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Studies on Diazepines. XIV.[1] Photolysis of Thieno-, Furo-, and Pyrrolo-[*c*]pyridine N-Imides: Formation of Novel Fused 1H-1,3- and 3H-2,3-Diazepines

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Irradiation of the methylpyridine N-imides (**3b**—**g**) condensed with a thiophene, furan, or pyrrole ring on the *c*-side of the pyridine ring gave the corresponding novel fused 1H-1,3- (**5**) and/or 3H-2,3-diazepines (**6**), together with the aminopyridines (**7**) and the parent fused pyridines (**1**), whereas the fused pyridine N-imide (**3a**) having no methyl group gave only the aminopyridine derivative (**4**).

This photolysis may proceed by rearrangement to two kinds of diaziridine intermediates, (**8**) and (**9**); the latter may give the 2,3-diazepines (**6**) directly by ring-expansion, whereas the former may further rearrange to the aziridine intermediate (**10**), followed by ring-expansion to give the 1,3-diazepines (**5**).

Some reactions of the diazepines (**5** and **6**) thus obtained were also examined.

Keywords——photolysis; rearrangement; ring-expansion; N-imides; thieno[*c*]-pyridines; furo[*c*]pyridines; pyrrolo[*c*]pyridines; 1H-1,3-diazepines; 3H-2,3-diazepines

We have previously reported the first synthesis of fully unsaturated 1,2-benzodiazepines[2] and the analogous 1,2-diazepines[3] condensed with aromatic heterocyclic rings such as pyridine, thiophene, furan, and pyrrole from the corresponding quinoline and quinoline-type fused pyridine N-imides by irradiation. In contrast, irradiation of isoquinoline N-imides had been shown to cause N–N fragmentation to the parent isoquinolines, as well as rearrangement to 1-aminoisoquinoline derivatives.[4,5] However, we have very recently reported that 1-substituted isoquinoline N-acylimides undergo a photo-induced two-step rearrangement to form novel 1,3-benzodiazepines.[6]

In connection with the above results, we were interested in examining the photochemical behavior of isoquinoline-type fused pyridine N-imides condensed with aromatic five-membered heterocyclic rings on the *c*-side of the pyridine ring. We now report that the photolysis of these fused pyridine N-imides affords the corresponding novel fused 1H-1,3- and 3H-2,3-diazepines.[7]

The pyridines (**1a**—**g**)[8] condensed with aromatic five-membered heterocyclic rings were aminated with O-mesitylenesulfonylhydroxylamine (H_2NOMes) according to the method of

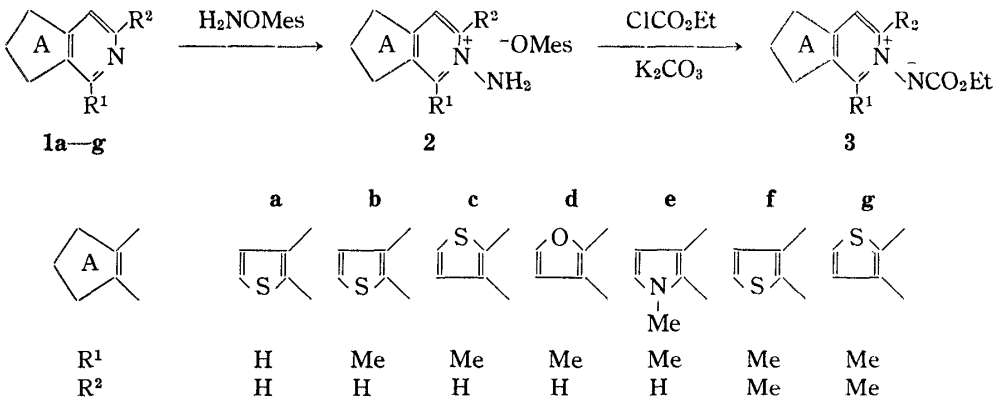


Chart 1

Tamura *et al.*[9] to give the corresponding N-aminopyridinium mesitylenesulfonates (**2a—g**) in 75—95% yields. Treatment of the salts (**2**) with ethyl chloroformate in ethanol in the presence of potassium carbonate gave the N-ethoxycarbonylimides (**3**) in good yields.

Irradiation of the 7-unsubstituted thieno[2,3-*c*]pyridine N-imide (**3a**) gave the 7-ethoxycarbonylaminothienopyridine (**4**) and the parent thienopyridine (**1a**) in 46% and 5% yields, but gave no ring-expansion products; these results are analogous to those observed for 1-unsubstituted isoquinoline N-imides.[4,5] In contrast, irradiation of the 7-methylthieno[2,3-*c*]-pyridine N-imide (**3b**) resulted in the formation of the 1H-1,3-thienodiazepine (**5b**) and the 3H-2,3-thienodiazepine (**6b**) in 10% and 35% yields, together with the 5-aminothienopyridine (**7b**) and the parent thienopyridine (**1b**) in 5—6% and 3—4% yields. Similarly, irradiation of 4-methylthieno[3,2-*c*]- (**3c**) and 1,7-dimethylpyrrolo[2,3-*c*]pyridine N-imide (**3e**) gave the four kinds of products in the yields shown in Chart 1. However, the 4-methylfuro[3,2-*c*]-pyridine N-imide (**3d**) gave only the 2,3-diazepine (**6d**) and no 1,3-diazepine.

