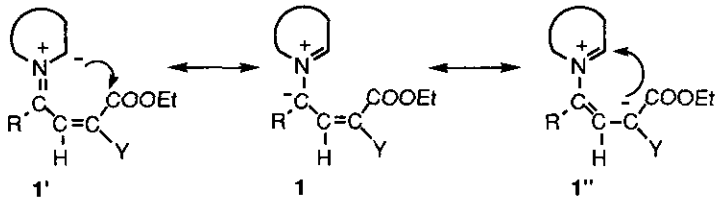
SYNTHESIS OF MESOMERIC "BETAINES, QUINOLIZINIUMIDES, *VIA* BACK-DONATED 1,6-CYCLIZATION

Yoshiro Matsuda,* Keisuke Katou, Takanobu Nishiyori, Takashi Uemura, and Maki Urakami

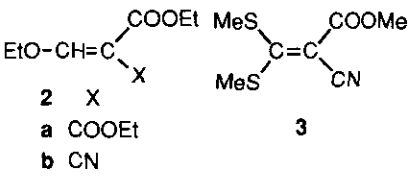
Faculty of Environmental Studies, Nagasaki University,
1-14 Bunkyo-machi Nagasaki 852, Japan

Abstract - The reaction of 3-aminopyridinium salts (**4**) with polarized olefins (**2a,b**, **3**) in the presence of triethylamine yielded the corresponding 3-aminopyridinium *N*-allylides (**5**). Thermolysis of 3-aminopyridinium *N*-allylides (**5a-c,h-j,l-n**) in refluxing xylene afforded the 1,5-dipolar cyclization products, 8-aminoindolizines (**6**) together with the back-donated 1,6-cyclization products, quinoliziniumides (**7**). In addition, thermolysis of *N*-allylides (**5a-c,h-j,l-n**) in refluxing AcOH gave quinoliziniumides (**7**).

Polarized olefins (ethoxymethylene compounds and ketene dithioacetals), when appropriately functionalized (cyano, methoxycarbonyl, nitro, sulfonyl, pyridyl, *etc.*), are versatile reagents which have been extensively utilized in heterocyclic synthesis.[1] We have been engaged in an ongoing investigation of these reagents, and have carried out extensive studies on the reaction of heteroaromatic compounds with various polarized olefins and their analogues.[2] In particular, it is well known that heterocyclic salts react with polarized olefins to produce heterocyclic *N*-allylides (**1**). These *N*-allylides (**1**), acting as extended dipoles, are of interest in heterocyclic chemistry,[3] and may be considered resonance hybrids of the representative structures (**1**, **1'**, **1"**) shown in Scheme 1.

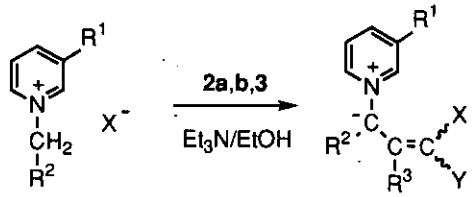


Scheme 1



Scheme 2

Many of the previous studies on *N*-allylides (**1**) have focused on the synthesis of bicyclic compounds with a bridgehead nitrogen by 1,5-dipolar cyclization according to the resonance structure (**1"**). In this study, we have taken advantage of an alternative *N*-allylide form (resonance structure **1'**) to realize a novel reaction which we have termed a 'back-donated 1,6-cyclization.'



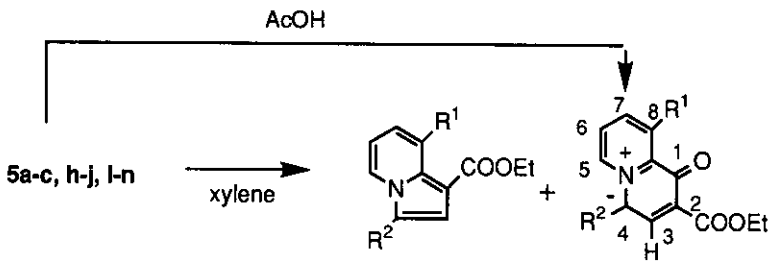
4

	R^1	R^2	X
a	NH_2	COOEt	Br
b	NH_2	CN	Cl
c	NH_2	COC_6H_5	Br
d	NHMe	COOEt	Br
e	NHMe	CN	Cl
f	NHMe	COC_6H_5	Br
g	NMe_2	COOEt	Br
h	NMe_2	CN	Cl
i	NMe_2	COC_6H_5	Br

5

	R^1	R^2	R^3	X	Y
a	NH_2	COOEt	H	COOEt	COOEt
b	NH_2	CN	H	COOEt	COOEt
c	NH_2	COC_6H_5	H	COOEt	COOEt
d	NH_2	COOEt	H	COOEt	CN
e	NH_2	COC_6H_5	H	COOEt	CN
f	NH_2	CN	SMe	COOMe	CN
g	NH_2	COC_6H_5	SMe	COOMe	CN
h	NHMe	COOEt	H	COOEt	COOEt
i	NHMe	CN	H	COOEt	COOEt
j	NHMe	COC_6H_5	H	COOEt	COOEt
k	NHMe	COOEt	H	COOEt	CN
l	NMe_2	COOEt	H	COOEt	COOEt
m	NMe_2	CN	H	COOEt	COOEt
n	NMe_2	COC_6H_5	H	COOEt	COOEt
o	NMe_2	COOEt	H	COOEt	CN
p	NMe_2	CN	H	COOEt	CN
q	NMe_2	COOEt	SMe	COOMe	CN
r	NMe_2	CN	SMe	COOMe	CN

Scheme 3



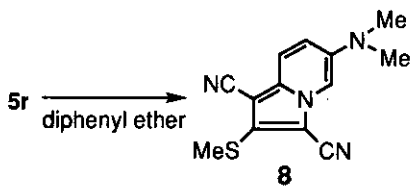
6

	R^1	R^2
a	NH_2	CN
b	NHMe	COOEt
c	NHMe	CN
d	NHMe	COC_6H_5

7

	R^1	R^2
a	NH_2	COOEt
b	NH_2	CN
c	NH_2	COC_6H_5
d	NHMe	COOEt
e	NHMe	CN
f	NHMe	COC_6H_5
g	NMe_2	COOEt
h	NMe_2	CN
i	NMe_2	COC_6H_5

