[Chem. Pharm. Bull. 27(9)2188—2193(1979)]

UDC 547.891.2.04 : 542.952.1.04

Studies on Diazepines. VIII.[1] Syntheses and Rearrangements of 3H-1,2-Pyrido- and 3H-1,2-Thieno-diazepines

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(Received April 25, 1979)

The previously unknown 3H-1,2-pyrido- (**3a, b**) and 3H-1,2-thieno- (**3c, d**) diazepines were prepared from the corresponding 1H-isomers. Treatment of **3** with bases or acids resulted in tautomerization to give the 1H-diazepines (**1**), and photolysis of **3** afforded the condensed 3-vinylpyrazoles (**4**). However, thermolysis of the pyridodiazepines (**3a, b**) gave **4a, b**, whereas the thienodiazepines (**3c, d**) gave the thienylpyrazoles (**5**) on irradiation *via* a [1, 5] hydrogen shift in the diazepine ring; this mechanism was confirmed by a deuterium-labelling experiment. The 3-acetoxy- (**13a**) and 3-methoxy- (**13b**) 3H-1,2-thienodiazepines were also prepared, and their photolysis afforded 3-vinylpyrazoles (**14**). However, thermolysis or base treatment of **13** resulted in loss of nitrogen to give compounds (**15**) and (**16**).

Keywords——rearrangement; photolysis; thermolysis; deuterium-labelling experiment; 3H-1,2-pyridodiazepines; 3H-1,2-thienodiazepines; pyridopyrazoles; thienopyrazoles; thienylpyrazoles

In previous papers,[3] we have reported that 3H-1,2-benzodiazepines, prepared from their 1H-isomers,[4] undergo both heat- and light-induced rearrangements to give 3-vinylindazoles in high yields. On the other hand, Sharp[5] recently reported that the thermolysis and photolysis of monocyclic 3H-1,2-diazepines take quite different paths; the former gives vinylpyrazoles by rearrangement and the latter gives bicyclic compounds by cyclization. In connection with these results and the similar rearrangements of other nitrogen-containing seven-membered ring systems such as 4H-1,2-diazepines,[6] triazepines,[7] and oxazepines,[8] it seemed of interest to examine analogous reactions of the title compounds as part of our studies on diazepines. We report here the syntheses of 3H-1,2-pyridodiazepines (**3a, b**) and 3H-1,2-thienodiazepines (**3c, d**) from the corresponding 1H-isomers reported in the preceding paper,[1] and describe their photochemical and thermal rearrangements.

The 2,3-dihydro-1H-1,2-diazepines (**2a—d**), prepared by lithium aluminum hydride reduction of the corresponding condensed 1H-1,2-diazepines (**1a—d**),[1] were dehydrogenated with 4-phenyl-1,2,4-triazoline-3,5-dione in benzene to give the desired 3H-1,2-diazepines (**3a—d**) in moderate yields.

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3) J. Kurita and T. Tsuchiya, *J. Chem. Soc. Chem. Commun.*, **1974**, 936; T. Tsuchiya and J. Kurita, *Chem. Pharm. Bull.* (Tokyo), **26**, 1890 (1978).
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6) H. Kolbinger, G. Reissenweber, and J. Sauer, *Tetrahedron Lett.*, **1976**, 4321; D.J. Harris, M.T. Thomas, V. Snieckus, N. Friedman, K. Schaumburg, K.B. Tomer, and O. Buchardt, *Can. J. Chem.*, **55**, 56 (1977).
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9) A part of this work has been published in a preliminary communication: T. Tsuchiya, M. Enkaku, and H. Sawanishi, *J. Chem. Soc. Chem. Commun.*, **1978**, 568.

