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Studies on Diazepines. XXII.[1] Synthesis of Monocyclic 1,4-Dihetero Seven-Membered Ring Compounds Using Thermal Valence Bond Isomerization of Tricyclo[4.1.0.0^{2,5}]heptane Systems

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The 3-azatricyclo[4.1.0.0^{2,5}]heptanes (**11**—**14**) prepared readily from pyridines *via* 2-azabicyclo[2.2.0]hexa-5-enes (**10**) were found to be useful synthons for seven-membered heterocycles. The thermolysis of the compounds (**11**—**13**) having an oxygen, a nitrogen, or a sulfur atom in the 7-position resulted in valence bond isomerization with ring opening, giving rise to the corresponding 1,4-dihetero seven-membered ring compounds, 1,4-oxazepine (**15**), 1,4-diazepine (**16**), and 1,4-thiazepine (**17**) derivatives. The 3-azatricycloheptane (**14**) having no hetero atom in the 7-position also afforded the azepine derivative (**18**).

Keywords——1,2-dihydropyridine; 2-azabicyclo[2.2.0]hexa-5-ene; 3-azatricyclo[4.1.0.0^{2,5}]-heptane; 1,4-oxazepine; 1,4-diazepine; 1,4-thiazepine; valence bond isomerization; ring-expansion; thermolysis

The chemistry of seven-membered heterocycles has recently been widely investigated and a large number of oxepin, azepine, and thiepin rings have been synthesized by a variety of methods.[2] As illustrated in Chart 1 using general formulas, most of the seven-membered heterocyclic rings (**1**) have been prepared by routes involving valence bond isomerization of various kinds of cyclic ring systems; *e.g.*, norcaradienes (**2**),[2] bicyclo[3.2.0]heptadienes (**3**),[3] conjugated cyclopropenes (**4**),[4] quadricyclanes (**5**),[5] and valenes (**6**).[6]

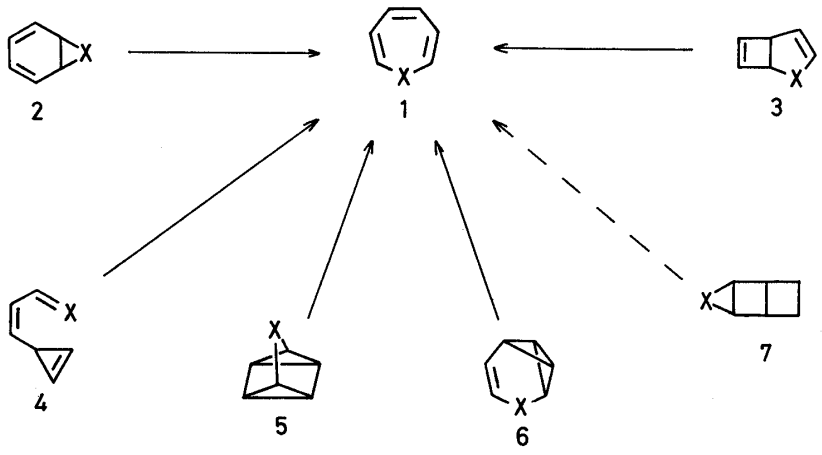


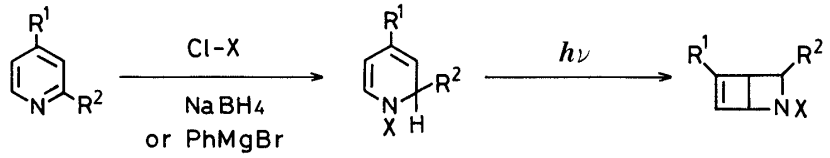
Chart 1

We have already reported the syntheses of fused 1,2-,[2c,7] 1,3-,[2d,8] 2,3-,[9] and 2,4-diazepines[1] condensed with aromatic rings such as benzene, pyridine, thiophene, furan, and pyrrole by photo-induced rearrangements of condensed pyridine *N*-imides or azides *via*

aziridine or diaziridine intermediates of the type of **2**. Among the three possible monocyclic dihetero seven-membered ring isomers due to the isomeric positions of the two hetero atoms, 1,2- and 1,3-dihetero compounds such as 1,2-[2b] and 1,3-diazepines[10] and 1,3-oxazepines[2a,4a] are known, but as for 1,4-dihetero isomers, only highly substituted 6*H*-1,4-diazepines[11] had been reported prior to the present work.[12]

Therefore, we were interested in the synthesis of 1,4-dihetero seven-membered rings, and we report here that tricyclo[4.1.0.0^{2,5}]heptane systems (**7**) prepared readily from pyridines can be used as new useful synthons for these novel seven-membered heterocyclic rings.[13]

Pyridines (**8a—c**) were reduced with sodium borohydride in the presence of methyl or benzyl chloroformate at −70 °C according to the reported procedure[14] to yield the corresponding 2-unsubstituted 1-methoxycarbonyl- (**9a, f, g**) and 1-benzyloxycarbonyl-1,2-dihydropyridines (**9b, c**). The 2-phenyl-1,2-dihydropyridines (**9d, e**) were prepared from **8a, b** by treatment with phenylmagnesium bromide in the presence of benzyl chloroformate.[15] In either reaction, the corresponding undesired 1,4-dihydropyridines were also formed, but the 1,2-isomers (**9**) were relatively unstable and readily decomposed during isolation. Therefore, they were used in the following photolysis without isolation. Irradiation of **9a—g** in methylene chloride for 10—18 h resulted in cyclization to give the 2-azabicyclo[2.2.0]hexa-5-enes (**10**) in 20—30% yields from the parent pyridines (**8**).



