Dioxopyrrolines. XLIV.[1] Thermal 1,3-Shift of 2-Azabicyclo[3.2.0]hept-2-ene Ring System. A New Entry to 3,4-Dihydropyridines and 2-Azanorborn-2-enes

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Thermolysis of 4-oxo-2-azabicyclo[3.2.0]hept-2-enes caused two reactions; one is the 1,3-shift of the C_1–C_7 bond to the C_3 carbon followed by cheletropic loss of CO from the intermediary formed 2-azanorborn-2-enes to yield the dihydropyridines, and the other is epimerization of the C_7-substituent. These two reactions occurred competitively depending on the nature of the C_7 substituent. Intermediary formation of the 2-azanorborn-2-enes in the rearrangement reaction was proved by trapping experiments with the use of 4-acetoxy derivatives. The mechanisms of the thermal 1,3-shift and 7-epimerization are discussed.

Keywords dioxopyrroline; 1*H*-pyrrole-2,3-dione; 2-azabicyclo[3.2.0]hept-2-ene; cyclobutane; thermolysis; 1,3-shift; epimerization; dihydropyridine; dihydropyridone; 2-azanorbornane

The 7-substituted 2-azabicyclo[3.2.0]heptane-3,4-diones (**2**), 2+2 photoadduct of olefins to 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione (**1**), readily undergo various skeletal rearrangements.[2] Recently, we reported that base treatment of the molecule caused epimerization at the C_7-substituent together with the ring expansion reaction, both reactions being due to C_1–C_5 bond fission.[1] The 7-*exo*-phenyl derivative (**2a**) gave the dioxopyrroline (**1**), a cycloreversione product, and a dihydropyridone (**9a**), though in low yield, when heated at 200 °C in toluene.[3] The latter is identical with the by-product of photocycloaddition of **1** to styrene,[4] and is suggested to be formed by cheletropic loss of CO from the intermediary 2-azanorbornene which may be formed *via* 1,3-shift from the lactim form as shown in Chart 1. This paper deals with this subject in detail.[5]

Results and Discussion

Thermal Reactions of 7-Substituted-3-ethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-ones: Formation of Dihydropyridines We thought that fixation of the double bond at N_2–C_3 would facilitate the rearrangement, and therefore, the imidates (**3**) were chosen as the substrates. These compounds were readily prepared by alkylation of 5-ethoxycarbonyl-1-phenyl-2-azabicyclo-[3.2.0]heptane-3,4-diones (**2**)[4] with triethyloxonium fluoroborate (Meerwein reagent) (Chart 2).

Thermolysis of **3** caused two reactions; one is a 1,3-shift of the C_1–C_7 bond and another is an epimerization at the C_7-substituent (Chart 3). The 7-*exo* and 7-*endo* isomers (**3a** and **3b**, **3c** and **3d**, and **3i** and **3j**) gave the same dihydropyridines (**7a**, **7b**, and **7c**) in good yields on heating in toluene