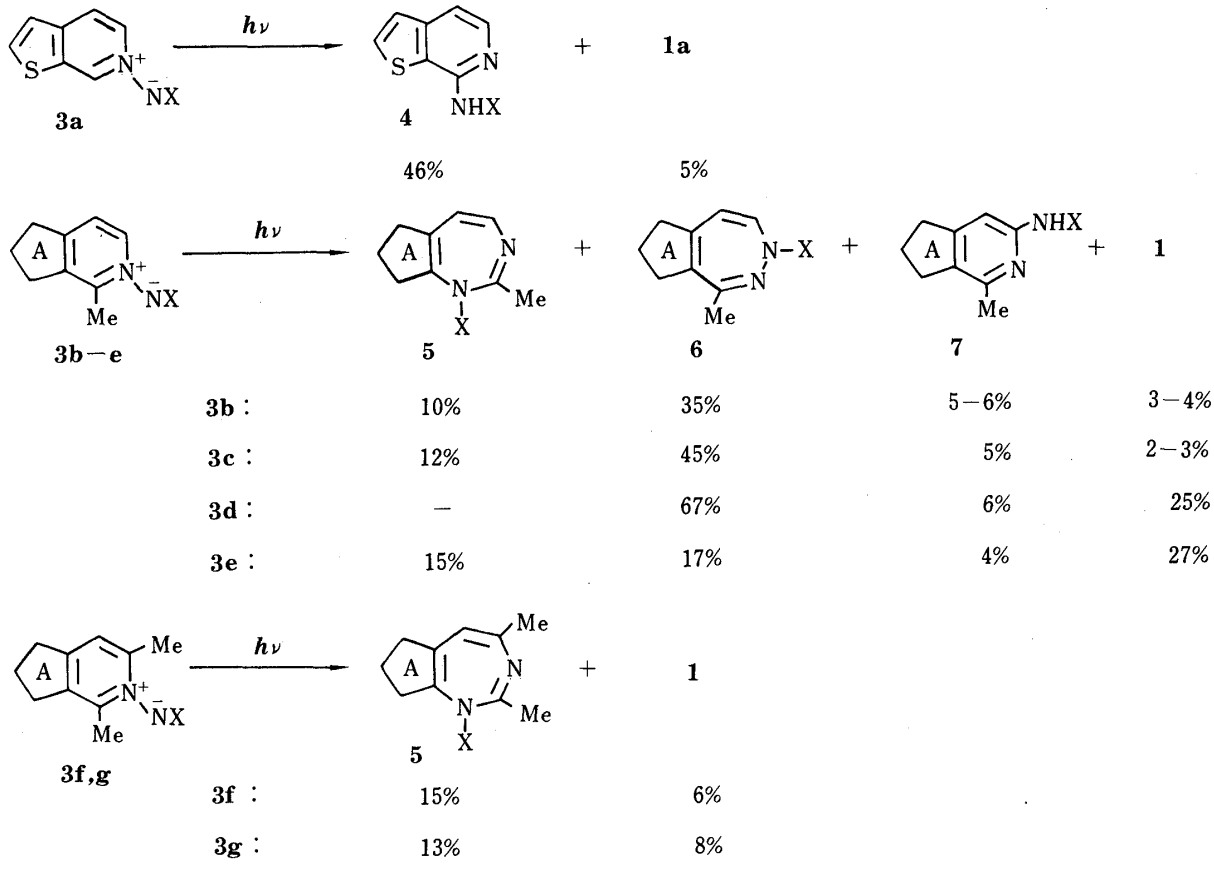


Chart 2

Next, the thienopyridines, (**3f**) and (**3g**), having another methyl group in the opposite α-position of the pyridine ring, upon irradiation, gave only the corresponding 1,3-diazepines (**5**) in *ca.* 15% yields and no 2,3-diazepine (**6**). The 2,3-diazepines (**6**) are stable, but the 1,3-diazepines (**5**) were found to be relatively unstable, tending to decompose during the course of the isolation procedure. This instability of the diazepines (**5**) may account for the low yields.

The present photolysis may proceed by photo-induced rearrangement to two kinds of diaziridine intermediates, (**8**) and (**9**), as shown in Chart 3. The latter intermediate (**9**) may undergo either ring-expansion to give the 2,3-diazepines (**6**) or N–N bond fission to give the aminopyridine derivatives (**7**), analogously with the results of photolysis of pyridine[10] and

quinoline N-imides[2,3] in which the corresponding 1,2-diazepines and/or 2-amino derivatives are formed. However, the intermediate (**8**) may further rearrange to the aziridine (**10**) by a [1, 5]-sigmatropic shift, followed by ring-expansion to give the 1,3-diazepines (**5**). In the case of **3a** (R^1=H), elimination of the hydrogen atom occurs after cleavage of the N–N bond of the diaziridine intermediate (**8**) to give the amino derivative (**4**) in preference to the second rearrangement into the aziridine (**10**). On the other hand, in the case of the other N-imides (**3b**—**g**: R≠H), such elimination cannot occur because of the presence of the substituent and the further rearrangement predominates to give the 1,3-diazepines by analogy with the case of 1-substituted isoquinoline N-imides.[6]

It should be noted that the initial rearrangement takes place to either side of the pyridine ring, in contrast with the reactions of quinolines[2,3] and isoquinolines.[4–6] However, in the cases of **3f** and **3g** having methyl groups on both sides of the imide function, the corresponding

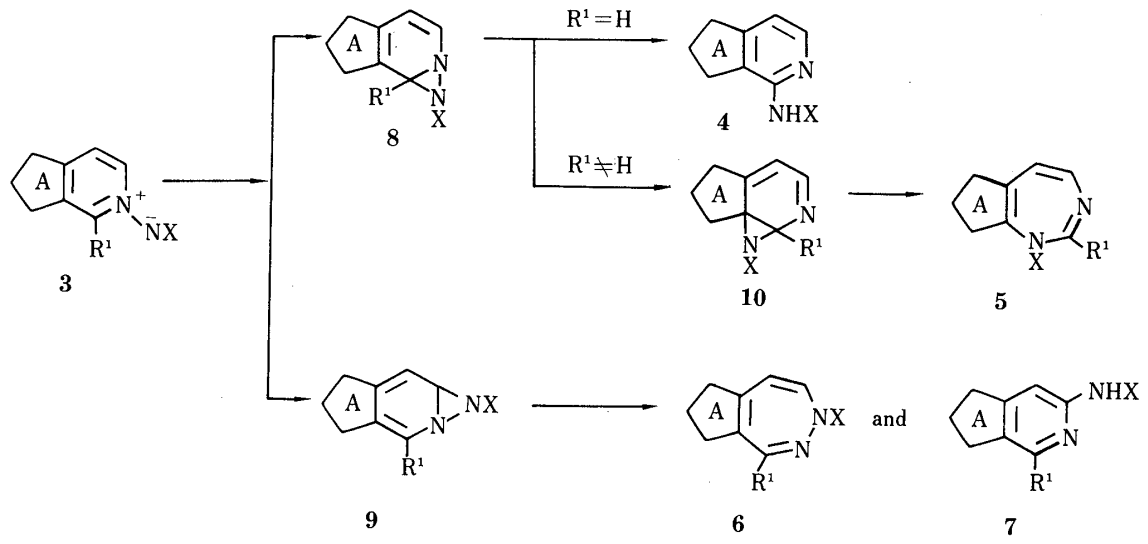


Chart 3

Table I. 1H-1,3-Diazepines (**5**) and 3H-2,3-Diazepines (**6**)