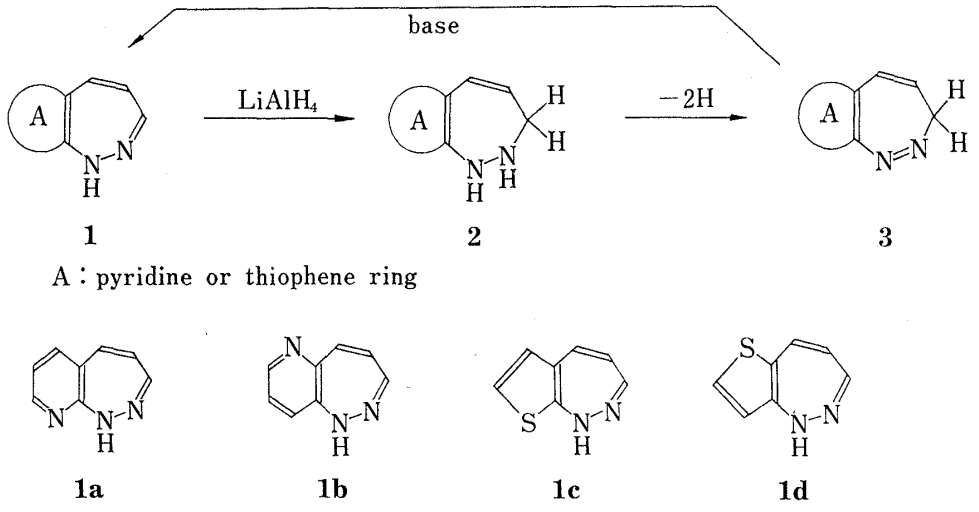

Chart 1

The ^{1}H-nuclear magnetic resonance (NMR) spectral data are consistent with the proposed 3H structures and the tautomeric 2H- and 5H-diazepine structures can be ruled out by analogy with the case of 3H-1,2-benzodiazepines.[3] As stated in the introductory paragraphs, the aza-cycloheptatrienes are known to be extremely susceptible to acid- and base-catalyzed, thermal, and photochemical rearrangements. Therefore, we examined such reactions of the new diazepines (**3**).

The 3H-diazepines (**3a—d**) were readily tautomerized to the parent 1H-diazepines (**1**) by treatment with both bases and acids. Treatment of **3** with sodium methoxide in methanol gave **1** quantitatively, and treatment with dry hydrogen chloride in ether also gave **1** in *ca.* 60% yield.

The 3H-pyridodiazepines (**3a, b**) were irradiated with a halogen lamp to give the corresponding 3-vinyl-pyridopyrazoles (**4a, b**) as the sole products in *ca.* 65% yields. Heating of **3a, b** in refluxing dry xylene also resulted in the formation of the same pyrazoles (**4a, b**)

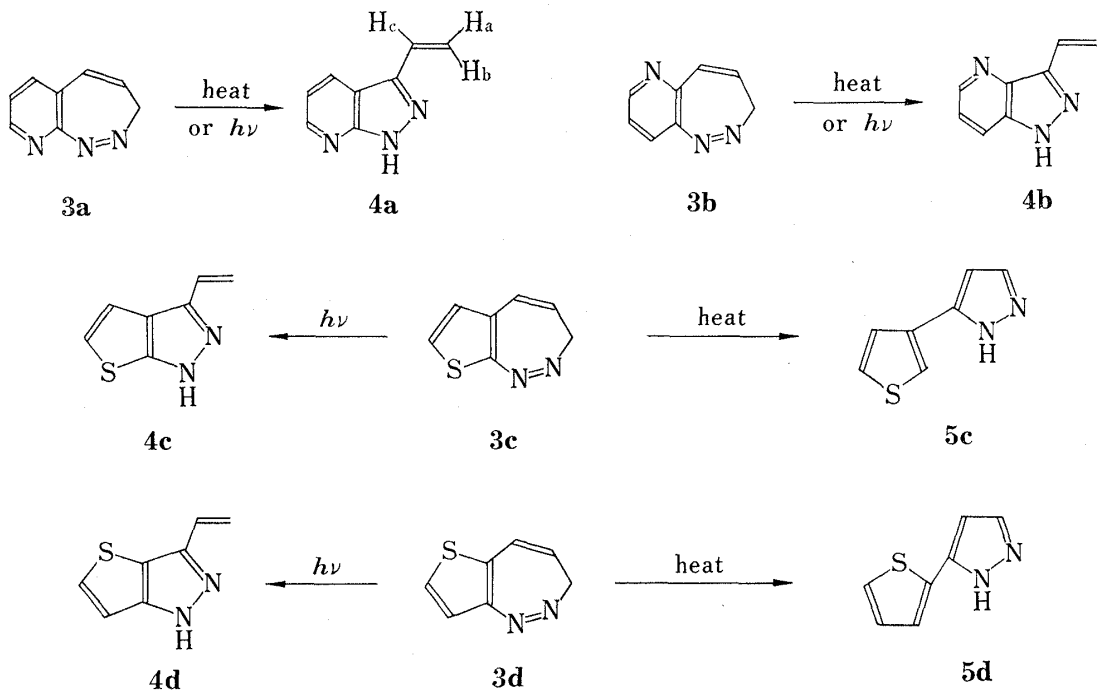

Chart 2

in 80% yields. However, whereas irradiation of the thienodiazepines (**3c**, **d**) yielded the 3-vinylthienopyrazoles (**4c**, **d**) in 60—65% yields analogous to the reactions of pyrido- and benzo-diazepines, thermolysis of **3c**, **d** in refluxing xylene gave different pyrazole derivatives, 3-thienylpyrazoles (**5c**, **d**), in *ca.* 50% yields.

