Studies on Seven-Membered Heterocycles. XXXI.[1] Synthesis of 1,4-Oxazepinones and 1,4-Diazepinones from 2-Pyridones and Their Conversion into Fully Unsaturated 1,4-Oxazepines and 1,4-Diazepines

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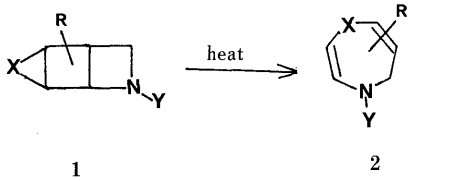
Thermolysis of the 6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-ones (8 and 21) and 3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-ones (9 and 22), prepared from the corresponding 2-pyridones (5) *via* the 2-azabicyclo[2.2.0]hex-5-en-3-ones (7 and 18), resulted in valence isomerization with ring opening to give the novel 1,4-oxazepin-5-ones (10a—e and 15a—c) and 1,4-diazepin-5-ones (11a—e and 16a—c), respectively. Treatment of the *N*-unsubstituted compounds 15 and 16 with triethyloxonium tetrafluoroborate afforded the fully unsaturated 1,4-oxazepines (23a—c) and 1*H*-1,4-diazepines (24a—c), respectively.

Keywords 2-pyridone; 1,4-oxazepin-5-one; 1,4-diazepin-5-one; 1,4-oxazepine; 1,4-diazepine; 6-aza-3-oxatricyclo[3.2.0.0^{2,4}]-heptan-7-one; 3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-one; thermal valence isomerization; ring expansion

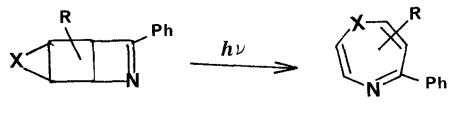
The synthesis of new seven-membered heterocyclic rings with two or more hetero atoms has recently been an object of extensive study.[2,3] Among the three possible fully unsaturated monocyclic dihetero seven-membered ring isomers (diheteroepines) due to the isomeric positions of the two hetero atoms, 1,2- and 1,3-diheteroepines such as 1,2-[3] and 1,3-diazepines[4,5] and 1,3-oxazepines[6,7] are known, but as regards the 1,4-isomers, only highly substituted 6*H*-1,4-diazepines had been reported[8] prior to our work.[7,9] We have recently shown that the tricyclic compounds **1** and **3** having a highly strained bicyclopentane ring system undergo thermal or photochemical valence isomerization with ring opening to give the dihydro (**2**)[10] and fully unsaturated 1,4-diheteroepines (**4**),[7] respectively. On the other hand, with regard to monocyclic diheteroepinones, only 1,2-diazepinones are known.[11] Therefore, we were interested in the ring opening of the oxo derivatives of **1** and we report here the synthesis of novel 1,4-oxazepin-5-ones and 1,4-diazepin-5-ones, and conversion of them into the corresponding fully unsaturated 5-ethoxy-1,4-diheteroepines.[12]

The *N*-methoxymethyl-2-pyridones (**6a—e**), prepared from the corresponding 2-pyridones (**5**) by treatment with chloromethyl methyl ether, were irradiated in benzene for 20—40 h to result in cyclization giving rise to the 2-aza-3-oxobicyclo[2.2.0]hex-5-enes (**7**) in 40—70% yields. Treatment of **7** with *m*-chloroperbenzoic acid (*m*-CPBA) gave the key tricyclic oxirane compounds **8a—e**, 6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-ones, in *ca.* 95% yields. the aziridine compounds **9a—e**, 3,6-diazatricyclo[3.2.0.0^{2,4}]-heptan-7-ones, were prepared in *ca.* 40% yields by the reaction of **7** with ethoxycarbonylnitrene generated from *N*-ethoxycarbonyl-*p*-nitrobenzenesulfonylhydroxylamine by treatment with benzyltriethylammonium bromide and sodium hydrogencarbonate.[13] when the *N*-protecting methoxymethyl (MOM) group is absent in the bicyclic compounds **7**, the yields of either the oxirane or aziridine compounds are very low (10—15%).



1 2

X=O, NCO_2Et, S, CH_2
Y=CO_2Me, CO_2CH_2Ph
R=H, Me, Ph



3 4

X=O, NCO_2Et
R=H, Me

Chart 1

The structures of the tricyclic compounds **8** and **9** were characterized on the basis of their spectral data, particularly by proton nuclear magnetic resonance (^{1}H-NMR) spectral comparison with the already reported compounds **1**[10] and **3**,[7] of which the stereochemistry, however, has not been examined in detail. In the ^{1}H-NMR spectrum of **8b**, a nuclear Overhauser effect (NOE) enhancement (15—20%) was observed only between the 2-Me (δ 1.63) and the 4-H (δ 4.23) signals; indicating that **8b** is the *anti*-stereostructure shown in Fig. 1 and not the *syn*-structure, and consequently, all of the tricyclic compounds reported are considered to have similar stereostructures.

Heating the tricyclic compounds **8a—d** and **9a—e** in dichlorobenzene at 150°C until almost all of the starting compounds had been consumed (for 4—6 h) resulted in valence isomerization with ring opening to give the novel 1,4-oxazepin-5-ones (**10a—d**) and 1,4-diazepin-5-ones (**11a—e**), respectively, in 70—90% yields. In the case of the oxirane compound **8e** (R^4=Me), thermolysis at 150°C for 5 h gave only the 5-hydroxy-2-pyridone derivative **12e** in 85% yield and no oxazepinone (**10e**), whereas that at 120°C for 2 h resulted in the formation of **10e** in 40% yield, together with **12e** (*ca.* 20%) and the starting **8e** (35%), showing that **10e** may readily undergo thermal rearrangement to give **12e**. Therefore, the thermal behavior of the diheteroepinones **10** and **11** was examined. The oxazepinones (**10a, b, e**) were heated in dichlorobenzene at 165°C in a sealed tube for 10 h to result in rearrangement giving the expected 5-hydroxy-2-pyridones (**12**) in moderate yields, probably by the path involving the aza-norcaradiene intermediates, as shown in Chart 2. The electron-donating 3-Me group (R^4) in **10e** may assist the formation of the norcaradiene intermediate, and thus **10e** might readily be converted to **12e** at lower temperature. On the contrary, even when the diazepinones

(**11a, b**) were heated at 200°C for 10 h, no reaction occurred. An analogous difference in thermolytic behavior between oxepines and azepines has been observed for a variety of heteroepines.[2,7]

Hydrolysis of the *N*-methoxymethyl(MOM)-diheteroepinones (**10a** and **11a**) with hydrogen chloride in acetone gave the *N*-hydroxymethyl compounds **13a** and **14a** in 47% and 35% yields, respectively. In the infrared (IR) spectra of **13a** and **14a**, the amide carbonyl absorption bands appeared at lower wave-lengths (**13a**: 1650 cm^{-1}; **14a**: 1652 cm^{-1}) than those of the MOM compounds **10a** and **11a** (1670 cm^{-1}); indicating that the carbonyl oxygen is hydrogen bonded with the OH hydrogen atom.

Treatment of **13a** and **14a** with ammonia in ether resulted in dehydroxymethylation to afford the desired *N*-unsubstituted parent 1,4-oxazepin-5-one (**15a**) and 1*H*-1,4-diazepin-5-one (**16a**), respectively, in *ca.* 50% yields. The *N*-unsubstituted compounds **15** and **16** could also be prepared by the following different route, shown in Chart 3.

The 2-aza-3-oxobicyclo[2.2.0]hex-5-enes (**17a—c**), prepared from the corresponding *N*-unsubstituted 2-pyridones (**5**) by irradiation, were treated with *tert*-butyldimethylsilyl