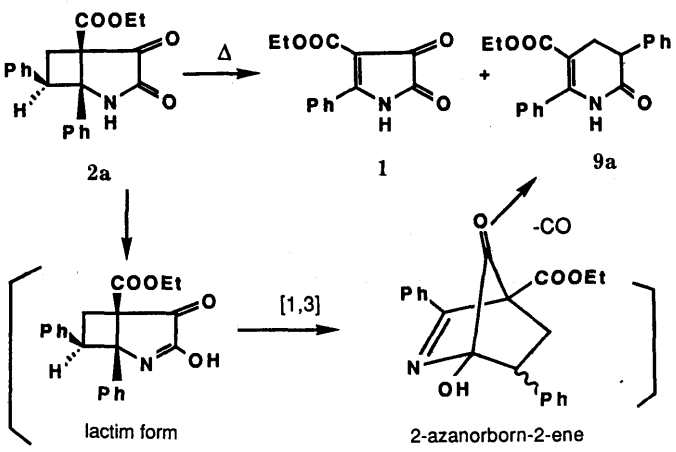
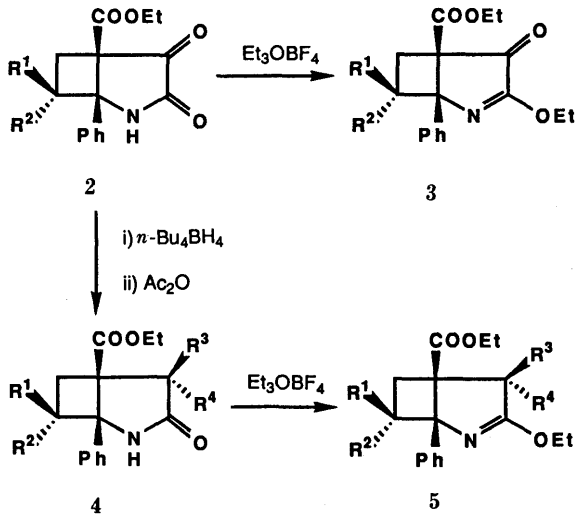


Chart 1



for compounds **2** and **3**

	R^1	R^2		R^1	R^2
a	Ph	H	**i**	Ph	Me
b	H	Ph	**j**	Me	Ph
c	OEt	H	**k**	Me	OAc
d	H	OEt	**l**	OAc	Me
e	OAc	H	**m**	Et	Me
f	H	OAc			
g	Et	H			
h	H	Et			

for compounds **4** and **5**

	R^1	R^2	R^3	R^4
a	Ph	H	OAc	H
b	Ph	H	H	OAc
c	H	Ph	H	OAc
d	H	OEt	H	OAc
e	Et	H	OAc	H
f	Ph	Me	OAc	H
g	Ph	Me	H	OAc
h	Me	Ph	H	OAc
i	Me	OAc	H	OAc

Chart 2

at 120—200 °C. Similar heating of the 7-Et–7-Me derivative (**3m**) at 200 °C formed **7e** in good yield. Pyrolysis of the 7-OAc–7-Me derivatives (**3k** and **3l**) yielded the same pyridine (**8**), which is a product of thermal loss of acetic acid from the dihydropyridine (**7d**). On the other hand, the 7-*exo*-Et derivative (**3g**) on heating at 200 °C underwent C_7-epimerization to form the 7-*endo*-isomer (**3h**) quantitatively. The *endo*-OAc derivative (**3f**) on similar heating partially epimerized to give a 1 : 2 mixture of **3e** and **3f**. The results are accumulated in Table I, and indicate that the reaction is greatly affected by the nature of the 7-substituent.

The structure of the dihydropyridines (**7**) were elucidated on the basis of the ultraviolet (UV) absorption at 293 nm, the ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectra, and the following chemical transformations (Chart 4). The compounds **7** were readily hydrolyzed on silica gel chromatography or on treatment with acid to give the dihydropyridones (**9**). They were proved to be identical with the compounds directly formed by the photocycloaddition reaction of **1** to olefins.[4] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) oxidation of **7** gave the 2-ethoxypyridine derivative (**10**).

Formation of **7** can be rationalized in terms of the 1,3-shift of the C_1–C_7 bond followed by cheletropic loss of CO from an intermediary 2-azanorbornen-7-one (**6**).