The formation of the 3-vinylpyrazoles (**4**) presumably involves proton transfer of the 3H-pyrazoles (**7**), which are formed *via* the diradical intermediate (**6**) or *via* a concerted process, and not tautomerization to the 5H- or 7H-isomers followed by cyclic addition of the aza-butadiene units to the bicyclic compounds analogous to that observed for 3H-1,2-diazepines[3,5,10] and 2,3-benzodiazepines.[11] However, thermolysis of the thienodiazepines (**3c**, **d**) may involve a thermally allowed [1,5] hydrogen shift in the diazepine ring to give the 7H-isomer (**8**), followed by successive C–N bond fission and ring closure to give the thienylpyrazoles (**5**). This assumption was tested by means of the following deuterium-labelling experiments.

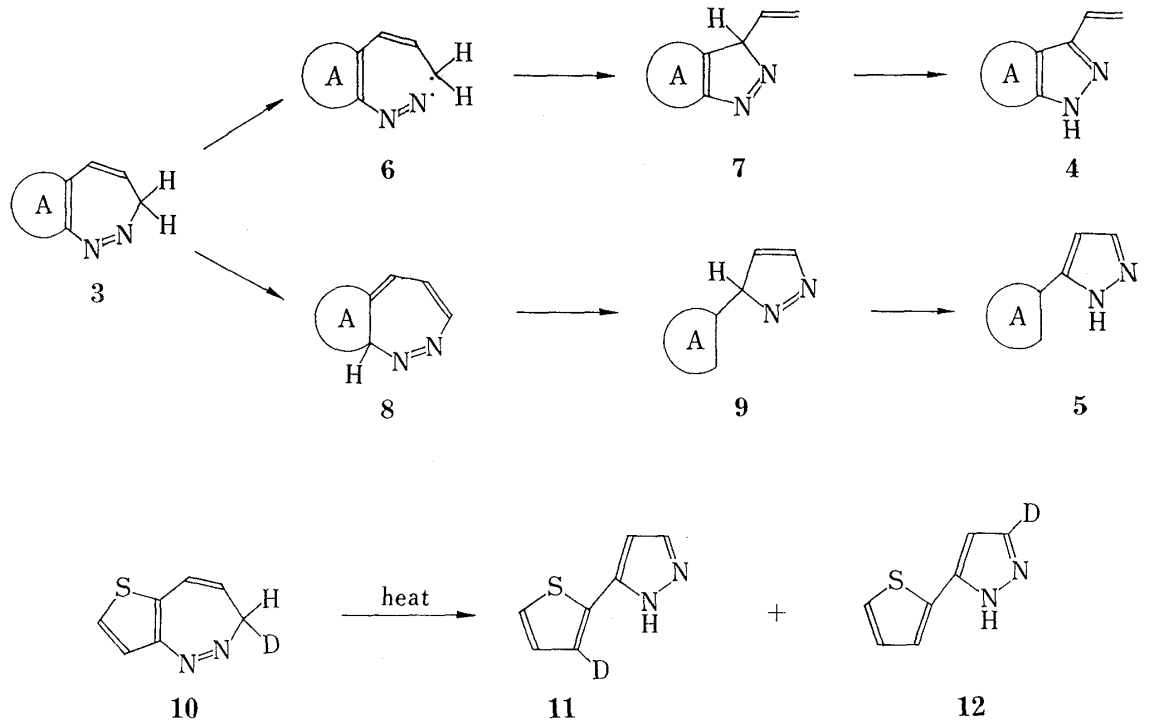

Chart 3

Thermolysis of the deuteriated diazepine (**10**), prepared from **1d** by successive $LiAlD_4$ reduction and dehydrogenation in the manner described for **3**, resulted in the formation of the labelled compounds (**11**) and (**12**) in a ratio of 1 : 3. This ratio was determined by ^1H-NMR spectral analysis and the isotope effect for the tautomerization (3)→(8) ($k_H/k_D=3$), is parallel with that for [1,5] hydrogen and deuterium migration in the other systems such as cyclopentadienes.[12] This result is clearly consistent with the foregoing mechanistic proposal.