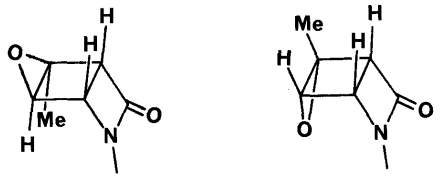
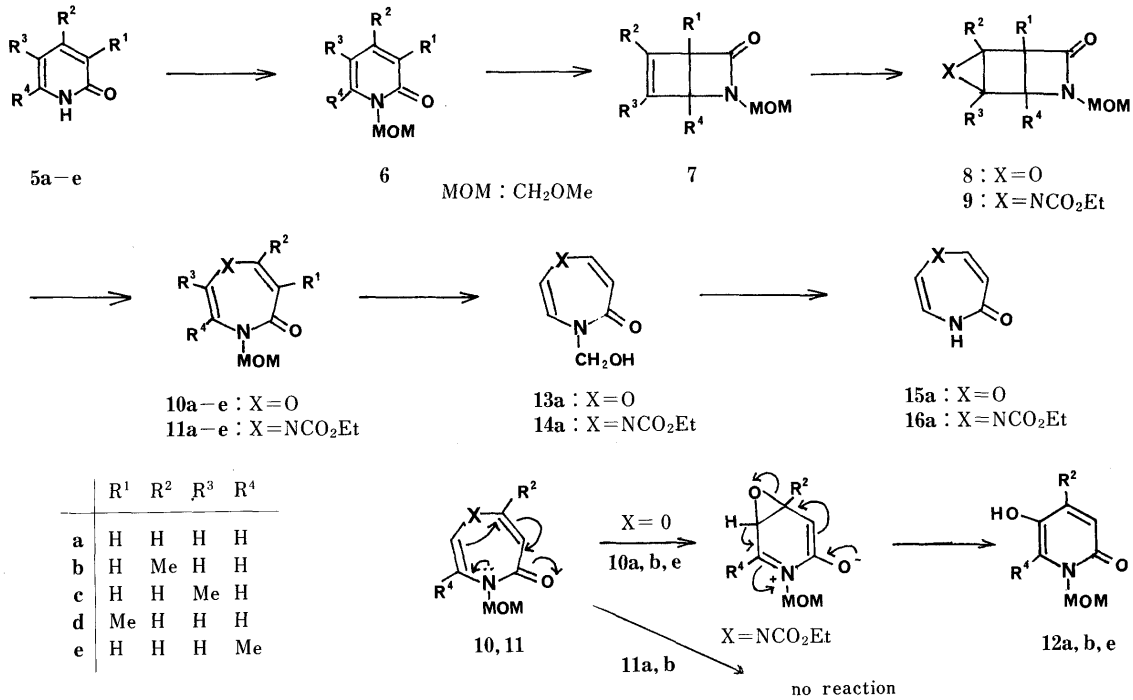


Fig. 1



	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	Me	H	H
c	H	H	Me	H
d	Me	H	H	H
e	H	H	H	Me

Chart 2

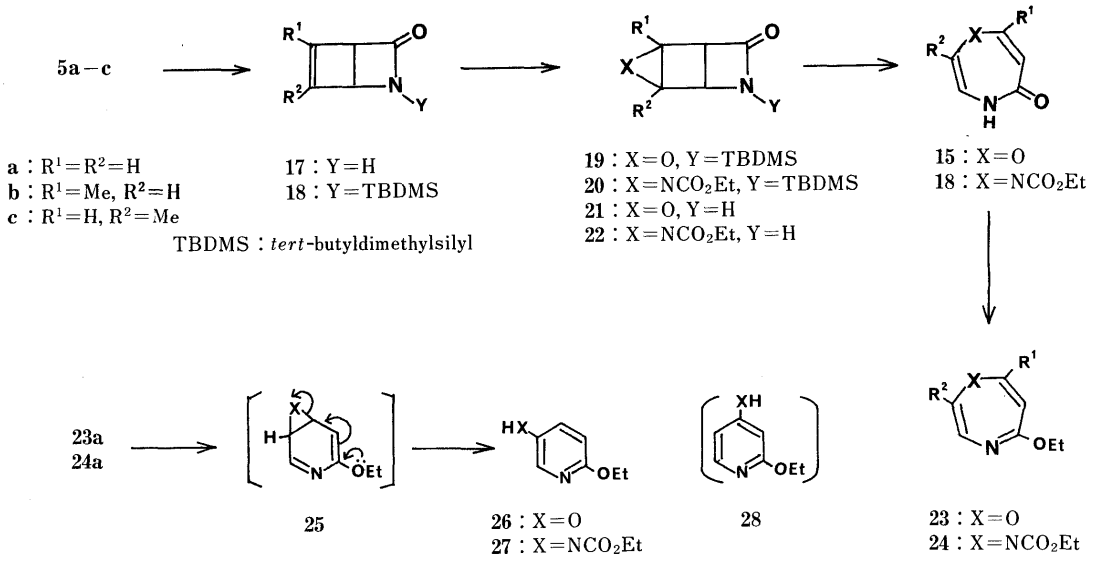


Chart 3

(TBDMS) chloride[14] in dimethylformamide to give the *N*-TBDMS derivatives **18** in *ca.* 90% yields. Treatment of **18a—c** with *m*-CPBA afforded the oxirane compounds **19** in 95—97% yields and treatment with ethoxycarbonylnitrene generated by the method described for **9** gave the aziridine compounds **20** in *ca.* 50% yields. The protecting TBDMS group in **19** and **20** could be readily removed only by passage through a short alumina column using ether–methanol (50 : 1) as an eluent, giving rise to the *N*-unsubstituted lactam compounds **21** and **22**, respectively, in quantitative yields. These compounds (**21** and **22**) were also obtained directly from the *N*-unsubstituted bicyclic compounds **17** by treatment with *m*-CPBA or ethoxycarbonylnitrene, but in very low yields (10—20%). Heating the tricyclic compounds **21** and **22** also resulted in ring opening to give the 1,4-oxazepin-5-ones (**15a—c**) and 1*H*-1,4-diazepin-5-ones (**16a—c**), respectively, in *ca.* 90% yields.

The structures of the new diheteroepinones were elucidated from their spectral data and the results of the following chemical studies. For example, the IR spectra of **15a** and **16a** showed a strong absorption band at 1670 cm^{-1} due to the conjugated amide carbonyl group. The ^{1}H-NMR of **15a** and **16a** showed two AB pairs of doublets at δ 5.52 and 4.99 (J=6 Hz) for **15a**; 5.58 and 5.18 (J=8 Hz) for **16a** assignable to 2-H and 3-H, and at δ 4.80 and 6.26 (J=7.5 Hz) for **15a**; 4.92 and 6.98 (J=10 Hz) for **16a** due to 6-H and 7-H, respectively, in addition to the signal at δ 7.5 (NH).

In order to convert the diheteroepinones into fully unsaturated diheteroepines, **15** and **16** were treated with TBDMS chloride in the presence of diethylamine or with *n*-butyl lithium followed by methyl iodide, but only decomposition occurred, and the expected *O*-silylation or *O*-methylation products could not be obtained. However, treatment of **15** and **16** with triethyloxonium tetrafluoroborate in dichloromethane resulted in *O*-ethylation predominantly to give the desired fully unsaturated 5-ethoxy-1,4-oxazepines (**23a—c**) and 5-ethoxy-1*H*-1,4-diazepines (**24a—c**), respectively, in 75–90% yields. As was expected, the 1,4-oxazepines (**23**) having an anti-aromatic ring system with 8π-electrons are relatively unstable and susceptible to decomposition in a silica gel or alumina column, whereas the 1,4-diazepines (**24**) stabilized by the electron-withdrawing ethoxycarbonyl group on the nitrogen atom are stable and can be purified by chromatography, by analogy with 1,3-diheteroepines,[2,4,5] 1,4-diheteroepines,[7,9] and 1-acylazepines.[2]

The structures of the diheteroepines **23** and **24** were characterized on the basis of the spectral data and the result of the following thermolysis. For example, in the ^{1}H-NMR spectra of **23a** and **24a**, signals due to four ring protons lie in the olefinic range (δ 5.1—5.9 for **23a**; δ 5.1—6.6 for **24a**) as two pairs of doublets. Heating the oxazepine (**23a**) at 45°C for 1 h in benzene gave 2-ethoxy-5-hydroxypyridine (**26**) in 60% yield, presumably *via* the aza-norcaradiene

TABLE I. ^{1}H-NMR Spectral Data for the 1,4-Diheteroepin-5-ones (**10**, **11**, **15**, and **16**)

