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

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Irradiation of the 2-methylpyridine N-acylimides (**12b—d** and **17a—c**) condensed with a thiophene, furan, or pyrrole ring on the b-side of the pyridine ring gave the corresponding fused 1H-1,2- (**13b—d** and **18a—c**) and 3H-1,3-diazepines (**14b—d** and **19a—c**), together with the parent fused pyridines (**10** and **15a—c**), whereas the N-unsubstituted N-imide (**12a**) gave only the 1H-1,2-diazepine (**13a**) and no 1,3-diazepine.

In this ring-expansion reaction, the initial photo-induced rearrengement may take place on either side of the pyridine nitrogen to give two kinds of diaziridine intermediates (**21**) and (**22**); the former may give 1,2-diazepines directly, whereas the latter may further rearrange to the aziridine intermediate (**23**), followed by ring-expansion to give the 1,3-diazepines.

Some reactions of the new diazepines thus obtained were also examined.

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

It is known that the 2-unsubstituted quinolines and related fused pyridine N-imides (**1a**: X=H) undergo photo-induced rearrangement to give the corresponding fully unsaturated 1H-1,2-benzodiazepines[2] and analogous fused 1,2-diazepines (**2**),[3] whereas irradiation of

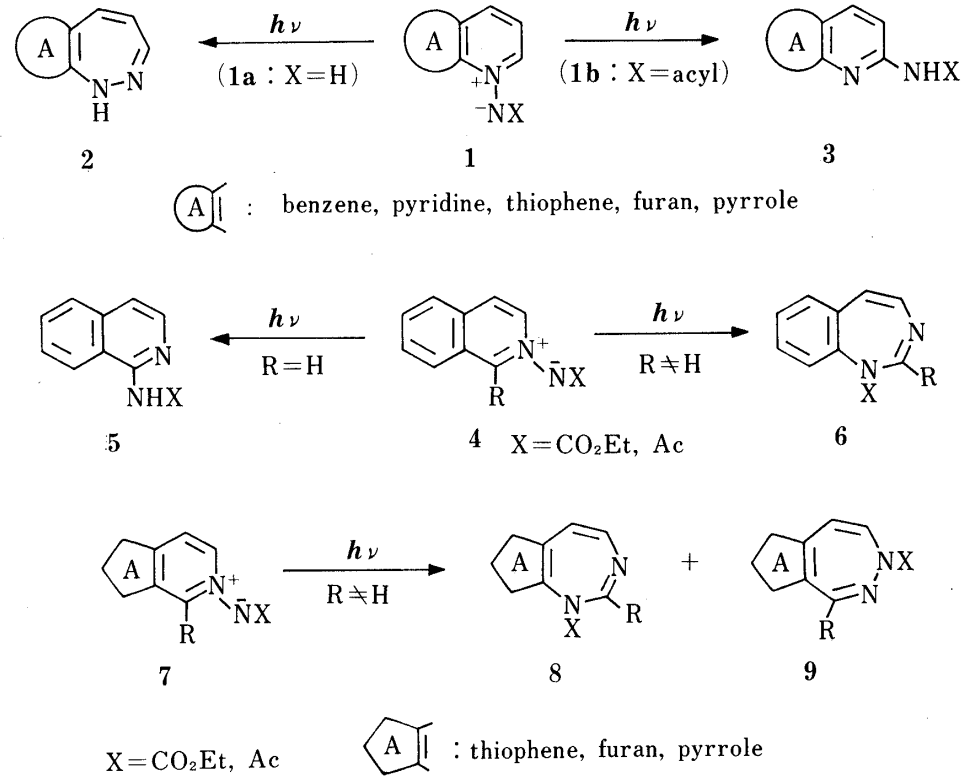


Chart 1

the N-acylimides (**1b**: X=CO_2Et, Ac, or COPh) gives only 2-aminopyridines (**3**) and no diazepines.[4] On the other hand, we have recently reported that the 1-substituted isoquinoline N-acylimides (**4**: R=Me or CO_2Et) undergo a photo-induced two-step rearrangement to generate the novel 1H-1,3-benzodiazepines (**6**),[5] while, in contrast, irradiation of the 1-unsubstituted isoquinoline N-imides (**4**: R=H) resulted in N–N fragmentation to the parent isoquinolines or rearrangement to the 1-aminoisoquinolines (**5**).[4,6] We have also reported that the photolysis of the similar 1-substituted isoquinoline-type fused pyridine N-acylimides (**7**) condensed with an aromatic five-membered ring such as thiophene, furan, or pyrrole ring gives the corresponding fused 1H-1,3-diazepines (**8**) and 3H-2,3-diazepines (**9**).[1,7]

In connection with the above results, we were interested in examining the photochemical behavior of quinoline-type fused pyridine N-imides having a methyl group in the α-position of the pyridine ring. We now report that the photolysis of these fused pyridine N-imides affords the corresponding new 1H-1,2- and 3H-1,3-diazepines.[8]