Next, the 3-substituted 3H-1,2-thienodiazepines (**13**) were prepared by a method similar to that used for 1,2-benzodiazepines[13] in order to examine this thermolysis in more detail. Namely, the thienodiazepine (**1c**) was treated with lead tetraacetate in dry benzene to give

10) R. McEwan and J.T. Sharp, *J. Chem. Soc. Chem. Commun.*, **1973**, 85; J.D. Done, J.H. Knox, R. McEwan, and J.T. Sharp, *ibid.*, **1974**, 532.
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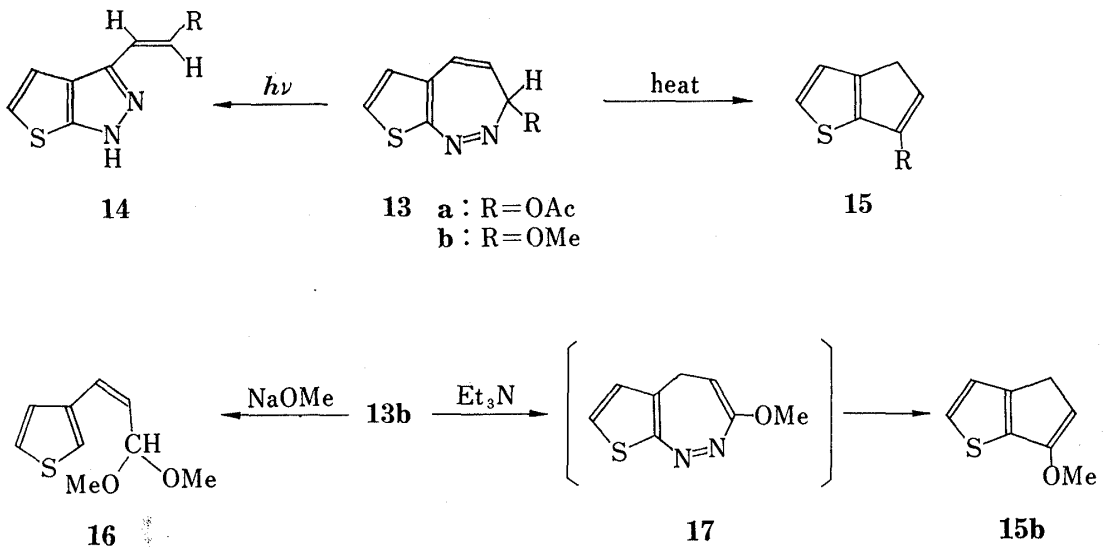

14 **13** **a** : R=OAc, **b** : R=OMe **15**

16 **17** **15b**

Chart 4

the 3-acetoxydiazepine (**13a**) in 36% yield. Treatment of **1c** with cuppric nitrate in methanol resulted in the formation of the 3-methoxydiazepine (**13b**) in 56% yield.

Photolysis of the 3-substituted diazepines (**13a, b**) also gave the corresponding 3-vinylthienopyrazoles (**14a, b**). However, thermolysis of **13** resulted in the formation of the cyclopentenothiophenes (**15a, b**) and yielded no pyrazole derivative. The methoxy compound (**15b**) was readily converted into 6-oxocyclopenta[*b*]thiophene[14] during separation. This result indicates that in the case of thermolysis of **13**, the loss of N_2 from the biradical intermediate (**6**) is much faster than the radical recombination, probably because of substituent effects.

Finally, base treatments of 3-methoxy-3H-diazepine (**13b**) unexpectedly gave different results from those obtained with the 3-unsubstituted diazepines (**3**), which were tautomerized to the parent 1H-isomers. Treatment of **13b** with sodium methoxide gave the ketal (**16**). On the other hand, treatment with triethylamine resulted in the formation of **15b**. The formation of **15b** may involve initial tautomerization to the 5H-diazepine intermediate (**17**), followed by extrusion of nitrogen.

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 JMS-D100 instrument. NMR spectra were recorded on a JEOL JNM-MH100 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard, and 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 spectrophotometer. Microanalyses were performed in the Microanalytical Laboratory of this School by Miss R. Hamano. Photolyses were carried out in an immersion apparatus equipped with a 200W halogen lamp (Ushio-JCV200W-GS), which was cooled internally with running water.