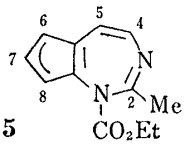
Compd. No.	mp[a] (°C)	MS *m/e* (M+)	IR $\nu_{max}^{CHCl_3}$ cm^{-1} (C=O)	IR (C=N)	UV λ_{max}^{EtOH} nm (ε)	Formula	Analysis (%) Found (Calcd) C	H	N
5b	Oil[b]	236	1720	1640	248(5600)	$C_{11}H_{12}N_2O_2S$	60.12 (55.93	5.11 5.12	11.91 11.86)
5c	52—53	236	1710	1640	265(7400)	$C_{11}H_{12}N_2O_2S$	55.95 (55.93	5.14 5.12	11.89 11.86)
5e	Oil	233	1720	1638	230(6500)	$C_{12}H_{15}N_3O_2$	61.93 (61.78	6.45 6.48	17.78 18.02)
5f	65—66	250	1720	1645	250(6400)	$C_{12}H_{14}N_2O_2S$	57.72 (57.59	5.60 5.64	11.02 11.20)
5g	Oil	250	1715	1640	263(7700)	$C_{12}H_{14}N_2O_2S$	57.63 (57.59	5.54 5.64	11.07 11.20)
6b	88—89	236	1700	1635	252(16300)	$C_{11}H_{12}N_2O_2S$	55.99 (55.93	5.21 5.12	11.83 11.86)
6c	119—120	236	1690	1620	250(17250)	$C_{11}H_{12}N_2O_2S$	55.82 (55.93	5.12 5.12	11.61 11.86)
6d	76—77	220	1690	1620	260(10600)	$C_{11}H_{12}N_2O_3$	59.87 (60.00	5.52 5.45	12.67 12.73)
6e	113—114	233	1680	1630	260(10600)	$C_{12}H_{15}N_3O_2$	61.70 (61.78	6.43 6.48	17.81 18.02)

a) Recrystallized from *n*-hexane-isopropyl ether.
b) Viscous oil.

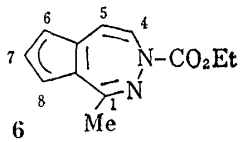
2,3-diazepines (**6**) could not be isolated. At present, the effect of the second methyl group on the photolysis is not clear. Monocyclic 1,3-diazepines,[11,12] 1,3-benzodiazepines,[6] and 2,3-benzodiazepines[13] have already been reported, whereas the products (**5**) and (**6**) are the first examples of 1,3- and 2,3-diazepines condensed with heterocyclic rings.[14]

The physical, analytical, and some spectral data for these novel 1,3- (**5**) and 2,3-diazepines (**6**) are collected in Table 1. The nuclear magnetic resonance (NMR) spectral data are also summarized in Table II.

Table II. NMR Spectral Data for the 1H-1,3- (**5**) and 3H-2,3-diazepines (**6**)



5



6

	δ ($CDCl_3$)
5b	2.26 (3H, s, 2-Me), 6.22 (1H, d, 5-H), 6.68 (1H, d, 6-H), 6.78 (1H, d, 4-H), 7.58 (1H, d, 7-H), $J_{4,5}=8$, $J_{6,7}=5$ Hz, 1.22 and 4.14 (3H, t, and 2H, q, CO_2Et)
5c	2.33 (3H, s, 2-Me), 6.32 (1H, d, 5-H), 6.78 (1H, d, 8-H), 6.86 (1H, d, 4-H), 7.34 (1H, d, 7-H), $J_{4,5}=8$, $J_{7,8}=5$ Hz, 1.26 and 4.18 (3H, t, and 2H, q, CO_2Et)
5e	2.38 (3H, s, 2-Me), 3.54 (3H, s, N-Me), 6.04 (1H, d, 6-H), 6.26 (1H, d, 5-H), 6.64 (1H, d, 7-H), 6.70 (1H, d, 4-H), $J_{4,5}=8$, $J_{6,7}=2.5$ Hz, 1.30 and 4.21 (3H, t, and 2H, q, CO_2Et)
5f	2.10 (3H, s, 4-Me), 2.32 (3H, s, 2-Me), 6.16 (1H, s, 5-H), 6.74 (1H, d, 6-H), 7.12 (1H, d, 7-H), $J_{6,7}=5$ Hz, 1.30 and 4.24 (3H, t, and 2H, q, CO_2Et)
5g	2.10 (3H, s, 4-Me), 2.34 (3H, s, 2-Me), 6.19 (1H, s, 5-H), 6.81 (1H, d, 8-H), 7.28 (1H, d, 7-H), $J_{7,8}=8$ Hz, 1.28 and 4.22 (3H, t, and 2H, q, CO_2Et)
6b	2.37 (3H, s, 1-Me), 6.20 (1H, d, 5-H), 6.34 (1H, d, 4-H), 6.90 (1H, d, 6-H), 7.40 (1H, d, 7-H), $J_{4,5}=7$, $J_{6,7}=5$ Hz, 1.31 and 4.27 (3H, t, and 2H, q, CO_2Et)
6c	2.33 (3H, s, 1-Me), 6.25 (1H, d, 5-H), 6.39 (1H, d, 4-H), 7.04 (1H, d, 8-H), 7.18 (1H, d, 7-H), $J_{4,5}=7$, $J_{7,8}=5$ Hz, 1.30 and 4.24 (3H, t, and 2H, q, CO_2Et)
6d	2.32 (3H, s, 1-Me), 6.22 (1H, d, 5-H), 6.36 (1H, d, 4-H), 6.50 (1H, d, 8-H), 7.30 (1H, d, 7-H), $J_{4,5}=7$, $J_{7,8}=2$ Hz, 1.32 and 4.30 (3H, t, and 2H, q, CO_2Et)
6e	2.18 (3H, s, 1-Me), 3.70 (3H, s, N-Me), 6.16 (2H, s, 4- and 5-H), 6.00 (1H, d, 6-H), 6.58 (1H, d, 7-H), $J_{6,7}=3$ Hz, 1.24 and 4.20 (3H, t, and 2H, q, CO_2Et)

These data and the results of the following chemical studies are consistent with the proposed structures, eliminating other possible structures such as 2H-2,3- and 4H-2,4-diazepines.