4,6-Dimethylthieno[2,3-*b*]pyridine (**10**)[9] was aminated with O-mesitylenesulfonylhydroxylamine (H_2NOMes) according to the method of Tamura *et al.*[10] to give the N-aminopyridinium mesitylenesulfonate (**11**) in 94% yield. Treatment of the salt (**11**) with ethyl chloroformate, acetic anhydride, or benzoyl chloride in the presence of alkali gave the corresponding N-acylimides (**12b—d**) as stable crystals in 50—70% yields. The N-unsubstituted N-imide (**12a**) was too unstable to be isolated; thus, treatment of the salt (**11**) with potassium hydroxide in methanol, followed by irradiation of the solution containing the imide (**12a**) resulted in the formation of the 1H-thieno[2,3-*c*]-1,2-diazepine (**13a**) and the parent thienopyridine (**10**) in *ca.* 60% and 15% yields, respectively; this result is analogous to those observed for 2-unsubstituted quinoline-type fused pyridine N-imides (**1a**).[2,3] In contrast, irradiation of the N-ethoxycarbonylimide (**12b**) gave the two kinds of diazepines, the 1H-1,2-diazepine (**13b**) and the 3H-1,3-diazepine (**14b**), in 12% and 57% yields, respectively, together with the parent thienopyridine (**10**) in *ca.* 10% yield. Similarly, the N-acetyl- (**12c**) and the N-benzoyl-imide (**12d**), upon irradiation, gave the 1,2-diazepines (**13c**, 8%; **13d**, 10%), the 1,3-diazepines (**14c**, 15%; **14d**, 20%), and the thienopyridine (**10**: 55% from **12c**; 35% from **12d**). In the cases of **12c**

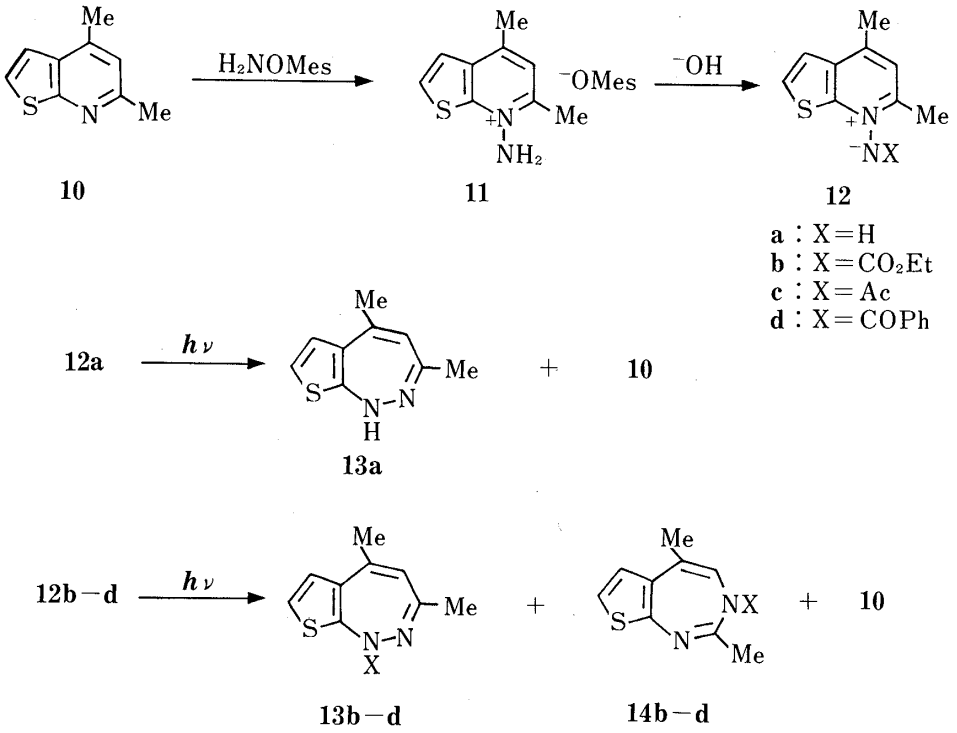


Chart 2

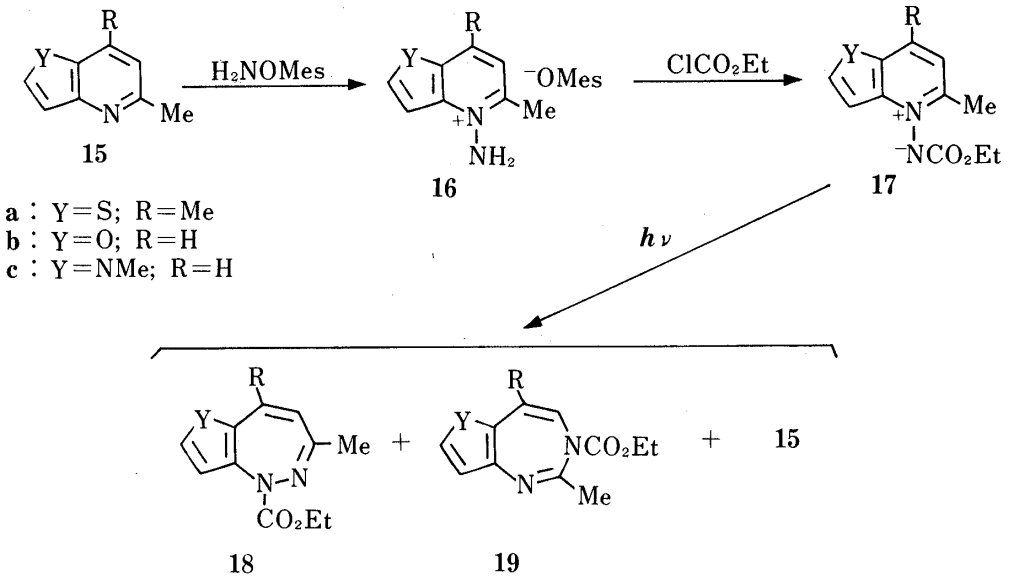


Chart 3

and **12d**, the formation of the N–N fragmentation product (**10**) predominates over that of the rearrangement products (**13** and **14**). Such a tendency is generally observed for the photolyses of various aromatic amine N-imides,[11] although the effect of acyl groups has not been clarified.

