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Studies on Diazepines. XX.[1] Acylations of 1*H*-1,2-Thienodiazepines and 1*H*-1,2-Benzodiazepines

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Treatment of the *N*-unsubstituted 3-methyl-1*H*-1,2-thieno[2,3-*c*]diazepine (**3**) with ethyl chloroformate, acetyl chloride, or benzoyl chloride in benzene resulted in ring-conversion to give the corresponding 3-acyl-3*H*-1,3-thieno[2,3-*d*]diazepines (**4**), whereas similar treatment of the *N*-substituted thieno[2,3-*c*]diazepine (**6**) gave the *exo*-methylene compound (**7**) and treatment of the fully unsubstituted thieno[2,3-*c*]diazepine (**8**) gave the thieno[2,3-*b*]pyridine derivatives (**9**) and (**10**). On the other hand, the *N*-unsubstituted 3-methyl-1*H*-1,2-benzo[*c*]diazepines (**16**), upon treatment with ethyl chloroformate in benzene, gave the *exo*-methylene compounds (**17**), and in the case of the diazepines (**16b, c**) having an electron-donating group in the 7-position, the 3-acyl-3*H*-1,3-benzo[*d*]diazepines (**19**) were also formed. The mechanisms of these acylations are discussed.

Keywords——acylation; ring-conversion; 1*H*-1,2-thieno[2,3-*c*]diazepine; 3*H*-1,3-thieno[2,3-*d*]diazepine; 1*H*-1,2-benzo[*c*]diazepine; 3*H*-1,3-benzo[*d*]diazepine

Recently, the chemistry of unsaturated seven-membered heterocycles has been widely investigated.[2] We have reported the syntheses and thermal and photochemical reactions of novel fused 1,2-,[3,4] 1,3-,[5-7] and 2,3-diazepines[1] condensed with aromatic rings such as benzene, pyridine, thiophene, furan, and pyrrole.

Monocyclic 4*H*-1,2-diazepines[8] and 5*H*-2,3-benzodiazepines[1] are known to undergo tautomerization with acetylation on treatment with acetyl chloride or acetic anhydride to give the corresponding 1-acetyl-1*H*-1,2-diazepines or 3-acetyl-3*H*-2,3-benzodiazepines. The acylations of 5*H*-2,3-benzodiazepines have also afforded various results depending on the acylating reagents and reaction conditions.[9] As for 1,2-benzodiazepines and related fused 1,2-diazepines, reductions,[3] oxidations,[10] and rearrangements[11] have been well studied, whereas their acylations have received little attention. Previously, we reported that the *N*-unsubstituted 1*H*-1,2-benzo[*c*]- (**1a**)[3,10a] and 1*H*-1,2-thieno[2,3-*c*]-diazepines (**1b**),[7] upon treatment with ethyl chloroformate or methyl iodide in the presence of *n*-butyllithium, give the corresponding 1-substituted 1*H*-1,2-diazepines (**2**).

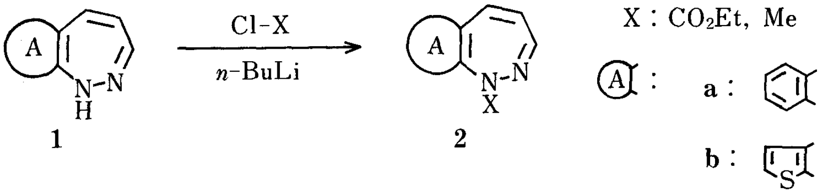
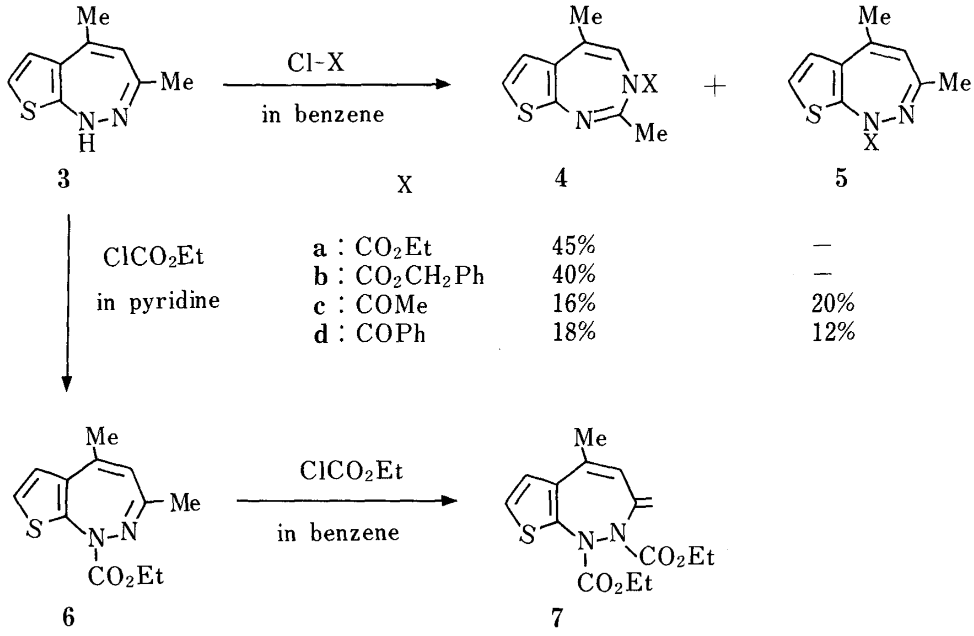