Scheme 4



8

Scheme 5

Our preliminary studies on the thermolyses of azolium *N*-allylides have led to a new heterocyclic ring closure that proceeds by back-donated 1,6-cyclization onto the carbonyl or cyano carbon at X to produce the mesomeric betaines.[4] Hence, the change of the azole moiety for the pyridine moiety offers interesting possibilities for studying the scope of the back-donated 1,6-cyclization. With regard to pyridinium *N*-allylides,[2c] there have been numerous reports of indolizines synthesis by 1,5-dipolar cyclization, but previously there has been no report of quinoliziniumides synthesis using back-donated 1,6-cyclization, due to the difficulty in introducing the electrophilic carbonyl group into the pyridinium ring. Furthermore, there have been no systematic studies on the thermolysis of stable 3-aminopyridinium *N*-allylides (**5**). Bradlow and Vanderwerf,[5] however, have pointed out that in the addition of 3-substituted pyridinium *N*-ylides and the hydroxide ion, the effect of any 3-substituents might be expected to lend added resonance stabilization to the pseudo-base. This fact suggests that in the thermolysis of 3-aminopyridinium *N*-allylides (**5**), the electron-donating amino group may be expected to lend added resonance stabilization to the resonance structure (**1'**). In this study, we carried out the thermolysis of **5**, and successfully determined that *N*-allylides (**5**), in refluxing xylene or AcOH, underwent the back-donated 1,6-cyclization to give the mesomeric betaines, 8-aminoquinoliziniumides (**7**). The polarized olefins (**2**,**3**)[6] used are shown in Scheme 2.

The reaction of the salts (**4a-i**) with polarized olefins (**2a**,**b**,**3**) in the presence of triethylamine in refluxing EtOH for 5 h gave 3-aminopyridinium *N*-allylides (**5a-r**) (Scheme 3). Refluxing of *N*-allylides (**5a-c**,**h-j**,**l-n**) in xylene for 10 h gave the 1,5-dipolar cyclization products, indolizines (**6a-d**), and/or the back-donated 1,6-cyclization products, 3-aminoquinoliziniu-mides (**7a-i**), in poor yields. In our attempt to find a more suitable method for synthesizing **7** from the thermolysis of **5** in refluxing diphenyl ether, pyridine, DMF, *etc.*, we happened to find that thermolysis of **5a-c** in refluxing AcOH for 2 h could be effected smoothly to give **7a-c** in 86, 32, and 43% yields, respectively. These effects of AcOH are of great interest, although we were not able to fully clarify them here. Furthermore, treatment of 3-(*N*-methylamino)-pyridinium (**5h**) or 3-(*N*,*N*-dimethylamino)pyridinium *N*-allylide (**5l**) in refluxing AcOH afforded demethylated quinoliziniumides (**7a**, **d**) (Scheme 4).

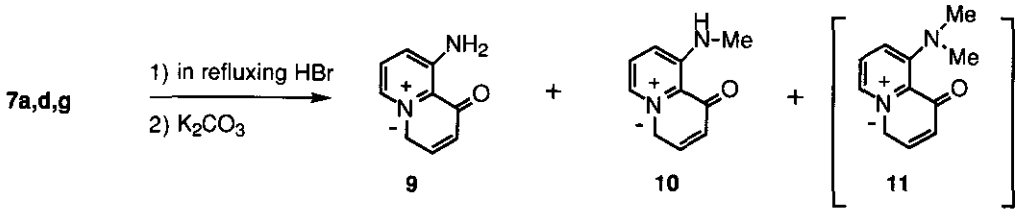
Table 1. Yields of **7d**,**g** from **5h**,**l** in Refluxing AcOH

Starting Material	Time (h)	**7a** (%)	**7d** (%)	**7g** (%)	Recovery (%)
5h	0.5				90
5h	1		trace		85
5h	2	5	56		
5h	3	36	40		
5h	10		10		
5l	0.5				90
5l	1			trace	80
5l	2	trace	35	48	
5l	3	trace	36	38	
5l	10			10	

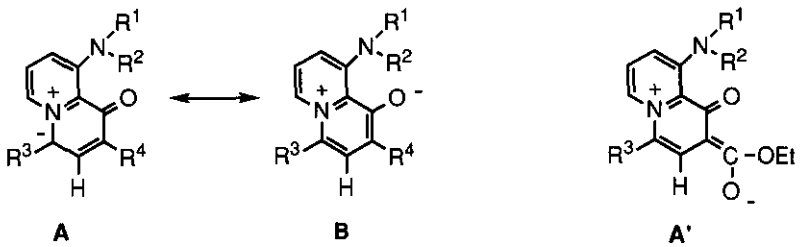
Table 2. Yields of **9**,**10** from **7a**,**d**,**g** in Refluxing 47% HBr

Starting Material	Time (h)	**9** (%)	**10** (%)	**11** (%)	Recovery (%)
7a	2	72			
7d	0.5		trace		64
7d	1	4	35		
7d	2	5	43		
7d	3	41			
7g	0.5			-	61
7g	1		trace	-	47
7g	2	4	48	-	
7g	3	20	38	-	

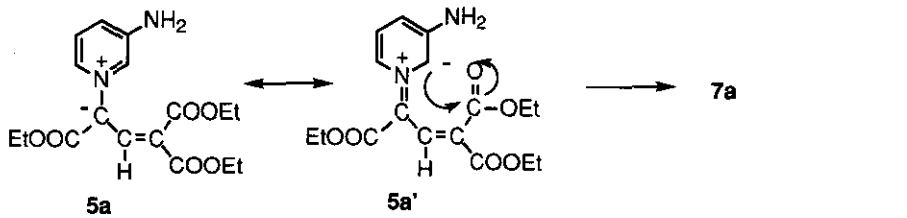
We next examined the ring closure of **5h,l** in refluxing AcOH to determine the effect of the various reaction times shown in Table 1. The optimal time for 1,6-cyclization was 2 h, and yielded quinoliziniumides (**7d, g**) in 56 and 48% yields, along with demethylated quinoliziniumides (**7a,d**) in 5 and 35% yields. Furthermore, the cyclization of *N*-allylides (**5i,j,m,n**) in refluxing AcOH for 2 h afforded the desired compounds (**7e,f,h,i**) in 38, 31, 31, and 28% yields, together with demethylated compounds (**7b,c,e,f**) in 12, 10, 10, and 16% yields. Our further attempts to obtain the mesomeric betaine, quinoliziniumide, from the thermolysis of *N*-allylides (**5d-g,k,o-r**) in refluxing xylene, diphenyl ether, or AcOH were fruitless: that is, only undesired materials and/or unknown decomposition products could be detected by ^{1}H-NMR spectroscopy and TLC. For example, treatment of **5r** in refluxing diphenyl ether for 30 min gave only 6-(*N*,*N*-dimethylamino)indolizine (**8**)[7] (Scheme 5).