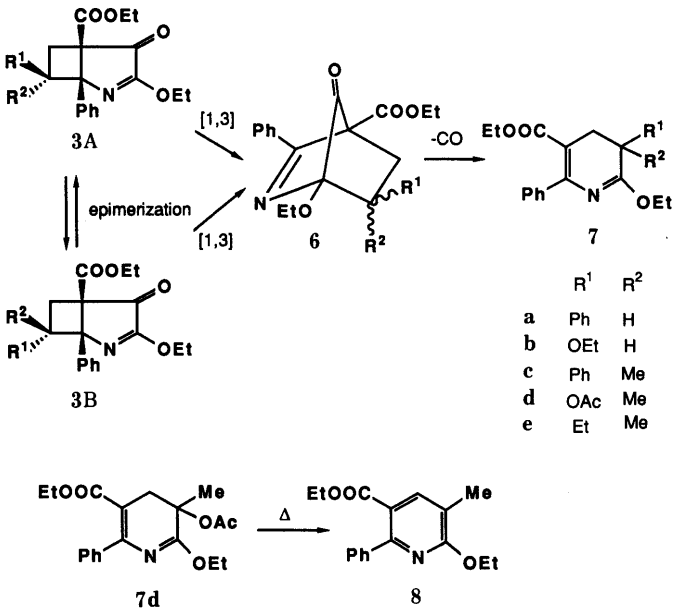


Chart 3

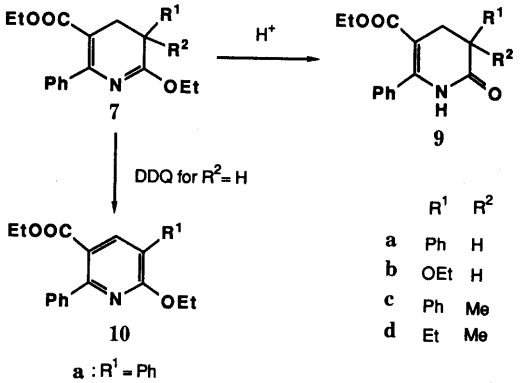


Chart 4

Thermal Reaction of 7-Substituted 4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-enes: Formation of 2-Azanorborn-2-enes In order to clarify the reaction pathway, we attempted to isolate the intermediate, 2-azanorborn-2-ene. The cheletropic loss of CO from the intermediate (**6**) could be avoided when the 4-oxo group was reduced to the alcohol. Therefore, we chose the 4-acetoxy imidates (**5**) as substrates, which were prepared by imidation of the corresponding 4-acetoxy lactams (**4**)[1] with Meerwein reagent (Chart 2).

The thermal reactions of the 4-acetoxy imidates required more drastic conditions than those of the corresponding 4-oxo imidates (Charts 5 and 6). Heating of the imidate (**5a**) in toluene at 160 °C for 8 h yielded two-2-azanorborn-2-enes (**11** and **12**), and a pyrrole (**13**) in yields of 29, 23, and 1%, respectively. As shown below, **11** and **12** are the expected 1,3 shift products of the C_1–C_7 bond with inversion and retention of the configuration at the migrating center (C_7), respectively. The pyrrole (**13**) was proved to be a pyrolysate of the 2-azanorbornenes, since it was quantitatively formed when **11** or **12** was heated at 300 °C. This is presumably be formed by the retro Diels–Alder reaction of the 2-azanorbornene followed by two consecutive 1,5-hydride shifts as shown in Chart 5. Such a thermal cyclopentadiene 1,5-hydride shift is known to occur very easily.[6] Similarly, the corresponding 4-*endo* isomer (**5b**) gave two 1,3-shift products, azanorbornenes (**14** and **15**), and the pyrrole (**13**) in 24, 47, and 1% yields, though it required rather drastic conditions (180 °C for 8 h). The 7-*endo* Ph imidate (**5c**) was stable at 200 °C but decomposed at 300 °C to yield the pyrrole (**13**) as a sole product in 21% yield. The 7-OEt (**5d**) and 7-Et imidate (**5e**) were extremely stable under thermal condition and remained unchanged. The results are summarized in Table II.

