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Studies on Diazepines. XVII.[1] Synthesis of Monocyclic 1,3-Diazepines. (2). Substituent Effects on the Thermal Ring-conversion of 1,2-Diazepines into 1,3-Diazepines

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The thermolysis of 1,2-diazepines (**7a**—**f** and **11**) having an electron-donating substituent in the 4- or 6-position resulted in the formation of the 1,3-diazepines (**9** and **12**) and 2-aminopyridines (**10**), whereas 1,2-diazepines (**7g**—**k**) having an electron-withdrawing substituent in the same position gave only 2-aminopyridines (**10**) and no 1,3-diazepines. However, the thermolysis of 3-, 5-, or 7-substituted 1,2-diazepines with either an electron-donating or -withdrawing substituent did not give 1,3-diazepines. Heating of the bicyclic compounds (**8**) also gave the corresponding 1,3-diazepines.

Based on these results, we concluded that the presence of an electron-donating substituent is essential for this ring-conversion of 1,2-diazepines into 1,3-diazepines. These substituent effects and the reaction mechanism are discussed.

Keywords——thermolysis; rearrangement; ring-conversion; substituent effect; 1,2-diazepines; 1,3-diazepines; pyridine N-imides; 2-acylaminopyridines

In the previous paper,[1] it was shown that 1,2-diazepines (**2**) having a methyl group in the 4- or 6-position, prepared from the corresponding 3-methylpyridine N-imides (**1**), undergo thermal rearrangement with ring-conversion to give the novel 1,3-diazepines (**3**), whereas 1,2-diazepines having no methyl group in these positions do not give 1,3-diazepines. In an attempt to clarify this substituent effect on the rearrangement, the thermolysis of various substituted 1,2-diazepines was examined. The results obtained indicated that the presence of an electron-donating substituent in the 4- and/or 6-position is essential for the thermal ring-conversion of 1,2-diazepines into 1,3-diazepines. This paper describes in detail these results and the substituent effects on the present thermolysis.[2]

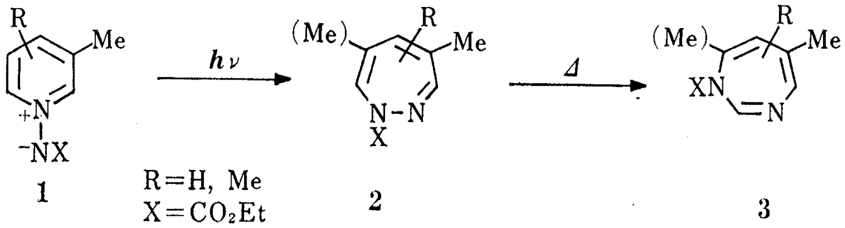
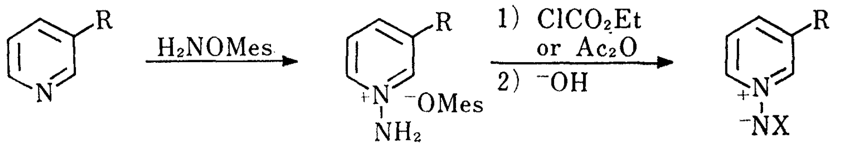


Chart 1

Various 3-substituted pyridines (**4a**—**h**) were aminated with O-mesitylenesulfonylhydroxylamine[3] to give the corresponding N-aminopyridinium mesitylenesulfonates (**5a**—**h**) in high yields. Treatment of the salts (**5**) with ethyl chloroformate in ethanol in the presence of potassium carbonate gave the N-ethoxycarbonylimides (**6**) in good yields. However, the acetoxy compound (**5d**) was readily hydrolyzed under these basic conditions and did not give 3-acetoxypyridine N-ethoxycarbonylimide. Therefore, the N-acetylimide (**6d**) was prepared by treatment of **5d** with acetic anhydride in 88% yield.

Irradiation of the N-imides (**6**) thus obtained resulted in the formation of the corresponding 1,2-diazepines (**7a**—**k**; see Table I) and/or the 2H-2,3-diazabicyclo[3.2.0]heptadienes (**8a**—**d**, **l**, **m**; see Table II) in the yields given in the experimental section. The pyridine N-imides

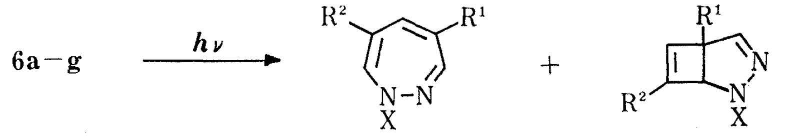


4 5 6

a: R=OMe
b: R=SMe
c: R=Ph
d: R=OAc

e: R=Br
f: R=CO_2Et
g: R=NHAc
h: R=NMe_2

6a—c: X=CO_2Et
6d: X=Ac
6e—h: X=CO_2Et

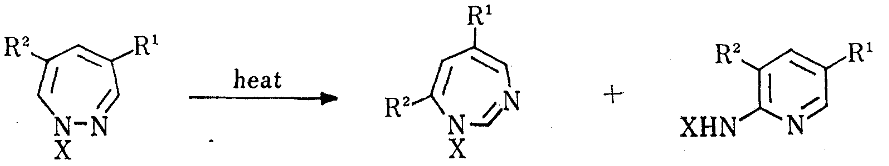


7a−k 8a−d,l,m

Chart 2

6a—**e**: R=OMe, SMe, Ph, OAc, or Br) gave the corresponding 4- and 6-substituted 1,2-diazepines, by analogy with the case of 3-methylpyridine N-imides,[1] whereas the N-imide (**6f**: R=CO_2Et) gave only the 4-substituted 1,2-diazepine (**7k**) in 71% yield.[4] Since the 1,2-diazepines (**7a**—**d**: R=OMe or SMe) are susceptible to photo-induced cyclization, the N-imides (**6a**, **b**), upon irradiation also gave the corresponding bicyclic compounds (**8a**—**d**) along with **7a**—**d**. In contrast, the N-imide (**6g**) (R=NHAc) gave only the bicyclic compounds (**8l**, **m**) and no 1,2-diazepines. The irradiation of the N-imide (**6h**) (R=NMe_2) gave a different result from those for the other N-imides, as will be discussed later.

Heating of the 1,2-diazepines (**7a**—**k**) thus obtained in refluxing benzene, toluene, xylene, or mesitylene resulted in the formation of 1,3-diazepines (**9**) and/or 2-aminopyridines (**10**). The yields of these products and the reaction conditions are summarized in Table I.