Chart 1

In connection with the above results for monocyclic 1,2-diazepines and 2,3-benzodiazepines, we examined the acylation of the title diazepines in more detail and now report our new results, including the first examples of the ring-conversion of 1,2-diazepines into 1,3-diazepines by acylating reagents.[12]

Acylations of 1*H*-1,2-Thienodiazepines

Treatment of 3,5-dimethyl-1*H*-1,2-thieno[2,3-*c*]diazepine (**3**),[7] prepared photochemically from 4,6-dimethylthieno[2,3-*b*]pyridine *N*-imine, with ethyl chloroformate in anhydrous benzene resulted in rearrangement with ring-conversion to give the 3-ethoxycarbonyl-3*H*-1,3-thieno[2,3-*d*]diazepine (**4a**) in 45% yield as the sole product. A similar result was obtained with benzyl chloroformate; the 3-benzyloxycarbonyl compound (**4b**) was obtained in 40% yield. However, treatment of **3** with acetyl chloride and benzoyl chloride in benzene gave the corresponding 3-acyl-3*H*-1,3-diazepines (**4**) and 1-acyl-1*H*-1,2-diazepines (**5**), respectively, in the yields shown in Chart 2. However, no reaction was obtained with acetic anhydride, tosyl chloride, or methyl iodide even on heating at 60—70 °C for 8—10 h.



X	4	5
a : CO_2Et	45%	–
b : CO_2CH_2Ph	40%	–
c : COMe	16%	20%
d : COPh	18%	12%

Chart 2

Treatment of the 1*H*-1,2-diazepine (**3**) with ethyl chloroformate in pyridine instead of benzene afforded only the 1-ethoxycarbonyl-1*H*-1,2-thieno[2,3-*c*]diazepine (**6**),[7] analogously to the reaction in the presence of *n*-butyllithium. In contrast to the case of the *N*-unsubstituted diazepine (**3**), treatment of the *N*-substituted diazepine (**6**) with ethyl chloroformate in benzene resulted in the formation of the 1,2-diethoxycarbonyl-3-*exo*-methylene compound (**7**) in 70% yield as the sole product and gave no other diazepine derivatives.

On the other hand, fully unsubstituted 1*H*-1,2-thieno[2,3-*c*]diazepine (**8**),[4] upon treatment with ethyl chloroformate or acetyl chloride in benzene, underwent rearrangement with ring-contraction to give two kinds of thieno[2,3-*b*]pyridines, 6-acylaminothienopyridines (**9**) and thienopyridine *N*-acylimides (**10**), in *ca.* 10 and 15% yields, respectively, but no diazepine derivatives. In addition, when ethanol was used as a solvent instead of benzene the 2-ethoxycarbonyl-3-ethoxy-2,3-dihydrothieno[2,3-*c*]diazepine (**11**) was obtained in 20% yield, together with **9a**. In this case, no other diazepine could be obtained.

These results indicate that the presence of a substituent at the 3-position of the diazepine ring is required for the ring-conversion of 1,2-diazepines into 1,3-diazepines. A possible mechanism for the present reactions is shown in Chart 4.

These reactions may proceed by initial formation of the 2-acyl salts (**12**), which then rearrange to the diaziridine intermediates (**13**) in the case of 1-unsubstituted diazepines (**3** and **8**, Y = H in **12**). The diaziridines (**13**) may then undergo either N–N bond fission (path a) or C–N bond cleavage (path b); the latter gives the thienopyridine *N*-acylimides (**10**) and the

