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Reaction of Pyridinium N-Ylides with Ketenethioacetal Derivatives

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Reaction of the pyridinium N-ylides with ketenethioacetals in the presence of triethylamine or potassium carbonate as a base in ethanol or dimethylformamide gave the pyridinium N-allylides which were readily cyclized to afford the indolizine derivatives.

Keywords——pyridinium ylide ketenethioacetal; methylpyridinium ylide ketenethioacetal; pyridinium allylide; synthesis of indolizine; cyclization of pyridinium allylide

It has previously been reported that the reaction of various types of active methylene compounds with ketenethioacetal derivatives gives the corresponding replacement products of methylthio group of the ketenethioacetals.[2] The present paper deals with the reaction of pyridinium N-ylide as active methylene compound with some ketenethioacetal derivatives and the successive cyclization.

The reaction of N-phenacylpyridinium bromide (**1a**) with ketenethioacetal, 2-cyano-3,3-bis(methylthio)acrylonitrile (**2a**) (CMAN) in the presence of triethylamine in refluxing ethanol gave the corresponding N-allylide (**3a**), mp 192°, in 67% yield. The reaction of **1a** with the other ketenethioacetal, methyl 2-cyano-3,3-bis(methylthio)acrylate (**2b**) (MCMA), was also carried out to give the corresponding N-allylide (**3b**) in 43% yield. In a similar manner, the other N-allylides (**3c—e**) were also prepared in good yields as shown in Chart 1. These pyridinium N-allylides (**3a—e**) were also obtained by the reaction of 1-[2,2-bis(methylthio)-vinyl]pyridinium iodide with malononitrile or methyl cyanoacetate in 60—90% yield.[3] The reaction of N-carbamoylmethylpyridinium chloride (**1e**) with **2b** did not give N-allylide, but afforded the glutaconimide derivatives (**4**) in 40% yield, which was also obtained by the

1) Location: *1–14, Bunkyo-machi, Nagasaki, 852, Japan.*

2) *a*) H.D. Edwards and J.D. Kendall, U.S. Patent 2533233 (1950) [*Chem. Abstr.*, **45**, 4052*h* (1951)]; *b*) R. Gompper and W. Töpfel, *Chem.* Ber., **95**, 2871 (1962); *c*) G. Kobayashi, S. Furukawa, Y. Matsuda, M. Nakamura, and R. Natsuki, *Yakugaku Zasshi*, **87**, 1044 (1967); *d*) G. Kobayashi, S. Furukawa, Y. Matsuda, R. Natsuki, and S. Matsunaga, *Chem. Pharm. Bull.* (Tokyo), **18**, 124 (1970); *e*) G. Kobayashi, Y. Matsuda, R. Natsuki, and M. Sone, *Chem. Pharm. Bull.* (Tokyo), **20**, 657 (1972); *f*) G. Kobayashi, Y. Matsuda, R. Natsuki, and Y. Tominaga, *Yakugaku Zasshi*, **92**, 713 (1972); *g*) G. Kobayashi, Y. Matsuda, R. Natsuki, and Y. Tominaga, *Yakugaku Zasshi*, **92**, 1468 (1972); *h*) Y. Tominaga, R. Natsuki, Y. Matsuda, and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **21**, 1658 (1973); *i*) Y. Tominaga, R. Natsuki, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, **93**, 1523 (1973); *j*) G. Kobayashi, Y. Matsuda, R. Natsuki, Y. Tominaga, and M. Sone, *Yakugaku Zasshi*, **93**, 612 (1973); *k*) M. Sone, Y. Tominaga, R. Natsuki, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, **93**, 1008 (1973); *l*) G. Kobayashi, Y. Matsuda, R. Natsuki, Y. Tominaga, C. Maseda, and H. Awaya, *Yakugaku Zasshi*, **94**, 50 (1974); *m*) C. Maseda, M. Sone, Y. Tominaga, R. Natsuki, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, **94**, 839 (1974); *n*) M. Matsuo, H. Awaya, C. Maseda, Y. Tominaga, R. Natsuki, Y. Matsuda, and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2765 (1974); *o*) S. Ueno, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2624 (1974); *p*) K. Mizuyama, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, **95**, 290 (1975); *q*) T. Hatada, M. Sone, Y. Tominaga, R. Natsuki, Y. Matsuda, and G. Kobayashi, *Yakugaku Zasshi*, **95**, 623 (1975); *r*) Y. Tominaga, Y. Morita, Y. Matsuda, and G. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **23**, 2390 (1975); *s*) H. Fujito, Y. Tominaga, Y. Matsuda, and G. Kobayashi, *Heterocycles*, **4**, 939 (1976).