Next, similar reactions were carried out for the other fused pyridine N-ethoxycarbonylimides (**17a—c**), which were prepared from 5,7-dimethylthieno- (**15a**),[9] 5-methylfuro-(**15b**),[12] and 1,5-dimethylpyrrolo-[3,2-*b*]pyridine (**15c**)[13] *via* the salts (**16**) according to the procedure described for the preparation of the imide (**12b**), respectively. Irradiation of the imides (**17a—c**) also gave the 1,2-diazepines (**18a**, 18%; **18b**, 46%; **18c**, 15%) and the 1,3-diazepines (**19a**, 45%; **19b**, 15%; **19c**, 35%), as well as the corresponding parent pyridines (**15a**, 11%; **15b**, 5%; **15c**, 7%).

The formation of the diazepines (**13** and **18**) and (**14** and **19**) may proceed by photo-induced rearrangement to two kinds of diaziridine intermediates, (**21**) and (**22**), as shown in Chart 4. The N-substituted 1,2-diazepines (**13** and **18**) are formed directly from the former intermediates (**21**), whereas the latter (**22**) may further rearrange to the aziridne intermediates (**23**) by a [1,5]-sigmatropic shift, followed by ring-expansion to give the 1,3-diazepines (**14** and **19**) by

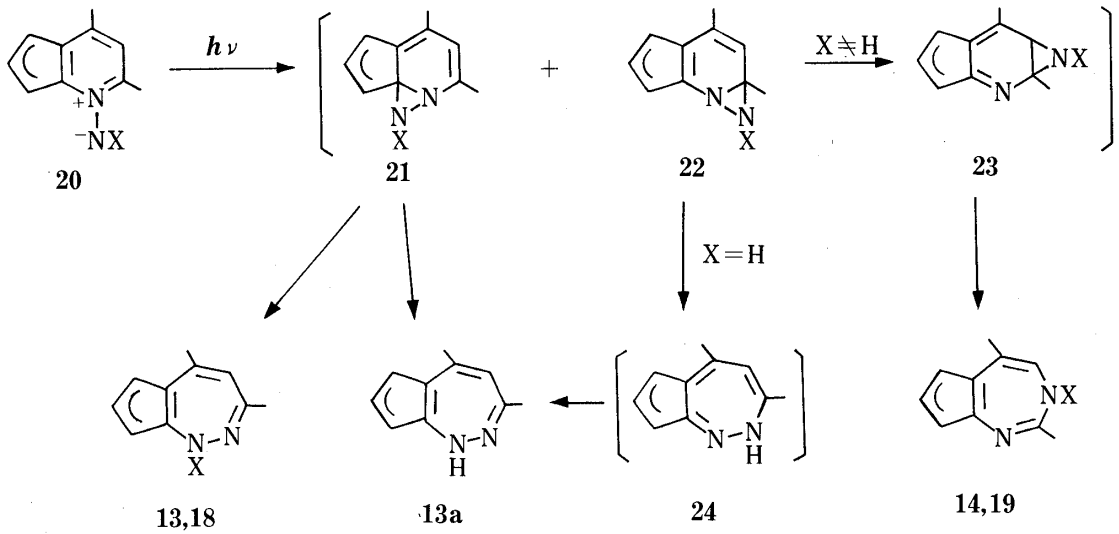


Chart 4

analogy with the cases of 1-substituted isoquinoline N-imides (**4**)[5] and related compounds (**7**).[1] In the case of N-unsubstituted imide (**12a**: X=H in **20**), the diaziridine (**22**) may undergo ring-expansion to the 1H-1,2-diazepine (**13a**) *via* the unstable *o*-quinonoid-type 2H-isomer (**24**) in preference to the second rearrangement into the aziridine (**23**). This may account for the fact that the imides (**1a**) and (**12a**) give only 1H-1,2-diazepines and no 1,3-diazepines. The initial photo-induced rearrangement clearly takes place to either side of the pyridine nitrogen, in contrast with the reactions of quinoline N-imides (**1**)[2,4], but analogous to the cases of isoquinoline-type fused pyridine N-imides (**7**).[1,7] However, it should be noted that the present result is the first example of the rearrangement of N-imides directly to a carbon that is part of a ring junction.

TABLE I. 1H-1,2-(**13** and **18**) and 3H-1,3-Diazepines (**14** and **19**)