Compd No.	2-H	3-H	6-H	7-H	Me	CH_3–O–CH_2–NH	CH_3–CH_2–O_2C–
10a	5.67 (d)	5.15 (d)	4.94 (d)	6.33 (d)	—	3.30 4.73	
	$J_{2,3}$=6, $J_{6,7}$=8						
10b	5.80 (d)	5.30 (d)	5.06 (q)	—	1.86 (d)	3.32 4.82	
	$J_{2,3}$=6, $J_{7\text{-Me},6}$=0.8						
10c	—	5.26 (q)	5.10 (d)	6.54 (d)	1.80 (d)	3.32 4.76	
	$J_{2\text{-Me},3}$=1, $J_{6,7}$=8						
10d	5.98 (d)	5.45 (d)	—	6.57 (q)	1.78 (d)	3.34 4.86	
	$J_{2,3}$=5, $J_{6\text{-Me},7}$=1.2						
10e	6.06 (q)	—	5.27 (d)	6.73 (d)	1.83 (d)	3.34 4.99	
	$J_{2,3\text{-Me}}$=1.5, $J_{6,7}$=7						
11a	6.05 (d)	5.38 (d)	5.08 (d)	7.01 (d)	—	3.32 4.80	1.32 4.28
	$J_{2,3}$=8, $J_{6,7}$=10						
11b	6.08 (d)	5.76 (d)	5.45 (q)	—	2.14 (d)	3.28 4.86	1.28 4.18
	$J_{2,3}$=6, $J_{6,7\text{-Me}}$=0.8						
11c	—	5.70 (q)	5.39 (d)	7.01 (d)	2.01 (d)	3.30 4.84	1.30 4.24
	$J_{2\text{-Me},3}$=1, $J_{6,7}$=9						
11d	6.12 (d)	5.56 (d)	—	6.90 (q)	1.91 (d)	3.34 4.87	1.32 4.26
	$J_{2,3}$=7, $J_{6\text{-Me},7}$=1						
11e	6.08 (q)	—	5.26 (d)	7.09 (d)	1.94 (d)	3.32 4.96	1.32 4.27
	$J_{2,3\text{-Me}}$=1, $J_{6,7}$=9						
15a	5.52 (d)	4.99 (dd)	4.80 (dd)	6.26 (d)	—	7.5 (br)	
	$J_{2,3}$=6, $J_{3,NH}$=6, $J_{NH,6}$=2.5, $J_{6,7}$=7.5						
15b	5.56 (d)	5.08 (dd)	4.90 (m)	—	1.82 (d)	7.3 (br)	
	$J_{2,3}$=6, $J_{3,NH}$=6, $J_{NH,6}$=2.5, $J_{6,7\text{-Me}}$=1						
15c	—	5.01 (m)	4.88 (dd)	6.37 (d)	1.71 (d)	7.2 (br)	
	$J_{2\text{-Me},3}$=1.2, $J_{3,NH}$=6, $J_{NH,6}$=2.5, $J_{6,7}$=7.5						
16a	5.85 (d)	5.18 (dd)	4.92 (dd)	6.98 (d)	—	7.4 (br)	1.32 4.27
	$J_{2,3}$=8, $J_{3,NH}$=6, $J_{NH,6}$=2, $J_{6,7}$=10						
16b	5.93 (d)	5.75 (dd)	5.49 (s)	—	2.16 (s)	8.6 (br)	1.30 4.23
	$J_{2,3}$=6, $J_{3,NH}$=5						
16c	—	5.68 (m)	5.40 (dd)	7.02 (d)	2.00 (d)	8.2 (br)	1.35 4.28
	$J_{2\text{-Me},3}$=1, $J_{3,NH}$=5, $J_{NH,6}$=2, $J_{6,7}$=9						

($CDCl_3$), J=Hz.

intermediate **25**. Similarly, thermolysis of **24a** afforded 2-ethoxy-5-ethoxycarbonylaminopyridine (**27**) in 78% yield, though somewhat more drastic conditions (heating in dichlorobenzene at 180°C for 12 h) were required.

These thermal behaviors are similar to those observed for 5-phenyl-1,4-diheteroepines.[7] In both cases (**23a** and **24a**), the formation of other possible rearrangement products (**28**) was not observed, probably because the electron-donating ethoxy group favors the C^4–X bond cleavage to give predominantly **26** and **27**, as shown in the structure **25**, and therefore, the C^5–X bond cleavage products **28** are not formed.

In conclusion, the present results provide the first examples of 1,4-diheteroepinones as well as a new route to fully unsaturated 1,4-oxazepines and 1,4-diazepines.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Hitachi 270—30 spectrometer and mass spectra (MS) were measured with a JEOL DX-300 instrument. ^{1}H-NMR spectra were recorded on a JEOL JNM-MH100 or GSX-400 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 Faculty 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, which was cooled internally with running water.

1-Methoxymethyl-2-pyridones (6a—e) General Procedure: A solution of chloromethyl methyl ether (1.2 mol eq) in CH_2Cl_2 (10 ml) was added with stirring to a solution of a 2-pyridone (**5a—e**;[15] *ca.* 10 g) in CH_2Cl_2 (150 ml). The reaction solution was stirred for 24 h at room temperature and then diluted with CH_2Cl_2 (200 ml). The mixture was successively washed with saturated $NaHCO_3$ and saturated NaCl, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 2) as an eluent to give **6** as a colorless oil.

1-Methoxymethyl-2-pyridone (**6a**): 54% yield, bp 102—103.5 °C (2.5 mmHg). IR (neat): 1660 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.39 and 5.35 (3H, s, and 2H, s, CH_3OCH_2), 6.30 (1H, m, 5-H), 6.62 (1H, m, 3-H), 7.40 (1H, m, 4-H), 7.50 (1H, m, 6-H), $J_{3,4}=9$ Hz, $J_{3,5}=1.5$ Hz, $J_{3,6}=2$ Hz, $J_{4,5}=7$ Hz, $J_{4,6}=2$ Hz, $J_{5,6}=7$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_7H_9NO_2$; 139.0633. Found: 139.0631.

1-Methoxymethyl-4-methyl-2-pyridone (**6b**): 66% yield, bp 107—109 °C (3.5 mmHg). IR (neat): 1672 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.38 and 5.30 (3H, s, and 2H, s, CH_3OCH_2), 2.19 (3H, s, 4-Me), 6.06 (1H, dd, 5-H), 6.35 (1H, d, 3-H), 7.36 (1H, d, 6-H), $J_{3,5}=1.5$ Hz, $J_{5,6}=7$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}N_2O$: 153.0790. Found: 153.0784.

1-Methoxymethyl-5-methyl-2-pyridone (**6c**): 61% yield, bp 111—113 °C (3 mmHg). IR (neat): 1674 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.40 and 5.31 (3H, s, and 2H, s, CH_3OCH_2), 2.08 (3H, br s, 5-Me), 6.54 (1H, dd, 3-H), 7.18 (1H, br dd, 6-H), 7.26 (1H, dd, 4-H), $J_{3,4}=9$ Hz, $J_{3,6}=2$ Hz, $J_{4,6}=2$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0796.

1-Methoxymethyl-3-methyl-2-pyridone (**6d**): 51% yield, bp 115—118 °C (3.5 mmHg). IR (neat): 1662 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.43 and 5.38 (3H, s, and 2H, s, CH_3OCH_2), 2.16 (3H, br s, 3-Me), 6.20 (1H, dd, 5-H), 7.28 (1H, m, 4-H), 7.36 (1H, dd, 6-H), $J_{3\text{-Me},4}=1$ Hz, $J_{4,5}=7$ Hz, $J_{4,6}=2$ Hz, $J_{5,6}=7$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0788.

1-Methoxymethyl-6-methyl-2-pyridone (**6e**): 55% yield, bp 112—114 °C (3.5 mmHg). IR (neat): 1664 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.33 and 5.43 (3H, s, and 2H, s, CH_3OCH_2), 2.38 (3H, s, 6-Me), 5.95 (1H, d, 5-H), 6.26 (1H, d, 3-H), 7.15 (1H, dd, 4-H), $J_{3,4}=9$ Hz, $J_{4,5}=7$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0781.

2-Methoxymethyl-2-azabicyclo[2.2.0]hex-5-en-3-ones (7a—e) General Procedure: A solution of a 2-pyridone (**6a—e**, 1—2 g) in benzene (300 ml) was irradiated; this photolysis was followed in terms of the disappearance of the spot of the starting **6** on silica gel thin-layer chromatography (TLC) and was complete in 20—40 h. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using ether–hexane (1 : 2) as an eluent to give **7** as a colorless viscous oil.

2-Methoxymethyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**7a**): 42% yield. IR (neat): 1755 (C=O), 1558 (C=C) cm^{-1}. ^{1}H-NMR δ: 3.28 and 4.54 (3H, s, and 2H, d, $J=11$ Hz, CH_3OCH_2), 4.27 (1H, m, 4-H), 4.47 (1H, dd, 1-H), 6.65 (1H, m, 5-H), 6.72 (1H, dd, 6-H), $J_{1,4}=2$ Hz, $J_{1,5}=3$ Hz, $J_{4,5}=0.8$ Hz, $J_{4,6}=1.2$ Hz, $J_{5,6}=2.5$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_7H_9NO_2$: 139.0633. Found: 139.0621.

2-Methoxymethyl-5-methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**7b**): 71% yield. IR (neat): 1750 (C=O), 1624 (C=C) cm^{-1}. ^{1}H-NMR δ: 3.25 and 4.43 (3H, s, and 2H, s, CH_3OCH_2), 1.90 (3H, m, 5-Me), 4.06 (1H, m, 4-H), 4.23 (1H, m, 1-H), 6.23 (1H, m, 6-H), $J_{1,4}=2$ Hz, $J_{1,5\text{-Me}}=0.8$ Hz, $J_{4,5\text{-Me}}=0.8$ Hz, $J_{4,6}=1.2$ Hz, $J_{5\text{-Me},6}=1.6$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0779.