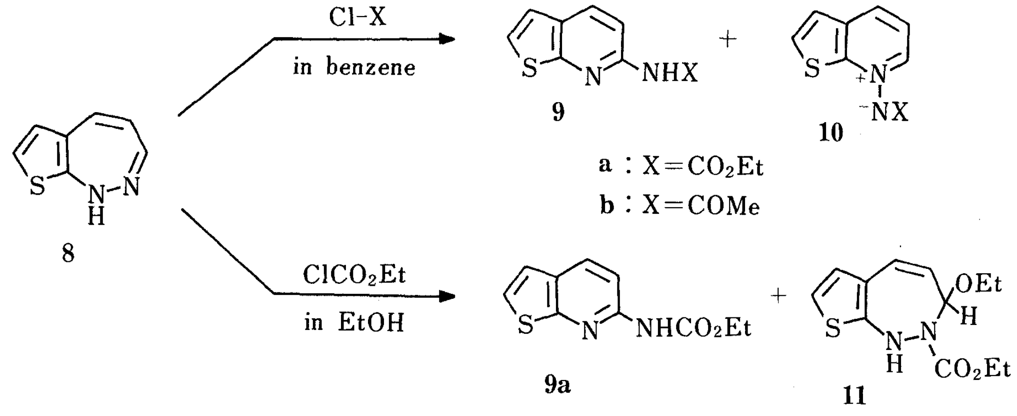


Chart 3

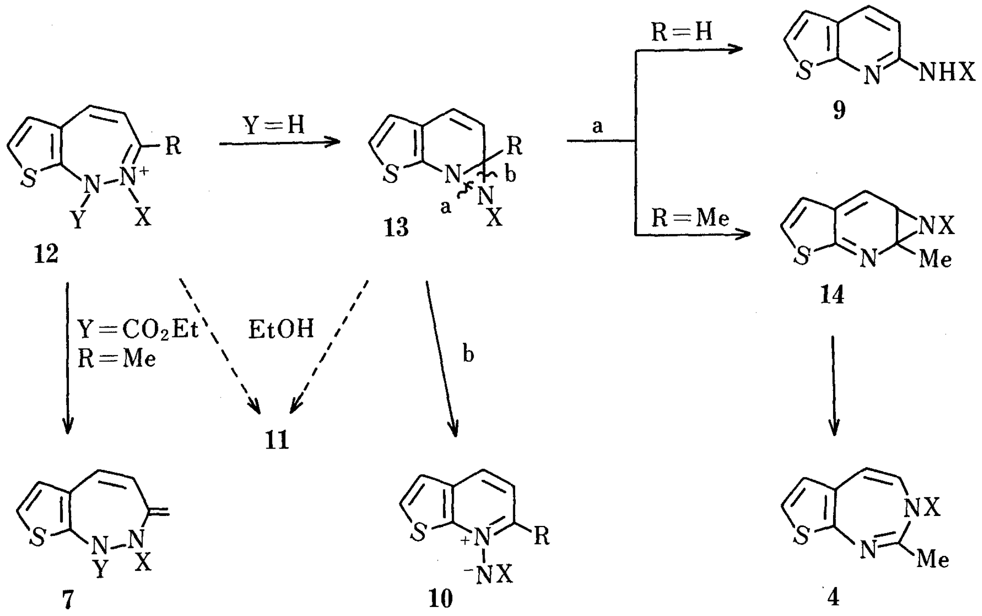


Chart 4

former affords either the 2-aminopyridines (**9**) in the case of R = H, or the 1,3-diazepines (**4**) by ring-expansion *via* the aziridine intermediates (**14**) in the case of R = Me. This substituent effect is analogous to that in the direct photochemical formation of condensed 1,3-diazepines from the corresponding fused pyridine *N*-imides.[5-7]

Acylations of 1*H*-1,2-Benzo[*c*]diazepines

Fully unsubstitued 1*H*-1,2-benzo[*c*]diazepine underwent ring-contraction on treatment with acylating reagents to give quinoline *N*-acylimides. This result is analogous to those for the thieno[2,3-*c*]diazepine (**8**). However, the acylation of 3-methyl-1*H*-1,2-benzo[*c*]diazepines (**16**) gave somewhat different results from those for the 3-methylthieno[2,3-*c*]diazepine (**3**).

The 3-methylbenzo[*c*]diazepines (**16a**—**c**) were prepared from the corresponding *N*-aminoquinolinium mesitylenesulfonates (**15**)[13] by irradiation in methanol in the presence of potassium hydroxide. 3-Methyl-1*H*-1,2-benzo[*c*]diazepine (**16a**) having no substituent in the benzene ring, upon treatment with ethyl chloroformate in benzene at room temperature, gave the *exo*-methylene compound (**17a**) and 2-methylquinoline *N*-ethoxycarbonylimide (**18a**) in 52 and 6% yields, but no 1,3-diazepine was obtained. However, the benzodiazepines (**16b, c**) having an electron-donating group such as a methyl or methoxy group at the 7-position gave the 3-ethoxycarbonyl-3*H*-1,3-benzo[*d*]diazepines (**19b, c**), in addition to the *exo*-methylene