7 9 10

Chart 3

These results show that the 1,2-diazepines (**7a**—**f**) having an electron-donating substituent such as methoxy, methylthio, and phenyl give both 1,3-diazepines (**9**) and 2-aminopyridines (**10**), analogous to the results observed for 4- or 6-methyl-1,2-diazepines.[1] In contrast, 1,2-diazepines (**7g**—**k**) having an electron-withdrawing substituent (such as acetoxy, bromo, and ethoxycarbonyl) give only 2-aminopyridines (**10**) and no 1,3-diazepines (**9**). In addition, the 1,2-diazepines (**7a**, **b**) (R=OMe) readily rearrange at lower temperature to give **9** in higher yields than in the cases of **7c**—**f** (R=SMe or Ph). The yields of 1,3-diazepines from the 4-substituted 1,2-diazepines (**7a**, **c**, **e**) are somewhat higher than those from the corresponding 6-substituted isomers (**7b**, **d**, **f**). It should be noted that **7k** (R=CO_2Et) with a strong electron-withdrawing group gives the parent N-imide (**6f**) together with the 2-aminopyridine derivative (**10k**).

Table I. Thermolysis of the 1,2-Diazepines (**7**)

	7		Solvent[a)]	Reaction time (h)	Product (Yield %)	
	R^1	R^2			**9**	**10**
a	OMe	H	B	1	60	35
b	H	OMe	B	1	50	45
c	SMe	H	T	2	55	35
d	H	SMe	X	1.2	35	60
e	Ph	H	X	2	40	40
f	H	Ph	X	1.5	(35)[b)]	55
g	OAc	H	X	40	—	75
h	H	OAc	X	38	—	70
i	Br	H	M	1.5	—	65
j	H	Br	M	1.5	—	75
k	CO_2Et	H	M	3	—	35[c)]

a) B, benzene (80°); T, toluene (110°); X, xylene (140°); M, mesitylene (165°).
b) The compound (**9f**) gradually decomposed during isolation.
c) The parent N-imide (**6f**) was also obtained in 35—40 % yield.

Next, the thermal behavior of the bicyclic compounds (**8**) was also examined and the results obtained are shown in Chart 4 and Table II. The methoxy (**8a, b**) and methylthio derivatives (**8c, d**) gave the corresponding 1,3-diazepines (**9**) and 2-aminopyridines (**10**), respectively, as was the case in the direct thermolysis of the 1,2-diazepines (**7a**—**d**). However, the acetylamino compounds **8l** and **8m** gave only one kind of product; the former gave the 1,3-diazepine (**9l**) and the latter gave the 2-aminopyridine (**10m**). As compared with the cases of 1,2-diazepines, higher temperatures or longer reaction times are needed for the thermolysis of the bicyclic compounds.

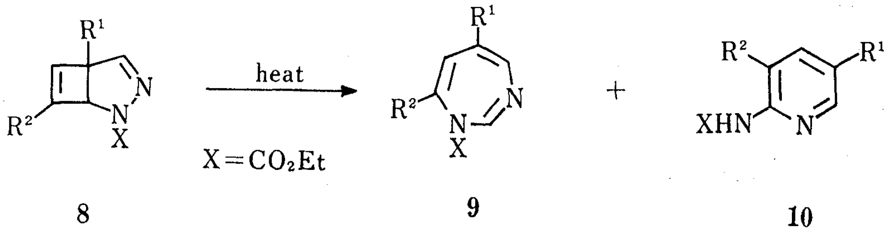
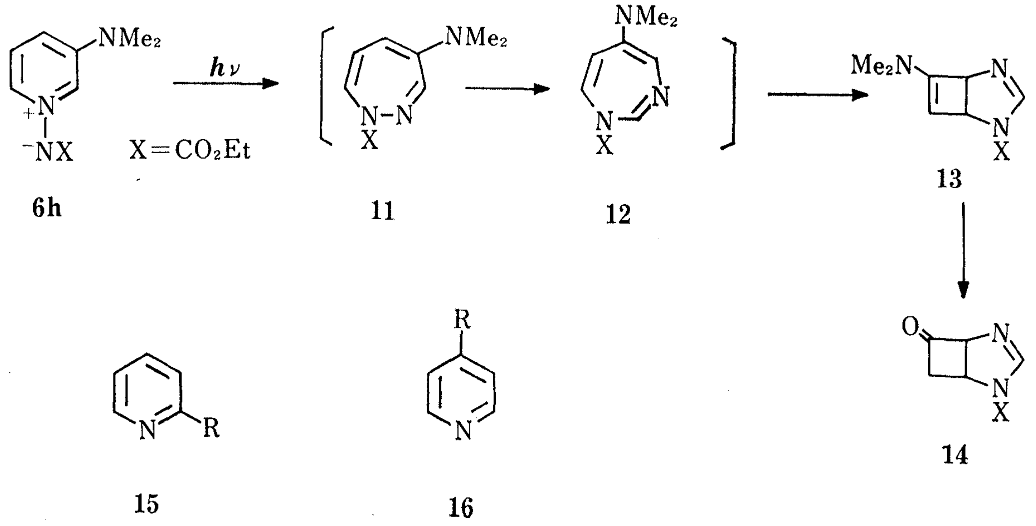


Chart 4

Table II. Thermolysis of the 2,3-Diazabicyclo[3.2.0]heptadienes (**8**)

	8		Solvent	Reaction time (h)	Product (Yield %)	
	R^1	R^2			**9**	**10**
a	OMe	H	T	0.5	55	35
b	H	OMe	M	5	40	20
c	SMe	H	X	1	45	35
d	H	SMe	M	2	35	35
l	NHAc	H	X	0.8	75	—
m	H	NHAc	M	5	—	45

As mentioned above, the 3-dimethylaminopyridine N-imide (**6h**) showed somewhat different photochemical behavior. Irradiation of **6h** in benzene for 2 h at room temperature resulted in the formation of the 2H-2,4-diazabicyclo[3.2.0]heptadiene (**13**) in *ca.* 80% yield; its formation was confirmed by nuclear magnetic resonance (NMR) spectral analysis of the residue obtained upon concentration of the reaction solution. However, the product (**13**) gradually decomposed during isolation by chromatography, so the residue was hydrolyzed without purificantion to give the 6-oxo compound (**14**) in 56% yield. The product (**13**) may be formed from the 1,3-diazepine (**12**) derived from the 1,2-diazepine (**11**) initially formed. This result indicates that the ring-conversion of **11** into **12** occurs readily below room temperature.