2-Methoxymethyl-6-methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**7c**): 52% yield. IR (neat): 1756 (C=O), 1624 (C=C) cm^{-1}. ^{1}H-NMR δ: 3.25 and 4.53 (3H, s, and 2H, d, $J=11$ Hz, CH_3OCH_2), 1.86 (3H, m, 6-Me), 3.97 (1H, m, 4-H), 4.23 (1H, m, 1-H), 6.16 (1H, m, 5-H), $J_{1,4}=2$ Hz, $J_{1,5}=3$ Hz, $J_{1,6\text{-Me}}=0.5$ Hz, $J_{4,5}=0.8$ Hz, $J_{4,6\text{-Me}}=1.5$ Hz, $J_{5,6\text{-Me}}=1.6$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0799.

2-Methoxymethyl-4-methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**7d**): 40% yield. IR (neat): 1760 (C=O), 1546 (C=C) cm^{-1}. ^{1}H-NMR δ: 3.24 and 4.47 (3H, s, and 2H, d, $J=11$ Hz, CH_3OCH_2), 1.49 (3H, s, 4-Me), 4.12 (1H, d, 1-H), 6.48 (1H, dd, 5-H), 6.57 (1H, d, 6-H), $J_{1,5}=3$ Hz, $J_{5,6}=2.5$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0785.

2-Methoxymethyl-1-methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**7e**): 54% yield. IR (neat): 1756 (C=O), 1550 (C=C) cm^{-1}. ^{1}H-NMR δ: 3.29 and 4.50 (3H, s, and 2H, d, $J=11$ Hz, CH_3OCH_2), 1.60 (3H, s, 1-Me), 3.91 (1H, dd, 4-H), 6.50 (1H, dd, 5-H), 6.61 (1H, dd, 6-H), $J_{4,5}=0.8$ Hz, $J_{4,6}=1.2$ Hz, $J_{5,6}=2.5$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0797.

6-Methoxymethyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-ones (8a—e) General Procedure: A solution of *m*-CPBA (1.2 mol eq) in CH_2Cl_2 (10 ml) was added dropwise with stirring to a solution of a bicyclic compound (**7a—e**, *ca.* 1 g) in CH_2Cl_2 (10 ml). Stirring was continued for an additional 8 h at room temperature, then the reaction mixture was diluted with CH_2Cl_2 (50—100 ml). The solution was successively washed with saturated $NaHCO_3$ and saturated NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 1) as an eluent to give **8** as a colorless viscous oil.

6-Methoxymethyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**8a**): 95% yield. IR (neat): 1766 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.27 and 4.48 (3H, s, and 2H, d, $J=12$ Hz, CH_3OCH_2), 3.72 (1H, dd, 5-H), 4.04 (1H, dd, 1-H), 4.14 (1H, dd, 4-H), 4.27 (1H, dd, 2-H), $J_{1,2}=3.5$ Hz, $J_{1,5}=1.8$ Hz, $J_{2,4}=2$ Hz, $J_{4,5}=4$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_7H_9NO_3$: 155.0582. Found: 155.0594.

6-Methoxymethyl-2-methyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**8b**): 97% yield. IR (neat): 1768 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.30 and 4.48 (3H, s, and 2H, d, $J=12$ Hz, CH_3OCH_2), 1.63 (3H, s, 2-Me), 3.68 (1H, dd, 5-H), 3.96 (1H, d, 1-H), 4.23 (1H, d, 4-H), $J_{1,5}=1.8$ Hz, $J_{4,5}=4$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_3$: 169.0739. Found: 169.0753.

6-Methoxymethyl-4-methyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**8c**): 96% yield. IR (neat): 1762 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.27 and 4.51 (3H, s, and 2H, d, $J=12$ Hz, CH_3OCH_2), 1.61 (3H, s, 4-Me), 3.60 (1H, d, 5-H), 4.01 (1H, dd, 1-H), 4.09 (1H, d, 2-H), $J_{1,2}=3.5$ Hz, $J_{1,5}=1.8$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_3$: 169.0739. Found: 169.0732.

6-Methoxymethyl-1-methyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**8d**): 94% yield. IR (neat): 1764 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.33 and 4.48 (3H, s, and 2H, d, $J=12$ Hz, CH_3OCH_2), 1.36 (3H, s, 1-Me), 3.83 (1H, d, 5-H), 4.02 (1H, dd, 4-H), 4.22 (1H, d, 2-H), $J_{2,4}=2$ Hz, $J_{4,5}=4$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_3$: 169.0739. Found: 169.0738.

6-Methoxymethyl-5-methyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**8e**): 94% yield. IR (neat): 1766 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.30 and 4.47 (3H, s, and 2H, d, $J=12$ Hz, CH_3OCH_2), 1.42 (3H, s, 5-Me), 3.41 (1H, d, 1-H), 4.06 (1H, d, 4-H), 4.15 (1H, dd, 2-H), $J_{1,2}=3.5$ Hz, $J_{2,4}=2$ Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_3$: 169.0739. Found: 169.0754.

3-Ethoxycarbonyl-6-methoxymethyl-3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-ones (9a—e) General Procedure: Benzyltriethylammonium bromide (0.2 mol eq) and saturated $NaHCO_3$ (*ca.* 5 mol eq) were added with stirring

to a solution of a bicyclic compound (**7a**—**e**, *ca.* 1 g) in CH_2Cl_2 (100 ml). *N*-Ethoxycarbonyl-*p*-nitrobenzenesulfonylhydroxylamine (1.5 mol eq) was added in small portions over a 0.5 h period to the above mixture with vigorous stirring in an ice bath. The reaction mixture was stirred for a further 5 h at room temperature and diluted with CH_2Cl_2 (100 ml). The organic layer was separated, washed with saturated NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 2—1 : 1) as an eluent to give **9** as a colorless viscous oil.

3-Ethoxycarbonyl-6-methoxymethyl-3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-one (**9a**): 35% yield. IR (neat): 1770 and 1726 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.29 and 4.19 (3H, t, and 2H, q, CO_2Et), 3.32 and 4.57 (3H, s, and 2H, d, J=11 Hz, CH_3OCH_2), 3.59 (1H, dd, 4-H), 3.74 (2H, m, 2- and 5-H), 4.12 (1H, dd, 1-H), $J_{1,2}$=3.5 Hz, $J_{1,5}$=1.8 Hz, $J_{2,4}$=2 Hz, $J_{4,5}$=3 Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_{10}H_{14}N_2O_4$: 226.0954. Found: 226.0959.

3-Ethoxycarbonyl-6-methoxymethyl-2-methyl-3,6-diazatricyclo-[3.2.0.0^{2,4}]heptan-7-one (**9b**): 40% yield. IR (neat): 1768 and 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 4.09 (3H, t, and 2H, q, CO_2Et), 3.72 and 4.49 (3H, s, and 2H, d, J=11.5 Hz, CH_3OCH_2), 1.55 (3H, s, 2-Me), 3.52 (1H, d, 4-H), 3.66 (1H, dd, 5-H), 3.96 (1H, d, 1-H), $J_{1,5}$=1.8 Hz, $J_{4,5}$=3.5 Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_{11}H_{16}N_2O_4$: 240.1110. Found: 240.1125.

3-Ethoxycarbonyl-6-methoxymethyl-4-methyl-3,6-diazatricyclo-[3.2.0.0^{2,4}]heptan-7-one (**9c**): 39% yield. IR (neat): 1774 and 1726 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.29 and 4.20 (3H, t, and 2H, q, CO_2Et), 3.35 and 4.60 (3H, s, and 2H, s, CH_3OCH_2), 1.61 (3H, s, 4-Me), 3.48 (1H, d, 2-H), 3.69 (1H, d, 5-H), 4.12 (1H, dd, 1-H), $J_{1,2}$=3.5 Hz, $J_{1,5}$=1.8 Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_{11}H_{16}N_2O_4$: 240.1110. Found: 240.1104.

3-Ethoxycarbonyl-6-methoxymethyl-1-methyl-3,6-diazatricyclo-[3.2.0.0^{2,4}]heptan-7-one (**9d**): 40% yield. IR (neat): 1768 and 1726 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.29 and 4.16 (3H, t, and 2H, q, CO_2Et), 3.33 and 4.53 (3H, s, and 2H, d, J=11.5 Hz, CH_3OCH_2), 1.37 (3H, s, 1-Me), 3.56 (1H, dd, 4-H), 3.68 (1H, d, 2-H), 3.95 (1H, d, 5-H), $J_{2,4}$=2 Hz, $J_{4,5}$= 3.5 Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_{11}H_{16}N_2O_4$: 240.1110. Found: 240.1096.