Preparation of 3H-1,2-Diazepines (3a—d)——General procedure: A solution of the 1H-1,2-diazepine (**1**, *ca.* 0.3 g) in ether (50 ml) was added dropwise with stirring to a suspension of $LiAlH_4$ (0.3—0.4 g) in anhydrous ether (20 ml), cooled in an ice bath. After stirring for an additional 30 min under ice cooling, the excess reagent was decomposed with water and the resulting precipitate of inorganic salt was filtered off. The filtrate was dried over $MgSO_4$ and evaporated to dryness *in vacuo* to give the 2,3-dihydrodiazepine derivative (**2**), which was dissolved in benzene (20—30 ml) without further purification. The benzene solution was treated with a solution of 1-phenyl-1,2,4-triazoline-3,5-dione (0.4—0.5 g) in benzene (20 ml) with stirring. After stirring for an additional 1 hr at room temperature, the resulting precipitate was filtered

14) D.W.H. McDowell, T.B. Patrick, B.K. Frame, and D.L. Ellison, *J. Org. Chem.*, 32, 1226 (1967).

off and the filtrate was evaporated to dryness *in vacuo*. The resulting residue was chromatographed on alumina using CH_2Cl_2 as an eluent to give the 3H-diazepine (**3**).

3H-1,2-Pyrido[2,3-*c*]diazepine (**3a**): 65% yield, mp 53.5—55.5°, yellow prisms [from isopropyl ether (IPE)]. MS *m/e*: 145 (M^+). NMR δ: 4.2 (2H, br, 3-H_2), 6.01 (1H, m, 4-H), 6.87 (1H, d, 5-H), 7.37 (1H, dd, 7-H), 7.84 (1H, d, 6-H), 8.66 (1H, d, 8-H), $J_{3,4}=7$, $J_{4,5}=9$, $J_{6,7}=7$, $J_{7,8}=4$ Hz. *Anal.* Calcd. for $C_8H_7N_3$: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.02; H, 4.88; N, 28.77.

3H-1,2-Pyrido[3,2-*c*]diazepine (**3b**): 75% yield, mp 34—36°, pale yellow prisms (from IPE). MS *m/e*: 145 (M^+). NMR δ: 4.2 (2H, br, 3-H_2), 6.05 (1H, m, 4-H), 7.06 (1H, d, 5-H), 7.32 (1H, dd, 8-H), 8.11 (1H, d, 9-H), 8.64 (1H, d, 7-H), $J_{3,4}=7$, $J_{4,5}=9$, $J_{7,8}=4$, $J_{8,9}=8$ Hz. *Anal.* Calcd. for $C_8H_7N_3$: C, 66.19: H, 4.86; N, 28.95. Found: C, 66.16; H, 4.96; N, 28.81.

3H-1,2-Thieno[2,3-*c*]diazepine (**3c**): 45% yield, yellow viscous oil. MS *m/e*: 150 (M^+). NMR δ: 4.2 (2H, br, 3-H_2), 5.51 (1H, m, 4-H), 7.00 (1H, d, 5-H), 7.00 (1H, d, 6-H), 7.39 (1H, d, 7-H), $J_{3'4}=7$, $J_{4,5}=9$, $J_{6,7}=5$ Hz. *Anal.* Calcd. for $C_7H_6N_2S$: C, 56.00; H, 4.03; N, 18.66. Found: C, 56.21; H, 3.96; N, 18.68.

3H-1,2-Thieno[3,2-*c*]diazepine (**3d**): 65% yield, yellow viscous oil. MS *m/e*: 150 (M^+). NMR δ: 4.2 (2H, br, 3-H_2), 5.44 (1H, m, 4-H), 6.99 (1H, d, 5-H), 7.24 (1H, d, 8-H), 7.45 (1H, d, 7 H), $J_{3,4}=7$, $J_{4,5}=9$, $J_{7,8}=5$ Hz. *Anal.* Calcd. for $C_7H_6N_2S$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.93; H, 4.01; N, 18.58.

Treatment of 3 with NaOMe. Isomerization to 1.——A mixture of 3H-diazepine (**3a—d**, 50 mg), NaOMe (10 mg), and MeOH (10 ml) was stirred for 3 hr at room temperature. The reaction mixture was evaporated to dryness *in vacuo* below 30° and the residue was extracted with ether. The extract was washed with water, dried, and concentrated. The residue was purified by chromatography on alumina to give the parent 1H-1, 2-diazepine (**1a—d**) almost quantitatively. These compounds were shown to be identical with authentic samples.

Photolysis of the 3H-Diazepines (3a—d)——A solution of 3H-diazepine (**3**, 100 mg) in CH_2Cl_2 (150 ml, for **3a, b**) or MeOH (150 ml, for **3c, d**) was irradiated with a halogen lamp under a nitrogen atmosphere for 8—12 hr. After removal of the solvent *in vacuo*, the resulting residue was chromatographed on alumina using CH_2Cl_2–MeOH (50: 1) or CH_2Cl_2–AcOEt (10: 1) as an eluent to give the corresponding 3-vinylpyrazole (**4a—d**).