8a—c **9a—g** **10a—g**

	R^1	R^2
a:	H	H
b:	Me	H
c:	Ph	H

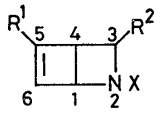
	R^1	R^2	X
a:	H	H	CO_2Me
b:	H	H	CO_2CH_2Ph
c:	Me	H	CO_2CH_2Ph
d:	H	Ph	CO_2CH_2Ph
e:	Me	Ph	CO_2CH_2Ph
f:	Me	H	CO_2Me
g:	Ph	H	CO_2Me

Chart 2

The key tricyclic compounds (**11—14**), 3-azatricyclo[4.1.0.0^{2,5}]heptanes, were prepared from **10** by the following procedures shown in Chart 3. Treatment of **10a—g** with *m*-chloroperbenzoic acid (*m*-CPBA) gave the 7-oxa compounds (**11a—g**) in 70—90% yields. The reaction of **10a—e** with ethoxycarbonyl nitrene generated from *N*-ethoxycarbonyl-*p*-nitrobenzenesulfonamide[16] by treatment with triethylbenzylammonium bromide and sodium hydrogencarbonate afforded the 7-aza compounds (**12a—e**) in 30—40% yields. Succinimide-*N*-sulfenyl chloride[17] reacted with the double bond of **10a** to give a mixture of the 6-chloro-5-(*N*-succinimidothio)-adduct and its regioisomer, both of which were reduced with lithium aluminum hydride monoethoxide at −75 °C to afford the 7-thia compound (**13**) in 80% yield. Treatment of **10a** with diazomethane in the presence of copper (I) chloride[18] gave the 7-methylene compound (**14**) in 21% yield. Although the stereochemistry of the tricyclic compounds (**11—14**) was not examined in detail, their stereostructures are tentatively assigned to be *trans*.

Heating the 3-azatricycloheptanes (**11—13**) having a hetero atom in the 7-position in refluxing toluene or xylene resulted in ring opening to give the corresponding novel 1,4-dihetero seven-membered ring compounds, *i.e.*, 4,5-dihydro-1,4-oxazepines (**15a—g**), 4,5-

TABLE I. 2-Azabicyclo[2.2.0]hexa-5-enes (**10a—g**)[a]



Compd. No.	Yield[b] (%)	Formula (MS *m/z*: M^+)	Analysis (%) Calcd (Found) C	H	N	^{1}H-NMR ($CDCl_3$) δ[c]
10a	24	$C_7H_9NO_2$ (139)	60.42 (60.51	6.52 6.48	10.07 9.87)	3.42 (2H, m, 3- and 4-H), 3.96 (1H, m, 3-H), 4.83 (1H, m, 1-H), 6.53 (2H, m, 5- and 6-H), 3.64 (3H, s, OMe)
10b	23	$C_{13}H_{13}NO_2$ (215)	72.54 (72.30	6.09 5.91	6.51 6.53)	3.44 (1H, m, 4-H), 3.57 and 4.03 (each 1H, m, 3-H_2), 4.92 (1H, m, 1-H), 6.59 (2H, m, 5- and 6-H), 5.15 (2H, s, CH_2Ph), 7.43 (5H, s, Ph-H)
10c	26	$C_{14}H_{15}NO_2$ (229)	73.34 (73.32	6.59 6.42	6.11 6.01)	3.16 (1H, m, 4-H), 3.44 and 3.84 (each 1H, m, 3-H_2), 4.53 (1H, m, 1-H), 6.11 (1H, m, 6-H), 1.73 (3H, s, 5-Me), 5.03 (2H, s, CH_2Ph), 7.22 (5H, s, Ph-H)
10d	15	$C_{19}H_{17}NO_2$ (291)	78.33 (78.19	5.88 5.95	4.81 4.58)	3.75 (1H, m, 4-H), 4.96 (1H, t, 1-H), 5.29 (1H, d, 3-H), 5.96 (1H, t, 5-H), 6.57 (1H, t, 6-H), 5.07 (2H, s, CH_2Ph), 7.21 (10H, s, Ph-H)
10e	18	$C_{20}H_{19}NO_2$ (305)	78.66 (78.61	6.27 6.02	4.59 4.42)	3.59 (1H, m, 4-H), 4.79 (1H, d, 1-H), 5.28 (1H, d, 3-H), 6.23 (1H, d, 6-H), 1.12 (3H, s, 5-Me), 5.02 (2H, s, CH_2Ph), 7.23 (10H, m, Ph-H)
10f	23	$C_8H_{11}NO_2$ (153)	62.72 (62.75	7.24 7.22	9.14 9.03)	3.32 (1H, m, 4-H), 3.48 and 3.92 (each 1H, m, 3-H_2), 4.65 (1H, m, 1-H), 6.24 (1H, m, 6-H), 1.82 (3H, s, 5-Me), 3.62 (3H, s, OMe)
10g	20	$C_{13}H_{13}NO_2$ (215)	72.54 (72.29	6.09 6.05	6.51 6.33)	3.65 (1H, m, 4-H), 3.47 and 3.95 (each 1H, m, 3-H_2), 4.72 (1H, m, 1-H), 6.51 (1H, m, 6-H), 3.52 (3H, s, OMe), 7.11 (5H, s, Ph-H)