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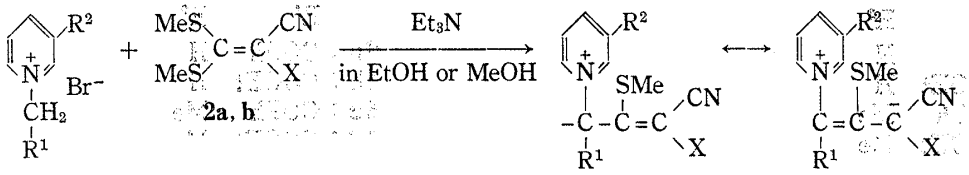
treatment of N-allylide (**3c**) with hydrochloric acid.[3] Compound (**4**) was identified with an authentic sample.[3]

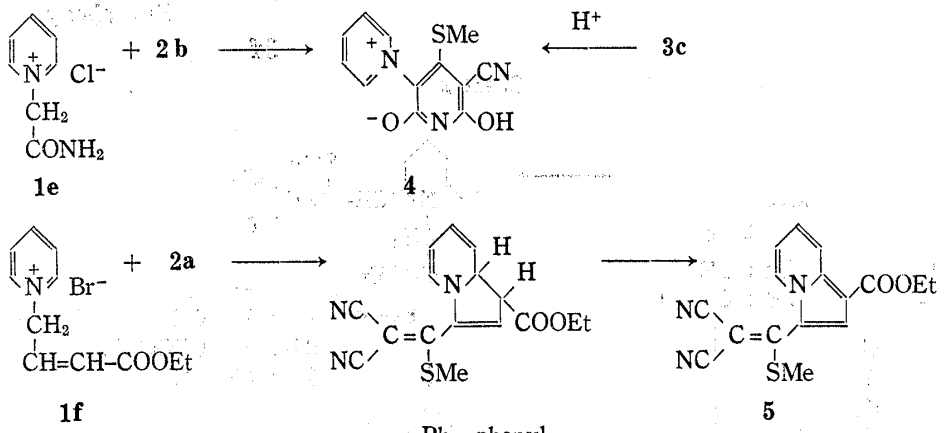
Similarly, the N-allylide derivative (**1f**) also reacted with 2a to give a yellow needles, mp 205—207°, which was assigned to be 1-ethoxycarbonyl-3-(2,2-cyano-1-methylthio)vinylindolizine (**5**) from elemental analysis and spectral data as shown in the experimental part. Compound (**5**) would be useful as synthetic intermediates for cycl[3,2,2]azine derivatives.[4]



	R^1	R^2
1a	COPh	H
1b	COOEt	H
1c	COPh	Me
1d	COOEt	Me

2a: X=CN (CMAN)
2b: X=COOMe (MCMA)

	R^1	R^2	X
3a	COPh	H	CN
3b	COPh	H	COOMe
3c	COOEt	H	CN
3d	COPh	Me	CN
3e	COOEt	Me	CN



Ph=phenyl

Chart 1

As we have recently reported that the reaction of N-[1-ethoxycarbonyl-2,2-bis(methylthio)vinyl]-3-methylpyridinium iodide (**1d**) with nitromethane in the presence of triethylamine in ethanol gave 3-ethoxycarbonyl-8-methyl-2-methylthioindolizine (**6b**) and that ethyl 2-methylthiopyrrolo[2,1-*c*]isoquinoline-3-carboxylate was prepared from the reaction of isoquinolinium N-ylide with 1-nitro-2,2-bis(methylthio)ethylene(**2c**)(NBME),[2s] this method afforded only 3-ethoxycarbonylindolizine derivatives.

The reaction of ethoxycarbonylmethyl-3-methylpyridinium bromide (**1d**) with **2c** in ethanol gave **6b** in 78% yield. In a similar reaction, the indolizine derivatives (**6a, c, d**) were synthesized by the reaction of **1c,g,** and **1h** with **2c** in good yields. This reaction of N-ylides with **2c** is more useful than that of ketenethioacetal, N-[2,2-bis(methylthio)vinyl]-pyridinium iodide (**7**), with nitromethane for the preparation of substituted indolizine derivatives.