6h **11** **12** **13** **14** **15** **16**

R=NMe$_2$, OMe, CO$_2$Et

Chart 5

The physical, analytical, and some spectral [infrared (IR), ultraviolet (UV), mass, and NMR)] data for the new 1,3-diazepines (**9**) are collected in Table III. The data are consistent with the proposed structures.

Table III. 1H-1,3-Diazepines (**9**)

Compd No.	IR $\nu_{max}^{CHCl_3}$ cm^{-1} (C=O)	UV λ_{max}^{EtOH} nm (ε)	Formula (MS m/e: M$^+$)	Analysis (%) Found (Calcd)			^{1}H-NMR (δ) CDCl$_3$, J=Hz[c)]				
				C	H	N	2-H	4-H	6-H	5-R^1	7-R^2
9a[a)]	1720	245 (5500) 305 (1700)	$C_9H_{12}N_2O_3$ (196)	55.33 (55.09	6.12 6.17	14.10 14.28)	6.63 (s)	6.21 (d)	5.42 (dd)	3.61 (s) OMe	5.91 (d) H
9b[a)]	1720	235 (5000) 304 (2000)	$C_9H_{12}N_2O_3$ (196)	55.00 (55.09	6.28 6.17	14.02 14.28)	6.73 (s)	6.79 (d)	5.23 (d)	5.96 (dd) H	3.72 (s) OMe
9c[a)]	1725	258 (6500) 318 (2800)	$C_9H_{12}N_2O_2S$ (212)	50.71 (50.92	5.80 5.70	13.13 13.20)	6.66 (s)	6.84 (d)	5.66 (dd)	2.26 (s) SMe	5.85 (d) H
9d[a)]	1720	260 (3800) 314 (2100)	$C_9H_{12}N_2O_2S$ (212)	50.68 (50.92	5.66 5.70	13.41 13.20)	6.61 (s)	6.98 (m)	5.95—6.10 (m)	H	2.43 (s) SMe
9e[a)]	1720	245 (11000) 291 (7300)	$C_{14}H_{14}N_2O_2$ (242)	69.53 (69.41	5.91 5.82	11.33 11.56)	6.68 (s)	7.13 (d)	5.72 (dd)	7.23 (s) Ph-H	5.92 (d) H
9l[b)]	1660 1720 3250 (NH)	231 (10000) 310 (3000)	$C_{10}H_{13}N_3O_3$ (223)	53.89 (53.81	5.88 5.87	18.76 18.82)	6.63 (s) 7.8 (br, NH)	7.20 (d)	5.72 (dd)	2.05 (s) NHAc-Me	5.85 (d) H

a) Pale yellow oil.

b) mp 140.5—142°C, yellow prisms (from AcOEt).

c) $J_{4,5}=8$, $J_{4,6}=1.5$, $J_{5,6}=6$, $J_{6,7}=7$, CO$_2$Et [1.30—1.33 (3H, t) and 4.24—4.28 (2H, q)].

On the other hand, attempts to develop an analogous route to 1,3-diazepines from 2- (**15**) and 4-substituted pyridines (**16**) with either an electron-donating or -withdrawing substituent have not been successful to date. The thermolysis of 3-, 5-, or 7-substituted 1,2-diazepines derived from pyridines having an electron-donating substituent in the 2- or 4-position undergo either rearrangement to give the parent N-imides or N–N fragmentation to give the starting pyridines, as observed for the 3-methyl-, 5-methyl-,[1] and 3,5,7-triphenyl-1H-1,2-diazepine derivatives.[5] In contrast, pyridines with an electron-withdrawing substituent such as an ethoxycarbonyl group do not give the corresponding 1,2-diazepines, as already reported.[6]

The above results clearly show that the presence of an electron-donating substituent in the 4- and/or 6-position is essential for the thermal rearrangement of 1,2-diazepines into 1,3-diazepines. The formation of the 1,3-diazepines (**9**) from **7** may involve the diaziridine intermediate (**17**), which then rearranges to the aziridine (**19**) followed by ring-expansion to **9** as suggested in the previous paper.[1]