3-Ethoxycarbonyl-6-methoxymethyl-5-methyl-3,6-diazatricyclo-[3.2.0.0^{2,4}]heptan-7-one (**9e**): 34% yield. IR (neat): 1766 and 1724 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 4.18 (3H, t, and 2H, q, CO_2Et), 3.33 and 4.55 (3H, s, and 2H, d, J=12 Hz, CH_3OCH_2), 1.43 (3H, s, 5-Me), 3.52 (1H, d, 1-H), 3.55 (1H, d, 4-H), 3.75 (1H, dd, 2-H), $J_{1,2}$=3.5 Hz, $J_{2,4}$=2 Hz. High-resolution MS *m/z*: M$^+$ Calcd for $C_{11}H_{16}N_2O_4$: 240.1110. Found: 240.1108.

Thermolysis of 8a—d: Formation of 4-Methoxymethyl-1,4-oxazepin-5-ones (10a—d) A solution of a tricyclic compound (**8a—d**, *ca.* 0.5 g) in dichlorobenzene (3—5 ml) was heated at 150 °C. The reaction was followed in terms of the disappearance of the spot of the starting **8** on thin layer chromatography (TLC) and was complete in 4—6 h. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using ether–hexane (1 : 3) as an eluent to give **10** as a yellow viscous oil. ^{1}H-NMR spectral data of **10a—d** are collected in Table I.

4-Methoxymethyl-1,4-oxazepin-5-one (**10a**): 72% yield. IR (neat): 1670 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_7H_9NO_3$: 155.0582. Found: 155.0580.

4-Methoxymethyl-7-methyl-1,4-oxazepin-5-one (**10b**): 87% yield. IR (neat): 1670 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_3$: 169.0739. Found: 169.0722.

4-Methoxymethyl-2-methyl-1,4-oxazepin-5-one (**10c**): 70% yield. IR (neat): 1671 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_3$: 169.0739. Found: 169.0745.

4-Methoxymethyl-6-methyl-1,4-oxazepin-5-one (**10d**): 75% yield. IR (neat): 1660 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_3$: 169.0739. Found: 169.0738.

Thermolysis of 8e i) At 150 °C for 5 h: A solution of **8e** (400 mg) in dichlorobenzene (4 ml) was heated at 150 °C for 5 h and worked up as described for the thermolysis of **8a—d** gave only 5-hydroxy-1-methoxymethyl-6-methyl-2-pyridone (**12e**: 340 mg, 85% yield).

ii) At 120 °C for 2 h: A solution of **8e** (400 mg) in dichlorobenzene (4 ml) was heated at 120 °C for 2 h. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using ether–hexane (1 : 3—1 : 2) as an eluent to give 4-methoxymethyl-3-methyl-1,4-oxazepin-5-one (**10e**: 160 mg, 40% yield), the starting **8e** (140 mg, 35% yield), and **12e** (80 mg, 20% yield), successively.

10e: Yellow viscous oil. IR (neat): 1662 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_8H_{11}NO_3$: 169.0739. Found: 169.0730. The ^{1}H-NMR spectral data of **10e** are collected in Table I.

12e: mp 122—124 °C, colorless prisms (from AcOEt). IR (KBr): 3200 (OH), 1678 (C=O) cm^{-1}. MS *m/z*: 169 (M$^+$). ^{1}H-NMR δ: 3.37 and 5.25 (3H, s, and 2H, s, CH_3OCH_2), 2.40 (3H, s, 6-Me), 6.48 (1H, d, 3-H), 7.42 (1H, d, 4-H), $J_{3,4}$=10 Hz. *Anal.* Calcd for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.23. Found: C, 56.71; H, 6.53; N, 8.10.

1-Ethoxycarbonyl-4-methoxymethyl-1*H*-1,4-diazepin-5-ones (11a—e) The tricyclic compounds (**9a—e**, *ca.* 0.5 g) were heated in dichlorobenzene and worked up as described for **10a—d** to give **11a—e**, of which spectral data are collected in Table I.

1-Ethoxycarbonyl-4-methoxymethyl-1*H*-1,4-diazepin-5-one (**11a**): 70% yield, yellow viscous oil. IR (neat): 1740 and 1670 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_{10}H_{14}N_2O_4$: 226.0954. Found: 226.0971.

1-Ethoxycarbonyl-4-methoxymethyl-7-methyl-1*H*-1,4-diazepin-5-one (**11b**): 86% yield, mp 65—66.5 °C, colorless prisms (from isopropyl ether (IPE)). IR (KBr): 1726 and 1670 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_{11}H_{16}N_2O_4$: 240.1110. Found: 240.1139.

1-Ethoxycarbonyl-4-methoxymethyl-2-methyl-1*H*-1,4-diazepin-5-one (**11c**): 76% yield, pale yellow viscous oil. IR (neat): 1730 and 1670 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_{11}H_{16}N_2O_4$: 240.1110. Found: 240.1094.

1-Ethoxycarbonyl-4-methoxymethyl-6-methyl-1*H*-1,4-diazepin-5-one (**11d**): 71% yield, pale yellow viscous oil. IR (neat): 1731 and 1665 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_{11}H_{16}N_2O_4$: 240.1110. Found: 240.1113.

1-Ethoxycarbonyl-4-methoxymethyl-3-methyl-1*H*-1,4-diazepin-5-one (**11e**): 73% yield, mp 71—72.5 °C, pale yellow prisms (from IPE). IR (KBr): 1728 and 1670 (C=O) cm^{-1}. High-resolution MS *m/z*: M$^+$ Calcd for $C_{11}H_{16}N_2O_4$: 240.1110. Found: 240.1121.

Thermolysis of 10a, b, e: Formation of 5-Hydroxy-1-methoxymethyl-2-pyridones (12a, b, e) General Procedure: A solution of **10** (*ca.* 100 mg) in dichlorobenzene (3 ml) was heated at 165 °C for 10 h in a sealed tube. After cooling, the reaction solution was chromatographed on silica gel using ether–hexane (1 : 2) as an eluent to give **12**.

5-Hydroxy-1-methoxymethyl-2-pyridone (**12a**): 60% yield, mp 157—159 °C, colorless prisms (from acetone–isopropyl alcohol). IR (KBr): 3200 (OH), 1670 (C=O) cm^{-1}. MS *m/z*: 155 (M$^+$). ^{1}H-NMR δ: 3.38 and 5.26 (3H, s, and 2H, s, CH_3OCH_2), 6.50 (1H, d, 3-H), 7.04 (1H, d, 6-H), 7.04 (1H, d, 6-H), 7.29 (1H, dd, 4-H), $J_{3,4}$=10 Hz, $J_{4,6}$=2.5 Hz. *Anal.* Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.15; H, 5.88; N, 8.92. The structure of **12a** was further confirmed by the following result. A solution of **12a** (30 mg) in 20% H_2SO_4 was heated at 50 °C for 8 h with stirring and then neutralized with Na_2CO_3. The mixture was evaporated *in vacuo* and the residue was extracted with boiling EtOH. The extract was evaporated and the residue was sublimed to give 5-hydroxy-2-pyridone (14 mg), which was identical with an authentic sample prepared by the reported method.[16]

5-Hydroxy-1-methoxymethyl-4-methyl-2-pyridone (**12b**): 41% yield, mp 131—133 °C, colorless prisms (from benzene–EtOH). IR (KBr): 3200 (OH), 1670 (C=O) cm^{-1}. MS *m/z*: 169 (M$^+$). ^{1}H-NMR δ: 3.35 and 5.20 (3H, s, and 2H, s, CH_3OCH_2), 2.17 (3H, s, 4-Me), 6.35 (1H, s, 3-H), 6.93 (1H, s, 6-H). *Anal.* Calcd for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.23. Found: C, 56.80; H, 6.41; N, 8.13.

12e: 85% yield.

Thermolysis of 11a, b A solution of **11** (*ca.* 50 mg) in dichlorobenzene was heated at 200 °C for 10 h in a sealed tube and worked up as described for the thermolysis of **10a, b, e** to result in recovery of the starting **11** (50—95%). No other characterizable product was obtained.

4-Hydroxymethyl-1,4-oxazepin-5-one (13a) A mixture of **10a** (200 mg), acetone (4 ml), and 0.5 N HCl (4 ml) was stirred for 4 h at room temperature and then diluted with CH_2Cl_2 (100 ml). The organic layer was separated, washed with water, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 3) as an eluent to give **13a**: 108 mg, 47% yield, mp 70.5—71.5 °C, yellow plates (from IPE). IR (KBr): 3330 (OH), 1650 (C=O) cm^{-1}. MS *m/z*: 141 (M$^+$). ^{1}H-NMR δ: 3.95 and 4.80 (1H, t, and 2H, d, J=8 Hz, $HOCH_2$), 5.00 (1H, d, 6-H), 5.32 (1H, d, 3-H), 5.72 (1H, d, 2-H), 6.40 (1H, d, 7-H), $J_{2,3}$=6 Hz, $J_{6,7}$=8 Hz. *Anal.* Calcd for $C_6H_7NO_3$: C, 51.06; H, 5.00; N, 9.93. Found: C, 51.13; H, 4.91; N, 9.92.