Treatment of the 1,3-diazepine (**5b**) with ethanol containing acetic acid resulted in the formation of the ring-opened product (**12**) presumably *via* the solvent adduct (**11**). Treatment of **12** with hydrogen chloride gave the thieno [2,3-*b*]pyrrole (**13**), which was also directly obtained from the 1,3-diazepine (**5b**) by treatment with hydrogen chloride in ethanol. Similarly, the 1,3-diazepine (**5g**), upon treatment with hydrogen chloride, gave the thienopyrrole (**15**). These results are analogous to those for 1H-1,3-benzodiazepines[6] and 1,3-benzoxazepines.[15]

Next, further irradiation of the 1,3-diazepine (**5b**) resulted in decomposition to give no characterizable products; however, the diazepine (**5g**), upon irradiation, gave the thienopyrrole (**15**) presumably *via* initial cyclization to the tricyclic valence isomer (**14**) followed by extrusion of acetonitrile, by analogy with the reactions of 1H-1,3-benzodiazepines[6] and triazepines.[16] In contrast, the 2,3-diazepines (**6**) are less susceptible to either acids or light. For example, both refluxing of a solution of **6b** in ethanol containing hydrogen chloride for 6 hr and irradiation of a solution of **6b** in methylene chloride for 5 hr resulted in the recovery of the starting diazepine unchanged. Finally, the 1,3-diazepine (**5b**) is less reactive to sodium borohydride reduction in ethanol, whereas the reduction of **5b** in ethanol containing aqueous sodium hydroxide gave the 4,5-dihydro compound (**18**) in 53% yield. On treatment with acetic anhydride,