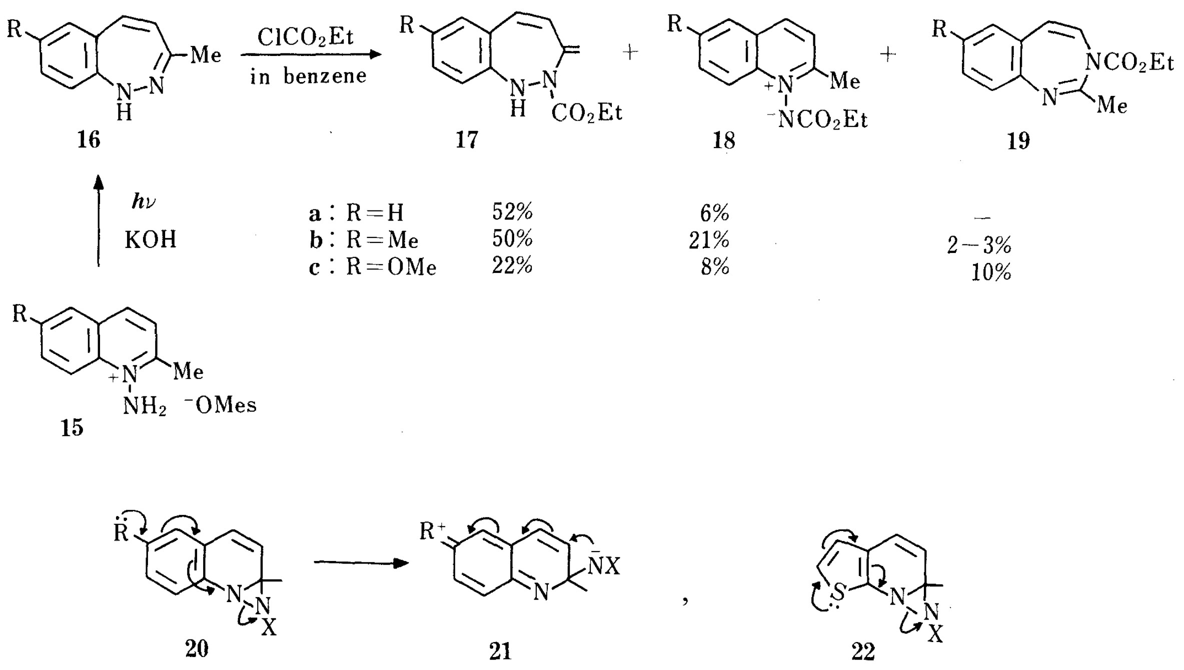


Chart 5

compounds (**17**) and the quinoline *N*-imides (**18**) in the yields shown in Chart 5.

In this *N*-unsubstituted benzo-series, the reaction could proceed by two competing pathways from the initially formed 2-acyl salts: i) deprotonation of the methyl group to give **17**, and ii) elimination of the NH proton to give **18** and **19** *via* the diaziridine intermediates, in contrast to the case of the thieno[2,3-*c*]diazepines (**12**). The substituent effect on this ring-conversion is illustrated by structures **20**—**22**. The electron-donating groups may provide assistance for breaking the N–N bond in the diaziridine (**20**) and for cyclization of the resulting dipolar intermediate (**21**) into aziridine. This effect is analogous to those observed in the thermal ring-conversion of monocyclic 1,2-diazepines into 1,3-diazepines[14] and the photochemical direct formation of 1,3-benzodiazepines from quinoline *N*-acylimides.[13] The formation of the 3*H*-1,3-thieno[2,3-*d*]diazepines (**4**) from the intermediates (**13**) can also be explained by a similar effect due to the sulfur atom in the thiophene ring as shown in the structure **22**.

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 spectra (MS) were recorded on a JEOL D-100 instrument. Proton nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-MH-100 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard; 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.

1*H*-1,2-Thienodiazepines (3 and 8)——3,5-Dimethyl-1*H*-1,2-thieno[2,3-*c*]diazepine (**3**)[7] and 1*H*-1,2-thieno[2,3-*c*]diazepine (**8**)[4] were prepared by the reported methods.

Acylations of the Thienodiazepine (3) in Benzene——a) With Ethyl Chloroformate: A solution of ethyl chloroformate (90 mg, 1.1 mol eq) in anhydrous benzene (5 ml) was added dropwise with stirring to a solution of **3** (125 mg) in benzene (8 ml). The reaction solution was stirred for an additional 2 h at room temperature and then 50% aq. K_2CO_3 (0.2 ml) was added to the solution. After vigorous stirring for 10 min, the mixture was diluted with CH_2Cl_2 (100 ml), then dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel using ether-*n*-hexane (1 : 3) as an eluent to give 3-ethoxycarbonyl-2,5-dimethyl-3*H*-1,3-thieno[2,3-*d*]diazepine (**4a**): 85 mg, 45% yield, mp 67—69 °C. This product was identical with an authentic sample.[7]