1-Ethoxycarbonyl-4-hydroxymethyl-1*H*-1,4-diazepin-5-one (14a) Compound **11a** (125 mg) was treated with 0.5 N HCl and worked up as described for **13a** to give **14a**: 32 mg, 35% yield, mp 97—98 °C, pale yellow prisms (from benzene). IR (KBr): 3380 (OH), 1740 and 1652 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.33 and 4.27 (3H, t, and 2H, q, CO_2Et), 3.43 and 4.78 (1H,

t, and 2H, d, J=8 Hz, $HOCH_2$), 4.27 (1H, d, 6-H), 5.06 (1H, d, 3-H), 5.45 (1H, d, 2-H), 7.00 (1H, d, 7-H), $J_{2,3}$=8 Hz, $J_{6,7}$=10 Hz. High-resolution MS m/z: M^+ Calcd for $C_9H_{12}N_2O_4$: 212.0797. Found: 212.0809.

1,4-Oxazepin-5-one (15a) Ammonia (0.1 N, 4 ml) was added dropwise over a 5 min period to a solution of **13a** (56 mg) in ether (10 ml) with stirring. The reaction mixture was diluted with CH_2Cl_2 (50 ml) and the organic layer was separated, washed with water, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 4) as an eluent to give **15a**: 18.5 mg, 42% yield, yellow viscous oil (solidified below 20 °C). IR (neat): 3240 (NH), 1670 (C=O) cm^{-1}. High-resolution MS m/z: M^+ Calcd for $C_5H_5NO_2$: 111.0320. Found: 111.0336. ^{1}H-NMR spectral data are collected in Table I.

1-Ethoxycarbonyl-1*H*-1,4-diazepin-5-one (16a) Compound **14a** (60 mg) was treated with aqueous ammonia and worked up as described for **15a** to give **16a**: 23 mg, 45% yield, mp 69—70 °C, yellow prisms (from benzene–IPE). IR (KBr): 3200 (NH), 1744 and 1674 (C=O) cm^{-1}. High-resolution MS m/z: M^+ Calcd for $C_8H_{10}N_2O_3$: 182.0691. Found: 182.0690. ^{1}H-NMR spectral data are collected in Table I.

2-Azabicyclo[2.2.0]hex-5-en-3-ones (17a—c) The pyridones (**5a—c**, 1—2 g) were irradiated and worked up as described for **7** to give **17a—c**.

2-Azabicyclo[2.2.0]hex-5-en-3-one (**17a**): 42% yield, mp 65—66 °C (lit.[17] mp 65.5—66.5 °C), colorless prisms (from benzene–IPE).

5-Methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**17b**): 65% yield, mp 55—56.5 °C, colorless prisms (from benzene–IPE). MS m/z: 109 (M^+). IR (KBr): 3262 (NH), 1734 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.91 (3H, m, 5-Me), 4.05 (1H, m, 4-H), 4.26 (1H, m, 1-H), 6.19 (1H, m, 6-H), 6.5 (1H, br, NH), $J_{1,4}$=2.2 Hz, $J_{1,5\text{-Me}}$=0.8 Hz, $J_{4,6}$=1.2 Hz, $J_{4,5\text{-Me}}$=0.8 Hz, $J_{5\text{-Me},6}$=1.6 Hz. *Anal.* Calcd for C_6H_7NO: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.84; H, 6.45; N, 12.63.

6-Methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**17c**): 36% yield, mp 48—49 °C, colorless prisms (from benzene–IPE). MS m/z: 109 (M^+). IR (KBr): 3232 (NH), 1734 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.81 (3H, m, 6-Me), 3.98 (1H, m, 4-H), 4.21 (1H, m, 1-H), 6.21 (1H, m, 5-H), 6.5 (1H, br, NH), $J_{1,4}$=2.2 Hz, $J_{1,5}$=2.8 Hz, $J_{1,6\text{-Me}}$=0.5 Hz, $J_{4,5}$=0.7 Hz, $J_{4,6\text{-Me}}$=1.5 Hz, $J_{5,6\text{-Me}}$=1.6 Hz. *Anal.* Calcd for C_6H_7NO: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.92; H, 6.38; N, 12.71.

2-(*tert*-Butyldimethylsilyl)-2-azabicyclo[2.2.0]hex-5-en-3-ones (18a—c) General Procedure: *tert*-Butyldimethylsilyl chloride (1.2 mol eq) and triethylamine (1.2 mol eq) were successively added to a solution of a bicyclic compound (**17a—c**, 1—2 g) in dimethylformamide (10—20 ml) with stirring in an ice bath. The reaction mixture was further stirred for 2 h at room temperature and then extracted with ether. The extract was washed with saturated NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 5) as an eluent to give **18** as a colorless viscous oil.

2-(*tert*-Butyldimethylsilyl)-2-azabicyclo[2.2.0]hex-5-en-3-one (**18a**): 90% yield. IR (neat): 1738 (C=O), 1556 (C=C) cm^{-1}. ^{1}H-NMR δ: 0.18 and 0.22 (each 3H, s, Si-Me), 0.95 (9H, s, *tert*-Bu), 4.05 (1H, m, 4-H), 4.25 (1H, dd, 1-H), 6.42 (1H, m, 5-H), 6.54 (1H, dd, 6-H), $J_{1,4}$=2 Hz, $J_{1,5}$=3 Hz, $J_{4,5}$=0.8 Hz, $J_{4,6}$=1.2 Hz, $J_{5,6}$=2.5 Hz. High-resolution MS m/z: M^+ Calcd for $C_{11}H_{19}NOSi$: 209.1236. Found: 209.1247.

2-(*tert*-Butyldimethylsilyl)-5-methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**18b**): 88% yield. IR (neat): 1737 (C=O), 1620 (C=C) cm^{-1}. ^{1}H-NMR δ: 0.18 and 0.22 (each 3H, s, Si-Me), 0.94 (9H, s, *tert*-Bu), 1.90 (3H, m, 5-Me), 4.05 (1H, m, 4-H), 4.16 (1H, m, 1-H), 6.16 (1H, m, 6-H), $J_{1,4}$=2 Hz, $J_{1,5\text{-Me}}$=0.8 Hz, $J_{4,5\text{-Me}}$=0.8 Hz, $J_{4,6}$=1.2 Hz, $J_{5\text{-Me},6}$=1.6 Hz. High-resolution MS m/z: M^+ Calcd for $C_{12}H_{21}NOSi$: 223.1392. Found: 223.1402.

2-(*tert*-Butyldimethylsilyl)-6-methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (**18c**): 85% yield. IR (neat): 1736 (C=O), 1630 (C=C) cm^{-1}. ^{1}H-NMR δ: 0.12 and 0.17 (each 3H, s, Si-Me), 0.90 (9H, s, *tert*-Bu), 1.75 (1H, m, 6-Me), 3.88 (1H, m, 4-H), 4.07 (1H, m, 1-H), 6.13 (1H, m, 5-H), $J_{1,4}$=2 Hz, $J_{1,5}$=3 Hz, $J_{1,6\text{-Me}}$=0.5 Hz, $J_{4,5}$=0.7 Hz, $J_{4,6\text{-Me}}$=1.5 Hz, $J_{5,6\text{-Me}}$=1.6 Hz. High-resolution MS m/z: M^+ Calcd for $C_{12}H_{21}NOSi$: 223.1392. Found: 223.1408.

6-(*tert*-Butyldimethylsilyl)-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-ones (19a—c) The bicyclic compounds (**18a—c**, 0.5—1 g) were treated with *m*-CPBA and worked up as described for **8** to give **19a—c** as colorless viscous oils.

6-(*tert*-Butyldimethylsilyl)-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**19a**): 97% yield. IR (neat): 1750 (C=O) cm^{-1}. ^{1}H-NMR δ: 0.25 and 0.30 (each 3H, s, Si-Me), 0.99 (9H, s, *tert*-Bu), 3.76 (1H, dd, 5-H), 3.95 (1H, dd, 1-H), 4.10 (1H, dd, 4-H), 4.19 (1H, dd, 2-H), $J_{1,2}$=3.5 Hz, $J_{1,5}$=1.8 Hz, $J_{2,4}$=2 Hz, $J_{4,5}$=4 Hz. High-resolution MS m/z: M^+ Calcd for $C_{11}H_{19}NO_2Si$: 225.1185. Found: 225.1174.

6-(*tert*-Butyldimethylsilyl)-2-methyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]-heptan-7-one (**19b**): 95% yield. IR (neat): 1750 (C=O) cm^{-1}. ^{1}H-NMR δ: 0.23 and 0.27 (each 3H, s, Si-Me), 0.96 (9H, s, *tert*-Bu), 1.63 (3H, s, 2-Me), 3.69 (1H, dd, 5-H), 3.82 (1H, d, 1-H), 4.08 (1H, d, 4-H), $J_{1,5}$=1.8 Hz, $J_{4,5}$=4 Hz. High-resolution MS m/z: M^+ Calcd for $C_{12}H_{21}NO_2Si$: 239.1342. Found: 239.1332.