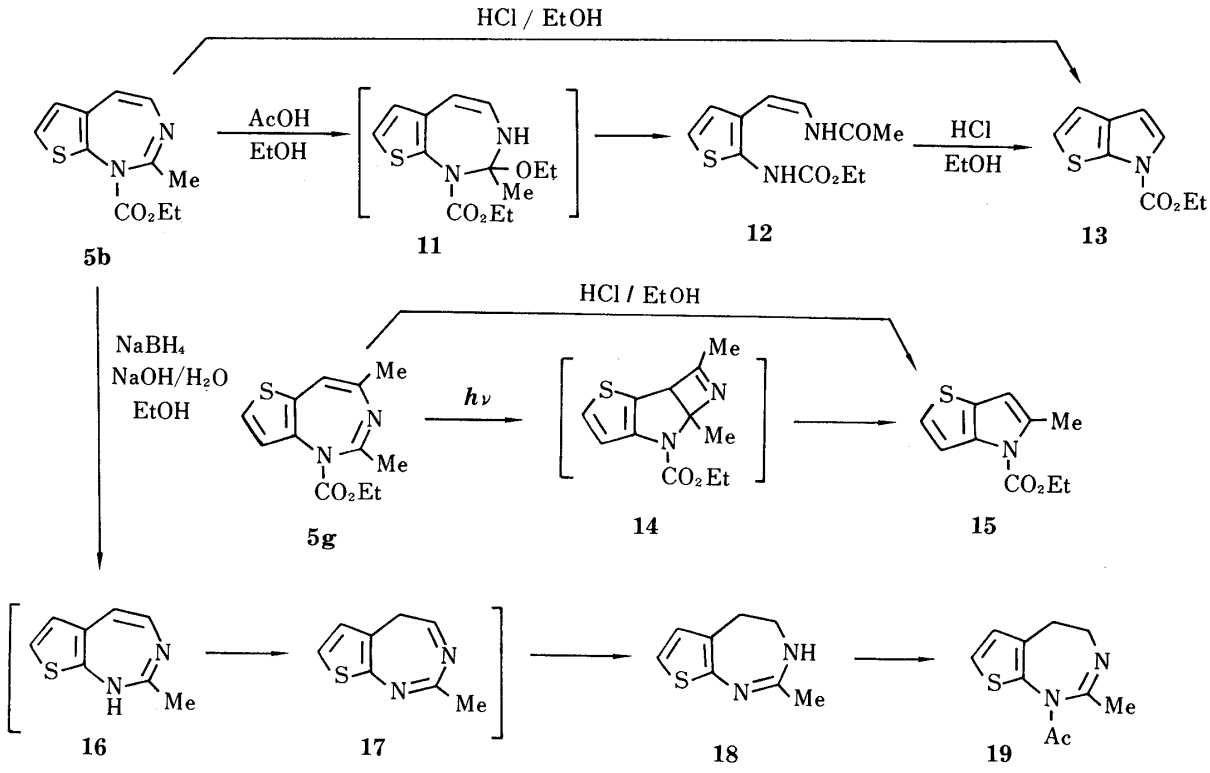


Chart 4

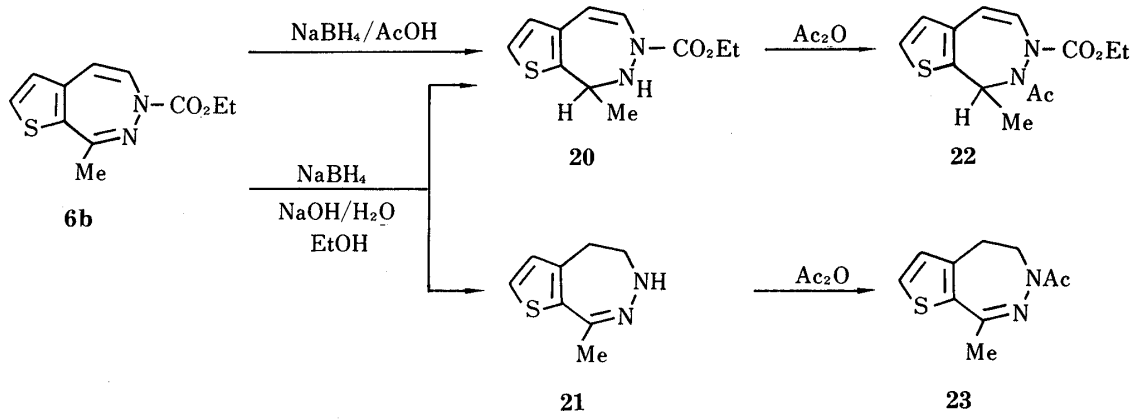


Chart 5

18 readily gave the 1-acetyl compound (**19**). The formation of **18** from **5b** may involve initial deethoxycarbonylation to the 1H-1,3-diazepine (**16**), which then tautomerizes to the 5H-isomer (**17**) followed by reduction, although all attempts to isolate the presumed intermediates (**16**) or (**17**) by treatment with alkali alone failed. In contrast, the reduction of the 2,3-diazepine (**6b**) with sodium borohydride in the presence of aqueous alkali gave the 1,2-dihydro (**20**) and 4,5-dihydro (**21**) compounds in 27% and 34% yields, respectively, whereas treatment of **6b** with sodium borohydride in acetic acid gave the 1,2-dihydro compound (**20**) in high yield as the sole product. Acetylation of the dihydro compounds (**20**) and (**21**) with acetic anhydride gave the corresponding acetates (**22**) and (**23**) in 90—95% yields.

Experimental

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. Infrared (IR) spectra were determined with a JASCO IRA-2 spectrometer and mass (MS) spectra were recorded on a JEOL D-100

instrument. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-MH100 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated; spectral assignments were confirmed by spin-decoupling experiments and, in the case of NH protons, by exchange with D_2O. Microanalyses were performed in the Microanalytical Laboratory of this school by Mrs R. Igarashi. Photolyses were carried out under a nitrogen atmosphere in an immersion apparatus equipped with a 400 W high-pressure Hg lamp and a Pyrex filter, which was cooled internally with running water.

Materials——All starting condensed pyridines (**1a—g**) were prepared by the reported procedure.[8]

N-Aminopyridinium Mesitylenesulfonates (2a—g)——General Procedure: A solution of O-mesitylenesulfonylhydroxylamine (1.1 mol eq) in CH_2Cl_2 (100—150 ml) was added dropwise to a solution of the condensed pyridine (**1**: 0.03—0.1 mol) in CH_2Cl_2 (*ca.* 50 ml) with constant stirring in an ice bath. The reaction mixture was stirred for an additional 1 hr. After addition of ether (300—500 ml) to the mixture, the resulting crystalline precipitates were collected by filtration and recrystallized from methanol or methanol–ethyl acetate to give the salts (**2**).

2a: 88% yield, mp 155—157°. NMR (CD_3OD) δ: 7.56 (1H, d, 3-H), 8.04 (1H, d, 2-H), 8.24—8.36 (2H, m, 4- and 5-H), 9.28 (1H, s, 7-H), $J_{2,3}=5$ Hz, $^-$OMes [2.08 (3H, s), 2.48 (6H, s), 6.61 (2H, s)]. *Anal.* Calcd for $C_{16}H_{18}N_2O_3S_2$: C, 54.85; H, 5.14; N, 8.00. Found: C, 55.02; H, 5.18; N, 7.93.

2b: 93% yield, mp 213.5—215°. NMR (CD_3OD) δ: 3.06 (3H, s, 7-Me), 7.70 (1H, d, 3-H), 8.13 (1H, d, 4-H), 8.52 (1H, d, 2-H), 8.56 (1H, d, 5-H), $J_{2,3}=5$, $J_{4,5}=7$ Hz, $^-$OMes [2.19 (3H, s), 2.56 (6H, s), 6.80 (2H, s)]. *Anal.* Calcd for $C_{17}H_{20}N_2O_3S_2$: C, 56.02; H, 5.53; N, 7.69. Found: C, 56.11; H, 5.50; N, 7.61.

2c: 82% yield, mp 214—215°. NMR (CD_3OD) δ: 3.02 (3H, s, 4-Me), 7.66 (1H, d, 3-H), 7.92 (1H, d, 2-H), 8.06 (1H, d, 7-H), 8.24 (1H, d, 6-H), $J_{2,3}=5$, $J_{6,7}=7$ Hz, $^-$OMes [2.16 (3H, s), 2.52 (6H, s), 6.56 (2H, s)]. *Anal.* Calcd for $C_{17}H_{20}N_2O_3S_2$: C, 56.02; H, 5.53; N, 7.69. Found: C, 56.26; H, 5.65; N, 7.73.

2d: 79% yield, mp 229—231°. NMR (CD_3OD) δ: 2.98 (3H, s, 4-Me), 7.32 (1H, d, 3-H), 7.86 (1H, d, 7-H), 8.12 (1H, d, 2-H), 8.56 (1H, d, 6-H), $J_{2,3}=2.5$, $J_{6,7}=7$ Hz, $^-$OMes [2.20 (3H, s), 2.56 (6H, s), 6.74 (2H, s)]. *Anal.* Calcd for $C_{17}H_{20}N_2O_4S$: C, 58.62; H, 5.75; N, 8.05. Found: C, 58.91; H, 5.90; N, 8.36.

2e: 93% yield, mp 194—195°. NMR (CD_3OD) δ: 3.20 (3H, s, 7-Me), 4.24 (3H, s, 1-Me), 6.78 (1H, d, 3-H), 7.76 (1H, d, 4-H), 7.88 (1H, d, 2-H), 9.18 (1H, d, 5-H), $J_{2,3}=2.5$, $J_{4,5}=7$ Hz, $^-$OMes [2.20 (3H, s), 2.56 (6H, s), 6.80 (2H, s)]. *Anal.* Calcd for $C_{18}H_{23}N_3O_3S$: C, 59.83; H, 6.37; N, 11.63. Found: C, 59.51; H, 6.23; N, 11.35.

2f: 76% yield, mp 198—200°. NMR (CD_3OD) δ: 2.82 (3H, s, 5-Me), 3.06 (3H, s, 7-Me), 7.62 (1H, d, 3-H), 8.02 (1H s 4-H) 8.42 (1H, d, 2-H), $J_{2,3}=5$ Hz, $^-$OMes [2.20 (3H, s) 2.52 (6H, s), 6.74 (2H, s)]. *Anal.* Calcd for $C_{18}H_{22}N_2O_3S_2$: C, 57.14; H, 5.82; N, 7.41. Found: C, 56.86; H, 5.76; N, 7.36.