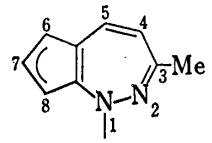
Compd. No.	mp[a] (°C)	MS *m/e* (M+)	IR $\nu_{max}^{CHCl_3}$ cm^{-1} (C=O)	UV λ_{max}^{EtOH} nm (ε)	Formula	Analysis (%) Calcd (Found) C	H	N
13a	95.5—97	178	3350 (NH)	244(9000) 259 (sh.)	$C_9H_{10}N_2S$	60.64 (60.97	5.66 5.87	15.71 15.23)
13b	134—135	250	1705	265(7000)	$C_{12}H_{14}N_2O_2S$	57.58 (57.82	5.64 5.76	11.19 11.45)
13c	102—104	220	1665	272(7200)	$C_{11}H_{12}N_2OS$	59.98 (59.90	5.49 5.41	12.72 12.48)
13d	Oil[b]	282	1655	225(18500) 280(8000)	$C_{16}H_{14}N_2OS$	68.06 (68.15	5.00 4.88	9.92 9.89)
18a	81—83	250	1710	279(5400)	$C_{12}H_{14}N_2O_2S$	57.58 (57.86	5.64 5.71	11.19 11.20)
18b	133—134	220	1710	227(14700) 259(8900)	$C_{11}H_{12}N_2O_3$	59.99 (59.95	5.49 5.45	12.72 12.77)
18c	155—156	233	1695	303(5900)	$C_{12}H_{15}N_3O_2$	61.79 (61.76	6.48 6.46	18.01 18.00)
14b	67—68.5	250	1700	228(10700) 305(2100)	$C_{12}H_{14}N_2O_2S$	57.58 (57.48	5.64 5.85	11.19 11.30)
14c	Oil	220	1665	226(13200) 300(3700)	$C_{11}H_{12}N_2OS$	59.98 (60.21	5.49 5.40	12.72 12.52)
14d	Oil	282	1655	229(13300) 270(4600)	$C_{16}H_{14}N_2OS$	68.06 (68.09	5.00 4.97	9.92 9.76)
19a	Oil	250	1710	259(14500)	$C_{12}H_{14}N_2O_2S$	57.58 (57.51	5.64 5.77	11.19 11.05)
19b	Oil	220	1710	256(5700)	$C_{11}H_{12}N_2O_3$	59.99 (60.21	5.49 5.29	12.72 12.75)
19c	Oil	233	1710	266(13100)	$C_{12}H_{15}N_3O_2$	61.79 (61.98	6.48 6.40	18.01 17.76)

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

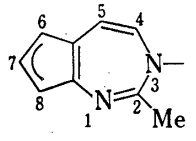
The physical, analytical, and some spectral data for these novel 1H-1,2- (**13** and **18** and 3H-1,3-diazepines (**14** and **19**) are collected in Table I. The ^{1}H-NMR spectral data are also summarized in Table II. These spectral data and the results of the following chemical studies are consistent with the proposed structures, eliminating other possible structures such as 2H-1,2- and 4H-2,4-diazepines.

Treatment of the N-unsubstituted 1H-1,2-diazepine (**13a**), whose structure was confirmed by comparison with the 1,2-diazepines (**2**) already reported,[3] with ethyl chloroformate in the presence of *n*-butyl lithium at −60°C gave a compound which is identical with the N-ethoxycarbonyldiazepine (**13b**) obtained from **12b**. Treatment of the 3H-1,3-diazepine (**14b**) with hydrochloric acid in methanol at room temperature resulted in the formation of the ring-opened product (**25**), which was further converted into the thieno[2,3-*b*]pyrrole derivative (**26**)

TABLE II. ^{1}H-NMR Spectral Data for the 1H-1,2- (**13** and **18**) and 3H-1,3-Diazepines (**14** and **19**) δ ($CDCl_3$)



13 and 18



14 and 19

13a	1.93 (3H, s, 3-Me), 2.06 (3H, br d, 5-Me), 5.94 (1H, br q, 4-H), 6.67 (1H, d, 6-H), 6.72 (1H, d, 7-H), 6.7 (1H, br, NH), $J_{4.5\text{-Me}}=1$, $J_{6,7}=6$ Hz
13b	2.09 (3H, s, 3-Me), 2.14 (3H, br d, 5-Me), 6.03 (1H, m, 4-H), 6.74 (1H, d, 6-H), 7.07 (1H, d, 7-H), $J_{4.5\text{-Me}}=1$, $J_{6,7}=5$ Hz, 1.34 and 4.27 (3H, t, and 2H, q, CO_2Et)
13c	2.12 (3H, s, 3-Me), 2.18 (3H, br d, 5-Me), 6.09 (1H, m, 4-H), 6.86 (1H, d, 6-H), 7.22 (1H, d, 7-H), $J_{4.5\text{-Me}}=1$, $J_{6,7}=5$ Hz, 2.31 (3H, s, Ac–Me)
13d	2.10 (3H, s, 3-Me), 2.26 (3H, br d, 5-Me), 6.23 (1H, m, 4-H), 6.89 (1H, d, 6-H), 7.17 (1H, d, 7-H), $J_{4.5\text{-Me}}=1$, $J_{6,7}=6$ Hz, 7.3—7.7 (5H, m, Ph–H)
18a	2.12 (3H, s, 3-Me), 2.19 (3H, br d, 5-Me), 6.08 (1H, m, 4-H), 6.94 (1H, d, 8-H), 7.33 (1H, d, 7-H), $J_{4.5\text{-Me}}=1$, $J_{7,8}=5$ Hz, 1.33 and 4.28 (3H, t, and 2H, q, CO_2Et)
18b	2.13 (3H, s, 3-Me), 6.10 (1H, d, 4-H), 6.38 (1H, d, 8-H), 6.72 (1H, d, 5-H), 7.41 (1H, d, 7-H), $J_{4.5}=12$, $J_{7,8}=2$ Hz, 1.34 and 4.29 (3H, t, and 2H, q, CO_2Et)
18c	2.13 (3H, s, 3-Me), 3.54 (3H, s, N–Me), 6.01 (1H, d, 4-H), 6.02 (1H, d, 8-H), 6.69 (1H, d, 7-H), 6.71 (1H, d, 5-H), $J_{4.5}=11$, $J_{7,8}=3$ Hz, 1.33 and 4.28 (3H, t, and 2H, q, CO_2Et)
14b	2.04 (3H, br d, 5-Me), 2.40 (3H, s, 2-Me), 5.66 (1H, m, 4-H), 6.84 (1H, d, 6-H), 6.96 (1H, d, 7-H), $J_{4.5\text{-Me}}=1$, $J_{6,7}=5$ Hz, 1.28 and 4.14 (3H, t, and 2H, q, CO_2Et)
14c	2.13 (3H, br d, 5-Me), 2.47 (3H, s, 2-Me), 5.78 (1H, m, 4-H), 6.98 (1H, d, 6-H), 7.09 (1H, d, 7-H), $J_{4.5\text{-Me}}=1$, $J_{6,7}=5$ Hz, 2.05 (3H, s, Ac–Me)
14d	2.14 (6H, s, 2- and 5-Me), 6.08 (1H, m, 4-H), 7.04 (1H, d, 6-H), 7.15 (1H, d, 7-H), $J_{6,7}=6$ Hz, 7.3—7.6 (5H, m, Ph–H)
19a	2.09 (3H, br d, 5-Me), 2.42 (3H, s, 2-Me), 5.77 (1H, m, 4-H), 6.96 (1H, d, 8-H), 7.16 (1H, d, 7-H), $J_{4.5\text{-Me}}=1$, $J_{7,8}=5$ Hz, 1.30 and 4.19 (3H, t, and 2H, q, CO_2Et)
19b	2.40 (3H, s, 2-Me), 5.79 (1H, d, 5-H), 6.39 (1H, d, 4-H), 6.47 (1H, d, 8-H), 7.26 (1H, d, 7-H), $J_{4,5}=7$, $J_{7,8}=2$ Hz, 1.31 and 4.22 (3H, t, and 2H, q, CO_2Et)
19c	2.41 (3H, s, 2-Me), 3.53 (3H, s, N–Me), 5.83 (1H, d, 5-H), 6.21 (1H, d, 8-H), 6.31 (1H, d, 4-H), 6.58 (1H, d, 7-H), $J_{4,5}=7$, $J_{7,8}=3$ Hz, 1.31 and 4.23 (3H, t, and 2H, q, CO_2Et)