a) Compounds **10a—c, f** are colorless viscous oils. Compounds **10d, e, g** are colorless prisms (from isopropyl ether); **10d** mp 91.5—92 °C; **10e** mp 56—57 °C; **10g** mp 77—78 °C. Compounds **1a—g** all showed absorptions at 1690 cm^{-1} due to C=O in the IR spectra. *b*) Isolated yields calculated from **8**. *c*) $J_{1,4}=3$, $J_{1,5}=3$, $J_{3,4}=8$, and $J_{4,5}=2$ Hz. These values of coupling constants were observed in spin-decoupling experiments, but others could not be clarified.

dihydro-1,4-diazepines (**16a—e**), and 4-methoxycarbonyl-4,5-dihydro-1,4-thiazepine (**17**), respectively, in 70—90% yields. The 7-methylene compounds (**14**) also gave the 2,5-dihydroazepine (**18**) in 79% yield on heating in refluxing xylene. The structures of the azepines (**15—18**) thus obtained were characterized by elemental and spectral analyses.

The isomerization of the tricyclic compounds (**11—14**) into the seven-membered heterocycles (**15—18**) may proceed *via* homolytic bond fission to the biradical intermediate (**19**) followed by ring opening of the azetidine ring. However, for the compounds with a hetero atom in the 7-position, the ionic mechanism *via* the intermediate (**20**) also seems likely, by analogy with to the thermal isomerization of butadienyloxiranes,[4c] but the concerted mechanism is less likely. In addition, photolysis of the tricyclic compounds did not occur.

Although it is well known that cyclobutene ring systems undergo thermal electrocyclic ring opening, little has been reported of such a reaction in fully saturated molecules similar to the present system. To cite two examples, the thermolysis of bicyclo[2.1.0]pentane yields penta-1,4-diene as a minor product in only 0.4% yield together with cyclopentene[19] and that of 3,4-diazabicyclo[4.1.0.$0^{2,5}$]heptanes affords 2,5-dihydro-1*H*-1,2-diazepines in high yields;[20]

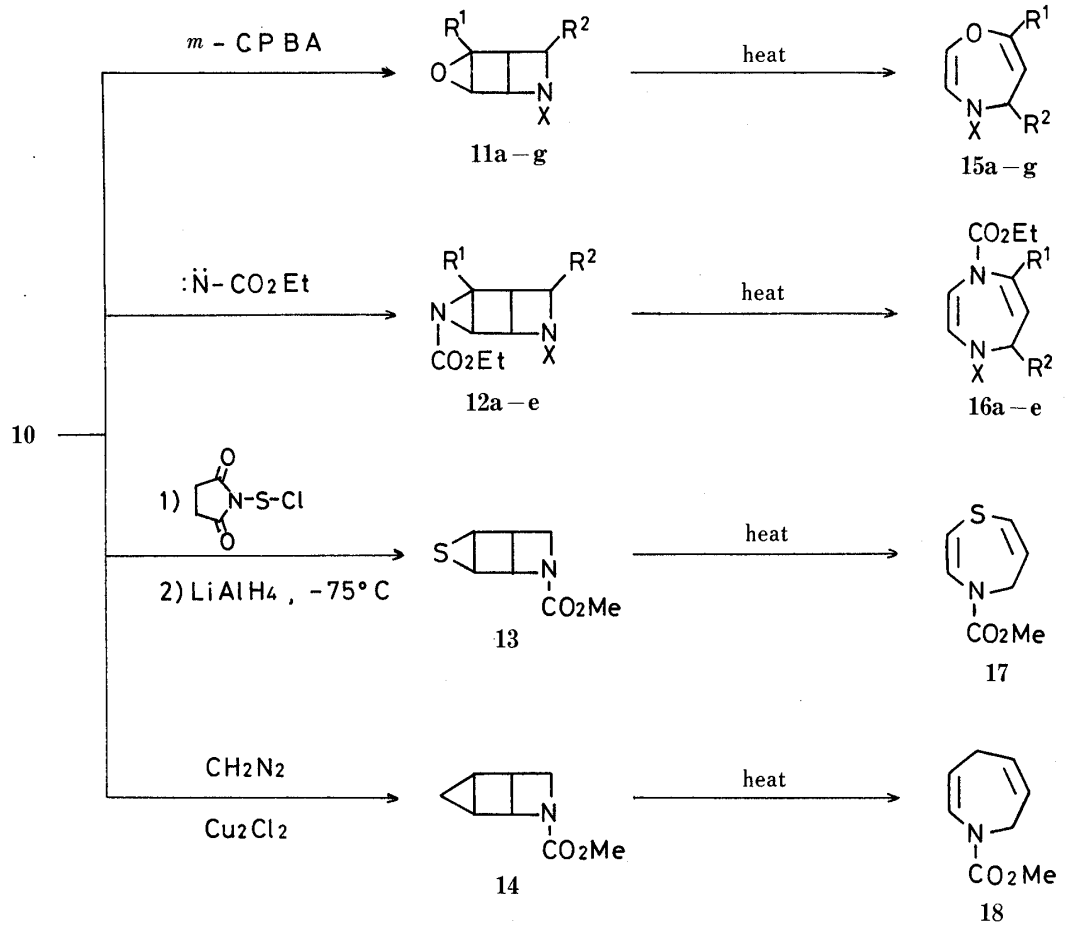
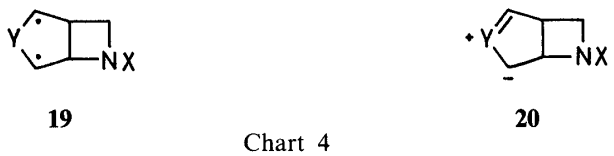


Chart 3



19 **20**

Chart 4

the latter example was reported after publication of our preliminary communication of the present work.[13)]

In conclusion, the present results provide a new class of synthons for the syntheses of seven-membered heterocyclic rings, and most of the 1,4-dihetero compounds reported represent novel ring systems.