3-Vinyl-1H-pyrido[2,3-*c*]pyrazole (**4a**): *ca.* 70% yield, mp 104—105°, colorless needles (from IPE). MS *m/e*: 145 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3150 (NH). NMR δ: 5.50 (1H, d, Ha), 6.00 (1H, d, Hb), 7.00 (1H, dd, Hc), 7.07 (1H, dd, 5-H), 8.17 (1H, d, 4-H), 8.52 (1H, d, 6-H), 13.5 (1H, br, NH), $J_{a,c}=11$, $J_{b,c}=17$, $J_{4,5}=8$, $J_{5,6}=4$ Hz. *Anal.* Calcd. for $C_8H_7N_3$: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.04; H, 4.81; N, 29.02.

3-Vinyl-1H-pyrido[3,2-*c*]pyrazole (**4b**): 60% yield, mp 162—163°, pale yellow prisms (from IPE). MS *m/e*: 145 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3100 (NH). NMR δ: 5.64 (1H, dd, Ha), 6.69 (1H, dd, Hb), 7.11 (1H, dd, Hc), 7.22 (1H, dd, 6-H), 7.73 (1H, d, 7-H), 8.55 (1H, d, 5-H), 11.4 (1H, br, NH), $J_{a,c}=11$, $J_{b,c}=18$, $J_{a,b}=3$, $J_{5,6}=4$, $J_{6,7}=8$ Hz. *Anal.* Calcd. for $C_8H_7N_3$: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.27; H, 4.79; N, 29.06.

3-Vinyl-1H-thieno[2,3-*c*]pyrazole (**4c**): 60% yield, mp 79—81°, colorless needles (from *n*-hexane). MS *m/e*: 150 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3150 (NH). NMR δ: 5.49 (1H, d, Ha), 5.89 (1H, d, Hb), 6.87 (1H, dd, Hc), 7.06 (2H, s, 4- and 5-H), 11.9 (1H, br, NH), $J_{a,c}=11$, $J_{b,c}=17$ Hz. *Anal.* Calcd. for $C_7H_6N_2S$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.80; H, 4.10; N, 18.38.

3-Vinyl-1H-thieno[3,2-*c*]pyrazole (**4d**): 65% yield, mp 122—123.5°, colorless needles (from IPE). MS *m/e*: 150 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3150 (NH). NMR δ: 5.46 (1H, d, Ha), 5.60 (1H, d, Hb), 6.84 (1H, dd, Hc), 6.85 (1H, d, 6-H), 7.30 (1H, d, 5-H), $J_{a,c}=11$, $J_{b,c}=17$. *Anal.* Calcd. for $C_7H_6N_2S$: C, 56.00; H, 4.03; N, 18.66. Found: C, 56.02; H, 3.94; N, 18.69.

Thermolysis of the 3H-Pyridodiazepines (3a, b)——A solution of diazepine (**3a, b**, 100 mg) in xylene (3 ml) was refluxed for 3—4 hr and the reaction mixture was evaporated to dryness *in vacuo*. The residue was chromatographed over alumina using CH_2Cl_2–MeOH (50: 1) as an eluent to give the corresponding pyridopyrazole (**4a**: 86% and **4b**: 75% yields), which were identical with authentic samples obtained by the photolysis of **3a, b**, respectively.

Thermolysis of the 3H-Thienodiazepines (3c, d)——A solution of diazepine (**3c, d**, 100 mg) in xylene (3 ml) was refluxed for 45 min and the reaction mixture was evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2–AcOEt (10: 1) as an eluent to give the corresponding thienylpyrazole (**5**).

3-(3′-Thienyl)pyrazole (**5c**): 55% yield, mp 107—108°, colorless prisms (from *n*-hexane—IPE). MS *m/e*: 150 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3150 (NH). NMR δ: 6.44 (1H, d, 4-H), 7.3—7.5 (3H, m, 2′-, 4′-, and 5′-H), 7.52 (1H, d, 5-H), 10.6 (1H, br, NH), $J_{4,5}=2.5$ Hz. *Anal.* Calcd. for $C_7H_6N_2S$: C, 56.00; H, 4.03; N, 18.66. Found: C, 56.06; H, 4.00: N, 18.85.

3-(2′-Thienyl)pyrazole (**5d**): 43% yield, mp 96.5—98°, colorless needles (from *n*-hexane—IPE). MS *m/e*: 150 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3150 (NH). NMR δ: 6.37 (1H, d, 4-H), 6.92 (1H, dd, 4′-H), 7.11 (1H, d, 5′-H), 7.20 (1H, d, 3′-H), 7.45 (1H, d, 5-H), 10.8 (1H, br, NH), $J_{4,5}=2.5$, $J_{3',4'}=3.5$, $J_{4',5'}=5$ Hz. *Anal.* Calcd. for $C_7H_6N_2S$: C, 56.00; H, 4.03; N, 18.66. Found: C, 56.25; H, 3.96; N, 18.63.