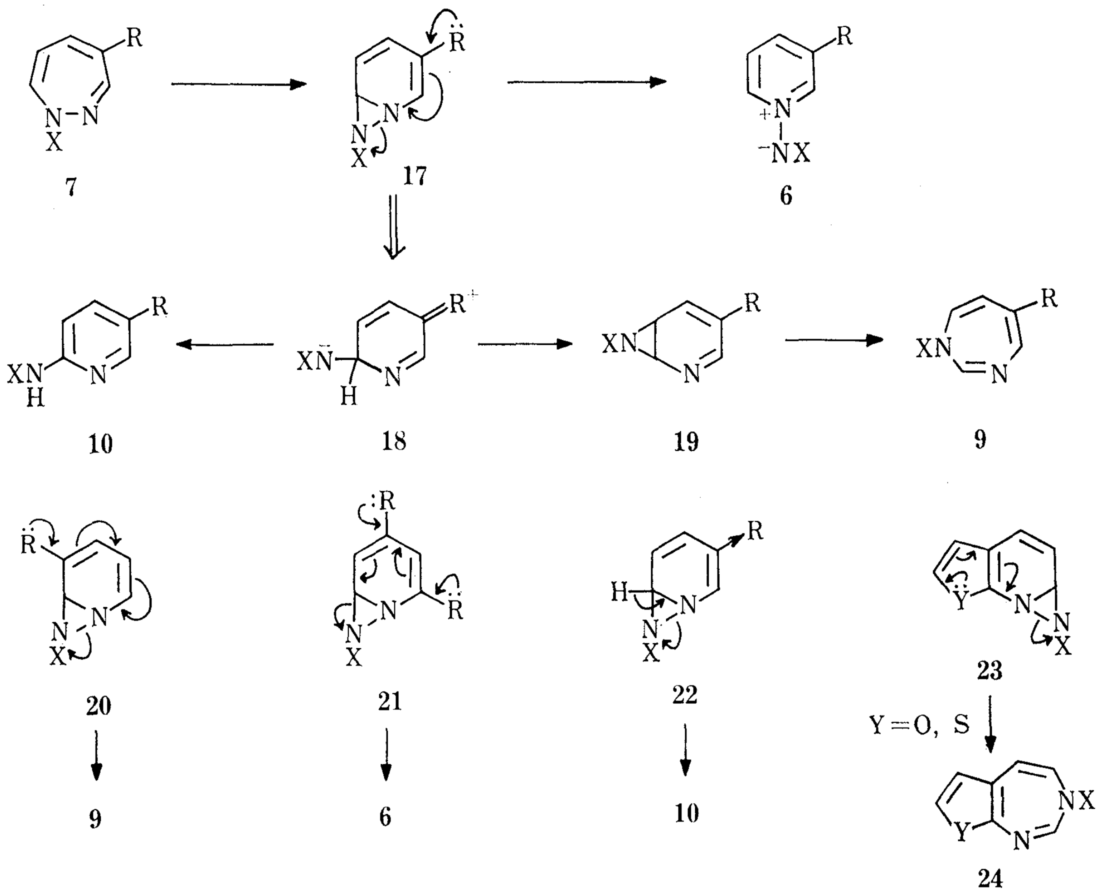


Chart 6

The electron-donating groups may provide assistance for breaking the N–N bond in the diaziridine (**17**) and for cyclization of the resulting dipolar intermediate (**18**) into the aziridine (**19**). This suggestion is supported by the results in Table I and Chart 5, which show that stronger electron-donating groups such as dimethylamino and methoxy groups are more favorable to the ring-conversion than weaker ones such as methylthio, phenyl, and methyl. It was also observed that the rates of the ring-conversion of **7** into **9** in a polar solvent such as pyridine and acetonitrile are about three times faster than those in benzene. This solvent effect supports the involvement of the dipolar intermediate (**18**), and thus another possible mechanism, a concerted [1,5]-sigmatropic process, for the rearrangement of **17** into **19** is unlikely. Similarly, electron-donating groups at C-5 in the diaziridine (**20**) may also assist the formation of **9**. In contrast, electron-donating groups in the 2- or 4-position would assist C–NX bond fission to provide the parent N-imides (**6**) as shown in the structure (**21**). The electron-withdrawing substituent at C-3 in the structure (**22**) may accelerate the elimination of the hydrogen atom at C-6 followed by N–N bond fission to give only 2-aminopyridines (**10**).

We have previously reported that the photolysis of fused pyridine N-acylimides (**23**)$^{7)}$ and related compounds$^{8)}$ gives the corresponding fused 1,3-diazepines, whereas quinoline N-acylimides give no 1,3-diazepines.$^{9)}$ These results can also be explained by this substituent effect, as shown in the structure (**23**); the benzene ring in the quinoline N-imides give no such assistance. Finally, Moore *et al.*$^{10)}$ reported a similar thermal ring-conversion of 1-benzoyl-4-acetoxy-5-methyl-6-phenyl-1H-1,2-diazepine and suggested that the 4-acetoxy group might assist this conversion. However, it seems that the key substituent is not the acetoxy group but the phenyl group in the 6-position in view of our present results; the acetoxy-1,2-diazepines (**7g, h**) did not give 1,3-diazepines (**9g, h**).

Experimental

The general experimental procedures were the same as in Part XVI.$^{1)}$

Starting Materials——3-Methoxy- (**4a**),$^{11)}$ 3-methylthio- (**4b**),$^{12)}$ 3-phenyl- (**4c**),$^{13)}$ 3-acetoxy- (**4d**),$^{14)}$ 3-acetylamino- (**4g**),$^{15)}$ and 3-dimethylamino-pyridine (**4h**)$^{16)}$ were prepared by the cited procedures. 3-Bromo- (**4e**) and 3-ethoxycarbonyl-pyridine (**4f**) were obtained from Tokyo Kasei Kogyo Co., Japan.

N-Aminopyridinium Mesitylenesulfonate (5a—h)——General Procedure: A solution of O-mesitylenesulfonylhydroxylamine (1.1 mol eq) in CH_2Cl_2 (100—150 ml) was added dropwise to a solution of the 3-substituted pyridines (**4**: *ca.* 0.05 mol) in CH_2Cl_2 (30—50 ml) with stirring in an ice bath. The reaction mixture was stirred for an additional 30 min at room temperature. After addition of ether (200—300 ml) to the mixture, the resulting crystalline precipitates were collected by filtration and recrystallized from ethanol or ethanol–ethyl acetate to give the salts (**5**).

5a: 92% yield, mp 104—106°C, colorless prisms. *Anal.* Calcd for $C_{15}H_{20}N_2O_4S$: C, 55.54; H, 6.21; N, 8.64. Found: C, 55.39; H, 6.20; N, 8.49.

5b: The N-amination of **4b** resulted in the formation of **5b** and the S-amino derivative in the ratio of *ca.* 2:1 (*ca.* 60% and 30% yields), as assessed by ^{1}H-NMR spectral analysis. However, since these products could not be separated, the mixture was used in the following reaction without isolation.

5c: 90% yield, mp 118—120°C, colorless prisms. *Anal.* Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.84; H, 5.99; N, 7.56. Found: C, 64.97; H, 6.01; N, 7.73.

5d: 87% yield, mp 131—133°C, colorless prisms. *Anal.* Calcd for $C_{16}H_{20}N_2O_5S$: C, 54.53; H, 5.72; H, 7.95. Found: C, 54.71; H, 5.88; N, 7.93.

5e: 88% yield, mp 157—160°C, colorless prisms. *Anal.* Calcd for $C_{14}H_{17}BrN_2O_3S$: C, 45.05; H, 4.59; N, 7.50. Found: C, 45.16; H, 4.57; N, 7.41.

5f: 92% yield, mp 132—134°C (lit.,$^{17)}$ mp 132—133°C), colorless prisms. *Anal.* Calcd for $C_{17}H_{22}N_2O_5S$: C, 55.72; H, 6.05; N, 7.64. Found: C, 55.84; H, 6.09; N, 7.55.

5g: 96% yield, mp 189—191°C, colorless prisms. *Anal.* Calcd for $C_{16}H_{21}N_3O_4S$: C, 54.68; H, 6.02; N, 11.96. Found: C, 54.78; H, 5.99; N, 12.03.

5h: 91% yield, mp 128—129.5°C, colorless needles. *Anal.* Calcd for $C_{16}H_{23}N_3O_3S$: C, 56.95; H, 6.87; N, 12.45. Found: C, 57.06; H, 6.90; N, 12.44.