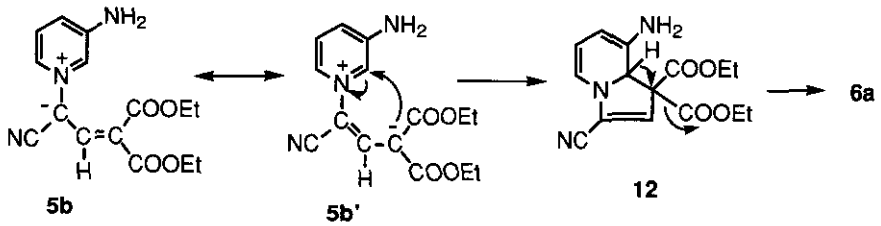
Scheme 6



Scheme 7



Scheme 8



Scheme 9

For removal of the ethoxycarbonyl groups of **7a,d,g** we examined the effect of various reaction times in refluxing 47% HBr (Table 2). In the case of **7d,g** the decarboxylation occurred to give aminoquinoliziniu-

mide together with demethylated compound, but 8-(*N*,*N*-dimethylamino)quinoliziniumide (**11**) could not be obtained (Scheme 6). The mesomeric betaines (**7a-i**,**9**,**10**) can be described to a first approximation by their resonance structures (A, B) as shown in Scheme 7. The 1-carbonyl absorption maxima for the mesomeric betaines (**7a-i**) in their IR spectra show at 1600-1630 cm^{-1}, while those for the other mesomeric betaines (**9**,**10**) show at 1580 cm^{-1}. This fact indicates that the former betaines have the dipole form A due to the resonance structure (A'), while the latter betaines have the dipole form B.

As pointed out in our previous paper,[4] a reasonable mechanism for the formation of the back-donated 1,6-cyclization product (**7a**) may proceed *via* the resonance structure (**5a'**) as outlined in Scheme 8. The formation of the 1,5-dipolar cyclization product (**6a**) may also be rationalized as outlined in Scheme 9, as pointed out by Acheson and Elmore[3k] and Meth-Cohn.[3e]

EXPERIMENTAL

Melting points were determined with a Mitamura Mel-Temp and are uncorrected. IR spectra were recorded in KBr pellets on an IR 810 (JASCO) spectrophotometer. UV spectra were recorded on a UV-310 (Shimazu) spectrophotometer. ^{1}H-NMR spectra were obtained on a Gemini 300 (VARIAN) and a VARIAN UNITY plus 500 (VARIAN) spectrometer with tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million (δ). Elemental analyses (C,H,N) of all compounds described here were performed on a Yanagimoto MT-2 CHN recorder.

General Procedure for the Preparation of 3-Aminopyridinium *N*-Allylides (5)

A mixture of the salt (**4a-d**,**g**,**h**) (2 mmol), an olefin (**2a**,**b**,**3**) (2 mmol), and triethylamine (0.40 g, 4 mmol) in EtOH (40 mL) was refluxed for 5 h, after which the mixture was evaporated under reduced pressure and the residue poured into ice-cold water (100 mL). The mixture was extracted with $CHCl_3$ (4x30 mL) and the combined extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was then submitted to column chromatography on silica gel. From a benzene-$CHCl_3$ (10:1) fraction, the product (**5a-g**,**k-m**,**o-r**) was obtained.

5a: mp 152-154 ℃ ($CHCl_3$-EtOH), yield 73%. IR (KBr) cm^{-1}: 1700 (CO), 1680 (CO), 1640 (CO); UV (EtOH) λmax (log ε) nm: 220 (4.27), 257 (4.16), 337 (4.61); ^{1}H-NMR ($CDCl_3$): 1.11-1.37 (9H, m, 3x$CH_2C\underline{H}_3$), 3.90-4.31 (6H, m, 3x$C\underline{H}_2CH_3$), 4.85 (2H, br s, NH_2), 7.31 (1H, s, =CH), 7.35-7.37 (2H, m, $C_{4,6}$-H), 8.37 (1H, s, C_2-H). *Anal.* Calcd for $C_{17}H_{22}N_2O_6$: C, 58.28; H, 6.33; N, 8.00. Found: C, 58.98; H, 6.11; N, 7.94.

5b: mp 120-122 ℃ ($CHCl_3$-EtOH), yield 32%. IR (KBr) cm^{-1}: 2180 (CN), 1670 (CO), 1640 (CO); UV (EtOH) λmax (log ε) nm: 223 (4.23), 255 (4.20), 329 (4.32), 446 (4.12); ^{1}H-NMR (DMSO-d_6): 1.34 (6H, m, 2x$CH_2C\underline{H}_3$), 4.20 (4H, m, 2x$C\underline{H}_2CH_3$), 5.20 (2H, br s, NH_2), 7.22-7.27 (2H, m, $C_{4,5}$-H), 7.70 (1H, s, =CH), 7.73-7.79 (1H, m, C_6-H), 8.00 (1H, s, C_2-H). *Anal.* Calcd for $C_{15}H_{17}N_3O_4$: C, 59.40; H, 5.65; N, 13.85. Found: C, 59.38; H, 5.64; N, 13.76.

5c: mp 203-205 ℃ ($CHCl_3$-EtOH), yield 36%. IR (KBr) cm^{-1}: 1690 (CO), 1650 (CO), 1620 (CO); UV

(EtOH) λmax (log ε) nm: 222 (4.34), 251 (4.21), 362 (4.50), 483 (2.68); ^{1}H-NMR (DMSO-d_6): 1.34 (6H, m, 2x$CH_2C\underline{H}_3$), 3.73 (4H, m, 2x$C\underline{H}_2CH_3$), 6.25 (2H, br s, NH_2), 7.44-7.57 (7H, m, Ph, $C_{4,5}$-H), 7.65-7.69 (2H, m, =CH, C_6-H), 7.79 (1H, s, C_2-H). *Anal.* Calcd for $C_{21}H_{22}N_2O_5$: C, 65.96; H, 5.80; N, 7.33. Found: C, 65.68; H, 6.02; N, 7.38.

5d: mp 220-222 ℃ ($CHCl_3$-EtOH), yield 26%. IR (KBr) cm^{-1}: 2180 (CN), 1680 (CO), 1660 (CO); UV (EtOH) λmax (log ε) nm: 222 (4.34), 251 (4.21), 362 (4.50), 483 (2.68); ^{1}H-NMR (DMSO-d_6): 1.17 (6H, t, J = 7 Hz, 2x$CH_2C\underline{H}_3$), 4.07 (4H, m, 2x$C\underline{H}_2CH_3$), 6.39 (2H, br s, NH_2), 7.65 (1H, s, =CH), 7.60 (1H, d, J = 5 Hz, C_4-H), 7.83-7.94 (2H, m, $C_{5,6}$-H), 9.98 (1H, s, C_2-H). *Anal.* Calcd for $C_{15}H_{17}N_3O_4$: C, 59.40; H, 5.65; N, 13.85. Found: C, 59.12; H, 5.58; N, 13.68.