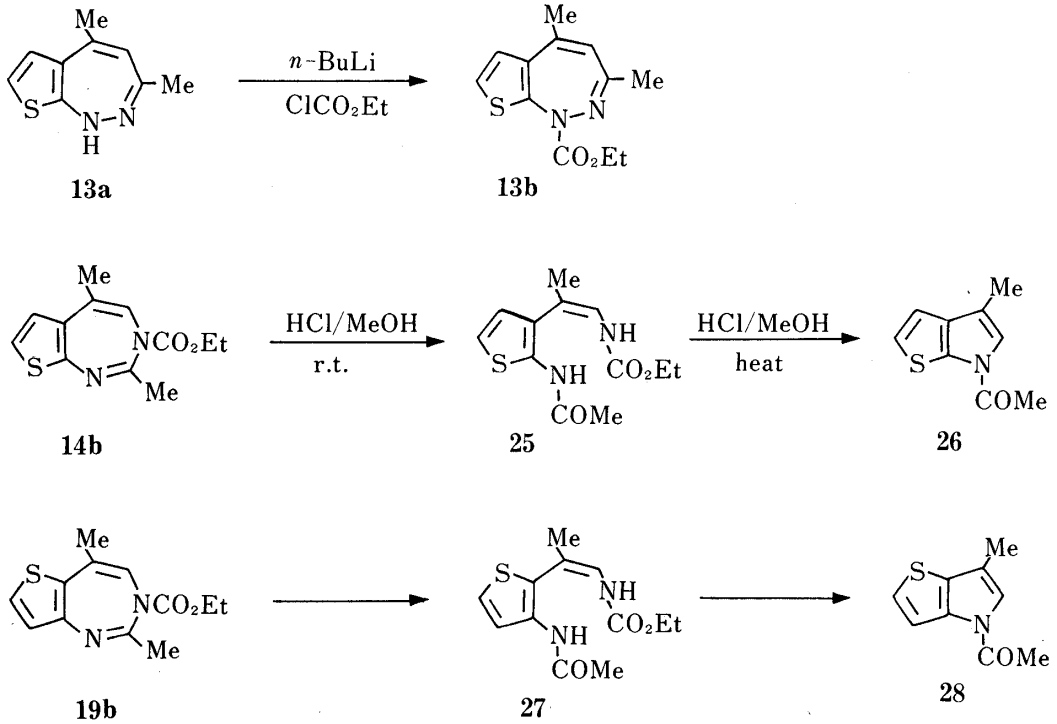


Chart 5

by refluxing in methanol containing hydrochloric acid. Similarly, the 1,3-diazepine (**19b**) gave the thieno[3,2-*b*]pyrrole (**28**) *via* the ring-opened compound (**27**). These results are analogous to those observed for 1H-[5] and 3H-1,3-benzodiazepines[14] and 1,3-benzoxazepines.[15]

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. Proton nuclear magnetic resonance (^{1}H-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. Ultraviolet (UV) spectra were recorded on a Hitachi 323 spectrometer. 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 fused pyridines (**10**),[9] (**15a**),[9] (**15b**),[12] and (**15c**)[13] were prepared by the reported procedures.