Preparation of 3-Deuterio-3H-1,2-thieno[3,2-*c*]diazepine (10)——The 1H-diazepine (**1d**, 280 mg) was reacted with $LiAlD_4$ (200 mg) and the products was worked up as described for **3a—d** to give (**10**): 59%

yield, yellow oil. MS *m/e*: 151 (M^+ for $C_7H_5D_1N_2S$). NMR δ: 4.1 (1H, br s, 3-H), 5.44 (1H, dd, 4-H), 7.00 (1H, d, 5-H), 7.24 (1H, d, 7-H), 7.45 (1H, d, 6-H), $J_{3,4}=7$, $J_{4,5}=8$, $J_{6,7}=6$ Hz.

Thermolysis of 10——A solution of **10** (160 mg) in xylene (4 ml) was refluxed for 1 hr and the reaction mixture was evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2–AcOEt (10: 1) as an eluent to give a mixture of 3'-D- (**11**) and 5-D- (**12**) 3-(2'-thienyl)-pyrazole in a ratio of 1: 3 in *ca.* 40% yield. NMR spectrum of the mixture: δ 6.44 (3/4 H, s, 4-H **12**), 6.45 (1/4 H, d, 4-H **11**), 6.95—7.1 (1H, m, 4'-H **11** and **12**), 7.19 (1H, d, 5'-H **11** and **12**), 7.27 (3/4 H, d, 3'-H **12**), 7.54 (1/4 H, d, 5-H **11**).

Preparation of 3-Acetoxy-3H-1,2-thieno[2,3-*c*]diazepine (13a)——A solution of $Pb(OAc)_4$ (3.23 g, 6.6 mmol) in dry benzene (150 ml) was added dropwise with stirring to a solution of the 1H-diazepine (**1c**, 820 mg, 5.5 mmol) in dry benzene (16 ml), cooled in an ice bath. After stirring for an additional 10 min, the excess reagent was decomposed with water and the resulting precipitate was filtered off. The filtrate was successively washed with satd. $NaHCO_3$ and satd. NaCl, then dried, and concentrated *in vacuo* below 20°. The residue was chromatographed on alumina using ether as an eluent to give **13a**: 36% yield, mp 90—91°, yellow prisms (from IPE). MS *m/e*: 180 [$(M-N_2)^+$]. IR ν_{max}^{KBr} cm^{-1}: 1750 (C=O). NMR δ: 2.28 (3H, s, OAc), 4.65 (1H, dd, 3-H), 5.39 (1H, dd, 4-H), 6.74 (1H, dd, 5-H), 6.83 (1H, d, 6-H), 7.25 (1H, d, 7-H). *Anal.* Calcd. for $C_9H_8N_2O_2S$: C, 51.92; H, 3.86; N, 13.46. Found: C, 52.03; H, 3.85; N, 13.39.

3-Methoxy-3H-1,2-thieno[3,2-*c*]diazepine (13b)——A mixture of **1c** (500 mg, 3.3 mmol), anhydrous cupric nitrate (675 mg, 3.6 mmol), and abs. MeOH (70 ml) was stirred for 1 hr at room temperature. The mixture was concentrated *in vacuo* below 15° and the residue was extracted with ether. The extract was successively washed with satd. $NaHCO_3$ and satd. NaCl, then dried, and concentrated. The residue was chromatographed on alumina using *n*-hexane–ether (1: 1) as an eluent to give **13b**: 56% yield, yellow oil. MS *m/e*: 152 [$(M-N_2)^+$]. NMR δ: 3.38 (1H, dd, 3-H), 3.82 (3H, s, OMe), 5.51 (1H, dd, 4-H), 6.84 (1H, dd, 5-H), 7.00 (1H, d, 6-H), 7.42 (1H, d, 7-H). *Anal.* Calcd. for $C_8H_8N_2OS$: C, 53.33; H, 4.48; N, 15.55. Found: C, 53.18; H, 4.51; N, 15.50.

Photolysis of 13a, b——A solution of **13** (150 mg) in MeOH (150 ml) was irradiated with a halogen lamp for 2.5 hr. After removal of the solvent *in vacuo* below 20°, the residue was chromatographed on silica gel using CH_2Cl_2–AcOEt (10: 1) as an eluent to give **14**.