5e: mp 223-222 ℃ ($CHCl_3$-EtOH), yield 32%. IR (KBr) cm^{-1}: 2200 (CN), 1690 (CO), 1650 (CO); UV (EtOH): λmax (log ε) nm: 222 (4.46), 255 (4.18), 362 (4.61); ^{1}H-NMR ($CDCl_3$): 1.09 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 3.94 (2H, q, J = 7 Hz, $C\underline{H}_2CH_3$), 6.37 (2H, br s, NH_2), 7.49-7.51 (5H, m, Ar-H), 7.61-7.69 (2H, m, $C_{4,5}$-H), 7.78 (1H, s, =CH), 7.90-7.95 (2H, m, $C_{6,2}$-H) . *Anal.* Calcd for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53. Found: C, 67.79; H, 5.35; N, 12.35.

5f: mp 238-240 ℃ ($CHCl_3$-EtOH), yield 28%. IR (KBr) cm^{-1}: 2190 (CN), 1650 (CO); UV (EtOH): λmax (log ε) nm: 225 (4.43), 256 (4.01), 286 (3.86), 329 (4.27), 440 (3.78); ^{1}H-NMR ($CDCl_3$): 2.47 (3H, s, SCH_3), 3.30 (3H, s, OCH_3), 7.46 (2H, br s, NH_2), 7.45-7.58 (2H, m, $C_{4,5}$-H), 7.95-8.09 (2H, m, $C_{2,6}$-H). *Anal.* Calcd for $C_{13}H_{12}N_4O_2S$: C, 54.15; H, 4.19; N, 19.43. Found: C, 54.21; H, 3.98; N, 19.25.

5g: mp 123-127 ℃ ($CHCl_3$-EtOH), yield 58%. IR (KBr) cm^{-1}: 2190 (CN), 1660 (CO), 1640 (CO); UV (EtOH) λmax (log ε) nm: 204 (4.06), 220 (4.15), 255 (3.92), 329 (3.62), 434 (3.83); ^{1}H-NMR ($CDCl_3$): 2.12 (3H, s, SCH_3), 3.42 (3H, s, OCH_3), 5.39 (2H, br s, NH_2), 7.27-7.538 (5H, m, Ar-H), 7.52-7.60 (3H, m, $C_{4,5,6}$-H), 7.80 (1H, s, C_2-H). *Anal.* Calcd for $C_{19}H_{17}N_3O_3S$: C, 62.11; H, 4.66; N, 11.44. Found: C, 62.40; H, 4.48; N, 11.25.

5k: mp 202-205 ℃ ($CHCl_3$-EtOH), yield 47%. IR (KBr) cm^{-1}: 2200 (CN), 1680 (CO), 1640 (CO); UV (EtOH): λmax (log ε) nm: 228 (4.44), 268 (4.08), 335 (4.69); ^{1}H-NMR ($CDCl_3$): 1.27 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 1.30 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 2.84 (3H, d, J = 5 Hz, $NHC\underline{H}_3$), 4.15 (4H, q, J = 7 Hz, 2x$C\underline{H}_2CH_3$), 5.34 (1H, br s, $N\underline{H}CH_3$), 7.39 (1H, d, J = 6 Hz, C_4-H), 7.50 (1H, s, =CH), 7.54-7.64 (2H, m, $C_{5,6}$-H), 8.29 (1H, s, C_2-H) . *Anal.* Calcd for $C_{15}H_{19}N_3O_4$: C, 59.01; H, 6.27; N, 13.76. Found: C, 59.29; H, 6.33; N, 14.00.

5l: mp 110-115 ℃ ($CHCl_3$-EtOH), yield 36% (B). IR (KBr) cm^{-1}: 1690 (CO), 1660 (CO), 1640 (CO); UV (EtOH): λmax (log ε) nm: 232 (4.24), 269 (4.23), 340 (4.62); ^{1}H-NMR ($CDCl_3$): 1.18 (6H, t, J = 7 Hz, 2x$CH_2C\underline{H}_3$), 1.32 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 3.06 (6H, s, -$N(CH_3)_2$), 3.89-3.98 (4H, m, 2x$C\underline{H}_2CH_3$),

4.21 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 7.28 (1H, d, J = 6 Hz, C_4-H), 7.46 (1H, t, J = 6 Hz, C_5-H), 7.69 (1H, s, =CH), 7.71 (1H, d, J = 6 Hz, C_6-H), 8.42 (1H, s, C_2-H). *Anal.* Calcd for $C_{19}H_{26}N_2O_6$: C, 60.31; H, 6.93; N, 7.40. Found: C,60.62; H, 6.74; N,7.16.

5m: mp 132-135 ℃ ($CHCl_3$-EtOH), yield 56%. IR (KBr) cm^{-1}: 2190 (CN), 1700 (CO), 1630 (CO); UV (EtOH) λmax (log ε) nm: 201 (3.93), 233 (4.29), 271 (4.24), 328 (4.36), 450 (4.13); ^{1}H-NMR ($CDCl_3$): 1.12 (6H, m, 2xCH$_2$C$\underline{H}_3$), 3.09 (6H, s, N(CH$_3$)$_2$), 3.95-4.16 (4H, m, 2xC$\underline{H}_2$CH$_3$), 7.35-7.58 (4H, m, $C_{4,5,6}$-H and =CH), 7.75 (1H, s, C_2-H) . *Anal.* Calcd for $C_{17}H_{21}N_3O_4$: C, 61.62; H, 6.39; N, 12.68. Found: C, 61.54; H, 6.35; N, 12.59.

5o: mp 102-108 ℃ ($CHCl_3$-EtOH), yield 38%. IR (KBr) cm^{-1}: 2190 (CN), 1680 (CO), 1660 (CO); UV (EtOH) λmax (log ε) nm: 231 (4.38), 274 (4.11), 335 (4.66); ^{1}H-NMR ($CDCl_3$): 1.26 (3H, t, J = 7 Hz, CH$_2$C$\underline{H}_3$), 1.03 (3H, t, J = 7 Hz, CH$_2$C$\underline{H}_3$), 3.11 (6H, s, N(CH$_3$)$_2$), 4.14 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 4.16 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 7.44 (1H, d, J = 7 Hz, C_4-H), 7.52-7.63 (2H, m, C_5-H and =CH), 7.69 (1H, d, J = 5 Hz, C_6-H), 8.31 (1H, s, C_2-H). *Anal.* Calcd for $C_{16}H_{21}N_3O_4$: C, 60.18; H, 6.63; N, 13.16. Found: C, 60.48; H, 6.33; N, 12.93.