b) With Benzyl Chloroformate: A solution of benzyl chloroformate (30% w/w in toluene, 350 mg, 1.1 mol eq) in benzene (3 ml) was added dropwise with stirring to a solution of **3** (100 mg) in benzene (5 ml). The mixture was stirred for an additional 3 h and then worked up as described for procedure a) to give the 3-benzyloxycarbonyl-1,3-thieno[2,3-*d*]diazepine (**4b**): 70 mg, 40% yield, pale yellow oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1710 (C=O). MS *m*/*e*: 312 (M$^+$). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 227 (13300), 255 (sh), 300 (3000). NMR δ: 2.06 (3H, br d, 5-Me), 2.42 (3H, s, 2-Me), 5.18 (2H, s, –CH$_2$Ph), 5.77 (1H, m, 4-H), 6.93 (1H, d, 6-H), 7.04 (1H, d, 7-H), 7.33 (5H, s, Ph-H), $J_{6,7}=6$ Hz. *Anal.* Calcd for $C_{17}H_{16}N_2O_2S$: C, 65.36; H, 5.16; N, 8.97. Found: C, 65.53; H, 5.11; N, 8.80.

c) With Acetyl Chloride: A solution of acetyl chloride (48 mg, 1.1 mol eq) in benzene (2 ml) was added dropwise with stirring to a solution of **3** (100 mg) in benzene (5 ml). The reaction solution was stirred for an additional 2 h and then worked up as described for procedure a) to give the 1-acetyl-1,2-diazepine (**5c**: 25 mg, 20% yield, mp 102—104 °C) and the 3-acetyl-1,3-diazepine (**4c**: 20 mg, 16% yield, pale yellow oil) successively. These products were identified by comparison with authentic samples.[7)]

d) With Benzoyl Chloride: A solution of benzoyl chloride (87 mg, 1.1 mol eq) in benzene (2 ml) was added dropwise with stirring to a solution of **3** (100 mg) in benzene (5 ml). The reaction solution was stirred for an additional 3 h and then worked up as described for procedure a) to give the 3-benzoyl-1,3-diazepine (**4d**: 29 mg, 18% yield, colorless oil) and the 1-benzoyl-1,2-diazepine (**5d**: 19 mg, 12% yield, colorless oil) successively. These products were identified by comparison with authentic samples.[7)]

Treatment of the Thienodiazepine (3) with Ethyl Chloroformate in Pyridine——A mixture of **3** (100 mg), ethyl chloroformate (50 mg), and pyridine (5 ml) was stirred for 2 h at room temperature. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using ether–*n*-hexane (3 : 1) as an eluent to give 1-ethoxycarbonyl-3,5-dimethyl-1*H*-1,2-thieno[2,3-*c*]diazepine (**6**): 59 mg, 42% yield, mp 134—135 °C. This product was identical with an authentic sample.[7)]

Treatment of the Thienodiazepine (6) with Ethyl Chloroformate in Benzene——Ethyl chloroformate (1 ml) was added dropwise with stirring to a solution of **6** (40 mg) in benzene (8 ml) at room temperature and the solution was then heated at 50 °C for 6 h. After cooling, the reaction solution was diluted with CH_2Cl_2 (50 ml). The mixture was successively washed with aq. sat. $NaHCO_3$ and aq. sat. NaCl, then dried and concentrated *in vacuo*. The residue was chromatographed on silica gel using ether–*n*-hexane (1 : 2) as an eluent to give the *exo*-methylene compound (**7**): 36 mg, 70% yield, pale yellow oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1725 (C=O). MS *m*/*e*: 322 (M$^+$). NMR δ: 1.23 (3H, t, 2-$CO_2CH_2C\underline{H}_3$), 1.31 (3H, t, 1-$CO_2CH_2C\underline{H}_3$), 2.16 (3H, br d, 5-Me), 4.0—4.4 (4H, m, 1- and 2-$CO_2C\underline{H}_2CH_3$), 5.13 (2H, br s, =CH_2), 6.16 (1H, br, 4-H), 6.85 (1H, d, 6-H), 7.03 (1H, d, 7-H), $J_{6,7}=5$ Hz. *Anal.* Calcd for $C_{15}H_{18}N_2O_4S$: C, 55.89; H, 5.63; N, 8.69. Found: C, 55.68; H, 5.65; N, 8.70.

Acylations of 1*H*-1,2-Thieno[2,3-*c*]diazepine (8)——a) With Ethyl Chloroformate in Benzene: A solution of ethyl chloroformate (175 mg, 1.1 mol eq) in benzene (5 ml) was added dropwise with stirring to a solution of **8** (220 mg) in benzene (5 ml). The reaction solution was stirred for an additional 30 min at room temperature and then aq. 50% K_2CO_3 (0.2 ml) was added to the solution. After stirring for 10 min, the mixture was diluted with CH_2Cl_2 (100 ml), then dried and concentrated *in vacuo*. The residue was chromatographed on silica gel. Elution with ether–*n*-hexane (1 : 5) gave 6-ethoxycarbonylaminothieno[2,3-*b*]pyridine (**9a**) and further elution with CH_2Cl_2–acetone (3 : 1) afforded the thienopyridine *N*-ethoxycarbonylimide (**10a**).