2g: 78% yield, mp 214—215°. NMR (CD_3OD) δ: 2.80 (3H, s, 6-Me), 3.08 (3H, s, 4-Me), 7.74 (1H, d, 3-H), 7.98 (1H, d, 2-H), 8.16 (1H, s, 7-H), $J_{2,3}=5$ Hz, $^-$OMes [2.16 (3H, s), 2.50 (6H, s), 6.70 (2H, s)]. *Anal.* Calcd for $C_{18}H_{22}N_2O_3S_2$: C, 57.14; H 5.82; N, 7.41. Found: C, 57.08; H, 6.02; N, 7.32.

Pyridine N-Ethoxycarbonylimides (3a—g)——General Procedure: Solid potassium carbonate (2.3 mol eq) and ethyl chloroformate (*ca.* 1.5—2.0 mol eq) were added to a solution of the salt (**2**: 0.01—0.02 mol) in ethanol (100—200 ml) with stirring. The mixture was stirred for an additional 8—12 hr at room temperature and the resulting inorganic precipitate was filtered off. The filtrate was evaporated to dryness *in vacuo* and the residue was extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and evaporated to dryness *in vacuo*. The resulting residue was chromatographed on silica gel using CH_2Cl_2–acetone as an eluent to give the imides (**3**) which were recrystallized from benzene or benzene–*n*-hexane.

3a: 82% yield mp 138—140°. IR ν_{max}^{KBr} cm^{-1}: 1610 (C=O). MS *m/e*: 222 (M^+). NMR δ: 7.44 (1H, d, 3-H), 7.85 (1H, d, 4-H), 8.00 (1H, d, 2-H), 8.26 (1H, d, 5-H), 9.32 (1H, s, 7-H) $J_{2,3}=5$, $J_{4,5}=6$ Hz, 1.30 and 4.18 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.05; H, 4.50; N, 12.61. Found: C, 54.04; H, 4.58; N, 12.50.

3b: 89% yield mp 88—89°. IR ν_{max}^{KBr} cm^{-1}: 1610 (C=O). MS *m/e*: 236 (M^+). NMR δ: 2.90 (3H, s 7-Me), 7.46 (1H, d, 3-H), 7.75 (1H, d, 4-H), 7.98 (1H, d, 2-H) 8.38 (1H, d, 5-H), $J_{2,3}=5$, $J_{4,5}=6$ Hz, 1.28 and 4.14 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.93; H 5.12; N, 11.86. Found: C 56.11; H, 5.19; N, 11.73.

3c: 94% yield, mp 116—117°. IR ν_{max}^{KBr} cm^{-1}: 1610 (C=O). MS *m/e*: 236 (M^+). NMR δ: 2.94 (3H, s, 4-Me), 7.50 (1H, d, 3-H), 7.74 (1H, d, 2-H), 7.88 (1H, d 7-H), 8.28 (1H, d, 6-H), $J_{2,3}=5$, $J_{6,7}=7$ Hz, 1.34 and 4.18 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.93; H, 5.12; N, 11.86. Found: C, 56.08; H, 5.20; N, 11.68.

3d: 91% yield, mp 147—148°. IR ν_{max}^{KBr} cm^{-1}: 1620 (C=O). MS *m/e*: 220 (M^+). NMR δ: 2.86 (3H, s, 4-Me), 6.94 (1H, d, 3-H), 7.52 (1H, d, 7-H), 7.80 (1H, d, 2-H), 8.36 (1H, d, 6-H), $J_{2,3}=2.5$, $J_{6,7}=7$ Hz, 1.34 and 4.16 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{12}N_2O_3$: C, 60.00; H, 5.45; N, 12.73. Found: C, 60.02; H, 5.60; N, 13.01.

3e: 65% yield, mp<30°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620 (C=O). MS *m/e*: 233 (M^+). NMR δ: 3.04 (3H, s, 7-Me), 4.10 (3H, s, 1-Me), 6.56 (1H, d, 3-H), 7.40 (1H, d, 2-H), 7.48 (1H, d, 4-H), 8.00 (1H, d, 5-H), $J_{2,3}=2.5$, $J_{4,5}=7$ Hz, 1.32 and 4.16 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{15}N_3O_2$: C, 61.78; H, 6.48; N, 18.02. Found: C, 61.97; H, 6.32; N, 17.79.

3f: 92% yield, mp<30°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620 (C=O). MS *m/e*: 250 (M$^+$). NMR δ: 2.70 (3H, s, 5-Me), 2.92 (3H, s, 7-Me), 7.36 (1H, d, 3-H), 7.70 (1H, s, 4-H), 7.92 (1H, d, 2-H), $J_{2,3}$=5 Hz, 1.36 and 4.18 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.73; H, 5.61; N, 11.08.

3g: 71% yield, mp<30°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620 (C=O). MS *m/e*: 250 (M$^+$). NMR δ: 2.72 (3H, s, 6-Me), 2.96 (3H, s, 4-Me), 7.50 (1H, d, 3-H), 7.64 (1H, d, 2-H), 7.85 (1H, s, 7-H), $J_{2,3}$=5 Hz, 1.26 and 4.20 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.81; H, 5.46; N, 10.96.

Photolysis of the Imides (3a—g)——General Procedure: A solution of the imide (**3**: 1—2 g) in CH_2Cl_2 or benzene (200—300 ml) was irradiated under a nitrogen atmosphere. The photolysis was followed in terms of the disappearance of the spot of the starting material on thin-layer chromatography, and was complete in 1—3 hr. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using CH_2Cl_2 as an eluent to give the 1,3-diazepines (**5**), the ethoxycarbonylaminopyridines (**4** or **7**), the 2,3-diazepines (**6**), and the parent pyridines (**1**) successively. The yields of these products are shown in Chart 2. Physical, analytical, and spectral (MS, IR, and UV) data for the novel diazepines (**5** and **6**) are collected in Table I. The NMR spectral data are summarized in Table II. Data for the ethoxycarbonylaminopyridines (**4** and **7b—e**) are as follows.