5p: mp 172-175 ℃ ($CHCl_3$-EtOH), yield 42%. IR (KBr) cm^{-1}: 2200 (CN), 1660 (CO); UV (EtOH) λmax (log ε) nm: 232 (4.37), 278 (4.15), 324 (3.85), 426 (4.51); ^{1}H-NMR ($CDCl_3$): 1.27 (3H, t, J = 7 Hz, CH$_2$C$\underline{H}_3$), 3.17 (6H, s, N(CH$_3$)$_2$), 4.18 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 7.44 (1H, d, J = 7 Hz, C_4-H), 7.63 (1H, t, J = 7 Hz, C_5-H), 7.68 (1H, s, =CH), 7.74 (1H, s, C_2-H), 7.82 (1H, d, J = 7 Hz, C_6-H). *Anal.* Calcd for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71. Found: C, 63.17; H, 5.81; N, 19.92.

5q: mp 160-163 ℃ ($CHCl_3$-EtOH), yield 32%. IR (KBr) cm^{-1}: 2190 (CN), 1680 (CO), 1650 (CO); UV (EtOH) λmax (log ε) nm: 230 (4.45), 275 (4.20), 388 (4.17); ^{1}H-NMR ($CDCl_3$): 1.27 (3H, t, J = 7 Hz, CH$_2$C$\underline{H}_3$), 2.45 (3H, s, SCH$_3$), 3.10 (6H, s, N(CH$_3$)$_2$), 3.58 (3H, s, OCH$_3$), 4.18 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 7.36 (1H, d, J = 6 Hz, C_4-H), 7.48 (1H, t, J = 6 Hz, C_5-H), 7.78-7.80 (2H, m, $C_{2,6}$-H). *Anal.* Calcd for $C_{17}H_{21}N_3O_4S$: C, 56.18; H, 5.82; N, 11.56. Found: C, 56.05; H, 5.81; N, 11.85.

5r: mp 193-195 ℃ ($CHCl_3$-EtOH), yield 45%. IR (KBr) cm^{-1}: 2190 (CN), 1680 (CO); UV (EtOH) λmax (log ε) nm: 233 (4.39), 278 (4.15), 329 (4.53), 446 (3.80); ^{1}H-NMR ($CDCl_3$): 2.60 (3H, s, SCH$_3$), 3.11 (6H, s, N(CH$_3$)$_2$), 3.46 (3H, s, OCH$_3$), 7.28 (1H, d, J = 7 Hz, C_4-H), 7.48 (1H, t, J = 7 Hz, C_5-H), 7.89 (1H, s, C_2-H), 7.92 (1H, d, J = 7 Hz, C_6-H). *Anal.* Calcd for $C_{15}H_{16}N_4O_2S$: C, 56.95; H, 5.10; N, 17.71. Found: C, 56.82; H, 5.27; N, 17.86.

General Procedure for the Reaction of 5a-c, h-j, l-n in Refluxing Xylene or AcOH

Method A: A solution of the *N*-allylide (**5a-c,l,m**) (2 mmol) in xylene (50 mL) was refluxed for 10 h, after which the mixture was evaporated under reduced pressure and the residue poured into ice-cold water (100 mL). The mixture was extracted with $CHCl_3$ (4x30 mL) and the combined extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was then submitted to column

chromatography on silica gel. From a benzene-$CHCl_3$ (10:1) fraction, the indolizine derivative (**6a**) was obtained. From a $CHCl_3$ fraction, the quinoliziniumide derivative (**7a-c,g,h**) was obtained.

Method B: A mixture of the salt (**4d-f,i**) (4 mmol), an olefin (**2a**) (0.86 g, 4 mmol), and triethylamine (0.81 g, 8 mmol) in EtOH (40 mL) was refluxed for 5 h, after which the mixture was evaporated under reduced pressure and the residue poured into ice-cold water (100 mL). The mixture was extracted with $CHCl_3$ (4x30 mL) and the combined extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. A benzene-$CHCl_3$ (10:1) fraction gave the oily *N*-allylide (**5h-j,n**). A solution of the crude *N*-allylide (**5h-j,n**) (2 mmol) in xylene (50 mL) was refluxed for 5 h. The resulting mixture was treated as described for method A. From a benzene-$CHCl_3$ (10:1) fraction, the indolizine derivative (**6b-d**) was obtained. From a $CHCl_3$ fraction, the quinoliziniumide derivative (**7d-f,i**) was obtained.

Method C: A solution of the *N*-allylide (**5a-c,l,m**) (2 mmol) in AcOH (50 mL) was refluxed for 2 h, after which the mixture was evaporated under reduced pressure and the residue poured into ice-cold water (100 mL) and made basic to litmus with K_2CO_3. The mixture was extracted with $CHCl_3$ (4x30 mL), and the combined extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a $CHCl_3$ fraction, the quinoliziniumide derivative (**7a-c,g,h**) was obtained (Table 3).

Method D: A mixture of the salt (**4d-f,i**) (4 mmol), an olefin (**2a**) (0.86 g, 4 mmol), and triethylamine (0.81 g, 8 mmol) in EtOH (40 mL) was refluxed for 5 h, after which the mixture was evaporated under reduced pressure and the residue poured into ice-cold water (100 mL). The mixture was extracted with $CHCl_3$ (4x30 mL) and the combined extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was then submitted to column chromatography on silica gel. From a benzene-$CHCl_3$ (10:1) fraction, the oily *N*-allylide (**5h-j,n**) was obtained. A solution of the crude *N*-allylide (**5h-j,n**) (2 mmol) in AcOH (50 mL) was refluxed for 2 h. The resulting mixture was treated as described for method C to give the quinoliziniumide derivative (**7d-f,i**) (Table 3).