However, the N-ylide (**1b**) was found to react with 3-(2,2-dicyano-1-methylthio)vinylindole to yield the pyridinium N-allylide (**3f**) in 92% yield.

Next, the reaction of the 2-picolinium N-ylide(**1i**) with 2a in the presence of potassium carbonate in dimethylformamide on a boiling water bath for 3 hr gave a colorless product

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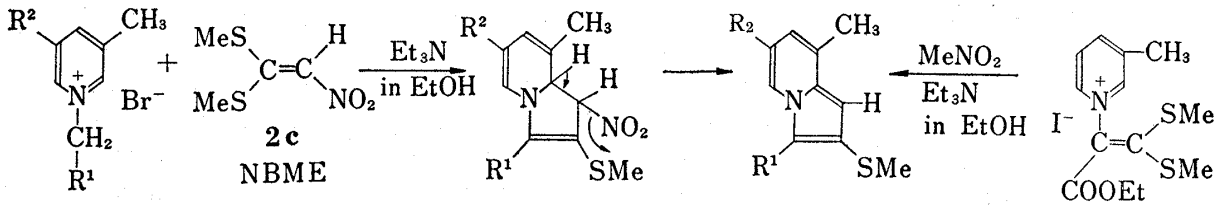
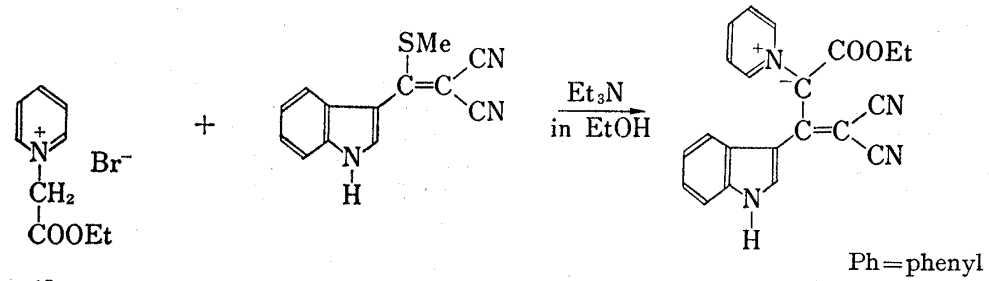


1c,d,g,h **2c** NBME **6a–d** **7**

	R^1	R^2
1c	COPh	H
1d	COOEt	H
1g	COPh	Me
1h	COOEt	Me

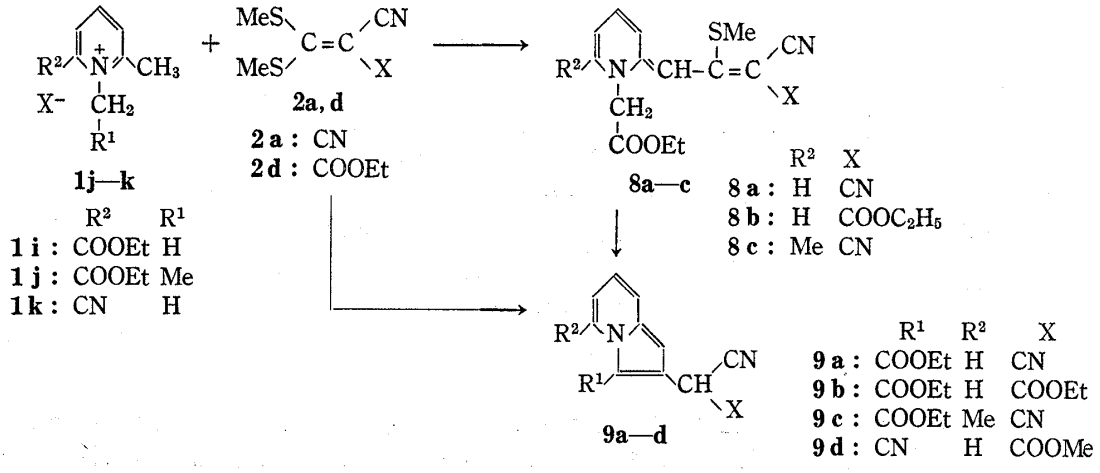
	R^1	R^2
6a	COPh	H
6b	COOEt	H
6c	COPh	Me
6d	COOEt	Me



