 (1H, d, J = 16.5 Hz, -CH=CH-), 8.22 (1H, s, naphthyl 1-H), 8.28 (2H, d, J = 6.9 Hz, 3- and 5-H), and 8.89 (2H, d, J = 6.9 Hz, 2- and 6-H). Fab ms *m/z* 246 $(M\text{-}I)^+$. Anal. Calcd for $C_{18}H_{16}NI$: C, 57.93; H, 4.32; N, 3.75. Found: C, 58.06; H, 4. 37; N, 3.68.

6-Methylisoquinolino[7,8-*a*]quinolizinium Perchlorate (**3**). A solution of **2** (250 mg; 0.7 mmol) and iodine (25 mg; 0.1 mmol) in acetonitrile (1000 ml) was irradiated for 21-23 h at room temperature with a 300 W high pressure mercury lamp inside a Pyrex immersion well. The progress of the reaction was monitored by the uv and visible spectra. After irradiation was completed, the solution was concentrated to 10 ml and ether was added. The solid precipitated was filtered, washed with ether to give crude **3**, which was reprecipitated with acetonitrile/ether to afford **3** (233 mg; 93 %): mp 239-242 °C (decomp.); λ_{max} (CH_3CN) 260 (log ε 4.43), 277 (4.29), *ca.* 286 (sh.), *ca.* 302 (sh.), 350 (3.69), 367 (3.93), and 386 nm (4.02); ir (KBr) 1088 and 1655 cm^{-1}; ^{1}H nmr (DMSO-d_6) δ = 2.87 (3H, s, 6-Me), 8.29 (1H, d, J = 5.3 Hz, 9-H), 8.32 (1H, dd, J = 7.3, 5.5 Hz, 3-H), 8.53 (1H, d, J = 8.9 Hz, 7-H), 8.62 (1H, dd, J = 9.6, 5.5 Hz, 2-H), 8.64 (1H, d, J = 8.9 Hz, 8-H), 8.95 (1H, d, J = 5.3 Hz, 10-H), 9.27 (1H, s, 5-H), 9.50 (1H, d, J = 7.3 Hz, 4-H), 9.54 (1H, d, J = 9.6 Hz, 1-H), and 10.21(1H, s, 12-H). Fab ms *m/z* 245 $(M\text{-}ClO_4)^+$. Anal. Calcd for $C_{17}H_{13}N_2O_4Cl{\cdot}H_2O$: C, 56.28; H, 4.17; N, 7.72. Found:

C, 56.03; H, 3.89; N, 7.88.

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