Experimental

The general experimental procedures were the same as in Part XXI.[1)]

2-Unsubstituted 1,2-Dihydropyridines (9a—c, f, g)——General Procedure: The procedure of Fowler[14)] for the preparation of **9a** was employed. A solution of methyl or benzyl chloroformate (0.2 mol) in ether (30 ml) was added dropwise with stirring to a solution of a pyridine (**8a—c**: 0.2 mol) and $NaBH_4$ (8.0 g) in anhydrous methanol (100 ml) in a dry ice–acetone bath. The rate of addition was controlled so that the temperature of the reaction mixture did not exceed −70 °C. The mixture was stirred for an additional 2 h at −70 °C and then poured into ice-water (200—300 ml). The aqueous mixture was extracted with ether and the extract was washed with water, dried over $MgSO_4$, and evaporated *in vacuo* to yield **9**, the identity of which was confirmed by the nuclear magnetic resonance (NMR) spectrum of the resulting residue. ^{1}H-NMR ($CDCl_3$) δ: (**9a**) 4.15 (2H, dd, J=3.5 and 2, 2-H_2), 4.82—5.95 (3H, m, 3-, 4-, and 5-H), 6.53 (1H, br d, J=7, 6-H), 3.63 (3H, s, OMe); (**9b**) 4.22 (2H, m, 2-H_2), 5.18 and 5.52 (each 1H, m, 4- and 5-H), 5.85 (1H, m, 3-H), 6.80 (1H, m, 6-H), 5.24 (2H, s, CH_2Ph), 7.43 (5H, br s, Ph-H); (**9c**) 1.58 (3H, m, 4-Me), 4.24 (2H, m, 2-H_2), 4.8—5.2 (2H, m, 3- and 5-H), 6.70 (1H, br d, J=7, 6-H), 5.16 (2H, s, CH_2Ph),

TABLE II. 3-Azatricyclo[4.1.0.$0^{2,5}$]heptanes (**11a—g**, **12a—e**, **13**, and **14**)

Compd. No.	Yield[a] (%)	mp[b] (°C)	IR ν_{max} cm^{-1} (C=O)	Formula (MS *m/z*: M$^+$)	Analysis (%) Calcd (Found)		
					C	H	N
11a	89	55—56[c]	1705	$C_7H_9NO_3$ (155)	54.19 (54.31	5.85 5.89	9.03 9.00)
11b	86	59—60[c]	1700	$C_{13}H_{13}NO_3$ (231)	67.52 (67.57	5.67 5.58	6.06 6.11)
11c	67	86—87[c]	1690	$C_{14}H_{15}NO_3$ (235)	68.55 (68.73	6.16 6.01	5.71 5.85)
11d	85	74—75[c]	1705	$C_{19}H_{17}NO_3$ (307)	74.25 (74.13	5.58 5.55	4.56 4.41)
11e	80	101—103[c]	1700	$C_{20}H_{19}NO_3$ (321)	74.74 (74.75	5.96 6.05	4.36 4.32)
11f	75	80—81[c]	1700	$C_8H_{11}NO_3$ (169)	56.79 (56.93	6.55 6.60	8.28 8.25)
11g	89	70—71[d]	1695	$C_{13}H_{13}NO_3$ (231)	67.52 (67.81	5.67 5.89	6.06 6.22)
12a	42	Oil	1690	$C_{10}H_{14}N_2O_4$ (226)	53.09 (52.87	6.24 6.23	12.38 12.09)
12b	33	57—58.5[e]	1705	$C_{16}H_{18}N_2O_4$ (302)	63.56 (63.66	6.00 5.91	9.27 9.21)
12c	30	Oil	1705	$C_{17}H_{20}N_2O_4$ (316)	64.54 (64.68	6.37 6.20	8.86 8.65)
12d	26	103—105[e]	1705	$C_{22}H_{22}N_2O_4$ (378)	69.82 (69.67	5.86 5.81	7.40 7.37)
12e	28	Oil	1705	$C_{23}H_{24}N_2O_4$ (392)	70.39 (70.46	6.16 6.04	7.14 6.99)
13	80	25—28[e]	1690	$C_7H_9NO_2S$ (171)	49.10 (49.35	5.30 5.48	8.18 8.03)
14	21	Oil	1690	$C_8H_{11}NO_2$ (153)	62.72 (62.94	7.24 7.14	9.14 9.02)

a) Yield of isolated product. *b*) Recrystallized from isopropyl ether. *c*) Colorless needles. *d*) Colorless plates. *e*) Colorless prisms.