N-Amino-4,6-dimethylthieno[2,3-*b*]pyridinium Mesitylenesulfonate (**11**)——A solution of O-mesitylenesulfonylhydroxylamine (4 g, 0.019 mol) in CH_2Cl_2 (100 ml) was added dropwise to a solution of 4,6-dimethylthieno[2,3-*b*]pyridine (**10**: 2.1 g; 0.013 mol) in CH_2Cl_2 (20 ml) with constant stirring in an ice bath. The reaction mixture was stirred for an additional 1 h. After addition of ether (*ca.* 500 ml) to the mixture, the resulting crystalline precipitates were collected by filtration and recrystallized from methanol to give the salt (**11**): 4.65 g, 94% yield, mp 252.5—253.5°C, colorless plates. IR ν_{max}^{KBr} cm^{-1}: 3225 (NH). ^{1}H-NMR (CD_3OD) δ: 2.77 (3H, s, 4-Me), 2.87 (3H, s, 6-Me), 7.60 (1H, d, 3-H), 7.61 (1H, s, 5-H), 7.84 (1H, d, 2-H), $J_{2,3}$=5 Hz, $^-$OMes [2.17 (3H, s), 2.52 (6H, s), 6.72 (2H, s)]. *Anal.* Calcd for $C_{18}H_{22}N_2O_3S_2$: C, 57.12; H, 5.86; N, 7.40. Found: C, 57.19; H, 5.80; N, 7.16.

4,6-Dimethylthieno[2,3-*b*]pyridine N-Ethoxycarbonylimide (**12b**)——Solid potassium carbonate (2.74 g; 0.02 mol) and ethyl chloroformate (1.58 g; 0.015 mol) were added to a solution of the salt (**11**: 5 g; 0.013 mol) in ethanol (100 ml) with stirring. The mixture was stirred for an additional 8 h 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 (1: 3) as an eluent to give the imide (**12b**): 4.12 g, 71% yield, mp 131.5—132.5°C, colorless prisms (from benzene). IR ν_{max}^{KBr} cm^{-1}: 1630 (C=O). MS *m/e*: 250 (M$^+$). ^{1}H-NMR δ: 2.55 (3H, s, 4-Me), 2.67 (3H, s, 6-Me), 7.24 (1H, d, 3-H), 7.27 (1H, s, 5-H), 7.49 (1H, d, 2-H), $J_{2,3}$=6 Hz, 1.35 and 4.19 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.58; H, 5.64; N, 11.19. Found: C, 57.84; H, 5.66; N, 11.27.

4,6-Dimethylthieno[2,3-*b*]pyridine N-acetylimide (**12c**)——A mixture of the salt (**11**: 1.5 g) and acetic anhydride (12 ml) was refluxed for 4 h with stirring. After removal of the reagent *in vacuo*, the residue was dissolved in CH_2Cl_2 (50 ml) and the solution was successively washed with satd. K_2CO_3 and satd. NaCl, then dried, and evaporated to dryness. The residue was chromatographed on silica gel using CH_2Cl_2–acetone (1: 1) as an eluent to give the imide (**12c**): 0.55 g, 64% yield, mp 152—153.5°C, colorless prisms (from benzene). IR ν_{max}^{KBr} cm^{-1}: 1580 (C=O). MS *m/e*: 220 (M$^+$). ^{1}H-NMR δ: 2.12 (3H, s, Ac-Me), 2.61 (3H, s, 4-Me), 2.66 (3H, s, 6-Me), 7.27 (1H, s, 5-H), 7.30 (1H, d, 3-H), 7.48 (1H, d, 2-H), $J_{2,3}$=6 Hz. *Anal.* Calcd for $C_{11}H_{12}N_2OS$: C, 59.98; H, 5.49; N, 12.72. Found: C, 59.90; H, 5.41; N, 12.42.

4,6-Dimethylthieno[2,3-*b*]pyridine N-Benzoylimide (**12d**)——Solid potassium carbonate (0.55 g; 4.0 mmol) and benzoyl chloride (0.45 g; 3.2 mmol) were added to a solution of the salt (**11**: 1 g; 2.65 mmol) in ethanol (30 ml) with stirring. The mixture was stirred for an additional 6h at room temperature and the resulting precipitate was filtered off. The filtrate was evaporated to dryness *in vacuo* and the residue was chromatographed on silica gel using CH_2Cl_2–acetone (1: 3) as an eluent to give the imide (**12d**): 370 mg, 51% yield, mp 165—166.5°C, colorless prisms (from benzene). IR ν_{max}^{KBr} cm^{-1}: 1590 (C=O). MS *m/e*: 282 (M$^+$). ^{1}H-NMR δ: 2.65 (3H, s, 4-Me), 2.72 (3H, s, 6-Me), 7.1—7.5 (6H, m), 8.1—8.3 (2H, m). *Anal.* Calcd for $C_{16}H_{14}N_2OS$: C, 68.06; H, 5.00; N, 9.92. Found: C, 67.86; H, 4.99; N, 9.81.

Photolysis of the N-Imide (**12a**)——A solution of potassium hydroxide (300 mg) in methanol (10 ml) was added dropwise to a solution of the salt (**11**: 1 g) in methanol (200 ml) over a 15 min period under irradiation. The mixture was further irradiated for an additional 1.5 h and then concentrated *in vacuo* below 30°C. The residue was extracted with ether and the extract was washed with satd. NaCl, dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The resulting residue was chromatographed on silica gel using ether–*n*-hexane (2: 1) as an eluent to give the parent thienopyridine (**10**: 63 mg, 15% yield) and the 1H-1,2-diazepine (**13a**: 280 mg, 60% yield) successively. Physical, analytical, and spectral data for the diazepine (**13a**) are collected in Tables I and II.

Photolysis of the N-Imides (**12b—d**)——A solution of the imide (**12b—d**: 0.3—1 g) in benzene (200—300 ml) was irradiated. The photolysis was followed in terms of the disappearance of the spot of the start-

ing materials on thin-layer chromatography, and was complete in 30—90 min. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using ether–*n*-hexane as an eluent to give the parent fused pyridine (**10**), the 1,3-diazepines (**14b—d**), and the 1,2-diazepines (**13b—d**) successively. The yields of these products are described in the text. Physical, analytical, and spectral (MS, IR, and UV) data for the diazepines obtained are collected in Table I. The ^{1}H-NMR spectral data are summarized in Table II.