9a: 32 mg, *ca.* 10% yield, mp 93.5—95 °C, colorless needles (from isopropyl ether–*n*-hexane). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1725 (C=O), 3225 (NH). MS *m*/*e*: 222 (M$^+$). NMR δ: 1.28 and 4.26 (3H, t, and 2H, q, CO_2Et), 7.13 (1H, d, 3-H), 7.27 (1H, d, 2-H), 7.97 (1H, d, 4-H), 8.09 (1H, d, 5-H), 8.6 (1H, br, NH), $J_{2,3}=5$, $J_{4,5}=8$ Hz. *Anal.* Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.54; N, 12.60. Found: C, 54.27; H, 4.55; N, 12.65.

10a: 26 mg, 8% yield, mp 127—128 °C, yellow prisms (from benzene–isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1640 (C=O). MS *m*/*e*: 222 (M$^+$). NMR δ: 1.37 and 4.23 (3H, t, and 2H, q, CO_2Et), 7.37 (1H, d, 3-H), 7.51 (1H, dd, 5-H), 7.60 (1H, d, 2-H), 8.08 (1H, d, 4-H), 9.47 (1H, d, 6-H), $J_{5,6}=6$, $J_{4,5}=8$, $J_{2,3}=5$ Hz. *Anal.* Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.54; N, 12.60. Found: C, 53.88; H, 4.34; N, 12.50.

b) With Acetyl Chloride in Benzene: A solution of acetyl chloride (115 mg, 1.1 mol eq) in benzene (3 ml) was added dropwise with stirring to a solution of **8** (200 mg) in benzene (10 ml). The solution was stirred for an additional 35 min at room temperature and then worked up as described for procedure a) to give 6-acetylaminothieno[2,3-*b*]pyridine (**9b**) and the thieno[2,3-*b*]pyridine *N*-acetylimide (**10b**).

9b: 32 mg, 14% yield, mp 155—156 °C, colorless prisms (from benzene–*n*-hexane), IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1670 (C=O), 3250 (NH). MS *m*/*e*: 192 (M$^+$). NMR δ: 2.23 (3H, s, COMe), 7.18 (1H, d, 3-H), 7.32 (1H, d, 2-H), 8.02 (1H, d, 4-H), 8.26 (1H, d, 5-H), 8.85 (1H, br, NH), $J_{4,5}=8$, $J_{2,3}=5$ Hz. *Anal.* Calcd for $C_9H_8N_2OS$: C, 56.23; H, 4.20; N, 14.57. Found: C, 56.40; H, 4.23; N, 14.68.

10b: 45 mg, 18% yield, mp 148—149 °C, colorless plates (from benzene–isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1570 (C=O). MS *m*/*e*: 192 (M$^+$). NMR δ: 2.16 (3H, s, COMe), 7.40 (1H, d, 3-H), 7.53 (1H, dd, 5-H), 7.60 (1H, d, 2-H), 8.18 (1H, d, 4-H), 9.13 (1H, d, 6-H), $J_{2,3}=5$, $J_{4,5}=8$, $J_{5,6}=6$ Hz. *Anal.* Calcd for $C_9H_8N_2OS$: C, 56.23; H, 4.20; N, 14.57. Found: C, 56.31; H, 4.20; N, 14.63.

c) With Ethyl Chloroformate in Ethanol: A solution of ethyl chloroformate (120 mg, 1.1 mol eq) in ethanol (2 ml) was added dropwise with stirring to a solution of **8** (150 mg) in ethanol (5 ml) in an ice bath. The reaction solution was stirred for an additional 30 min at room temperature and then aq. 50% K_2CO_3 (0.2 ml) was added to the solution. After stirring for 10 min, the mixture was diluted with CH_2Cl_2 (100 ml), then dried and evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel using ether–*n*-hexane (1 : 4) as an eluent to give **9a** (22 mg, 10% yield) and 3-ethoxy-2-ethoxycarbonyl-2,3-dihydro-1*H*-1,2-thieno[2,3-*c*]diazepine (**11**) successively.