1b **3f**

Ph=phenyl

Chart 2

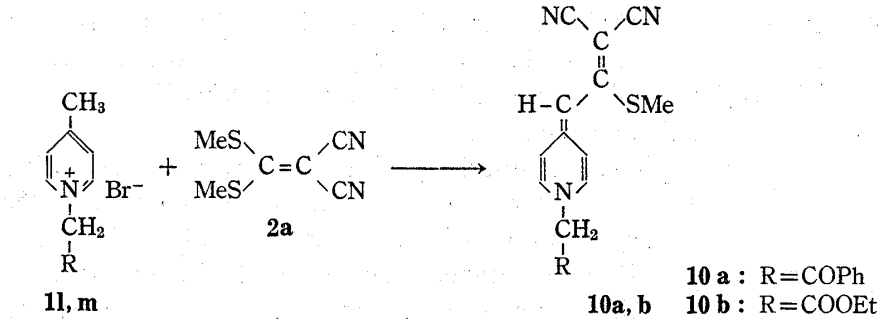


1j–k **2a, d** (**2a**: CN; **2d**: COOEt) **8a–c** **9a–d**

	R^2	R^1
1i	COOEt	H
1j	COOEt	Me
1k	CN	H

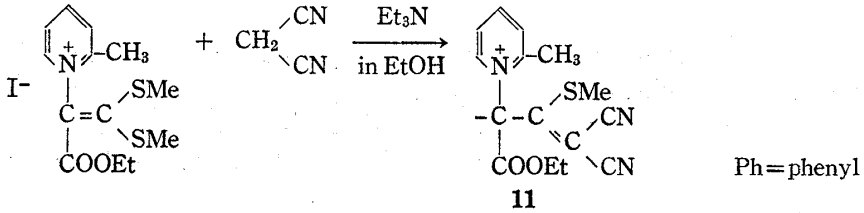
	R^2	X
8a	H	CN
8b	H	$COOC_2H_5$
8c	Me	CN

	R^1	R^2	X
9a	COOEt	H	CN
9b	COOEt	H	COOEt
9c	COOEt	Me	CN
9d	CN	H	COOMe



1l, m **2a** **10a, b**

10a: R=COPh **10b**: R=COOEt



11

Ph=phenyl

Chart 3

(**9a**), mp 192—193°, in a good yield, which had the composition corresponded to $C_{14}H_{11}N_3O_2$ from elemental analysis and exhibited infrared (IR) absorptions at 2190 cm^{-1} due to a cyano group and at 1740 cm^{-1} due to a carbonyl group of ester, and its nuclear magnetic resonance (NMR) spectrum ($CDCl_3$) of a triplet peak of methyl protons at δ 5.88 (3H,O-CH_2-C$\underline{H}_3$), a quartet of methylene protons at δ 4.52 (2H,O-CH_2-), a singlet of methine proton at δ 5.88 (1H, -$CH(CN)_2$), a singlet of aromatic proton at δ6.89 (1H, 1-H), a multiplet of aromatic protons at δ 6.96—7.35 (2H, 6-H and 7-H), and two doublet of aromatic protons at δ 7.64 and 9.50 (1H, J=9 Hz, 8-H and 1H, J=6 Hz, 5-H). From these data, this compond (**9a**) was assigned to be 2-dicyanomethyl-3-ethoxycarbonylindolizine. When this reaction was carried out at room temperature, two products the indolizine derivative (**9a**) and the 2-allylidene-1,2-dihydropyridine derivative (**8a**), which were assigned from elemental analysis and spectral data as shown in the experimental, were obtained in 14% and 70% yield, respectively. The ultraviolet (UV) spectrum of 8a was shown in Fig. 1. Compound (**8a**) was converted into **9a** by heating on a boiling water bath in the presence of potassium carbonate in 86% yield. Similarly, the reactions of **1i,j**, and **1k** with CMAN and ethyl 2-cyano-3,3-bis(methylthio)acrylate (ECMA) gave indolizine derivatives (**9b—d**) upon heating and the 2-allylidene-1,2-dihydropyridine derivatives (**8a,c**) at room temperature. These 2-allylidene-1,2-dihydropyrines (**8b, c**) were also converted into indolizine derivatives (**9b, c**) in the presence of potassium carbonate upon heating.

In the same manner, the reaction of 4-picolinium salts (**1l, m**) with ketenethioacetal (**2a**) also gave 4-allylidene-1,4-dihydropyridine derivatives (**10a, b**) in good yields.

However, the picolinium N-allylides having strong enamine character could not be obtained from the corresponding 2- or 4-picolinium salts by the similar method as above.