The structure and stereochemistry of 2-azanorbornenes were determined as follows. Both compounds (**11** and **12**) have the same molecular formula $C_{25}H_{27}NO_5$ as evidenced by the high resolution mass spectra (HRMS) and showed an intense UV absorption at 240 nm attributable to the Ph-C=N– chromophore, thus indicating that they are ster-

TABLE I. Thermolyses of 7-Substituted 3-Ethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-ene-4-ones (**3**)

Substrate			Conditions			Yield	Remarks
	R^1	R^2	Temp (°C)	Time (h)	Product	(%)	
3a	Ph	H	120	4	**7a**	70[a]	[1,3]
3b	H	Ph	200	2	**7a**	85[a]	[1,3]
3c	OEt	H	200	2	**7b**	75[a]	[1,3]
3d	H	OEt	200	20	**7b**	70[a]	[1,3]
3f	H	OAc	200	16	**3e**[b]	100	7-Epimerization
3g	Et	H	200	20	**3h**	88	7-Epimerization
3h	H	Et	200	40	**3h**	100	Unchanged
3i	Ph	Me	120	2	**7c**	91	[1,3]
3j	Me	Ph	120	2	**7c**	92	[1,3]
3k	Me	OAc	200	16	**8**	34	[1,3], 7-Epi[c]
3l	OAc	Me	200	16	**8**	47	[1,3], 7-Epi[c]
3m	Et	Me	200	20	**7e**	75[a]	[1,3]

a) Yields were calculated from those of dihydropyridones (**9**). *b*) This was obtained as a 1 : 2 mixture of **3e** and **3f**. *c*) The starting material recovered was contaminated with the 7-isomer.