11: 91 mg, 34% yield, mp 60—62 °C, colorless prisms (from isopropyl ether–*n*-hexane). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 1670 (C=O). MS *m*/*e*: 268 (M^+). NMR δ: 1.24 (3H, t, 3-$OCH_2C\underline{H}_3$), 1.29 and 4.14 (3H, t, and 2H, q, CO_2Et), 3.6—3.9 (3H, m, 3-H and 3-$OC\underline{H}_2CH_3$), 5.78 (1H, dd, 4-H), 6.47 (1H, d, 5-H), 6.62 (1H, d, 6-H), 6.71 (1H, d, 7-H), $J_{3,4}=4$, $J_{4,5}=12$ Hz. *Anal.* Calcd for $C_{12}H_{16}N_2O_3S$: C, 53.71; H, 6.01; N, 10.44. Found: C, 53.90; H, 6.04; N, 10.28.

Preparation of the 1*H*-1,2-Benzo[*c*]diazepines (16a—c)——General Procedure: The *N*-aminoquinolinium mesitylenesulfonates (**15a—c**) were prepared from the corresponding quinolines by *N*-amination with *O*-mesitylenesulfonylhydroxylamine according to the reported method.[13] A solution of KOH (2—3 mol eq) in methanol (10 ml) was added dropwise to a stirred suspension of a salt (**15a—c**: 3—5 g) in CH_2Cl_2 (300—350 ml) during 10 min under irradiation. The photolysis was followed in terms of the disappearance of the ultraviolet (UV) absorption at *ca.* 250 nm due to the salt (**15**) or the imine formed from **15** by treatment with the base, and was complete in 1—3 h. The reaction mixture was concentrated *in vacuo* below 25 °C and the residue was extracted with ether. The extract was washed with aq. sat. NaCl, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel using ether–*n*-hexane mixture as an eluent to give the corresponding parent quinoline derivative (10—20% yield) and the 1*H*-1,2-diazepine (**16**), successively.

16a: 60% yield, mp 62—63 °C, yellow needles (from isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 3270 (NH). MS *m*/*e*: 158 (M^+). NMR δ: 1.95 (3H, s, 3-Me), 5.98 (1H, d, 4-H), 6.72 (1H, d, 5-H). 6.4 (1H, br, NH), 6.5—7.1 (4H, m, Ar-H), $J_{4,5}=11$ Hz. *Anal.* Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.86; H, 6.41; N, 17.61.

16b: 58% yield, mp 104—105 °C, orange prisms (from isopropyl ether–*n*-hexane). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 3250 (NH). MS *m*/*e*: 172 (M^+). NMR δ: 1.98 (3H, s, 3-Me), 2.26 (3H, s, 7-Me), 6.16 (1H, d, 5-H), 6.6—7.1 (4H, m, 4- and Ar-H), $J_{4,5}=11$ Hz. *Anal.* Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.03; N, 16.26. Found: C, 76.70; H, 6.91; N, 16.29.

16c: 37% yield, mp 116—117 °C, red needles (from isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 3275 (NH). MS *m*/*e*: 188 (M^+). NMR δ 2.00 (3H, s, 3-Me), 3.80 (3H, s, 7-OMe), 6.21 (1H, d, 5-H), 6.4 (1H, br, NH), 6.6—6.8 (3H, m, Ar-H), 6.91 (1H, d, 4-H), $J_{4,5}=11$ Hz. *Anal.* Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.88. Found: C, 70.02; H, 6.51; N, 14.98.

Treatment of the Benzo[*c*]diazepines (16a—c) with Ethyl Chloroformate in Benzene——General Procedure: A solution of ethyl chloroformate (1.1 mol eq) in benzene (2—3 ml) was added dropwise to a solution of a 1*H*-1,2-diazepine (**16a—c**: 200—300 mg) in benzene (5—10 ml) with stirring. The reaction solution was stirred for an additional 2—3 h and then worked up as described for **3**. The resulting residue was chromatographed on silica gel. Elution with CH_2Cl_2–*n*-hexane (1 : 1) gave the *exo*-methylene compound (**17**) and the 1,3-diazepine (**19**) successively. Further elution with CH_2Cl_2–methanol (10 : 1) gave the quninoline *N*-imide (**18**). The yields of these products are shown in Chart 5.

17a: Yellow oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}\,\mathrm{cm}^{-1}$: 1700 (C=O), 3350 (NH). MS *m*/*e*: 230 (M^+). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 224 (11700), 241 (12200), 289 (10400), 299 (sh.). NMR δ: 1.19 and 4.09 (3H, t, and 2H, q, CO_2Et), 5.09 and 5.17 (each 1H, s, $C=CH_2$), 6.34 (2H, s, 4- and 5-H), 6.4 (1H, br, NH), 6.9—7.3 (4H, m, Ar-H). *Anal.* Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.69; H, 6.22; N, 12.13.