Pyridine N-Ethoxycarbonylimides (6a—h)——General Procedure: Ethyl chloroformate (1.1—1.3 mol eq) and solid potassium carbonate (2 mol eq) were added to a solution of the salt (**5**: 0.02—0.04 mol) in ethanol (100—200 ml) with stirring in an ice bath. The mixture was further stirred for 5—6 h at room temperature and the resulting inorganic precipitate was filtered off. The filtrate was concentrated *in vacuo* and the residue was extracted with CH_2Cl_2. The extract was evaporated to dryness *in vacuo* and the residue was chromatographed on silica gel using CH_2Cl_2–MeOH as an eluent to give the imides (**6**).

6a: 95% yield, hygroscopic solid, picrate [mp 141—143°C, yellow prisms (from EtOH)]. MS *m/e*: 196 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640 (C=O). NMR δ: 3.91 (3H, s, OMe), 7.28 (1H, m, 4-H), 7.41 (1H, m, 5-H), 8.39 (1H, m, 6-H), 8.63 (1H, br s, 2-H), $J_{4,5}=9$, $J_{5,6}=6$ Hz, 1.32 and 4.14 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{15}H_{15}N_5O_{10}$ (picrate): C, 42.36; H, 3.56; N, 16.47. Found: C, 42.17; H, 3.52; N, 16.35.

6b: 56% yield (from **4d**), mp 68—70°C, colorless prisms (from benzene). MS *m/e*: 212 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1650 (C=O). NMR δ: 2.55 (3H, s, SMe), 7.39 (1H, dd, 5-H), 7.55 (1H, m, 4-H), 8.50 (1H, m, 6-H), 8.69 (1H, br s, 2-H), $J_{4,5}=8$, $J_{5,6}=6$ Hz, 1.32 and 4.13 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20. Found: C, 50.77; H, 5.68; N, 13.27.

6c: 93% yield, mp 136—138°C, colorless plates (from benzene–$CHCl_3$). MS *m/e*: 242 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1625 (C=O). NMR δ: 7.5—7.7 (5H, m, Ph-H), 7.67 (1H, dd, 5-H), 8.05 (1H, m, 4-H), 8.90 (1H, m, 6-H), 9.23 (1H, m, 2-H), $J_{4,5}=8$, $J_{5,6}=6$ Hz, 1.37 and 4.26 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.36; H, 5.82; N, 11.46.

6e: 90% yield, mp 79—81°C, colorless prisms (from benzene–isopropyl ether). MS *m/e*: 244 and 246 (1:1) (M^+). IR ν_{max}^{KBr} cm^{-1}: 1630 (C=O). NMR δ: 7.39 (1H, dd, 5-H), 7.82 (1H, m, 4-H), 8.74 (1H, m, 6-H), 9.23 (1H, m, 2-H), $J_{4,5}=9$, $J_{5,6}=6$ Hz, 1.31 and 4.15 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_8H_9N_2O_2Br$: C, 39.21; H, 3.70; N, 11.43. Found: C, 39.03; H, 3.74; N, 11.36.

6f: 88% yield, mp 91—92°C (lit.,[4] 93°C), colorless prisms (from benzene–isopropyl ether).

6g: 73% yield, 153—155°C, colorless prisms (from $CHCl_3$–AcOEt). MS *m/e*: 223 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3200 (NH), 1700 and 1580 (C=O). NMR δ: 2.13 (3H, s, Ac), 7.45 (1H, dd, 5-H), 8.16 (1H, d, 6-H), 8.47 (1H, d, 4-H), 9.03 (1H, br s, 2-H), 10.8 (1H, br, NH), $J_{4,5}=9$, $J_{5,6}=6$ Hz, 1.33 and 4.18 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{13}N_3O_3$: C, 53.81; H, 5.87; N, 18.82. Found: C, 54.03; H, 5.80; N, 18.69.

6h: 89% yield, mp 107—109°C, colorless prisms (from benzene–isopropyl ether). MS *m/e*: 209 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1650 (C=O). NMR δ: 3.01 (6H, s, NMe_2), 6.98 (1H, dd, 4-H), 7.27 (1H, dd, 5-H), 7.99 (1H, d, 6-H), 8.16 (1H, d, 2-H), $J_{2,4}=2$, $J_{4,5}=9$, $J_{5,6}=6$ Hz, 1.31 and 4.11 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{15}N_3O_2$: C, 57.40; H, 7.23; N, 20.08. Found: C, 57.36; H, 7.21; N, 20.01.

3-Acetoxypyridine N-Acylimide (6d)——A mixture of the salt (**5d**: 10 g) and acetic anhydride (80 ml) was heated at 85—90°C with stirring for 6 h. After removal of excess acetic anhydride *in vacuo*, the residue was dissolved in CH_2Cl_2 (200 ml) and the solution was washed with 50% K_2CO_3, dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The resulting solid residue was recrystallized from benzene to give the imide (**6d**): 4.9 g, 88% yield, mp 130—132°C, colorless needles. MS *m/e*: 194 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1740 and 1600 (C=O). NMR δ: 2.06 (3H, s, N-Ac), 2.35 (3H, s, OAc), 7.55 (1H, dd, 5-H), 7.70 (1H, m, 4-H), 8.37 (1H, m, 6-H), 8.83 (1H, m, 2-H), $J_{4,5}=8$, $J_{5,6}=6$ Hz. *Anal.* Calcd for $C_9H_{10}N_2O_3$: C, 55.66; H, 5.19; N, 14.43. Found: C, 55.68; H, 5.18; N, 14.48.

Photolysis of the N-Imides (6): Preparation of the 1,2-Diazepines (7a—k) and 2H-2,3-Diazabicyclo[3.2.0]-heptadienes (8a—d, 8l, and 8m)——General Procedure: A solution of an imide (**6**: *ca.* 0.01 mol) in benzene (350 ml) was irradiated and the photolysis was followed in terms of the disappearance of the spot of the starting material on thin-layer chromatography. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using ether–*n*-hexane as an eluent to give **7** and/or **8**.

Irradiation of the 3-methoxypyridine N-imide (**6a**) for 2 h gave **7a** (15%), **7b** (20%), **8a** (30%), and **8b** (5%).

7a (4-OMe): mp 46.5—48°C, yellow prisms (from *n*-hexane–isopropyl ether). MS *m/e*: 196 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1710 (C=O). NMR δ: 3.61 (3H, s, OMe), 5.54 (1H, dd, 5-H), 5.63 (1H, t, 6-H), 5.98 (1H, d, 7-H), 7.23 (1H, d, 3-H), $J_{3,5}=1.5$, $J_{5,6}=6$, $J_{6,7}=6$ Hz, 1.35 and 4.29 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.16; H, 6.18; N, 14.22.