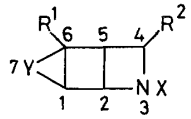
7.24 (5H, br s, Ph-H); (**9f**) 1.71 (3H, m, 4-Me), 3.80 (3H, s, OMe), 4.36 (2H, m, 2-H), 5.08 (1H, br d, J=8, 5-H), 5.26 (1H, m, 3-H), 6.75 (1H, br d, J=8, 6-H); (**9g**) 3.78 (3H, s, OMe), 4.38 (2H, d, 2-H_2), 5.40 (1H, br d, 5-H), 5.56 (1H, m, 3-H), 6.67 (1H, br d, 6-H), 7.12 (5H, m, Ph-H), $J_{2,3}$=4, $J_{5,6}$=8 Hz.

However, the dihydropyridines (**9**) thus obtained were unstable and readily decomposed during isolation by chromatography, so the resulting residue was used in the following photolysis without separation.

2-Phenyl-1,2-dihydropyridines (9d, e)——General Procedure: The reported method[15] for the synthesis of 2-substituted 1,2-dihydropyridines was modified. A solution of PhMgBr (0.1 mol) in tetrahydrofuran (THF: 100 ml) was added dropwise with stirring to a solution of a pyridine (**8a**, **b**: 0.1 mol) in THF (20 ml) in an ice bath. A solution of benzyl chloroformate (0.1 mol) in toluene (100—150 ml) was then added dropwise with stirring to the above stirred mixture at below −5 °C. The reaction mixture was stirred for an additional 2 h at −5 °C, allowed to warm to room temperature, and then stirred for a further 1 h. After addition of water (100 ml), the reaction mixture was extracted with ether. The extract was successively washed with satd. $NaHCO_3$ and satd. NaCl, and then concentrated *in vacuo* to give **9d**, **e**, which were also unstable, and so were used in the following photolysis without purification. ^{1}H-NMR ($CDCl_3$) δ: (**9d**) 5.0—5.4 (3H, m, 2-H and CH_2Ph), 5.5—6.1 (3H, m, 3-, 4-, and 5-H), 6.80 (1H, m, 6-H), 7.0—7.6 (10H, m, Ph-H); (**9e**) 1.75 (3H, m, 4-Me), 5.0—5.2 (3H, m, 2-H and CH_2Ph), 5.36 and 5.77 (each 1H, m, 3- and 5-H), 6.98 (1H, m, 6-H), 7.1—7.4 (10H, m, Ph-H).

2-Azabicyclo[2.2.0]hexa-5-enes (10a—g)——General Procedure: A solution of the residue containing a dihydropyridine (**9a—g**) obtained by the above procedure in CH_2Cl_2 (300 ml) was irradiated (400 W, high-pressure Hg lamp; Pyrex filter; under N_2); this photolysis was followed in terms of the disappearance of the signals of the starting dihydropyridine in the ^{1}H-NMR spectrum, and was complete in 10—18 h. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using *n*-hexane–ether (4 : 1) as an eluent to give **10**. Yields and analytical

TABLE III. ^{1}H-NMR Spectral Data for 3-Azatricycloheptanes (**11**—**14**)