17b: Yellow oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}\,\mathrm{cm}^{-1}$: 1690 (C=O), 3350 (NH). MS *m*/*e*: 244 (M^+). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 225 (9900), 242 (10000), 289 (8600), 298 (sh.). NMR δ: 1.21 and 4.15 (3H, t, and 2H, q, CO_2Et), 2.30 (3H, s, 7-Me), 5.18 and 5.26 (each 1H, s, $C=CH_2$), 6.23 (2H, s, 4- and 5-H), 6.24 (1H, br, NH), 6.9—7.2 (3H, m, Ar-H). *Anal.* Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.85; H, 6.49; N, 11.25.

17c: mp 85—86 °C, pale yellow prisms (from isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 1710 (C=O), 3300 (NH). MS *m*/*e*: 260 (M^+). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 235 (9300), 242 (9300), 287 (8100), 296 (sh.). NMR δ: 1.22 and 4.20 (3H, t, and 2H, q, CO_2Et); 3.84 (3H, s, 7-OMe), 5.24 and 5.30 (each 1H, s, $C=CH_2$), 6.49 (3H, s, 4-, 5-, and N–H), 6.8—7.1 (3H, m, Ar-H). *Anal.* Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.64; H, 6.26; N, 10.83.

The quinoline *N*-ethoxycarbonylimides (**18a—c**) and the 1,3-benzo[*d*]diazepines (**19a, c**) were identical with corresponding authentic samples.[13]

References and Notes

1) Part XIX: J. Kurita, M. Enkaku, and T. Tsuchiya, *Chem. Pharm. Bull.*, **30**, 3764 (1982).
2) For reviews, see A. G. Archer and L. H. Sternbach, *Chem. Rev.*, **68**, 747 (1969); M. Nastasi, *Heterocycles*, **4**, 1509 (1976); T. Mukai, T. Kumagai, and Y. Yamashita, *ibid.*, **15**, 1569 (1981); V. Snieckus and J. Streith, *Acc. Chem. Res.*, **14**, 348 (1981); T. Tsuchiya, *Yuki Gosei Kagaku Kyokai Shi*, **39**, 99 (1981).
3) T. Tsuchiya, J. Kurita, and V. Snieckus, *J. Org. Chem.*, **42**, 1856 (1977); T. Tsuchiya and J. Kurita, *Chem. Pharm. Bull.*, **26**, 1890 (1978).
4) T. Tsuchiya, M. Enkaku, J. Kurita, and H. Sawanishi, *Chem. Pharm. Bull.*, **27**, 2183 (1979).

5) T. Tsuchiya, M. Enkaku, J. Kurita, and H. Sawanishi, *J. Chem. Soc., Chem. Commun.*, **1979**, 534; T. Tsuchiya, M. Enkaku, and S. Okajima, *Chem. Pharm. Bull.*, **28**, 2602 (1980).

6) T. Tsuchiya, H. Sawanishi, M. Enkaku, and T. Hirai, *Chem. Pharm. Bull.*, **29**, 1539 (1981).

7) T. Tsuchiya, M. Enkaku, and S. Okajima, *J. Chem. Soc., Chem. Commun.*, **1980**, 454; *idem, Chem. Pharm. Bull.*, **29**, 3173 (1981).

8) D. J. Harris, G.Y.-P. Kan, V. Snieckus, and O. Buchardt, *Synthesis*, **1975**, 603.

9) D. P. Munro and J. T. Sharp, *Tetrahedron Lett.*, **23**, 345 (1982).

10) *a*) T. Tsuchiya, K. Takayama, and J. Kurita, *Chem. Pharm. Bull.*, **27**, 2476 (1979); *b*) T. Tsuchiya and J. Kurita, *J. Chem. Soc., Chem. Commun.*, **1979**, 803; *idem, Chem. Pharm. Bull.*, **28**, 1842 (1980).

11) J. Kurita and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, **1974**, 936; T. Tsuchiya, M. Enkaku, and H. Sawanishi, *ibid.*, **1978**, 568.

12) A part of this work has been published in a preliminary communication: J. Kurita, M. Enkaku, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, **1982**, 990.

13) The photolysis of the quinoline *N*-acylimides having an electron-donating substituent at the 6- or 8-position gave the corresponding 3*H*-1,3-benzodiazepines, whereas quinolines having an electron-donating group at some other position or an electron-withdrawing group gave no diazepines. [T. Tsuchiya, S. Okajima, M. Enkaku, and J. Kurita, *J. Chem. Soc., Chem. Commun.*, **1981**, 211; *idem, Chem. Pharm. Bull.*, **30**, 3757 (1982)].

14) The presence of an electron-donating substituent at the 4- and/or 6-position of the 1,2-diazepines is essential for these thermal ring-conversions. [T. Tsuchiya, J. Kurita, and H. Kojima, *J. Chem. Soc., Chem. Commun.*, **1980**, 444; J. Kurita, H. Kojima, M. Enkaku, and T. Tsuchiya, *Chem. Pharm. Bull.*, **29**, 3696 (1981)].