3-(2'-Acetoxyvinyl)-1H-thieno[2,3-*c*]pyrazole (**14a**): 28% yield, mp 116—118°, colorless granules (from *n*-hexane–IPE). MS *m/e*: 208 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1740 (C=O), 3300 (NH). NMR δ: 2.23 (3H, s, OAc), 6.53 (1H, d, 1'-H), 7.04 (2H, s, 4- and 5-H), 8.01 (1H, d, 2'-H), 6.9 (1H, br, NH), $J_{1',2'}=13$ Hz. *Anal.* Calcd. for $C_9H_8N_2O_2S$: C, 51.92; H, 3.86; N, 13.46. Found: C, 51.82; H, 3.88; N, 13.43.

3-(2'-Methoxyvinyl)-1H-thieno[2,3-*c*]pyrazole (**14b**): 35% yield, mp 120—121°, colorless needles (from IPE). MS *m/e*: 180 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3150, 3200 (NH). NMR δ: 3.72 (3H, s, OMe), 5.90 (1H, d, 1'-H), 6.92 (2H, s, 4- and 5-H), 7.25 (1H, d, 2'-H), 10.9 (1H, br, NH). *Anal.* Calcd. for $C_8H_8N_2OS$: C, 53.32; H, 4.47; N, 15.54. Found: C, 53.55; H, 4.47; N, 15.66.

Thermolysis of 13a——A solution of **13a** (300 mg) in xylene (5 ml) was refluxed for 2 hr, then the reaction mixture was concentrated *in vacuo*. The residue was distilled to give 6-acetoxy-4H-cyclopenteno[*b*]-thiophene (**15a**): *ca.* 25% yield, bp 95—100°/bath temp. (2.5 mmHg), colorless oil. MS *m/e*: 180 (M^+). IR ν_{max}^{film} cm^{-1}: 1760 (C=O). NMR δ: 2.28 (3H, s, OAc), 3.25 (2H, d, 4-H_2), 6.17 (1H, dd, 5-H), 7.01 (1H, d, 3-H), 7.24 (1H, d, 2-H), $J_{2,3}=5$, $J_{4,5}=3$ Hz. *Anal.* Calcd. for $C_9H_8O_2S$: C, 60.00; H, 4.48. Found: C, 60.18; H, 4.45.

Thermolysis of 13b——A solution of **13b** (300 mg) in benzene (5 ml) was refluxed for 30 min, then the reaction mixture was concentrated *in vacuo* to yield 6-methoxy-4H-cyclopenteno[*b*]thiophene (**15b**), the identity of which was confirmed by the ^1H-NMR spectrum of the resulting residue [δ: 3.10 (2H, d, 4-H_2), 3.72 (3H, s, OMe), 5.20 (1H, dd, 5-H), 2.95 (1H, d, 3-H), 7.15 (1H, d, 2-H). However, the compound (**15b**) was readily converted into 6-oxo-cyclopenta[b]thiophene, *ca.* 55% yield, mp 93—94° (lit.[14] 92—93°), colorless needles from IPE, during purification by chromatography on silica gel or alumina.

Treatment of 13b with NaOMe——A mixture of **13b** (50 mg), NaOMe (20 mg), and abs. MeOH (5 ml) was stirred for 40 hr at room temperature. Ether (100 ml) was added, then the solution was washed with satd. NaCl, dried over $MgSO_4$, and concentrated *in vacuo* below 20°. The residue was chromatographed on silica gel using *n*-hexane–ether (5: 1) as an eluent to give the acetal (**16**): *ca.* 25% yield, yellow oil. MS *m/e*: 184 (M^+). NMR δ: 3.37 (6H, s, OMe), 5.21 (1H, d, 3'-H), 5.68 (1H, dd, 2'-H), 6.66 (1H, d, 1'-H), 7.18 (1H, d, 4-H), 7.33 (1H, d, 5-H), 7.44 (1H, s, 2-H), $J_{1',2'}=12$, $J_{2',3'}=6$, $J_{4,5}=5$ Hz. *Anal.* Calcd. for $C_9H_{12}O_2S$: C, 58.69; H, 6.57. Found: C, 58.84; H, 6.41.

Treatment of 13b with Triethylamine——A mixture of **13b** (100 mg), triethylamine (100 mg), and dry benzene (10 ml) was stirred for *ca.* 2 hr under ice cooling. After removal of the solvent *in vacuo*, the residue was distilled under reduced pressure to give **15b** in *ca.* 35% yield.

Acknowledgement A part of this work was supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture, Japan, which is gratefully acknowledged.