Table 3. Yields from *N*-Allylides (**5a-c, h-j,l-n**) in Refluxing AcOH for 2 h

Starting Materials	Products (%)	Products (%)	Products (%)
5a	86 (**7a**)		
5b	32 (**7b**)		
5c	43 (**7c**)		
5h	5 (**7a**)	56 (**7d**)	
5i	12 (**7b**)	38 (**7e**)	
5j	10 (**7c**)	31 (**7f**)	
5l	trace (**7a**)	35 (**7d**)	48 (**7g**)
5m	trace (**7b**)	10 (**7e**)	31 (**7h**)
5n	trace (**7c**)	16 (**7f**)	28 (**7i**)

6a: mp 151-154 ℃ (EtOH) , yield 17% (A). IR (KBr) cm^{-1}: 2200 (CN), 1740 (CO); UV (EtOH) λmax (log ε) nm: 251 (4.16), 347 (4.19); ^{1}H-NMR ($CDCl_3$): 1.39 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 4.34 (2H, q, J = 7 Hz, $C\underline{H}_2CH_3$), 6.36 (1H, d, J = 7 Hz, C_7-H), 6.83 (1H, t, J = 7 Hz, C_6-H), 7.23 (1H, s, C_2-H), 7.77 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 63.14; H, 4.58; N, 18.59.

6b: mp 101-105 ℃ (EtOH), yield 5% (B). IR (KBr) cm^{-1}: 1700 (CO), 1670 (CO); UV (EtOH) λmax (log

ε) nm: 227 (4.38), 264 (4.35), 339 (4.18), 355 (4.19) nm; ^{1}H-NMR ($CDCl_3$): 1.41 (3H, t, J = 7 Hz, 2x$CH_2C\underline{H}_3$), 2.93 (3H, d, J = 5 Hz, NHC$\underline{H}_3$), 4.36 (4H, q, J = 7 Hz, 2xC$\underline{H}_2CH_3$), 6.16 (1H, d, J = 7 Hz, C_7-H), 6.86 (1H, t, J = 7 Hz, C_6-H), 7.92 (1H, s, C_2-H), 8.61 (1H, br s, N$\underline{H}CH_3$), 8.95 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{15}H_{18}N_2O_4$: C, 62.06; H, 6.25; N, 9.65. Found: C, 61.98; H, 6.15 ; N, 9.51.

6c: mp 115-120 ℃ (EtOH), yield 4% (B). IR (KBr) cm^{-1}: 2210 (CN), 1680 (CO); UV (EtOH) λmax (log ε) nm: 244 (4.63), 255 (4.34), 263 (4.33), 348 (4.36); ^{1}H-NMR ($CDCl_3$): 1.25 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 2.92 (3H, d, NHC$\underline{H}_3$), 4.34 (4H, q, J = 7 Hz, C$\underline{H}_2CH_3$), 6.11 (1H, d, J = 7 Hz, C_7-H), 6.89 (1H, t, J = 7 Hz, C_6-H), 7.65 (1H, d, J = 7 Hz, C_5-H), 7.68 (1H, s, C_2-H), 8.62 (1H, br s, N$\underline{H}CH_3$). *Anal.* Calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 64.43; H, 5.46; N, 17.31.

6d: mp 120-123 ℃ (EtOH), yield 2% (B). IR (KBr) cm^{-1}: 1680 (CO), 1620 (CO); UV (EtOH) λmax (log ε) nm: 244 (4.44), 286 (4.41), 406 (4.26); ^{1}H-NMR ($CDCl_3$): 1.35 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 2.97 (3H, d, NHC$\underline{H}_3$), 4.29 (4H, q, J = 7 Hz, C$\underline{H}_2CH_3$), 6.31 (1H, d, J = 7 Hz, C_7-H), 6.98 (1H, t, J = 7 Hz, C_6-H), 7.55-7.79 (6H, m, C_2- and Ar-H), 9.35 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.61; H, 5.44; N, 8.54.

7a: mp 283-285 ℃ (orange crystals, $CHCl_3$-EtOH), yield 5% (A). IR (KBr) cm^{-1}: 1710 (CO), 1680 (CO), 1620 (CO); UV (EtOH) λmax (logε) nm: 216 (4.35), 232 (4.40), 285 (3.77), 330 (4.18), 386 (3.95), 455 (4.46); ^{1}H-NMR ($CDCl_3$): 1.41 (3H, t, J = 7 Hz, 2x$CH_2C\underline{H}_3$), 4.36 (2H, q, J = 7 Hz, C$\underline{H}_2CH_3$), 4.41 (2H, q, J = 7 Hz, C$\underline{H}_2CH_3$), 6.90 (1H, d, J = 7 Hz, C_7-H), 7.31 (1H, t, J = 7 Hz, C_6-H), 8.84 (1H, s, C_3-H), 9.87 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{15}H_{16}N_2O_5$: C, 59.21; H, 5.30; N, 9.21. Found: C, 58.96; H, 5.26; N, 9.17.

7b: mp 227-231 ℃ (orange crystals, $CHCl_3$-EtOH), yield 22% (A). IR (KBr) cm^{-1}: 2200 (CN), 1720 (CO), 1620 (CO); UV (EtOH) λmax nm: 204, 249, 283, 292, 369, 402; ^{1}H-NMR ($CDCl_3$) 1.12-1.51 (3H, m, $CH_2C\underline{H}_3$), 4.18-4.43 (2H, m, C$\underline{H}_2CH_3$), 7.05 (1H, t, J = 7 Hz, C_6-H), 7.83 (1H, s, C_3-H), 8.07 (1H, d, J = 7 Hz, C_7-H), 8.58 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{13}H_{11}N_3O_3$: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.98; H, 4.04; N, 16.24.

7c: mp 283-284 ℃ (orange crystals, $CHCl_3$-EtOH), yield 3% (A). IR (KBr) cm^{-1}: 1720 (CO), 1630 (CO), 1610 (CO); UV (EtOH) λmax nm: 230, 254, 344, 393, 469 nm; ^{1}H-NMR ($CDCl_3$): 1.16 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 4.10 (2H, q, J = 7 Hz, C$\underline{H}_2CH_3$), 7.30 (1H, d, J = 7 Hz, C_7-H), 7.55-7.63 (6H, m, Ar and C_6-H), 8.01 (1H, s, C_3-H), 8.40 (2H, br s, NH_2), 9.55 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 68.09; H, 4.56; N, 8.08.

7d: mp 115-120 ℃ (orange crystals, $CHCl_3$-EtOH), yield 5% (B). IR (KBr) cm^{-1}: 1710 (CO), 1680 (CO), 1600 (CO); UV (EtOH) λmax (log ε) nm: 217 (4.35), 233 (4.53), 290 (3.87), 337 (4.28), 388 (3.96), 468 (4.42); ^{1}H-NMR ($CDCl_3$): 1.41 (6H, t, J = 7 Hz, 2x$CH_2C\underline{H}_3$), 2.93 (3H, d, J = 5 Hz, NHC$\underline{H}_3$), 4.37 (2H,

q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 4.45 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 6.85 (1H, d, J = 7 Hz, C_7-H), 7.36 (1H, t, J = 7 Hz, C_6-H), 8.82 (1H, s, C_3-H), 9.75 (1H, d, J = 7 Hz, C_5-H), 11.40 (1H, br s, N$\underline{H}$CH$_3$). *Anal.* Calcd for $C_{16}H_{18}N_2O_5$: C, 60.37; H, 5.70; N, 8.80. Found: C, 60.20; H, 5.61; N, 8.66.