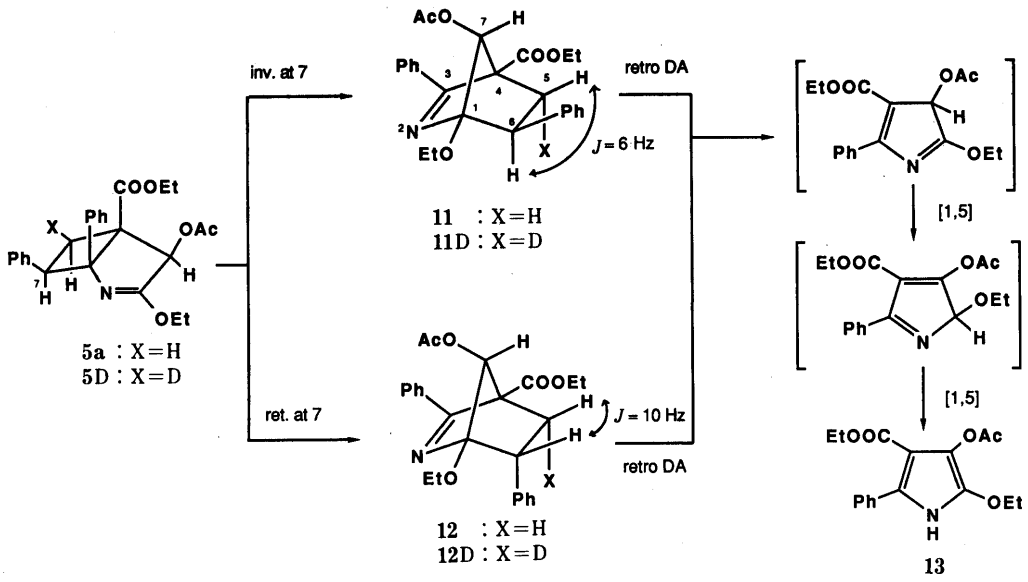


Chart 5

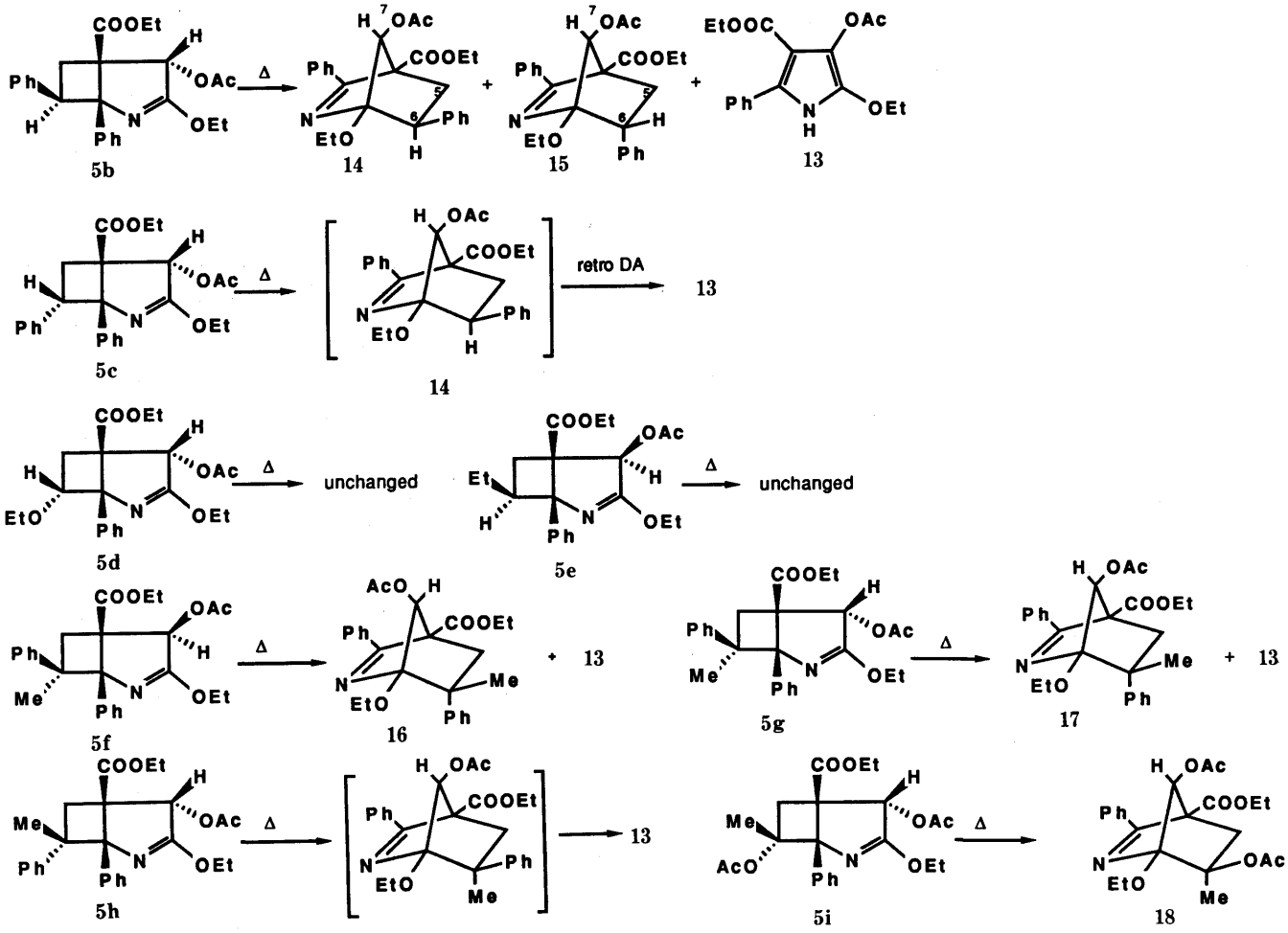


Chart 6

eoisomers. The stereochemistries of the C_6-phenyl group in **11** and **12** were established by analyses of the ^{1}H-NMR spectra. The assignment of the signals was made by comparison with those of the 5-*endo*-deuterium labeled compounds (**11D** and **12D**) obtained by similar pyrolysis of the 6-*exo*-deuterium labeled imidate (**5D**).[1,7] The coupling constant between C_5-*exo*-H and C_6-H was found to be 6 Hz in **11D** and 10 Hz in **12D** as shown in Chart 5, indicating that the relationship of C_5-H and C_6-H is *exo–endo* in the former and *exo–exo* in the latter.[8,9] Thus, the configuration

TABLE II. Thermolyses of 7-Substituted 4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-enes (5)