11a	2.97 (1H, m, 5-H), 3.89 and 4.16 (each 1H, m, 4-H_2), 4.08 (1H, m, 6-H), 4.24 (1H, m, 1-H), 4.45 (1H, m, 2-H), 3.72 (3H, s, CO_2Me)
11b	2.96 (1H, m, 5-H), 3.8—4.3 (4H, m, 1-H, 6-H, and 4-H_2), 4.51 (1H, m, 2-H), 5.16 (2H, s, CH_2Ph), 7.39 (5H, s, Ph-H)
11c	2.84 (1H, m, 5-H), 3.83 and 4.05 (each 1H, m, 4-H_2), 4.09 (1H, m, 1-H), 4.35 (1H, m, 2-H), 1.49 (3H, s, 6-Me), 5.05 (2H, s, CH_2Ph), 7.25 (5H, s, Ph-H)
11d	3.30 (1H, m, 5-H), 3.55 (1H, dd, J=3 and 4, 6-H), 4.26 (1H, dd, J=2 and 4, 1-H), 4.65 (1H, dd, J=3 and 4, 2-H), 5.52 (1H, d, J=7, 4-H), 5.14 (2H, br s, CH_2Ph), 7.31 (10H, m, Ph-H)
11e	3.19 (1H, m, 5-H), 4.22 (1H, d, J=4, 1-H), 4.49 (1H, d, J=3, 2-H), 5.51 (1H, d, J=7, 4-H), 0.70 (3H, s, 6-Me), 5.09 (2H, s, CH_2Ph), 7.23 (10H, s, Ph-H)
11f	2.85 (1H, m, 5-H), 3.78 and 4.07 (each 1H, m, 4-H_2), 4.10 (1H, m, 1-H), 4.24 (1H, m, 2-H), 1.52 (3H, s, 6-Me), 3.58 (3H, s, CO_2Me)
11g	3.36 (1H, m, 5-H), 4.00 and 4.23 (each 1H, m, 4-H_2), 4.53 (1H, m, 2-H), 4.70 (1H, m, 1-H), 3.62 (3H, s, CO_2Me)
12a	3.06 (1H, m, 5-H), 3.43 (1H, m, 6-H), 3.65 (1H, m, 1-H), 3.96 and 4.20 (each 1H, m, 4-H_2), 4.52 (1H, m, 2-H), 1.31 and 4.29 (3H, t, and 2H, q, CO_2Et)
12b	3.07 (1H, m, 5-H), 3.42 (1H, m, 6-H), 3.64 (1H, m, 1-H), 4.00 and 4.22 (each 1H, m, 4-H_2), 4.57 (1H, m, 2-H), 5.20 (2H, s, CH_2Ph), 7.43 (5H, s, Ph-H), 1.30 and 4.24 (3H, t, and 2H, q, CO_2Et)
12c	1.55 (3H, s, 6-Me), 3.02 (1H, m, 5-H), 3.48 (1H, m, 1-H), 3.96 and 4.16 (each 1H, m, 4-H_2), 4.45 (1H, m, 2-H), 5.13 (2H, s, CH_2Ph), 7.35 (5H, s, Ph-H), 1.24 and 4.27 (3H, t, and 2H, q, CO_2Et)
12d	2.77 (1H, m, 6-H), 3.30 (1H, m, 5-H), 3.53 (1H, m, 1-H), 4.60 (1H, m, 2-H), 5.53 (1H, d, J=8, 4-H), 5.08 (2H, s, CH_2Ph), 7.27 (10H, br s, Ph-H), 1.25 and 4.14 (3H, t, and 2H, q, CO_2Et)
12e	0.64 (3H, s, 6-Me), 3.26 (1H, m, 5-H), 3.54 (1H, d, J=4, 1-H), 4.51 (1H, d, J=3, 2-H), 5.56 (1H, d, J=8, 4-H), 5.07 (2H, br s, CH_2Ph), 7.26 (10H, br s, Ph-H), 1.26 and 4.11 (3H, t, and 2H, q, CO_2Et)
13	2.88 (1H, m, 5-H), 3.51 (1H, m, 6-H), 3.72 (1H, m, 1-H), 3.87 and 4.03 (each 1H, m, 4-H_2), 4.28 (1H, m, 2-H), 3.61 (3H, s, CO_2Me)
14	0.43 and 0.84 (each 1H, m, 7-H_2), 1.83 and 2.12 (each 1H, m, 1- and 6-H), 2.50 (1H, m, 5-H), 3.78 and 4.06 (each 1H, m, 4-H_2), 4.13 (1H, m, 2-H), 3.59 (3H, s, CO_2Me)

δ ($CDCl_3$), J=Hz.

and spectral data of the products (**10a**—**g**) are collected in Table I.

3-Aza-7-oxatricyclo[4.1.0.0^{2,5}]heptanes (11a—g)——General Procedure: A solution of *m*-CPBA (1.5 mol eq) in CH_2Cl_2 (10 ml) was added dropwise with stirring to a solution of a bicyclic compound (**10a**—**g**: 0.5—1.0 g) in CH_2Cl_2 (10 ml). After stirring for an additional 10 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (50—100 ml). The solution was successively washed with satd. $NaHCO_3$ and satd. NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on alumina using *n*-hexane–ether (1 : 1) as an eluent to give **11**.

Yields and physical, analytical, and spectral data of the oxirane compounds (**11a**—**g**) are collected in Tables II and III.

3,7-Diazatricyclo[4.1.0.0^{2,5}]heptanes (12a—e)——General Procedure: The reported procedure[16] for the formation of aziridines was applied. *N*-Ethoxycarbonyl-*p*-nitrobenzenesulfonamide (1.5 mol eq) and triethylbenzylammonium bromide (0.2 mol eq) were added to a solution of a bicyclic compound (**10a**—**e**: 4—6 g) in CH_2Cl_2 (50—100 ml) with stirring. Then, 4% $NaHCO_3$ (3 mol eq) was added dropwise with stirring to the above solution at room temperature. The reaction mixture was stirred for a further 5 h and diluted with CH_2Cl_2 (100 ml). The organic layer was separated, washed with satd. NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane–ether (4 : 1) as an eluent to give the starting compound (**10**: 60—70%) and **12**, successively.

Yields and physical, analytical, and spectral data of the aziridine compounds (**12a**—**e**) are collected in Tables II

TABLE IV. 1,4-Oxazepines (**15a—g**), 1,4-Diazepines (**16a—e**), 1,4-Thiazepine (**17**), and Azepine (**18**)