7e: mp 168-170 ℃ (orange crystals, $CHCl_3$-EtOH), yield 3% (B). IR (KBr) cm^{-1}: 2200 (CN), 1710 (CO), 1600 (CO); UV (EtOH) λmax (log ε) nm: 228 (4.56), 290 (3.86), 335 (4.21), 391 (3.88), 441 (4.28), 465 (4.39); ^{1}H-NMR ($CDCl_3$): 1.40 (3H, t, J = 7 Hz, CH$_2$C$\underline{H}_3$), 2.94 (3H, d, J = 5 Hz, NHC$\underline{H}_3$), 4.396 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 6.82 (1H, d, J = 7 Hz, C_7-H), 7.45 (1H, t, J = 7 Hz, C_6-H), 8.17 (1H, d, J = 7 Hz, C_5-H), 8.25 (1H, s, C_3-H), 11.29 (1H, br s, N$\underline{H}$CH$_3$). *Anal.* Calcd for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.86; H, 5.05; N, 15.29.

7f: mp 132-138 ℃ (orange crystals, $CHCl_3$-EtOH), yield 3% (B). IR (KBr) cm^{-1}: 1730 (CO), 1610 (CO), 1600 (CO); UV (EtOH) λmax (log ε) nm: 259 (4.28), 351 (4.15), 395 (4.04), 484 (4.33); ^{1}H-NMR ($CDCl_3$): 1.31 (3H, t, J = 7 Hz, CH$_2$C$\underline{H}_3$), 2.95 (3H, d, J = 5 Hz, NHC$\underline{H}_3$), 4.33 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 6.95 (1H, d, J = 7 Hz, C_7-H), 7.50 (1H, t, J = 7 Hz, C_6-H), 7.50-7.58 (3H, m, Ar-H), 7.75 (2H, d, J = 7 Hz, Ar-H), 8.31 (1H, s, C_3-H), 9.57 (1H, d, J = 7 Hz, C_5-H), 11.31 (1H, br s, N$\underline{H}$CH$_3$). *Anal.* Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N,7.48. Found: C, 70.81; H, 4.61; N, 7.64.

7g: mp 112-115 ℃ (orange crystals, $CHCl_3$-EtOH), yield 6% (A). IR (KBr) cm^{-1}: 1710 (CO), 1680 (CO), 1620 (CO); UV (EtOH) λmax (log ε) nm: 223 (4.28), 242 (4.41), 315 (3.98), 359 (4.02), 402 (3.95), 465 (4.18); ^{1}H-NMR ($CDCl_3$): 1.40 (6H, t, J = 7 Hz, 2xCH$_2$C$\underline{H}_3$), 3.06 (6H, s, N(CH$_3$)$_2$), 4.34 (4H, q, J = 7 Hz, 2xC$\underline{H}_2$CH$_3$), 7.18 (1H, d, J = 7 Hz, C_7-H), 7.31 (1H, t, J = 7 Hz, C_6-H), 8.82 (1H, s, C_3-H), 9.80 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{17}H_{20}N_2O_5$: C, 61.44; H, 6.07; N, 8.43. Found: C, 61.29; H, 5.98; N, 8.35.

7h: mp 170-175 ℃ (orange crystals, $CHCl_3$-EtOH), yield 5% (A). IR (KBr) cm^{-1}: 2200 (CN), 1670 (CO), 1630 (CO); UV (EtOH) λmax (log ε) nm: 234 (4.47), 254 (4.25), 310 (3.87), 358 (4.00), 407 (3.96), 463 (4.25); ^{1}H-NMR ($CDCl_3$): 1.37 (3H, t, J = 7 Hz, CH$_2$C$\underline{H}_3$), 3.08 (6H, s, N(CH$_3$)$_2$), 4.31 (2H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 7.18 (1H, d, J = 7 Hz, C_7-H), 7.40 (1H, t, J = 7 Hz, C_6-H), 8.23 (1H, s, C_3-H), 8.30 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{15}H_{15}N_3O_3$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.88; H, 5.47; N, 14.61.

7i: mp 160-163 ℃ (orange crystals, $CHCl_3$-EtOH), yield 4% (B). IR (KBr) cm^{-1}: 1710 (CO), 1630 (CO), 1610 (CO); UV (EtOH) λmax nm: 254, 299, 344, 393, 469; ^{1}H-NMR ($CDCl_3$): 1.32 (3H, t, J = 7 Hz, CH$_2$C$\underline{H}_3$), 2.99 (6H, s, N(CH$_3$)$_2$), 4.31 (4H, q, J = 7 Hz, C$\underline{H}_2$CH$_3$), 6.92 (1H, d, J = 7 Hz, C_7-H), 7.50-7.59 (4H, m, C_6- and Ar-H), 7.72 (2H, d, J = 6 Hz, Ar-H), 8.31 (1H, s, C_3-H), 9.57 (1H, d, J = 7 Hz, C_5-H). *Anal.* Calcd for $C_{21}H_{20}N_2O_4$: C, 69.22; H, 5.53; N, 7.69. Found: C, 69.35; H, 5.48; N, 7.75.

1,3-Dicyano-2-methylthio-6-(*N*,*N*-dimethylamino)indolizine (8)

A solution of the *N*-allylide (**5r**) (0.63 g, 2 mmol) in diphenyl ether (50 mL) was refluxed for 30 min and hexane was then added to the solution. The precipitate was collected by filtration, washed with hexane,

dried, and submitted to column chromatography on silica gel. From a benzene-$CHCl_3$ (10:1) fraction, the indolizine derivative (**8**) was obtained.

8: mp 182-185 ℃ (EtOH), yield 0.06 g, 12%. IR (KBr) cm^{-1}: 2200 (CN); UV (EtOH) λmax (log ε) nm: 205 (4.23), 270 (4.66); ^{1}H-NMR ($CDCl_3$): 2.70 (3H, s, SCH_3), 3.00 (6H, s, $N(CH_3)_2$), 7.17 (1H, d, J = 7 Hz, C_7-H), 7.45 (1H, s, C_5-H), 7.52 (1H, d, J = 7 Hz, C_8-H). *Anal.* Calcd for $C_{13}H_{12}N_4S$: C, 60.91; H, 4.72; N, 21.86. Found: C, 60.93; H, 4.76; N, 21.60.