On the other hand, 2-picolinium N-allylide (**11**), which was synthesized by the reaction of N-[1-ethoxycarbonyl-2,2-bis-(methylthio)vinyl]-2-methylpyridinium iodide with malononitrile, was not converted into the indolizine derivative under the similar condition. Thus, it can be assumed that difference in their nucleophilicity of the methyl groups at 2- and 4-positions would be considered as one of the reasons for their different reactivity.

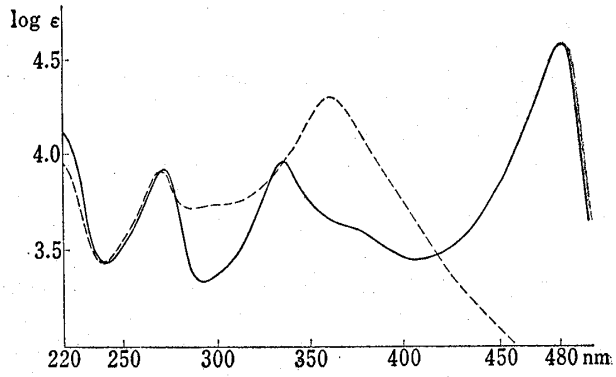


Fig. 1. UV Spectra of **8a** and **11**
——, 8a; – – –, 11.

Experimental

All melting points were determined in a capillary tube and are uncorrected. IR spectra were recorded in KBr pellets on a JASCO IRA-2 spectrometer, UV absorption spectra were determined on a Hitachi EP-S2 spectrometer in 95% EtOH, and NMR spectra were obtained using a JNM-PS-100 (100 MHz) spectrometer with tetramethylsilane as an internal standard, unless otherwise indicated.

Synthesis of The Pyridinium N-Allylides (3a—e)——To a solution of 0.01 mol of ketenethioacetal derivative (**2a, b**) and 0.01 mol of pyridinium salt (**1a—d**) in 80 ml of EtOH, 10 ml of Et_3N was added and the mixture was refluxed on a boiling water bath for 4 hr. When Et_3N was added, the mixture turned reddish brown. After evaporation of the solvent, the reddish oil was chromatographed over Al_2O_3 with benzene–EtOH (10: 1) to give the N-allylides in good yields, respectively. These products (**3a—c**) were identified respectively with authentic samples which were prepared by the reaction of N-[2,2-*bis*(methylthio)vinyl]-pyridinium iodides with the corresponding active methylene compounds.[3] **3d**: Orange needles, mp 189°, yield 60%. *Anal.* Calcd. for $C_{19}H_{15}N_3OS$: C, 68.46; H, 4.54; N, 12.61; S, 9.60. Found: C, 68.47; H, 4.48; N, 12.53; S, 9.66. IR ν(KBr) cm^{-1}: 2190 (CN). UV λ_{max}^{EtOH} nm (log ε): 265 (4.10), 325 (3.75), 405 (4.26).

NMR ($CDCl_3$) δ: 2.26 (3H, s, CH_3), 2.58 (3H, s, SCH_3), 7.40—7.80 (5H, m, phenyl), 7.86 (1H, t, J=8 Hz, 5-H), 8.18 (1H, dd, J=1 Hz, 8 Hz, 4-H), 8.36 (1H, s, 2-H), 8.38 (1H, d, J=5 Hz, 6-H). **3e**: Yellow needles, mp 193°, yield 87%. *Anal.* Calcd. for $C_{15}H_{15}N_3O_2S$: C, 59.79; H, 5.02; N, 13.95. Found: C, 59.70; H, 5.02; N, 13.94. IR ν (KBr) cm^{-1}: 2160 (CN), 1675 (C=O). UV λ_{max}^{EtOH} nm (log ε): 270 (3.75), 360 (4.28). NMR ($CDCl_3$) δ: 1.24 (3H, t, O–CH_2–CH_3), 2.44 (3H, s, 3-CH_3), 4.20 (2H, q, O–CH_2–), 7.78 (1H, t, J=7 Hz, 5-H), 8.11 (1H, dd, J=1 Hz, 4-H), 8.34 (1H, s, 2-H), 8.36 (1H, d, J=5 Hz, 6-H).