Compd. No.	Yield[a,b] (%)	IR $\nu_{max}^{CHCl_3}$ cm^{-1} (C=O)	Formula	(MS m/z: M$^+$)	Analysis (%) Calcd (Found)		
					C	H	N
15a	95	1700	$C_7H_9NO_3$	(155)	54.19	5.85	9.03
					(54.31	5.72	8.89)
15b	88	1705	$C_{13}H_{13}NO_3$	(231)	67.52	5.67	6.06
					(67.28	5.63	5.93)
15c	76	1700	$C_{14}H_{15}NO_3$	(245)	68.55	6.16	5.71
					(68.50	6.09	5.65)
15d	91	1710	$C_{19}H_{17}NO_3$	(307)	74.25	5.58	4.56
					(74.03	5.67	4.60)
15e	72	1705	$C_{20}H_{19}NO_3$	(321)	74.74	5.96	4.36
					(75.00	6.10	4.41)
15f	78	1710	$C_8H_{11}NO_3$	(169)	56.79	6.55	8.28
					(56.61	6.59	8.11)
15g	87	1710	$C_{13}H_{13}NO_3$	(231)	67.52	5.67	6.06
					(67.28	5.60	5.79)
16a	84	1700	$C_{10}H_{14}N_2O_4$	(226)	53.09	6.24	12.38
					(53.23	6.20	12.33)
16b	89	1700	$C_{16}H_{18}N_2O_4$	(302)	63.56	6.00	9.27
					(63.59	5.79	9.18)
16c	68	1690	$C_{17}H_{20}N_2O_4$	(316)	64.54	6.37	8.86
					(64.29	6.37	8.75)
16d	64	1690	$C_{22}H_{22}N_2O_4$	(378)	69.82	5.86	7.40
					(69.73	5.63	7.38)
16e	57	1695	$C_{23}H_{24}N_2O_4$	(392)	70.39	6.16	7.14
					(70.30	6.01	7.23)
17	72	1700	$C_7H_9NO_2S$	(171)	49.10	5.30	8.18
					(48.87	5.07	8.09)
18	79	1695	$C_8H_{11}NO_2$	(153)	62.72	7.24	9.14
					(62.83	7.08	8.98)

a) All compounds are colorless viscous oils except **15g**, mp 55—57 °C, colorless needles (from isopropyl ether). *b*) Yield of isolated product.

and III.

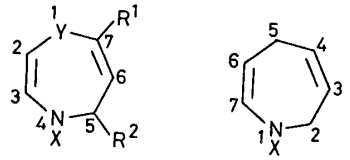
3-Methoxycarbonyl-3-aza-7-thiatricyclo[4.1.0.0^{2,5}]heptane (13)——A solution of succinimide-*N*-sulfenyl chloride[17] (1.2 g) in CH_2Cl_2 (10 ml) was added dropwise with stirring to a solution of the bicyclic compound (**10a**: 1.0 g) in CH_2Cl_2 (20 ml) in an ice bath. The reaction mixture was stirred for an additional 2 h at room temperature and then concentrated *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2–acetone (20 : 1) as an eluent to give the 6-chloro-5-(*N*-succinimidothio)-adduct (A) and its regioisomer (B), successively.

Adduct (A): 1.24 g, 57% yield, mp 106—108 °C, colorless needles (from $CHCl_3$–isopropyl ether). MS m/z: 304 and 306 (3 : 1) (M$^+$). IR ν_{max}^{KBr} cm^{-1}: 1700 and 1730 (C=O). ^{1}H-NMR δ: 2.80 (4H, s, succinimido-H), 3.35 (1H, m, 4-H), 4.0—4.6 (5H, m, 1-, 3-, 5-, and 6-H), 3.56 (3H, s, OMe).

Adduct (B): 0.22 g, 10% yield, mp 143—145 °C, colorless prisms (from AcOEt–isopropyl ether). MS m/z: 304 and 306 (3 : 1) (M$^+$). IR ν_{max}^{KBr} cm^{-1}: 1705 and 1730 (C=O). ^{1}H-NMR δ: 2.81 (4H, s, succinimido-H), 2.78 (1H, m, 4-H), 3.90 and 3.25 (each 1H, m, 3-H$_2$), 3.95, 4.50, and 4.76 (each 1H, m, 1-, 5-, and 6-H), 3.57 (3H, s, OMe).

Ethanol (160 mg) in THF (8 ml) was added dropwise with stirring to a suspension of $LiAlH_4$ (140 mg) in THF (5 ml) in an ice bath. Then, a solution of either the adduct (A: 440 mg) or (B: 190 mg) in THF (10 ml) was added dropwise to the above mixture at −75 °C. After stirring for a further 30 min at −75 °C, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. The mixture was diluted with ether (100 ml) and the organic layer was washed with satd. NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on alumina using *n*-pentane–ether (1 : 1) as an eluent to give **13**: from A, 421 mg, 80% yield; from B, 92 mg, 85% yield. Physical, analytical, and spectral data of the thiirane compound (**13**) are given in Tables II and III.

TABLE V. ^{1}H-NMR Spectral Data for the Azepines (**15**—**18**)