4: mp 156—157° (from *n*-hexane–benzene). MS *m/e*: 222 (M$^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (C=O). NMR δ: 7.32 (1H, d, 3-H), 7.50 (1H, d, 4-H), 7.76 (1H, d, 2-H), 8.26 (1H, d, 5-H), $J_{2,3}$=5, $J_{4,5}$=6 Hz, 1.32 and 4.32 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.05; H, 4.50; N, 12.61. Found: C, 53.98; H, 4.48; N, 12.61.

7b: mp 87—88° (from *n*-hexane). MS *m/e*: 236 (M$^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (C=O). NMR δ: 2.62 (3H, s, 7-Me), 7.24 (1H, d, 3-H), 7.56 (1H, d, 2-H), 8.14 (1H, s, 4-H), 8.10 (1H, br, NH), $J_{2,3}$=5 Hz, 1.23 and 4.23 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.93; H, 5.12; N, 11.86. Found: C, 56.14; H, 5.10; N, 12.01.

7c: mp 109—110° (*n*-hexane–CH_2Cl_2). MS *m/e*: 236 (M$^+$). IR ν_{max}^{KBr} cm^{-1}: 1723 (C=O). NMR δ: 2.72 (3H, s, 4-Me), 7.24 (2H, br, 2- and 3-H), 8.16 (1H, br, NH), 8.25 (1H, s, 7-H), 1.30 and 4.22 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.93; H, 5.12; N, 11.86. Found: C, 56.07; H, 5.08; N, 11.66.

7d: mp 136—137° (from *n*-hexane–benzene). MS *m/e*: 220 (M$^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (C=O). NMR δ: 2.60 (3H, s, 4-Me), 6.66 (1H, d, 3-H), 7.46 (1H, d, 2-H), 7.80 (1H, br, NH), 7.88 (1H, br, 7-H), $J_{2,3}$=2 Hz, 1.28 and 4.20 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 60.00; H, 5.46; N, 12.69.

7e: mp 127—128° (from *n*-hexane–benzene). MS *m/e*: 233 (M$^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (C=O). NMR δ: 2.80 (3H, s, 7-Me), 3.98 (3H, s, N–Me), 6.31 (1H, d, 3-H), 7.00 (1H, d, 2-H), 7.44 (1H, br, NH), 7.84 (1H, s, 4-H), $J_{2,3}$=3 Hz, 1.30 and 4.22 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{15}N_3O_2$: C, 61.78; H, 6.48; N, 18.02. Found: C, 61.59; H, 6.28; N, 17.81.

Treatment of the Diazepine (5b) with Ethanol Containing Acetic Acid——A mixture of the diazepine (**5b**: 80 mg), ethanol (10 ml), and acetic acid (3 ml) was refluxed for 5.5 hr then evaporated to dryness *in vacuo*. The residue was chromatographed on alumina using CH_2Cl_2 as an eluent to give the ring-opened product (**12**): *ca.* 50 mg, 58% yield, mp 154—155° (from benzene). MS *m/e*: 254 (M$^+$). IR ν_{max}^{KBr} cm^{-1}: 3254 and 3300 (NH), 1710 and 1670 (C=O). UV λ_{max}^{EtOH} nm (ε): 248 (23200), 284 (23400). NMR δ: 2.00 (3H, s, Ac–Me), 1.28 and 4.20 (3H, t, and 2H, q, CO_2Et), 5.24 (1H, d, J=9 Hz, –CH=CH–NH–), 6.98 (1H, d, J=9 Hz, –CH=CH–NH–), 6.70 and 6.90 (each 1H, d, J=5 Hz, thiophene-H). *Anal.* Calcd for $C_{11}H_{14}N_2O_3S$: C, 51.97; H, 5.51; N, 11.02. Found: C, 52.23; H, 5.47; N, 10.78.

Treatment of 12 with Hydrogen Chloride——A mixture of **12** (45 mg), ethanol (8 ml), and 10% hydrogen chloride (2 ml) was heated at 50—60° for 2 hr with stirring. After cooling, the reaction mixture was diluted with CH_2Cl_2 (100 ml) and successively washed with satd. Na_2CO_3 and satd. NaCl, then dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel using benzene as an eluent to give 1-ethoxycarbonylthieno[2,3-*b*]pyrrole (**13**): *ca.* 20 mg, 60% yield, oil. MS *m/e*: 195 (M$^+$). IR ν_{max}^{film} cm^{-1}: 1740 (C=O). NMR δ: 6.56 (1H, d, 3-H), 7.00 (1H, d, 4-H), 7.06 (1H, d, 5-H), 7.44 (1H, d, 2-H), $J_{2,3}$=5, $J_{4,5}$=5 Hz, 1.44 and 4.50 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_9NO_2S$: C, 55.38; H, 4.65; H, 7.18. Found: C, 55.58; H, 4.61; N, 7.01.

Treatment of the Diazepine (5b) with Hydrogen Chloride——A mixture of **5b** (60 mg), ethanol (10 ml), and 10% HCl (2 ml) was heated at 50—60° for 2 hr with stirring and worked up as described for **12** to give the thienopyrrole (**13**: 35 mg, 70% yield), which was identical with the product obtained from **12** by treatment with HCl.

Treatment of the Diazepine (5g) with Hydrogen Chloride——A mixture of **5g** (50 mg), ethanol (10 ml), and 10% HCl (2 ml) was heated at *ca.* 50° for 2 hr with stirring and then worked up as described for **12** to give the thienopyrrole (**15**): 26 mg, 62% yield, oil. MS *m/e*: 209 (M$^+$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1745 (C=O). NMR δ: 2.53 (3H, s, 2-Me), 6.17 (1H, s, 3-H), 6.96 (1H, d, 6-H), 7.98 (1H, d, 5-H), $J_{5,6}$=5 Hz, 1.44 and 4.39 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{11}NO_2S$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.31; H, 5.42; N, 6.58.

Photolysis of the Diazepine (5g)——A solution of **5g** (80 mg) in CH_2Cl_2 (150 ml) was irradiated under a nitrogen atmosphere for *ca.* 2 hr. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using CH_2Cl_2 as an eluent to give the thienopyrrole (**15**: 30 mg, 45% yield), which was identical with the product obtained from **5g** by treatment with HCl.