Substrate 7-Subst.	4-OAc	Conditions Temp (°C)	Time (h)	Product (Yield %) si[a]	sr[b]	py[c]	rec[d]	si/sr
5a *exo*-Ph	*exo*	160	8	29	23	1	—	1.2
5b *exo*-Ph	*endo*	180	8	24	47	1	—	0.5
5c *endo*-Ph	*endo*	300	5.5	—	—	21	—	
5d *endo*-OEt	*endo*	350	5	—	—	—	80	
5e *exo*-Et	*exo*	300	5	—	—	—	80	
5f di[e] (Ph, Me)	*exo*	180	3	—	30	35	—	(ret)
5g di (Ph, Me)	*endo*	180	18	—	25	30	30	(ret)
5h di (Me, Ph)	*endo*	250	2.5	—	—	88	—	
5i di (Me, OAc)	*endo*	350	1	—	9	—	67	(ret)

a) The [1,3]shift product with inversion. *b*) The [1,3]shift product with retention. *c*) Pyrrole (**13**). *d*) Starting material was recovered. *e*) 7,7-Disubstituted.

of the C_6-phenyl group was established as *exo* in **11D** and *endo* in **12D**. It was, therefore, concluded that the compounds (**11** and **12**) are the 1,3-shift products with inversion and retention of the configuration at the migrating center, respectively.

Analytical and spectral data for **14** and **15** also indicate that they are stereoisomers of the 2-azanorborn-2-ene. The stereochemistry at C_6 was also deduced from the ^{1}H-NMR spectra. Although the C_6-proton signals of **15** exhibited unresolved bands overlapped with those of the C_5-protons, **14** exhibited a W type long range coupling between C_7-H and C_6-*endo*-H ($J=1$ Hz), thus establishing that the C_6-phenyl group of **14** has *exo*-configuration. Thus, **14** is the 1,3-shift product with C_7-inversion and **15** is that with C_7-retention.

The 7,7-disubstituted 4-acetoxy imidates also underwent the 1,3-shift on similar thermolysis as shown in Chart 6. The 7-*exo*-Ph–7-*endo*-Me–4-OAc imidate (**5f**) on heating at 180 °C for 2 h gave the 2-azanorborn-2-ene (**16**) and the pyrrole (**13**) is 30 and 35% yields, respectively. The corresponding 4-*endo*-OAc isomer (**5g**) also gave the 2-azanorborn-2-ene (**17**) (25%) and the pyrrole (**13**) (30%) on prolonged (18 h) heating at 180 °C. The stereoisomer (**5h**) was stable at 180 °C and rearranged at 250 °C. However, the pyrrole (**13**) was the sole product. The imidate (**5i**) was thermally very stable and on heating at 350 °C for 1 h gave the azanorbornene (**18**) in only 9% yield. Prolonged heating of this merely caused profound decomposition. The results are accumulated in Table II.

2-Azanorborn-2-enes derived from the 7,7-disubstituted imidates were always single stereoisomers. Although no direct evidence is available, we consider that they are the product with retention of configuration of the C_7-substituent from the mechanistic point of view (see next section).

Mechanistic Consideration The above rearrangement is essentially identical with the thermal rearrangement of 7-substituted bicyclo[3.2.0]heptenes to 6-substituted bicyclo[2.2.1]heptenes reported by Berson.[10,11] He showed that this suprafacial rearrangement occurs stereoselectively in both "allowed" and "forbidden" manners. The allowed process is expected from a usual highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) interaction that accompanies inversion of stereochemistry at the migrating center (si-process) and proceeds through an *anti*-clockwise rotation of the C_6–C_7 bond to take an R^2 inside configuration at the transition