15a	4.21 (2H, dd, 5-H_2), 4.91 (1H, m, 6-H), 5.63 (1H, d, 2-H), 5.97 (1H, d, 3-H), 6.32 (1H, m, 7-H), 3.77 (3H, s, CO_2Me)
15b	4.24 (2H, dd, 5-H_2), 4.96 (1H, m, 6-H), 5.70 (1H, d, 2-H), 6.11 (1H, d, 3-H), 6.39 (1H, m, 7-H), 5.22 (2H, s, CH_2Ph), 7.41 (5H, s, Ph-H)
15c	1.78 (3H, s, 7-Me), 4.18 (2H, d, 5-H_2), 5.01 (1H, t, 6-H), 5.61 (1H, d, 2-H), 5.97 (1H, m, 3-H), 5.14 (2H, s, CH_2Ph), 7.29 (5H, s, Ph-H)
15d	5.04 (1H, m, 5-H), 5.76 (2H, m, 2- and 6-H), 6.06 (1H, br, 3-H), 6.43 (1H, d, 7-H), 5.16 (2H, s, CH_2Ph), 7.29 (10H, m, Ph-H)
15e	5.01 (1H, d, 6-H), 5.69 (2H, m, 2- and 5-H), 5.89 (1H, br, 3-H), 1.89 (3H, s, 7-Me), 5.17 (2H, s, CH_2Ph), 7.31 (10H, m, Ph-H)
15f	1.73 (3H, s, 7-Me), 4.06 (2H, d, 5-H_2), 4.90 (1H, t, 6-H), 5.52 (1H, d, 2-H), 5.80 (1H, d, 3-H), 3.60 (3H, s, CO_2Me)
15g	4.41 (2H, d, 5-H_2), 5.84 (2H, m, 2- and 6-H), 6.06 (1H, d, 3-H), 3.68 (3H, s, CO_2Me), 7.3—7.5 (5H, m, Ph-H)
16a	4.29 (2H, d, 5-H), 5.37 (1H, m, 6-H), 6.22 (2H, br, 2- and 3-H), 6.95 (1H, d, 7-H), 3.88 (3H, s, CO_2Me), 1.32 and 4.32 (3H, t, and 2H, q, CO_2Et)
16b	4.32 (2H, d, 5-H_2), 5.36 (1H, m, 6-H), 6.25 (2H, br, 2- and 3-H), 6.97 (1H, d, 7-H), 5.23 (2H, s, CH_2Ph), 7.41 (5H, s, Ph-H), 1.32 and 4.32 (3H, t, and 2H, q, CO_2Et)
16c	2.01 (3H, s, 7-Me), 4.27 (2H, d, 5-H_2), 5.4—6.3 (3H, m, 2-, 3-, and 6-H), 5.14 (2H, s, CH_2Ph), 7.33 (5H, s, Ph-H), 1.29 and 4.19 (3H, t, and 2H, q, CO_2Et)
16d	5.20 (1H, m, 6-H), 5.88 and 6.08 (each 1H, m, 2- and 3-H), 6.28 (1H, br d, 5-H), 7.08 (1H, d, 7-H), 5.16 (2H, s, CH_2Ph), 7.2—7.5 (10H, m, Ph-H), 1.33 and 4.27 (3H, t, and 2H, q, CO_2Et)
16e	1.99 (3H, s, 7-Me), 5.44 (1H, d, 6-H), 5.83 (2H, br, 2- and 3-H), 6.25 (1H, d, 5-H), 5.12 (2H, s, CH_2Ph), 7.0—7.3 (10H, m, Ph-H), 1.01 and 3.76 (3H, t, and 2H, q, CO_2Et)
17	4.32 (2H, m, 5-H_2), 4.87 (1H, d, 2-H), 6.20 (2H, m, 6- and 7-H), 6.71 (1H, d, 3-H), 3.71 (3H, s, CO_2Me)
18	2.92 (2H, m, 5-H_2), 4.22 (2H, m, 2-H_2), 4.66 (1H, m, 3-H), 5.81 (2H, m, 4- and 6-H), 6.49 (1H, br, 7-H), 3.69 (3H, s, CO_2Me)

δ ($CDCl_3$), coupling constants—**15**: $J_{2,3}=6$, $J_{5,6}=6$, $J_{5,7}=1.5$, $J_{6,7}=7$—8 Hz. **16**: $J_{2,3}=0$—0.5, $J_{5,6}=6$—8, $J_{5,7}=0$—0.5, $J_{6,7}=9$ Hz. **17**: $J_{2,3}=9$ Hz.

3-Methoxycarbonyl-3-azatricyclo[4.1.0.0^{2,5}]heptane (14)——Dry diazomethane gas was passed through a mixture of the bicyclic compound (**10a**: 1.27 g), copper (I) chloride (0.45 g), and CCl_4 (30 ml) under nitrogen.[18] The inorganic precipitates were filtered off and the filtrate was concentrated *in vacuo*. The residue was chromatographed on alumina using *n*-pentane–CH_2Cl_2 (2 : 1) as an eluent to give **14**. The yield and physical, analytical, and spectral data are given in Tables II and III.

4,5-Dihydro-1,4-oxazepines (15a—g)——General Procedure: A solution of an oxirane compound (**11a—g**: 50—100 mg) in toluene (3—6 ml) was refluxed. The reaction was followed in terms of the disappearance of the spot of the starting **11** on thin-layer chromatography and was complete in 5—10 h. After removal of the solvent *in vacuo*, the residue was chromatographed on alumina using *n*-hexane–ether (4 : 1) as an eluent to give **15**. Yields and physical, analytical, and spectral data of the oxazepines (**15a—g**) are collected in Tables IV and V.

4,5-Dihydro-1,4-diazepines (16a—e)——General Procedure: A solution of an aziridine compound (**12a—e**: 50—100 mg) in xylene (3—6 ml) was refluxed for 6—10 h and worked up as described for **15** to give **16**. Yields and physical, analytical, and spectral data of the diazepines (**15a—e**) are collected in Tables IV and V.

4-Methoxycarbonyl-4,5-dihydro-1,4-thiazepine (17)——A solution of the thiirane compound (**13**: 51 mg) in toluene (3 ml) was refluxed for 6 h and then worked up as described for **15** to give **17**. The yield and analytical and spectral data of the thiazepine (**17**) are given in Tables IV and V.

1-Methoxycarbonyl-2,5-dihydroazepine (18)——A solution of the cyclopropene compound (**14**: 117 mg) in xylene

(6 ml) was refluxed for 20 h and then worked up as described for **15** to give **18**. The yield and analytical and spectral data of the azepine (**18**) are given in Tables IV and V.

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