Reduction of the 1,3-Diazepine (5b) with $NaBH_4$ in Ethanol Containing Aqueous NaOH——Solid $NaBH_4$ (150 mg) was added in small portions to a solution of **5b** (80 mg) in ethanol (8 ml) containing 10% NaOH (0.5 ml), with stirring at room temperature. The solution was further stirred at 50—55° for 3 hr and was then diluted with CH_2Cl_2 (150 ml). The mixture was washed with satd. NaCl, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2–MeOH (4: 1) as an eluent to give the 4,5-dihydro-3H-1,3-thienodiazepine (**18**): 30 mg, 53% yield, oil. MS *m/e*: 166 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3250 (NH), 1620 (C=N). NMR δ: 2.06 (3H, s, 2-Me), 2.92 (2H, br t, $J=4$ Hz, 5-H_2), 3.50 (2H, br t, $J=4$ Hz, 4-H_2), 6.00 (1H, br, NH), 6.55 (1H, d, 6-H), 6.70 (1H, d, 7-H), $J_{6,7}=5$ Hz. *Anal.* Calcd for $C_8H_{10}N_2S$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.66; H, 6.04; N, 16.58.

Acetylation of 18 with Acetic Anhydride——A mixture of **18** (28 mg) and acetic anhydride (2 ml) was heated at 95—100° with stirring for 1 hr and then concentrated to dryness *in vacuo*. The residue was dissolved in CH_2Cl_2 (50 ml) and the solution was successively washed with satd. $NaHCO_3$ and satd. NaCl, then dried, and evaporated to dryness. The residue was chromatographed on alumina using *n*-hexane–ether (1: 2) as an eluent to give the acetate (**19**): 30 mg, 86% yield, mp 100—101° (from isopropyl ether). MS *m/e*: 208 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1670 (C=O). NMR δ: 2.16 (3H, s, Ac), 2.47 (3H, s, 2-Me), 3.00 (2H, t, $J=7$ Hz, 5-H_2), 3.65 (2H, t, $J=7$ Hz, 4-H_2), 6.79 (1H, d, 6-H), 7.11 (1H, d, 7-H), $J_{6,7}=5$ Hz. *Anal.* Calcd for $C_{10}H_{12}N_2OS$: C, 57.67; H, 5.81; N, 13.45. Found: C, 57.69; H, 5.73; N, 13.29.

Reduction of the 2,3-Diazepine (6b) with $NaBH_4$——i) In Ethanol Containing Aqueous NaOH: Solid $NaBH_4$ (600 mg) was added in small portions to a solution of **6b** (300 mg) in ethanol (10 ml) containing 10% NaOH (0.5 ml) with stirring at room temperature. The solution was further stirred at 50° for 5 hr and then diluted with CH_2Cl_2 (150 ml). The mixture was washed with satd. NaCl, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with a benzene–CH_2Cl_2 mixture to give the dihydro compounds (**20**) and (**21**) successively.

20: 80 mg, 27% yield, oil. MS *m/e*: 238 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300 (NH), 1710 (C=O). NMR δ: 1.44 (3H, d, $J=8$ Hz, 1-Me), 4.42 (1H, q, 1-H), 5.60 (1H, d, 5-H), 6.63 (1H, d, 6-H), 6.75 (1H, d, 4-H), 6.85 (1H, d, 7-H), $J_{4,5}=8$, $J_{6,7}=4$ Hz, 1.24 and 4.16 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.45; H, 5.92; N, 11.76. Found: C, 55.70; H, 5.97; N, 11.62.

21: 71 mg, 34% yield, oil. MS *m/e*: 166 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3330 (NH). NMR δ: 2.28 (3H, s, 1-Me), 3.04 (2H, t, $J=4$ Hz, 5-H_2), 3.24 (2H, t, $J=4$ Hz, 4-H_2), 5.6 (1H, br, NH), 6.78 (1H, d, 6-H), 7.10 (1H, d, 7-H), $J_{6,7}=4$ Hz. *Anal.* Calcd for $C_8H_{10}N_2S$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.88; H, 5.91; N, 16.75.

ii) In Acetic Acid: Solid $NaBH_4$ (100 mg) was added in small portions to a solution of **6b** (50 mg) in acetic acid (5 ml) with stirring in an ice bath. The reaction solution was stirred for an additional 20 min and was then diluted with CH_2Cl_2 (100 ml). After removal of acetic acid by extraction with satd. $NaHCO_3$, the solution was washed with satd. NaCl, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel using benzene–CH_2Cl_2 (1: 1) as an eluent to give the 1,2-dihydro-2,3-diazepine (**20**): 46 mg, *ca.* 90% yield.

Acetylation of 20 with Acetic Anhydride——A mixture of **20** (47 mg) and acetic anhydride (2 ml) was heated at *ca.* 100° with stirring for 2 hr and worked up as described for **18** to give the acetate (**22**): 50 mg, 91% yield, oil. MS *m/e*: 280 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680 and 1730 (C=O). NMR δ: 1.40 (3H, d, $J=8$ Hz, 1-Me), 1.97 (3H, s, Ac), 5.86 (1H, d, 5-H), 6.10 (1H, q, 1-H), 6.76 (1H, d, 6-H), 7.01 (1H, d, 4-H), 7.04 (1H, d, 7-H), $J_{4,5}=9$, $J_{6,7}=5$ Hz, 1.36 and 4.34 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{13}H_{16}N_2O_3S$: C, 55.71; H, 5.75; N, 10.00. Found: C, 55.84; H, 5.74; N, 9.81.

Acetylation of 21 with Acetic Anhydride——A mixture of **21** (55 mg) and acetic anhydride (1 ml) was stirred for 1 hr at room temperature and then worked up as described for **18** to give the acetate (**23**): 65 mg, 94% yield, mp 92—93.5° (from *n*-hexane–isopropyl ether). MS *m/e*: 208 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1660 (C=O). NMR δ: 2.29 (3H, s, Ac), 2.51 (3H, s, 1-Me), 3.11 (2H, t, 5-H_2), 3.95 (2H, t, 4-H_2), 6.98 (1H, d, 6-H), 7.37 (1H, d, 7-H), $J_{4,5}=4$, $J_{6,7}=4$ Hz. *Anal.* Calcd for $C_{10}H_{12}N_2OS$: C, 57.67; H, 5.81; N, 13.45. Found: C, 57.79; H, 5.86; N, 13.21.

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