3-(2,2-Dicyano-1-methylthio)vinyl-1-ethoxycarbonylindolizine (5)——To a solution of 0.544 g of **1f** and 0.34 g of **2a** in 7 ml of EtOH, 0.65 ml of Et_3N was added and then the mixture was refluxed for 6 hr on a boiling water bath. After evaporation of the solvent, the residue was chromatographed over Al_2O_3 with benzene–EtOH (100: 1) to give **5** as pale yellow needles, mp 205—207°, in 32% yield. *Anal.* Calcd. for $C_{16}H_{13}N_3O_2S$: C, 61.73; H, 4.21; N, 13.50; S, 10.30. Found: C, 61.49; H, 4.20; N, 13.45; S, 10.47. IR ν (KBr) cm^{-1}: 2220 (CN), 1708 (C=O). UV λ_{max}^{EtOH} nm (log ε): 260 (4.39), 360 (3.99), 375 (4.11), 394 (3.86). NMR ($CDCl_3$) δ: 1.46 (3H, t, O–CH_2–$\underline{CH_3}$), 2.64 (3H, s, SCH_3), 4.50 (2H, q, O–CH_2–), 7.12 (1H, td, J=7 Hz, 6-H), 7.69 (1H, td, J=7 Hz, 1 Hz, 7-H).

Reaction of Carbamoylmethylpyridinium Chloride (1e) with MCMA——To a solution of 1.58 g of **1e** and 2.20 g of **2e** in 50 ml of dimethylformamide, 2 g of K_2CO_3 was added and the mixture was stirring for 4 hr at room temperature. The reaction mixture was poured into 200 ml of ice-water. The precipitate was collected by filtration and recrystallized from MeOH to give a glutaconimide derivative (**4**), mp 300°, in 80% yield, which was identified with an authentic sample prepared by the reaction of N-[2,2-bis(methylthio)-vinyl]pyridinium iodide with malononitrile in the presence of K_2CO_3.[3]

Reaction of the 3 or 5-Substituted Pyridinium Salts with NBME——To a solution of 0.01 mol of the pyridinium salt (**1c, d, g, h**) and 0.01 mol of NBME in 100 ml of EtOH, 15 ml of Et_3N was added and the mixture was refluxed on a boiling water bath for 10 hr. After evaporation of the solvent, the residue was poured into 200 ml of water. The precipitate was collected by decantation and recrystallized from EtOH or MeOH to give the indolizine derivative (**6a—d**) in good yields. Compound (**6b**) was identified with an authentic sample, prepared by the reaction of N-[1-ethoxycarbonyl-2,2-bis(methylthio)vinyl]pyridinium iodide with nitromethane in the presence of Et_3N.[3] **6a**: mp 150°, yield 52%. *Anal.* Calcd. for $C_{17}H_{15}NOS$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.71; H, 5.30; N, 4.83. UV λ_{max}^{EtOH} nm (log ε): 230 (4.21), 260 (4.27), 282 (4.30), 390 (4.11). **6b**: mp 87°, yield 82%. **6c**: mp 239°, yield 62%. *Anal.* Calcd. for $C_{18}H_{17}NOS$: C, 73.20; H, 5.80; N, 4.75; S, 10.83. Found: C, 73.61, H, 5.75; N, 4.56; S, 10.85. UV λ_{max}^{EtOH} nm (log ε); 260 (4.28), 284 (4.30), 395 (4.09). NMR ($CDCl_3$) δ: 2.42, 2.68, 2.72 (3H, 3H, 3H, s, s, s, 6-CH_3, 8-CH_3 or SCH_3), 6.57 (1H, s, 1-H), 7.30 (1H, s, 7-H), 7.45—8.28 (6H, m, phenyl and 5-H).

Reaction of 1b with 3-(2,2-Dicyano-1-methylthio)vinylindole——To a solution of 1.3 g of 1b and 1.2 g of 3-(2,2-dicyano-1-methylthio)vinylindole in 50 ml of EtOH, 5 ml of Et_3N was added and the mixture was refluxed on a boiling water bath for 2 hr. When the Et_3N was added, the mixture turned reddish brown. After evaporation of the solvent, the reddish oil was chromatographed over Al_2O_3 with benzene–EtOH (10: 1) to give the corresponding N-allylide (**3f**): Orange needles, mp 186°, in 92% yield. *Anal.* Calcd. for $C_{21}H_{16}N_4O_2$: C, 70.77; H, 4.53; N, 15.72. Found: C, 70.14; H, 4.78; N, 15.22. IR ν (KBr) cm^{-1}: 2160, 2170 (CN), 1643 (C=O). UV λ_{max}^{EtOH} nm (log ε): 220 (4.62), 261 (4.14), 360 (4.45), 447 (3.69).