7b (6-OMe): Yellow oil. MS *m/e*: 196 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1705 (C=O). NMR δ: 3.60 (3H, s, OMe), 6.65 (1H, br s, 7-H), 6.22 (1H, dd, 4-H), 6.44 (1H, d, 5-H), 7.38 (1H, d, 3-H), $J_{3,4}=4$, $J_{4,5}=11$ Hz, 1.33 and 4.25 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 54.91; H, 6.21; N, 14.16.

8a (5-OMe): Colorless oil. MS *m/e*: 196 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 (C=O). NMR δ: 3.32 (3H, s, OMe), 4.88 (1H, d, 1-H), 5.90 (1H, d, 7-H), 6.45 (1H, dd, 6-H), 6.92 (1H, s, 4-H), $J_{1,6}=1.5$, $J_{6,7}=3$ Hz, 1.33 and 4.27 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 54.98; H, 6.33; N, 14.00.

8b (7-OMe): Colorless oil. MS *m/e*: 196 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 (C=O). NMR δ: 3.57 (3H, s, OMe), 3.73 (1H, d, 5-H), 4.90 (1H, d, 6-H), 5.14 (1H, dd, 1-H), 6.95 (1H, s, 4-H), $J_{1,5}=4$, $J_{1,6}=2$ Hz, 1.33 and 4.27 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 54.83; H, 6.05; N, 14.01.

Irradiation of the 3-methylthiopyridine N-imide (**6b**) for 3 h gave **7c** (16%), **7b** (21%), **8c** (30%), and **8d** (4%).

7c (4-SMe): Yellow oil. MS *m/e*: 212 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715 (C=O). NMR δ: 2.29 (3H, s, SMe), 5.67 (1H, dd, 6-H), 6.16 (1H, d, 7-H), 6.35 (1H, dd, 5-H), 7.29 (1H, d, 3-H), $J_{3,5}=1.5$, $J_{5,6}=6$, $J_{6,7}=7$ Hz, 1.36 and 4.32 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20. Found: C, 50.68; H, 5.61; N, 13.52.

7d (6-SMe): Yellow oil. MS *m/e*: 212 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710 (C=O). NMR δ: 2.29 (3H, s, SMe), 6.04 (1H, s, 7-H), 6.30 (1H, dd, 4-H), 6.55 (1H, d, 5-H), 7.40 (1H, d, 3-H), $J_{3,4}=4$, $J_{4,5}=11$ Hz, 1.34 and 4.30 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20. Found: C, 50.68; H, 5.77; N, 13.07.

8c (5-SMe): Colorless oil. MS *m/e*: 212 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 (C=O). NMR δ: 2.13 (3H, s, SMe), 4.85 (1H, d, 1-H), 6.16 (1H, d, 7-H), 6.37 (1H, dd, 6-H), 6.84 (1H, s, 4-H), $J_{1,6}=1.5$, $J_{6,7}=3$ Hz, 1.34 and 4.38 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20. Found: C, 50.67; H, 5.79; N, 13.02.

8d (7-SMe): Colorless oil. MS *m/e*: 212 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 (C=O). NMR δ: 2.22 (3H, s, SMe), 4.07 (1H, br d, 5-H), 5.06 (1H, dd, 1-H), 5.95 (1H, d, 6-H), 6.94 (1H, br s, 4-H), $J_{1,5}=4$, $J_{1,6}=2$ Hz, 1.34 and 4.30 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20. Found: C, 50.86; H, 5.73; N, 13.01.

Irradiation of the 3-phenylpyridine N-imide (**6c**) for 4.5 h gave **7e** (42%) and **7f** (39%).

7e (4-Ph): mp 70—72°C, red prisms (from isopropyl ether). MS *m/e*: 242 (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1730 (C=O). NMR δ: 5.75 (1H, dd, 6-H), 6.24 (1H, d, 7-H), 6.74 (1H, dd, 5-H), 7.27 (5H, s, Ph-H), 7.69 (1H, d, 3-H), $J_{3,5}=1.5$, $J_{5,6}=6$, $J_{6,7}=7$ Hz, 1.36 and 4.30 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.38; H, 5.81; N, 11.63.

7f (6-Ph): mp 107—108.5°C, yellow plates (from benzene-isopropyl ether). MS *m/e*: 242 (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1710 (C=O). NMR δ: 6.50 (1H, dd, 4-H), 6.61 (1H, s, 7-H), 7.02 (1H, d, 5-H), 7.5 (5H, s, Ph-H), 7.68 (1H, d, 3-H), $J_{3,4}=4$, $J_{4,5}=11$ Hz, 1.41 and 4.44 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.44; H, 5.81; N, 11.46.

Irradiation of the 3-acetoxypyridine N-imide (**6d**) for 3.5 h gave **7g** (28%), **7h** (17%), and 3-acetoxypyridine (**4d**) (*ca.* 40%).

7g (4-OAc): mp 82—83°C, yellow needles (from *n*-hexane–isopropyl ether). MS *m/e*: 194 (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1750 and 1670 (C=O). NMR δ: 2.22 and 2.26 (each 3H, s, Ac–Me), 5.74 (1H, t, 6-H), 6.27 (1H, dd, 5-H), 6.30 (1H, d, 7-H), 7.26 (1H, d, 3-H), $J_{3,5}=1.5$, $J_{5,6}=6$, $J_{6,7}=6$ Hz. *Anal.* Calcd for $C_9H_{10}N_2O_3$: C, 55.66; H, 5.19; N, 14.43. Found: C, 55.75; H, 5.20; N, 14.50.

7h (6-OAc): mp 103—105°C, orange prisms (from isopropyl ether). MS *m/e*: 194 (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1755 and 1670 (C=O). NMR δ: 2.17 and 2.22 (each 3H, s, Ac–Me), 6.3 (3H, m, 3-, 4-, and 5-H), 7.44 (1H, br s, 7-H). *Anal.* Calcd for $C_9H_{10}N_2O_3$: C, 55.66; H, 5.19; N, 14.43. Found: C, 55.72; H, 5.15; N, 14.49.

Irradiation of the 3-bromopyridine N-imide (**6e**) for 4 h gave **7i** (45%) and **7j** (40%).