6-(*tert*-Butyldimethylsilyl)-4-methyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]-heptan-7-one (**19c**): 95% yield. IR (neat): 1745 (C=O) cm^{-1}. ^{1}H-NMR δ: 0.23 and 0.38 (each 3H, s, Si-Me), 0.99 (9H, s, *tert*-Bu), 1.60 (3H, s, 4-Me), 3.72 (1H, d, 5-H), 3.94 (1H, dd, 1-H), 4.18 (1H, d, 2-H), $J_{1,2}$=3.5 Hz, $J_{1,5}$=1.8 Hz. High-resolution MS m/z: M^+ Calcd for $C_{12}H_{21}NO_2Si$: 239.1342. Found: 239.1339.

6-(*tert*-Butyldimethylsilyl)-3-ethoxycarbonyl-3,6-diazatricyclo-[3.2.0.0^{2,4}]heptan-7-ones (20a—c) The bicyclic compounds **18a—c** (0.5—1 g) were treated with *N*-ethoxycarbonyl-*p*-nitrobenzenesulfonylhydroxylamine (1.5 mol eq) and worked up as described for **9** to give **20a—c** as colorless viscous oils.

6-(*tert*-Butyldimethylsilyl)-3-ethoxycarbonyl-3,6-diazatricyclo-[3.2.0.0^{2,4}]heptan-7-one (**20a**): 46% yield. IR (neat): 1756 and 1734 (C=O) cm^{-1}. ^{1}H-NMR δ: 0.26 and 0.31 (each 3H, s, Si-Me), 0.98 (9H, s, *tert*-Bu), 1.31 and 4.21 (3H, t, and 2H, q, CO_2Et), 3.49 (1H, dd, 4-H), 3.60 (1H, dd, 2-H), 3.74 (1H, dd, 5-H), 3.94 (1H, dd, 1-H), $J_{1,2}$=3.5 Hz, $J_{1,5}$=1.8 Hz, $J_{2,4}$=2 Hz, $J_{4,5}$=3 Hz. High-resolution MS m/z: M^+ Calcd for $C_{14}H_{24}N_2O_3$: 268.1787. Found: 268.1782.

6-(*tert*-Butyldimethylsilyl)-3-ethoxycarbonyl-2-methyl-3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-one (**20b**): 52% yield. IR (neat): 1754 and 1732 (C=O) cm^{-1}. ^{1}H-NMR δ: 0.26 and 0.29 (each 3H, s, Si-Me), 0.98 (9H, s, *tert*-Bu), 1.36 and 4.23 (3H, t, and 2H, q, CO_2Et), 1.59 (3H, s, 2-Me), 3.37 (1H, d, 4-H), 3.73 (1H, dd, 5-H), 3.88 (1H, d, 1-H), $J_{1,5}$=1.8 Hz, $J_{4,5}$=3 Hz. High-resolution MS m/z: M^+ Calcd for $C_{15}H_{26}N_2O_3$: 282.1943. Found: 282.1949.

6-(*tert*-Butyldimethylsilyl)-3-ethoxycarbonyl-4-methyl-3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-one (**20c**): 49% yield. IR (neat): 1740 and 1725 (C=O) cm^{-1}. ^{1}H-NMR δ: 0.21 and 0.37 (each 3H, s, Si-Me), 1.01 (9H, s, *tert*-Bu), 1.29 and 4.20 (3H, t, and 2H, q, CO_2Et), 1.56 (3H, s, 4-Me), 3.43 (1H, d, 2-H), 3.68 (1H, d, 5-H), 3.92 (1H, dd, 1-H), $J_{1,2}$=3.5 Hz, $J_{1,5}$=1.8 Hz. High-resolution MS m/z: M^+ Calcd for $C_{15}H_{26}N_2O_3$: 282.1943. Found: 282.1944.

6-Aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-ones (21a—c) General Procedure: A solution of a silyl compound (**19a—c**: 0.2—0.3 g) in ether–MeOH (50 : 1) was passed through a short alumina column (0.25 × 3 cm). The eluent was evaporated *in vacuo* and the resulting solid residue was recrystallized from benzene–IPE to give **21** as colorless prisms.

6-Aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**21a**): 97% yield, mp 105—106 °C. MS m/z: 111 (M^+). IR (KBr): 3284 (NH), 1734 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.81 (1H, dd, 5-H), 4.08 (1H, dd, 1-H), 4.25 (1H, dd, 4-H), 4.28 (1H, dd, 2-H), 6.7 (1H, br, 6-NH), $J_{1,2}$=3.4 Hz, $J_{1,5}$=1.7 Hz, $J_{2,4}$=2 Hz, $J_{4,5}$=3.7 Hz. *Anal.* Calcd for $C_5H_5NO_2$: C, 54.05; H, 4.54; N, 12.61. Found: C, 54.03; H, 4.49; N, 12.48.

2-Methyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**21b**): 95% yield, mp 112.5—113.5 °C. MS m/z: 125 (M^+). IR (KBr): 3305 (NH), 1740 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.68 (3H, s, 2-Me), 3.76 (1H, dd, 5-H), 3.98 (1H, d, 1-H), 4.23 (1H, d, 4-H), 6.6 (1H, br, 6-NH), $J_{1,5}$=1.5 Hz, $J_{4,5}$=3.7 Hz. *Anal.* Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.65; H, 5.64; N, 11.09.

4-Methyl-6-aza-3-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**21c**): 95% yield, mp 89—90 °C. MS m/z: 125 (M^+). IR (KBr): 3280 (NH), 1756 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.66 (3H, s, 4-Me), 3.69 (1H, d, 5-H), 4.02 (1H, dd, 1-H), 4.18 (1H, d, 2-H), 6.8 (1H, br, 6-NH), $J_{1,2}$=3.4 Hz, $J_{1,5}$=1.7 Hz. *Anal.* Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.49; H, 5.78; N, 11.18.

3-Ethoxycarbonyl-3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-ones (22a—c) The silyl compounds **20a—c** (0.3—0.5 g) were passed through a short alumina column and worked up as described for **21** to give **22a—c** as colorless needles (from benzene–IPE).

3-Ethoxycarbonyl-3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-one (**22a**): 96% yield, mp 110—112 °C. MS m/z: 182 (M^+). IR (KBr): 3272 (NH), 1742 and 1722 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.29 and 4.20 (3H, t, and 2H, q, CO_2Et), 3.60 (2H, m, 2- and 4-H), 3.75 (1H, dd, 5-H), 4.05 (1H, dd, 1-H), 7.04 (1H, br, 6-NH), $J_{1,2}$=3.5 Hz, $J_{1,5}$=1.8 Hz, $J_{4,5}$=3.5 Hz. *Anal.* Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.60; H, 5.52; N, 15.31.

3-Ethoxycarbonyl-2-methyl-3,6-diazatricyclo[3.2.0.0^{2,4}]heptan-7-one (**22b**): 95% yield, mp 91.5—92.5 °C. MS m/z: 196 (M^+). IR (KBr): 3270 (NH), 1734 and 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.30 and 4.19 (3H, t,

and 2H, q, CO_2Et), 1.60 (3H, s, 2-Me), 3.50 (1H, d, 4-H), 3.75 (1H, dd, 5-H), 3.97 (1H, d, 1-H), 6.75 (1H, br, NH), $J_{1,5}=1.8$ Hz, $J_{4,5}=3.5$ Hz. *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 54.97; H, 6.19; N, 14.25.

3-Ethoxycarbonyl-4-methyl-3,6-diazatricyclo[3.2.0.$0^{2,4}$]heptan-7-one (**22c**): 96% yield, mp 92.5—93.5 °C. MS *m/z*: 196 (M^+). IR (KBr): 3216 (NH), 1746 and 1718 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.30 and 4.18 (3H, t, and 2H, q, CO_2Et), 1.56 (3H, s, 4-Me), 3.44 (1H, d, 2-H), 3.68 (1H, d, 5-H), 4.04 (1H, dd, 1-H), 7.04 (1H, br, NH), $J_{1,2}=3.5$ Hz, $J_{1,5}=1.8$ Hz. *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.05; H, 6.10; N, 14.13.

Thermal Isomerization of 21a—c: Formation of 1,4-Oxazepin-5-ones (15a—c) Compounds **21a—c** (0.1—0.2 g) were heated in dichlorobenzene at 145 °C for 1—2 h and worked up as described for **10** to give **15a—c**. The ^{1}H-NMR spectral data for these compounds are collected in Table I.

1,4-Oxazepin-5-one (**15a**): 89% yield; this compound was identical with the product obtained from **13a**.