Synthesis of The Indolizines (9a—d) from 2-Picolinium N-Ylides (1i—k) and Ketenethioacetals——To a solution of 0.005 mol of **1i**, **1j**, or **1k** and 0.005 mol of the ketenethioacetal, (2-cyano-3,3-bis(methylthio)-acrylate, methyl 2-cyano-3,3-bis(methylthio)acrylate, ethyl 2-cyano-3,3-bis(methylthio)acrylate), in 10—15 ml of dimethylformamide, 0.01 mol of K_2CO_3 was added and the mixture was heated on a boiling water bath for 3 hr. The reaction mixture was poured into 200 ml of ice-water and acidified with 10% HCl solution. The precipitate was collected by filtration, washed with water and recrystallized from EtOH to give indolizine derivatives (**9a—d**) in good yields. **9a**: Colorless needles, mp 190—191°, yield 80%. *Anal.* Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59. Found: C, 66.57; H, 4.20; N, 16.56. IR ν (KBr) cm^{-1}: 2190 (CN), 1740 (C=O). UV λ_{max}^{EtOH} nm (log ε): 221 (4.51), 252 (4.42), 330 (4.14), 344 (4.20). NMR ($CDCl_3$) δ: 1.50 (3H, t, O–CH_2–$\underline{CH_3}$), 4.52 (2H, q, O–CH_2–), 5.88 (1H, s, $CH(CN)_2$), 6.89 (1H, s, 1-H), 6.96—7.35 (2H, m, 6-H and 7-H), 7.64 (1H, d, J=9 Hz, 8-H), 9.50 (1H, d, J=6 Hz, 5-H). **9b**: Yellow plates, mp 115°, yield 83%. *Anal.* Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 64.08; H, 5.36; N, 9.32. IR ν (KBr) cm^{-1}: 2200 (CN), 1750, 1675 (C=O). UV λ_{max}^{EtOH} nm (log ε): 221 (4.55), 254 (4.48), 330 (4.14), 345 (4.21). NMR ($CDCl_3$) δ: 2.31 and 2.41 2×(3H, t, O–CH_2–CH_3), 4.30 and 4.41 2×(2H, q, O–CH_2–$\underline{CH_3}$), 5.59 (1H, s, $-CH\langle^{CH}_{COOEt}$), 6.70 (1H, s, 1-H), 6.87 (1H, t, J=7 Hz, 6-H), 7.10 (1H, t, J=7 Hz, 7-H), 7.51 (1H, d, J=7 Hz, 8-H), 9.42 (1H, d, J=6 Hz, 5-H). **9c**: Orange needles, mp 142—143°, yield 71%. *Anal.* Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.84; H, 4.77; N, 15.66. IR ν (KBr) cm^{-1}: 2180, 2160 (CN), 1740 (C=O). UV λ_{max}^{EtOH} nm (log ε): 345 (4.35), 483 (4.26). **9d**: Orange needles, mp 159—156°, yield 36%. *Anal.* Calcd. for $C_{13}H_9N_3O_2$: C, 65.26; H, 3.79; N, 17.59. Found: C, 65.43; H, 3.63; N, 17.33. IR ν (KBr) cm^{-1}: 2100 (CN), 1753 (C=O). UV λ_{max}^{EtOH}nm (log ε): 241 (4.39), 249 (4.46), 300 (4.05), 317 (4.08). NMR ($CDCl_3$) δ: 3.86 (3H, s, OCH_3), 5.04 (1H, s, $CH\langle^{CN}_{COOMe}$), 6.70 (1H, s, 1-H), 6.93 (1H, t, J=7 Hz, 6-H), 7.14 (1H, t, J=8 Hz, 7-H), 7.55 (1H, d, J=8 Hz, 8-H), 8.26 (1H, d, J=7 Hz, 5-H).