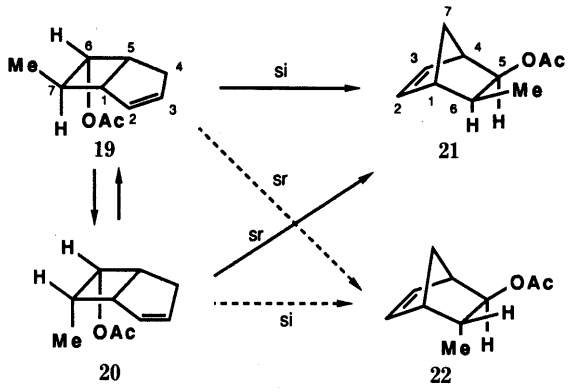


Chart 7. Thermal 1,3-Shift of 7-Substituted Bicyclo[3.2.0]heptenes (according to Berson)[11]

state. However, when this rotation is difficult for steric reasons, the rearrangement proceeds through the forbidden process which results in retention of the configuration at the migrating center (sr-process). Thus, the 7-*exo*-methyl isomer (**19**) gave the product (**21**) with inversion of the methyl group (si/sr = 9.3), while the 7-*endo*-methyl isomer (**20**) gave the product (**21**) with retention of the methyl configuration predominantly (si/sr = 0.14).

Berson argued from the kinetic observation that this forbidden but concerted process is energetically more favored than the biradical process which may produce stereorandamization of the substituent. Its occurrence was explained in terms of a contribution of a subjacent orbital of the allyl system which would overlap with the 2*p* orbital of the migrating carbon.

Later, Fukui[12] pointed in his textbook, that, in **20**, the detaching bond in the favorable reaction form is already weakened by the steric compression of the *endo*-methyl group and, in such a situation, the reaction proceeds by a consecutive multi-step process with retention of the stereochemical relationship at the migrating terminus, even if it is biradical-like. Therefore, in a forbidden but concerted reaction, Berson's subjacent orbital control should be interpreted as the interaction between the 1π orbital of the allyl system and the 2*p* orbital of the migrating bond (SOMO). His argument implies the importance of steric congestion initially present at the migrating center owing to the substituent, which weakens the migrating bond in the early stage of the reaction so as to facilitate the migration.

In our thermolysis of 7-substituted 3-ethoxy-2-azabicyclo[3.2.0]hept-2-ene the 1,3-shift occurs more easily, *i.e.*

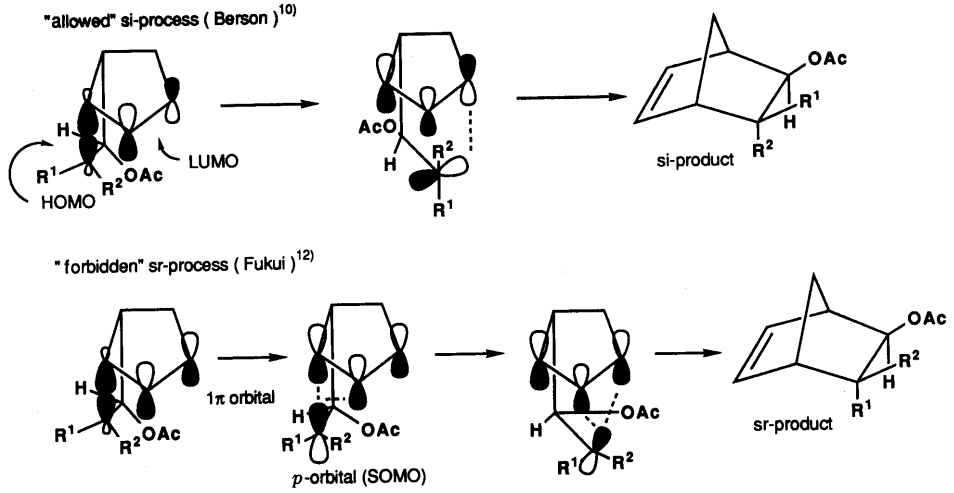
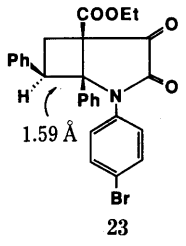


Chart 8. Proposed Mechanisms of Thermal Bicycloheptane Rearrangement



23

Chart 9

at lower temperature, than in Berson's cases. This can be explained by the larger LUMO amplitude at C-3 due to substitution of an OEt group. However, the ease of the reaction is greatly affected by the nature of substituent at the migrating center. Rearrangement of 7-Ph derivatives is particularly easy compared to the 7-OEt, 7-OAc, and 7-Et derivatives. Some of the latters (**3f** and **3g**) did not give the rearranged product, and only underwent the 7-epimerization (see below).