1,4-Dihydro-1-oxo-8-aminoquinolizin-4a-ium-4-ides (9,10)

A solution of quinoliziniumide (**7a,d,j**) (4 mmol) in 47% HBr (20 mL) was refluxed. The reaction mixture was evaporated under reduced pressure. A solution of the residue in water (20 mL) was made basic to litmus with K_2CO_3 and extracted with $CHCl_3$ (3x10 mL). The extract was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene-$CHCl_3$ (10:1) fraction, the quinoliziniumide derivative (**9,10**) was obtained (Table 2).

9: mp 110-113 ℃ (yellow crystals, EtOH). IR (KBr) cm^{-1}: 1580 (CO); UV (EtOH) λmax (log ε) nm: 209 (4.44), 252 (3.55), 305 (3.76), 366 (3.65), 425 (4.30); ^{1}H-NMR ($CDCl_3$): 6.29 (1H, d, J = 8 Hz, C_4-H), 6.74 (1H, d, J = 8 Hz, C_2-H), 6.94 (1H, t, J = 8 Hz, C_3-H), 7.11 (1H, t, J = 6 Hz, C_6-H), 7.28 (1H, d, J = 6 Hz, C_7-H), 7.41 (1H, d, J = 6 Hz, C_5-H), 7.55-7.80 (2H, br, NH_2). *Anal.* Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.35; H, 5.11; N, 17.32.

10: mp 112-115 ℃ (yellow crystals, EtOH). IR (KBr) cm^{-1}: 1580 (CO); UV (EtOH) λmax (log ε) nm: 211 (4.57), 252 (3.65), 270 (3.66), 311 (4.03), 366 (3.76), 429 (4.37); ^{1}H-NMR ($CDCl_3$): 2.86 (3H, d, J = 3 Hz, $NHC\underline{H}_3$), 6.11 (1H, d, J = 8 Hz, C_4-H), 6.75 (1H, d, J = 8 Hz, C_2-H), 7.01 (1H, t, J = 8 Hz, C_3-H), 7.13 (1H, t, J = 7 Hz, C_6-H), 7.28 (1H, d, J = 7 Hz, C_7-H), 7.32 (1H, d, J = 7 Hz, C_5-H), 11.40 (1H, br s, $N\underline{H}CH_3$). *Anal.* Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 69.05; H, 5.79; N, 16.22.

REFERENCES AND NOTES

1. a) Y. Tominaga and Y. Matsuda, *J. Heterocycl. Chem.*, 1985, **22**, 937. b) M. Kolb, *Synthesis*, **1990**, 171.
2. a) Y. Tominaga and Y. Matsuda, *J. Syn. Org. Chem. Japan*, 1985, **43**, 669. b) Y. Matsuda and H. Gotou, *Heterocycles*, 1987, **26**, 2757. c) Y. Matsuda, H. Gotou, M. Yamashita, K. Takahashi, S. Ide, K. Furuno, K. Torisu, T. Itou, and C. Motokawa, *ibid.*, 1992, **34**, 2277.
3. a) V. Boekelheide and N. A. Fedoruk, *J. Am. Chem. Soc.*, 1968, **90**, 3830. b) H. G. O. Becker, D. Nagel, and H. J. Timpe, *J. Prakt. Chem.*, 1973, **315**, 97. c) K. Matsumoto, *J. Syn. Org. Chem. Japan*, 1974, **32**, 731. d) Y. Tamura, Y. Sumida, S. Haruki, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 575. e) O. Meth-Cohn, *Tetrahedron Lett.*, **1975**, 413. f) T. Uchida and K. Matsumoto, *Synthesis*, **1976**, 209. g) A. Kakehi, S. Ito, T. Funahashi, and Y. Ota, *J. Org. Chem.*, 1976, **41**, 1570.

h) A. Kakehi, S. Ito, K. Uchiyama, Y. Konno, and K. Kondo, *ibid.*, 1977, **42**, 443. i) H. J. Timpe, H. G. O. Becker, and R. Radeglia, *J. Prakt. Chem.*, 1977, **319**, 945. j) F. J. Swinbourene, J. H. Hunt, and G. Klinkert, *Adv. Heterocycl. Chem.*, 1978, **23**, 103. k) R. M. Acheson and N. F. Elmore, *ibid.*, 1978, **23**, 263. l) E. C. Taylor and I. J. Turchi, *Chem. Rev.*, 1979, **79**, 181. m) Y. Tamura and M. Ikeda, *Adv. Heterocycl. Chem.*, 1981, **29**, 71.

4. a) Y. Matsuda, H. Gotou, K. Katou, H. Matsumoto, M. Yamashita, K. Takahashi, and S. Ide, *Heterocycles*, 1990, **31**, 977. b) Y. Matsuda, H. Gotou, K. Katou, H. Matsumoto, M. Yamashita, K. Takahashi, S. Ide, K. Furuno, and K. Torisu, *ibid.*, 1991, **32**, 2217. c) Y. Matsuda, M. Yamashita, K. Takahashi, S. Ide, K. Torisu, and K. Furuno, *ibid.*, 1992, **33**, 295. d) Y. Matsuda, M. Yamashita, K. Takahashi, S. Ide, T. Itou, C. Motokawa, and Y. Chiyomaru, *Chem. Pharm. Bull.*, 1994, **42**, 454. e) Y. Matsuda, Y. Chiyomaru, C. Motokawa, and T. Nishiyori, *Heterocycles*, 1995, **41**, 329 and 2777.
5. a) H. L. Bradlow and C. A. Vanderwerf, *J. Org. Chem.*, 1951, **16**, 73.
6. a) E. G. de Bollemount, *Bull. Soc. Chim. Fr.*, 1902, **25**, 20. b) O. Diels, H. Gütner, and R. Kaack, *Ber.*, 1922, **55**, 3439. c) R. Gompper and W. Töfl, *Chem. Ber.*, 1962, **95**, 2861. d) M. Prystas and J. Gut, *Coll. Czech. Chem. Commun.*, 1963, **28**, 2501. e) B. S. Thyagarajan and P. V. Gopalakrishnan, *Tetrahedron*, 1964, **20**, 1051.
7. This regioselectivity may be accounted for by the presence of a steric factor as pointed out by Tamura. In the case of the 1,5-dipolar cyclization process, the production of **8** may be considered to reflect the steric effect of the dimethylamino group rather than the general tendency for preferential attack at C-2 of pyridinium moiety owing to stabilization by resonance.[5] Y. Tamura, Y. Sumida, Y. Miki, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 406.

Received, 29th July, 1997