2-Allylidene-1,2-dihydropyridine Derivatives (8a—c)——To a solution of 0.005 mol of pyridinium salt (**1i, j**) and 0.005 mol of ketenethioacetal (**2a, b**) in 20 ml dimethylformamide, 1.54 g of K_2CO_3 was added and the mixture was stirred at room temperature for 1 hr. The reaction mixture was poured into 200 ml of ice-water. The precipitate was collected by filtration and recrystallized from EtOH to give the 2-allylidene-1,2-dihydropyridine derivative (**8a—c**) in good yields. The filtrate was acidified with 10% solution, washed with water, and recrystallized from EtOH to give the indolizine derivative (**9a—c**) in about 10—20% yield. **8a**: Orange needles, mp 150—151°, yield 70%. *Anal.* Calcd. for $C_{15}H_{15}N_3O_2S$: C, 59.79; H, 5.02; N, 14.00; S, 10.62. Found: C, 59.62; H, 4.94, N, 13.83; S, 10.65. IR ν (KBr) cm^{-1}: 2190 (CN), 1740 (C=O). UV λ_{max}^{EtOH} nm (log ε): 334 (3.95), 485 (4.59). NMR ($CDCl_3$) δ: 1.30 (3H, t, O–CH_2–$\underline{CH_3}$), 2.37 (3H, s, SCH_3), 4.28 (2H, q, O–CH_2–), 4.59 (2H, s, NCH_2–), 4.85 (1H, s, C=C–H), 6.59 (1H, t, J=7 Hz, 4-H), 7.32 (1H, t, J=7 Hz, 5-H), 7.50 (1H, d, J=7 Hz, 3-H), 7.62 (1H, d, J=8 Hz, 6-H). **8b**: Orange needles, mp 150°, yield 69%. *Anal.* Calcd. for $C_{17}H_{20}N_2O_4S$: C, 58.61; H, 5.79; N, 8.04; S, 9.39. Found: C, 58.51; H, 5.81; N, 7.82; S, 9.04. IR ν (KBr) cm^{-1}: 2160 (CN), 1740, 1650 (C=O). UV λ_{max}^{EtOH} nm (log ε): 254 (4.04), 344 (3.96), 490 (4.45). NMR ($CDCl_3$) δ: 2.36 (3H, s, SCH_3), 4.60 (2H, s, N–CH_2–), 5.26 (1H, s, C=C–H), 6.44 (1H, t, J=7 Hz, 4-H), 7.20—7.40 (2H, m, 3 and 5-H), 7.66 (1H, d, J=9 Hz, 6-H). **8c**: Orang needles, mp 143—144°. Yield 32%. *Anal.* Calcd. for $C_{16}H_{17}N_3O_2S$: C, 60.94; H, 5.43; N, 13.33. Found: C, 60.91; H, 5.39; N, 13.35. IR ν (KBr) cm^{-1}: 2160 (CN), 1742 (C=O). UV λ_{max}^{EtOH} nm (log ε): 255 (3.66), 336 (3.94), 487 (4.35).

4-Allylidene-1,4-dihydropyridine Derivatives (10a, b)——To a solution of 0.005 mol of the 4-methylpyridinium salt (**1l, m**) 0.005 mol of **2a** in 20 ml of dimethylformamide, 0.2 mol of K_2CO_3 was added and the mixture was stirred at room temperature for 2 hr. The reaction mixture was poured into 200 ml ice-water. The precipitate was collected by filtration, washed with water, and recrystallized from EtOH to give the 4-allylidene-1,4-dihydropyridine (**10a, b**). **10a**: Orange needles, mp 83°, yield 78%. *Anal.* Calcd. for $C_{15}H_{15}N_3O_2S$: C, 59.79; H, 5.02; N, 13.95. Found: 59.62; H, 4.83; N, 13.82. IR ν (KBr) cm^{-1}: 2170 (CN). 1740 (C=O). UV λ_{max}^{EtOH} nm (log ε): 250 (3.59), 343 (3.65), 492 (4.55). NMR ($(CD_3)_2C$=O) δ: 1.26 (3H, t, O–CH_2–CH_3), 2.46 (3H, s, SCH_3), 4.16 (2H, q, O–CH_2–), 5.12 (2H, s, N–CH_2–), 5.71 (1H, s, C=C–H), 7.26 (2H, d, J=8 Hz, 3 and 5-H), 7.86 (2H, d, J=8 Hz, 2 and 6-H). **10b**: Red prisms, mp 182°, yield 78%. *Anal.* Calcd. for $C_{19}H_{15}N_3OS$: C, 68.46; H, 4.54; N, 12.61; S, 9.60. Found: C, 68.34; H, 4.42; N, 12.55; S, 9.60. IR ν (KBr) cm^{-1}: 2160 (CN), 1705 (C=O). UV λ_{max}^{EtOH} nm (log ε): 249 (3.65), 344 (3.62), 495 (4.58).