N-Aminopyridinium Mesitylenesulfonates (16a—c)——General procedure: A solution of O-mesitylenesulfonylhydroxylamine (1.3 mol eq) in CH_2Cl_2 (100—150 ml) was added dropwise to a solution of the fused pyridine (**15**: 0.02—0.03 mol) in CH_2Cl_2 (20—30 ml) with constant stirring in an ice bath. The reaction mixture was stirred for an additional 1 h. After addition of ether (*ca.* 500 ml) to the mixture, the resulting crystalline precipitates were collected by filtration and recrystallized from methanol to give the salt (**16**).,

N-Amino-5,7-dimethylthieno[3,2-*b*]pyridinium Mesitylenesulfonate (**16a**): 72% yield, mp 199—201°C, colorless plates. IR ν_{max}^{KBr} cm^{-1}: 3250 (NH). ^{1}H-NMR (CD_3OD) δ: 2.75 (3H, s, 7-Me), 2.87 (3H, s, 5-Me), 7.54 (1H, s, 6-H), 7.87 (1H, d, 3-H), 8.35 (1H, d, 2-H), $J_{2,3}$=5 Hz, $^-$OMes [2.18 (3H, s), 2.51 (6H, s), and 6.71 (2H, s)]. *Anal.* Calcd for $C_{18}H_{22}N_2O_3S_2$: C, 57.12; H, 5.86; N, 7.40. Found: C, 56.89; H, 5.86; N, 7.25.

N-Amino-5-methylfuro[3,2-*b*]pyridinium Mesitylenesulfonate (**16b**): 87% yield, mp 221—222.5°C, colorless plates. IR ν_{max}^{KBr} cm^{-1}: 3230 (NH). ^{1}H-NMR (CD_3OD) δ: 2.87 (3H, s, 5-Me), 7.46 (1H, d, 3-H), 7.69 (1H, d, 6-H), 8.36 (1H, d, 7-H), 8.41 (1H, d, 2-H), $J_{2,3}$=2, $J_{6,7}$=9 Hz, $^-$OMes [2.20 (3H, s), 2.54 (6H, s), and 6.76 (2H, s)]. *Anal.* Calcd for $C_{17}H_{20}N_2O_4S$: C, 58.60; H, 5.79; N, 8.04. Found: C, 58.96; H, 5.93; N, 8.05.

N-Amino-1,5-dimethylpyrrolo[3,2-*b*]pyridinium Mesitylenesulfonate (**16c**): 81% yield, mp 169—170.5°C, colorless plates. IR ν_{max}^{KBr} cm^{-1}: 3250 (NH). ^{1}H-NMR (CD_3OD) δ: 2.83 (3H, s, 5-Me), 3.96 (3H, s, N-Me), 6.92 (1H, d, 3-H), 7.42 (1H, d, 6-H), 7.84 (1H, d, 2-H), 8.25 (1H, d, 7-H), $J_{2,3}$=4, $J_{6,7}$=8 Hz, $^-$OMes [2.20 (3H, s), 2.56 (6H, s), and 6.76 (2H, s)]. *Anal.* Calcd for $C_{18}H_{23}N_3O_3S$: C, 59.81; H, 6.41; N, 11.63. Found: C, 60.09; H, 6.45; N, 11.81.

Fused Pyridine N-Ethoxycarbonylimides (17a—c)——General Procedure: Solid potassium carbonate (1.5 mol eq) and ethyl chloroformate (1.1 mol eq) were added to a solution of the salt (**16**: 5—10 mmol) in ethanol (100—150 ml) with stirring. The mixture was stirred for an additional 8—10 h 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 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 (**17**).

17a: 73% yield, mp 103—104°C, colorless prisms (from benzene). IR ν_{max}^{KBr} cm^{-1}: 1620 (C=O). MS *m/e*: 250 (M$^+$). ^{1}H-NMR δ: 2.65 (3H, s, 5-Me), 2.74 (3H, s, 7-Me), 7.23 (1H, br s, 6-H), 7.67 (1H, d, 3-H), 7.82 (1H, d, 2-H), $J_{2,3}$=6 Hz, 1.35 and 4.17 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.58; H, 5.64; N, 11.19. Found: C, 57.84; H, 5.66; N, 11.27.

17b: 76% yield, oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1615 and 1635 (C=O). ^{1}H-NMR δ: 2.75 (3H, s, 5-Me), 7.08 (1H, d, 3-H), 7.36 (1H, d, 6-H), 7.87 (1H, d, 7-H), 7.89 (1H, d, 2 H), $J_{2,3}$=2, $J_{6,7}$=8 Hz, 1.35 and 4.17 (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, 59.81; H, 5.52; N, 12.76.

17c: 68% yield, mp 72—74°C, pale yellow prisms (from benzene–isopropyl ether). IR ν_{max}^{KBr} cm^{-1}: 1630 (C=O). MS *m/e*: 233 (M$^+$). ^{1}H NMR δ: 2.69 (3H, s, 5-Me), 3.74 (3H, s, N-Me), 6.60 (1H, d, 3-H), 7.12 (1H, d, 7-H), 7.32 (1H, d, 2-H), 7.72 (1H, d, 6-H), $J_{2,3}$=3, $J_{6,7}$=8 Hz, 1.37 and 4.20 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.55; H, 6.33; N, 17.93.