7-Methyl-1,4-oxazepin-5-one (**15b**): 92% yield, mp 94—95 °C, pale yellow prisms (from benzene–IPE). MS *m/z*: 125 (M^+). IR (KBr): 3250 (NH), 1670 (C=O) cm^{-1}. *Anal.* Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.66; H, 5.40; N, 11.06.

2-Methyl-1,4-oxazepin-5-one (**15c**): 87% yield, mp 30—32 °C, pale yellow prisms (from IPE). MS *m/z*: 125 (M^+). IR (KBr): 3248 (NH), 1692 (C=O) cm^{-1}. *Anal.* Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.54; H, 5.57; N, 11.18.

Thermal Isomerization of 22a—c: Formation of 1*H*-1,4-Diazepin-5-ones (16a—c) Compounds **22a—c** (0.1—0.2 g) were heated in dichlorobenzene at 160 °C for 1—2 h and worked up as described for **10** to give **16a—c**, which were recrystallized from benzene–IPE to give colorless prisms. These ^{1}H-NMR spectral data are collected in Table I.

1-Ethoxycarbonyl-1*H*-1,4-diazepin-5-one (**16a**): 90% yield. This compound was identical with the product from **14a**.

1-Ethoxycarbonyl-7-methyl-1*H*-1,4-diazepin-5-one (**16b**): 95% yield, mp 139—140 °C. MS *m/z*: 196 (M^+). IR (KBr): 3200 (NH), 1722 and 1686 (C=O) cm^{-1}. *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 54.86; H, 6.16; N, 14.22.

1-Ethoxycarbonyl-2-methyl-1*H*-1,4-diazepin-5-one (**16c**): 87% yield, mp 139—139.5 °C. MS *m/z*: 196 (M^+). IR (KBr): 3200 (NH), 1714 and 1668 (C=O) cm^{-1}. *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.10; H, 6.06; N, 14.18.

5-Ethoxy-1,4-oxazepines (23a—c) General Procedure: A solution of an oxazepinone (**15a—c**, *ca.* 100 mg) and triethyloxonium tetrafluoroborate (1.5 mol eq) in CH_2Cl_2 (10 ml) was stirred for 3 h in an ice bath and then diluted with CH_2Cl_2 (50 ml). The reaction solution was successively washed with saturated $NaHCO_3$ and saturated NaCl, dried, and evaporated *in vacuo* to give **23** in 75—85% yield as a yellow viscous oil in a nearly pure state. However, the products **23a—c** were unstable and readily decomposed in a column (silica gel, alumina, or Sephadex LH-20), so they could not be further purified.

5-Ethoxy-1,4-oxazepine (**23a**): IR (neat): 1650 (C=N) cm^{-1}. ^{1}H-NMR (toluene-d_8) δ: 1.23 and 4.20 (3H, t, and 2H, q, OEt), 5.09 (1H, d, 6-H), 5.45 (1H, d, 2-H), 5.89 (1H, d, 3-H), 5.93 (1H, d, 7-H), $J_{2,3}=4.5$ Hz, $J_{6,7}=6$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_7H_9NO_2$: 139.0633. Found: 139.0626.

5-Ethoxy-7-methyl-1,4-oxazepine (**23b**): IR (neat): 1640 (C=N) cm^{-1}. ^{1}H-NMR (toluene-d_8) δ: 1.26 and 4.09 (3H, t, and 2H, q, OEt), 1.85 (3H, s, 7-Me), 5.13 (1H, br s, 6-H), 5.63 (1H, d, 2-H), 5.81 (1H, d, 3-H), $J_{2,3}=4.5$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0783.

5-Ethoxy-2-methyl-1,4-oxazepine (**23c**): IR (neat): 1652 (C=N) cm^{-1}. ^{1}H-NMR (toluene-d_8) δ: 1.30 and 4.24 (3H, t, and 2H, q, OEt), 1.75 (3H, d, 2-Me), 5.19 (1H, d, 6-H), 5.94 (1H, q, 3-H), 6.08 (1H, d, 7-H), $J_{2\text{-Me},3}=1$ Hz, $J_{6,7}=6$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0779.

5-Ethoxy-1-ethoxycarbonyl-1*H*-1,4-diazepines (24a—c) The diazepinones (**16a—c**, *ca.* 100 mg) were treated with triethyloxonium tetrafluoroborate and worked up as described for **23** to give **24a—c**, which were purified by chromatography on alumina using ether–hexane (1 : 10) as an eluent.

5-Ethoxy-1-ethoxycarbonyl-1*H*-1,4-diazepine (**24a**): 86% yield, mp 36.5—37 °C, yellow prisms (from IPE–hexane). IR (KBr): 1720 (C=O), 1660 (C=N) cm^{-1}. ^{1}H-NMR δ: 1.28 and 1.30 (each 3H, t, $OCH_2C\underline{H}_3$), 4.09 and 4.23 (each 2H, q, OCH_2), 5.12 (1H, d, 6-H), 5.55 (1H, d, 2-H), 5.87 (1H, d, 3-H), 6.57 (1H, d, 7-H), $J_{2,3}=6$ Hz, $J_{6,7}=9$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_{10}H_{14}N_2O_3$: 210.1004. Found: 210.1011.

5-Ethoxy-1-ethoxycarbonyl-7-methyl-1*H*-1,4-diazepine (**24b**): 88% yield, pale yellow viscous oil (solidified at below 25 °C). IR (neat): 1722 (C=O), 1668 (C=N) cm^{-1}. ^{1}H-NMR δ: 1.28 and 1.30 (each 3H, t, $OCH_2C\underline{H}_3$), 4.12 and 4.20 (each 2H, q, OCH_2), 2.20 (3H, s, 7-Me), 5.48 (1H, s, 6-H), 5.66 (1H, d, 2-H), 6.20 (1H, d, 3-H), $J_{2,3}=5$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_{11}H_{16}N_2O_3$: 224.1161. Found: 224.1180.

5-Ethoxy-1-ethoxycarbonyl-2-methyl-1*H*-1,4-diazepine (**24c**): 80% yield, pale yellow viscous oil. IR (neat): 1720 (C=O), 1648 (C=N) cm^{-1}. ^{1}H-NMR δ: 1.28 and 1.30 (each 3H, t, $OCH_2C\underline{H}_3$), 4.12 and 4.19 (each 2H, q, OCH_2), 1.97 (1H, d, 2-Me), 5.42 (1H, d, 6-H), 6.10 (1H, q, 3-H), 6.57 (1H, d, 7-H), $J_{2\text{-Me},3}=1.5$ Hz, $J_{6,7}=9$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_{11}H_{16}N_2O_3$: 224.1161. Found: 224.1168.

Thermolysis of 23a A solution of **23a** (50 mg) in toluene (3 ml) was heated at 45 °C for 1 h and then evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 10) as an eluent to give 2-ethoxy-5-hydroxypyridine (**26**): 30 mg, 60% yield, mp 56—57 °C, colorless prisms (from benzene–IPE). MS *m/z*: 139 (M^+). IR (KBr): 3300—3500 (br, OH) cm^{-1}. ^{1}H-NMR δ: 1.36 and 4.24 (3H, t, and 2H, q, OEt), 6.64 (1H, d, 3-H), 7.20 (1H, dd, 4-H), 7.74 (1H, d, 6-H), $J_{3,4}=9$ Hz, $J_{4,6}=2.5$ Hz. *Anal.* Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.54; H, 6.38; N, 10.01. The structure of **26** was further confirmed by the following result. Compound **26** was treated with 48% HBr and worked up as reported for 4-hydroxy-2-methoxypyridine[18] to give 4-hydroxy-2-pyridone, which was identical with an authentic sample prepared by the reported method.[16]

Thermolysis of 24a A solution of **24a** (50 mg) in dichlorobenzene (2 ml) was heated at *ca.* 180 °C for 12 h in a sealed tube and then chromatographed on silica gel using ether–hexane (1 : 5) as an eluent to give 2-ethoxy-5-ethoxycarbonylaminopyridine (**27**): 39 mg, 78% yield, mp 94—95 °C, colorless prisms (from EtOH). MS *m/z*: 210 (M^+). IR (KBr): 3322 (NH), 1698 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.30 and 1.38 (each 3H, t, $OCH_2C\underline{H}_3$), 4.22 and 4.30 (each 2H, q, OCH_2), 6.68 (1H, d, 3-H), 7.76 (1H, dd, 4-H), 8.02 (1H, d, 6-H), $J_{3,4}=9$ Hz, $J_{4,6}=2$ Hz. *Anal.* Calcd for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.33. Found: C, 57.07; H, 6.63; N, 13.30.

References and Notes

1) The title of the series of "Studies on Diazepines" is replaced by the present title. Studies on Diazepines. XXX: J. Kurita, N. Kakusawa, and T. Tsuchiya, *Chem. Pharm. Bull.*, **36**, 4706 (1988).
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