7i (4-Br): mp 81—83°C, orange prisms (from *n*-hexane–isopropyl ether). MS *m/e*: 244 and 246 (1: 1) (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1715 (C=O). NMR δ: 5.58 (1H, dd, 6-H), 6.23 (1H, d, 7-H), 6.83 (1H, dd, 5-H), 7.30 (1H, d, 3-H), $J_{3,5}=1.5$, $J_{5,6}=6$, $J_{6,7}=7$ Hz, 1.37 and 4.31 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_8H_9BrN_2O_2$: C, 39.21; H, 3.70; N, 11.43. Found: C, 39.44; H, 3.80; N, 11.26.

7j (6-Br): mp 61—62°C, orange prisms (from *n*-hexane–isopropyl ether). MS *m/e*: 244 and 246 (1: 1) (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1710 (C=O). NMR δ: 6.20 (1H, dd, 4-H), 6.44 (1H, s, 7-H), 6.51 (1H, d, 5-H), 7.38 (1H, d, 3-H), $J_{3,4}=4$, $J_{4,5}=11$ Hz, 1.35 and 4.30 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_8H_9BrN_2O_2$: C, 39.21; H, 3.70; N, 11.43. Found: C, 39.26; H, 3.66; N, 11.31.

Irradiation of the 3-ethoxycarbonylpyridine N-imide (**6f**) for 8 h gave only **7k** (4-CO_2Et) in 71% yield. It was characterized by comparison of spectral data with the reported values.[4)]

Irradiation of the 3-acetylaminopyridine N-imide (**6g**) for 8 h gave **8l** (12%), **8m** (6%), the parent pyridine (**4g**: 40%), and ethoxycarbonylamino-3-acetylaminopyridine (**10m**: 20%).

8l (5-NHAc): mp 146—148°C, colorless prisms (from AcOEt–isopropyl ether). MS *m/e*: 223 (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3300 (NH), 1720 and 1650 (C=O). NMR δ: 1.97 (3H, s, Ac–Me), 4.84 (1H, d, 1-H), 5.95 (1H, d, 7-H), 6.50 (1H, dd, 6-H), 6.95 (1H, s, 4-H), 8.2 (1H, br, NH), $J_{1,6}=1.5$, $J_{6,7}=3$ Hz, 1.32 and 4.23 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{13}N_3O_3$: C, 53.81; H, 5.87; N, 18.82. Found: C, 53.77; H, 5.91; N, 18.69.

8m (7-NHAc): mp 177—179°C, colorless needles (from $CHCl_3$–AcOEt). MS *m/e*: 223 (M^+). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3250 (NH), 1690 and 1670 (C=O). NMR δ: 2.05 (3H, s, Ac–Me), 3.97 (1H, d, 5-H), 4.97 (1H, dd, 1-H), 5.78 (1H, d, 6-H), 6.98 (1H, d, 4-H), 7.6 (1H, br, NH), $J_{4,5}=1$, $J_{1,5}=4$, $J_{1,6}=2$ Hz, 1.37 and 4.26 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{13}N_3O_3$: C, 53.81; H, 5.87; N, 18.82. Found: C, 53.94; H, 5.91; N, 18.75.

Thermolysis of the 1,2-Diazepines (7a—k): Formation of the 1,3-Diazepines (9) and/or 2-Aminopyridines (10)——General Procedure: A solution of **7** (0.5 mmol) in benzene, toluene, xylene, or mesitylene (10—20 ml) was heated under reflux until the spot of the starting material had disappeared on silica gel thin-layer chromatography. The reaction mixture was concentrated *in vacuo* and the residue was extracted with *n*-hexane. The extract was concentrated *in vacuo* and the residue was chromatographed on Sephadex (LH-20) using $CHCl_3$–*n*-hexane (4: 1) as an eluent to give the 1,3-diazepines (**9**). The above *n*-hexane-insoluble fraction was chromatographed on silica gel using CH_2Cl_2–*n*-hexane as an eluent to give the 2-aminopyridines (**10**).

Reaction conditions for thermolysis and the yields of these products are shown in Table I. The physical, analytical, and spectral data for the 1,3-diazepines (**9**) are collected in Table III. The data for **10** are given below.

10a (5-OMe): mp 154—156°C, colorless prisms (from AcOEt). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200 (NH), 1725 (C=O). NMR δ: 3.81 (3H, s, OMe), 7.22 (1H, dd, 4-H), 7.90 (1H, d, 3-H), 7.98 (1H, d, 6-H), 9.3 (1H, br, NH), $J_{3,4}=9$, $J_{4,6}=2$ Hz, 1.36 and 4.23 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.14; H, 6.18; N, 14.34.

10b (3-OMe): mp 97—99°C, colorless needles (from AcOEt–isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3100 (NH), 1710 (C=O). NMR δ: 3.83 (3H, s, OMe), 6.88 (1H, dd, 5-H), 7.05 (1H, dd, 4-H), 7.4 (1H, br, NH), 7.92 (1H, dd, 6-H), $J_{4,5}=7$, $J_{4,6}=1.5$, $J_{5,6}=5$ Hz, 1.31 and 4.21 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.01; H, 6.14; N, 14.11.

10c (5-SMe): mp 133—135°C, colorless plates (from benzene–isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200

(NH), 1720 (C=O). NMR δ: 2.43 (3H, s, SMe), 7.60 (1H, dd, 4-H), 7.93 (1H, d, 3-H), 8.25 (1H, d, 6-H), 9.6 (1H, br, NH), $J_{3,4}=9$, $J_{4,6}=2$ Hz, 1.36 and 4.24 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20. Found: C, 51.02; H, 5.76; N, 13.07.

10d (3-SMe): mp 93—94°C, colorless prisms (from isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3150 (NH), 1730 (C=O). NMR δ: 2.37 (3H, s, SMe), 6.97 (1H, dd, 5-H), 7.66 (1H, dd, 4-H), 7.7 (1H, br, NH), 8.30 (1H, dd, 6-H), $J_{4,5}=7$, $J_{4,6}=1.5$, $J_{5,6}=5$ Hz, 1.33 and 4.25 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20. Found: C, 50.99; H, 5.68; N, 13.11.

10e (5-Ph): mp 169—171°C, colorless plates (from benzene). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200 (NH), 1720 (C=O). NMR δ: 7.1—7.5 (5H, m, Ph-H), 7.75 (1H, dd, 4-H), 7.97 (1H, d, 3-H), 8.44 (1H, d, 6-H), 9.7 (1H, br, NH), $J_{3,4}=9$, $J_{4,6}=2$ Hz, 1.33 and 4.22 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.47; H, 5.82; N, 11.43.