Photolysis of the Imides (17a—c)——A solution of the imide (**17**: 0.5—1.0 g) in benzene (200—250 ml) was irradiated and then worked up as described for **12b—d** to give the 1,3-diazepines (**19**), the parent pyridines (**15**), and the 1,2-diazepines (**18**) successively. The yields of these products are described in the text. Physical, analytical, and spectral (MS, IR, and UV) data for the diazepines (**18** and **19**) are collected in Table I. The ^{1}H-NMR spectral data are also summarized in Table II.

N-Ethoxycarbonylation of the 1H-1,2-Diazepine (13a)——A solution of *n*-butyl lithium (15% w/w in *n*-hexane, d=0.68, 1.02 ml, 1.2 mol eq) was added dropwise with stirring, to a solution of the diazepine (**13a**: 244 mg, 1.37 mmol) in anhydrous tetrahydrofuran cooled in a dry ice–acetone bath, then a solution of ethyl chloroformate (164 mg, 1.1 mol eq) in tetrahydrofuran (3 ml) was further added dropwise to the reaction mixture. After stirring for an additional 20 min at *ca.* −60°C, the reaction mixture was warmed to room temperature and diluted with ether (100 ml). The mixture was washed with satd. NaCl, dried, and concentrated *in vacuo*. The resulting residue was chromatographed on silica gel using ether–*n*-hexane (2: 1) as an eluent to give the N-ethoxycarbonyldiazepine (**13b**: 140 mg, *ca.* 40% yield).

Treatment of the 1,3-Diazepine (14b) with Hydrochloric Acid——A mixture of **14b** (100 mg), methanol (5 ml), and 10% hydrochloric acid (0.5 ml) was stirred for 1 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (100 ml) and successively washed with satd. $NaHCO_3$ and satd. NaCl, then dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The solid residue was recrystallized from benzene–*n*-hexane to give the ring-opened product (**25**): 75% yield, mp 175—176.5°C, colorless needles. IR ν_{max}^{KBr} cm^{-1}: 3200 and 3300 (NH), 1670 and 1700 (C=O). MS *m/e*: 268 (M$^+$). ^{1}H-NMR (CD_3OD) δ: 1.91 (3H, br d, J= 1 Hz, vinyl-Me), 2.08 (3H, s, Ac-Me), 6.39 (1H, m, vinyl-H), 6.61 and 6.90 (each 1H, d, J=5 Hz, thiophene-

H), 1.21 and 4.04 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{16}N_2O_3S$: C, 53.71; H, 6.01; N, 10.44. Found: C, 53.45; H, 6.07; N, 10.16.

Treatment of 25 with Hydrochloric Acid——A mixture of **25** (30 mg), methanol (6 ml) and 10% hydrochloric acid (0.5 ml) was refluxed for *ca.* 2 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 (100 ml) and successively washed with satd. $NaHCO_3$ and satd. NaCl, then dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel using ether–*n*-hexane (1 : 5) as an eluent to give 1-acetyl-3-methylthieno[2,3-*b*]pyrrole (**26**): *ca.* 45% yield, mp 80—81°C, colorless prisms (from *n*-hexane). IR ν_{max}^{KBr} cm^{-1}: 1690 (C=O). MS *m/e*: 179 (M^+). ^{1}H-NMR δ: 2.26 (3H, br d, 3-Me), 2.56 (3H, s, Ac-Me), 6.95 (1H, d, 4-H), 7.00 (1H, m, 2-H), 7.06 (1H, d, 5-H), $J_{4,5}=6$, $J_{2,3\text{-Me}}=1$ Hz. *Anal.* Calcd for C_9H_9NOS: C, 60.31; H, 5.06; N, 7.81. Found: C, 60.43; H, 4.98; N, 7.89.

Treatment of the 1,3-Diazepine (19b) with Hydrochloric Acid——A mixture of **19b** (90 mg), methanol (5 ml), and 10% hydrochloric acid (0.5 ml) was stirred for 1 h at room temperature and then worked up as described for **14b** to give the ring-opened product (**27**): *ca.* 80% yield, mp 152.5—154°C, colorless needles (from benzene). IR ν_{max}^{KBr} cm^{-1}: 3250 and 3300 (NH), 1670 and 1710 (C=O). MS *m/e*: 268 (M^+). ^{1}H-NMR δ: 1.99 (3H, br d, $J=1$ Hz, vinyl-Me), 2.12 (3H, s, Ac-Me), 6.70 (1H, m, vinyl-H), 7.30 and 7.72 (each 1H, d, $J=5$ Hz, thiophene-H), 1.26 and 4.16 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{12}H_{16}N_2O_3S$: C, 53.71; H, 6.01; N, 10.44. Found: C, 53.46; H, 5.93; N, 10.31.

Treatment of 27 with Hydrochloric Acid——A mixture of **27** (120 mg), methanol (5 ml), and 10% hydrochloric acid (0.8 ml) was refluxed for 3.5 h, and then worked up as described for **25** to give 1-acetyl-3-methylthieno[3,2-*b*]pyrrole (**28**): 58% yield, mp 111.5—112.5°C, colorless prisms (from *n*-hexane). IR ν_{max}^{KBr} cm^{-1}: 1680 (C=O). MS *m/e*: 179 (M^+). ^{1}H-NMR δ: 2.22 (3H, s, 3-Me), 2.55 (3H, s, Ac-Me), 7.2 (3H, br, 2-H and thiophene-H). *Anal.* Calcd for C_9H_9NOS: C, 60.31; H, 5.06; N, 7.81. Found: C, 60.28; H, 5.01; N, 7.66.

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