10f (3-Ph): mp 113—115°C, colorless prisms (from benzene–isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200 (NH), 1740 (C=O). NMR δ: 7.00 (1H, dd, 5-H), 7.1—7.4 (5H, m, Ph-H), 7.44 (1H, dd, 4-H), 7.4 (1H, br, NH), 8.29 (1H, dd, 6-H), $J_{4,5}=7$, $J_{4,6}=1.5$, $J_{5,6}=5$ Hz, 1.18 and 4.04 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.43; H, 5.82; N, 11.42.

10g (5-OAc): mp 164—166°C, colorless needles (from benzene). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} : 3300 (NH), 1760 and 1690 (C=O). NMR δ: 7.42 (1H, dd, 4-H), 8.02 (1H, d, 6-H), 8.21 (1H, d, 3-H), 9.0 (1H, br, NH), $J_{3,4}=8$, $J_{4,6}=3$ Hz, 2.17 and 2.39 (each 3H, s, Ac-Me). *Anal.* Calcd for $C_9H_{10}N_2O_3$: C, 55.66; H, 5.19; N, 14.43. Found: C, 55.57; H, 5.20; N, 14.49.

10h (3-OAc): mp 118—120°C, colorless needles (from benzene–isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200 (NH), 1760 and 1690 (C=O). NMR δ: 2.26 (6H, s, Ac-Me), 7.03 (1H, dd, 5-H), 7.42 (1H, dd, 4-H), 8.07 (1H, dd, 6-H), $J_{4,5}=7$, $J_{4,6}=1.5$, $J_{5,6}=5$ Hz. *Anal.* Calcd for $C_9H_{10}N_2O_3$: C, 55.66; H, 5.19; N, 14.43. Found: C, 55.54; H, 5.16; N, 14.41.

10i (5-Br): mp 188—189°C, colorless needles (from AcOEt). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200 (NH), 1725 (C=O). NMR δ: 7.78 (1H, dd, 4-H), 7.97 (1H, d, 3-H), 8.38 (1H, d, 6-H), 8.8 (1H, br, NH), $J_{3,4}=9$, $J_{4,6}=2$ Hz, 1.37 and 4.28 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_8H_9BrN_2O_2$: C, 39.21; H, 3.70; N, 11.43. Found: C, 39.31; H, 3.69; N, 11.21.

10j (3-Br): mp 77—78.5°C, colorless prisms (from isopropyl ether). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200 (NH), 1725 (C=O). NMR δ: 7.03 (1H, dd, 5-H), 7.6 (1H, br, NH), 7.96 (1H, dd, 4-H), 8.53 (1H, dd, 6-H), $J_{4,5}=7$, $J_{4,6}=1.5$, $J_{5,6}=5$ Hz, 1.38 and 4.35 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_8H_9BrN_2O_2$: C, 39.21; H, 3.70; N, 11.43. Found: C, 39.26; H, 3.75; N, 11.31.

10k (5-CO_2Et): mp 165—167°C, colorless needles (from benzene). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200 (NH), 1730 and 1700 (C=O). NMR δ: 7.97 (1H, d, 3-H), 8.16 (1H, dd, 4-H), 8.85 (1H, d, 6-H), 9.8 (1H, br, NH), $J_{3,4}=8$, $J_{4,6}=2$ Hz, [1.40 and 1.42 (each 3H, t), 4.28 and 4.32 (each 2H, q), $2CO_2Et$]. *Anal.* Calcd for $C_{11}H_{14}N_2O_4$: C, 55.45; H, 5.92; N, 11.76. Found: C, 55.47; H, 5.90; N, 11.59.

Thermolysis of the 2,3-Diazabicyclo[3.2.0]heptadienes (8a—d, l, m)——A solution of **8** (*ca.* 0.5 mmol) in toluene, xylene, or mesitylene (10—15 ml) was refluxed and then worked up as described for the 1,2-diazepines (**7**) to give the corresponding 1,3-diazepines (**9**) and/or 2-aminopyridines (**10**). The reaction conditions and the yields of these products are listed in Table II. The physical, analytical, and spectral data for the 1,3-diazepine (**9l**) are also given in Table III.

10m (3-NHAc): mp 215—218°C, colorless prisms (from EtOH). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3250 (NH), 1720 and 1690 (C=O). NMR δ: 2.17 (3H, s, Ac-Me), 7.16 (1H, dd, 5-H), 8.14 (1H, br d, 6-H), 8.30 (1H, br d, 4-H), 9.2—9.3 (2H, br, NH), $J_{4,5}=7$, $J_{5,6}=5$ Hz, 1.37 and 4.29 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{13}N_3O_3$: C, 53.81; H, 5.87; N, 18.82. Found: C, 53.55; H, 5.90; N, 18.88.

Photolysis of the 3-Dimethylaminopyridine N-Imide (6h)——A solution of **6h** (1.0 g) in benzene (350 ml) was irradiated for 2 h and then concentrated *in vacuo* to yield 6-dimethylamino-2-ethoxycarbonyl-2,4-diazabicyclo[3.2.0]heptadiene (**13**), the identity of which was confirmed by the NMR spectrum of the resulting residue [δ: 2.73 (6H, s, NMe_2), 3.57 (2H, m, 1- and 5-H), 4.09 (1H, m, 7-H), 7.54 (1H, s, 3-H)]. However, the compound (**13**) was readily decomposed during purification by chromatography. Therefore, tetrahydrofuran (16 ml) and water (4 ml) were added to the residue and the mixture was stirred for 1 h at room temperature. After concentration *in vacuo*, the resulting residue was chromatographed on silica gel using *n*-hexane–ether as an eluent to give 2-ethoxycarbonyl-6-oxo-2,4-diazabicyclo[3.2.0]hepta-3-ene (**14**): 493 mg, 56% yield, colorless oil. MS *m/e*: 182 (M^+). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1800 and 1730 (C=O). NMR δ: 3.23 and 3.64 (each 1H, m, 7-H_2), 4.64 (1H, m, 5-H), 5.52 (1H, m, 1-H), 7.65 (1H, br s, 3-H), $J_{7,7'}=19$ Hz, 1.36 and 4.28 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.55; H, 5.56; N, 15.13.

References and Notes

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