For 4-oxo derivatives, 7-*exo*-Ph (**3a**) rearranged more easily than 7-*endo*-Ph (**3b**) in agreement with Berson's results. The former compound rearranged at 120 °C, while the latter was recovered unchanged at the same temperature and gave the rearranged product at 200 °C. This clearly indicates that the rearrangement does not proceed through (*exo*→*endo*) 7-epimerization. Weakening of the migrating bond in the 7-*exo*-Ph derivatives at the ground state is suggested by the X-ray analysis of **23**, which clearly indicated that C_1–C_7 bond is unusually elongated (1.590 Å).[4,13] In addition to this bond-weakening effect, the 7-phenyl group should decrease the energy of the transition state by conjugation with the developing orbital of the migrating carbon.

In contrast to 7-mono-substituted derivatives (**3f** and **3g**), the 7,7-disubstituted derivatives, 7-OAc–7-Me (**3k** and **3l**) and 7-Et–7-Me (**3m**), gave the rearrangement products. Apparently the increase of steric congestion at C-7 arising from di-substitution produces weakening of the C_1–C_7 bond, thus facilitating the 1,3-shift as suggested by Fukui.[12]

The stereochemical results for the 4-acetoxy derivatives are more instructive (Table II). These derivatives required more drastic conditions than those used for the reaction of the 4-oxo derivatives. The 4-*exo*–7-*exo* derivative (**5a**) reacted most easily among the three stereoisomeric 4-OAc–7-Ph derivatives, producing the inversion product with only a slight preference over the retention product (si/sr = 1.2). Apparently, the 7-Ph group (when compared to Berson's results) is violating the allowed si-process. On the other hand, the 4-*endo*–7-*exo* derivative (**5b**) gave the retention product preferentially (si/sr = 0.5). Obviously the 4-*endo*-OAc group blocks the Ph-inside configuration at the transition state for this compound, thus reducing the si-process.

In 4-*endo*–7-*endo* derivatives, the si and sr processes are both severely blocked, so the rearrangement in difficult or does not occur (**5c** and **5d**). However, in 7,7-di-substituted 4-*endo* derivatives (**5f**, **5g** and **5h**), where one of the 7-substituents has *endo* configuration, the rearrangement was again observed, though the reaction was accompanied with further degradation of the product to the pyrrole (**13**). This again indicates that steric congestion at C-7 weakens the C_1–C_7 bond to facilitate the rearrangement.

Comparing **5g** and **5h** or **5b** and **5c**, the former (**5g** and **5b**) rearrange far more easily than the latter (**5h** and **5c**). This means that the 7-*exo*-Ph group has a greater bond-weakening effect than the 7-*endo*-Ph group.

For all the 7,7-disubstituted derivatives, the 1,3-shift products are stereochemically homogeneous. For the reasons discussed above, we argue that these should be the sr-products produced by the consecutive multi-step process suggested by Fukui,[12] since in all cases the si-process should suffer serious steric hindrance in the transition states. In our case, the central atom of the allyl system is nitrogen whose large HOMO amplitude due to the N= C–OEt system may also assist the migration of SOMO at C-7.

Some comments are called for on the 7-epimerization observed for several 4-oxo derivatives. The reaction was also observed in Berson's examples[10] and always occurs towards the thermodynamically more stable isomer; *endo* to *exo* in Berson's and *exo* to *endo* in our cases.[1] It was observed even in disubstituted derivatives (**3k** and **3l**), suggesting that epimerization is competitive to rearrangement. These results appear to suggest that both rearrangement and epimerization involve the same biradical intermediate formed by C_1–C_7 bond cleavage. However, it

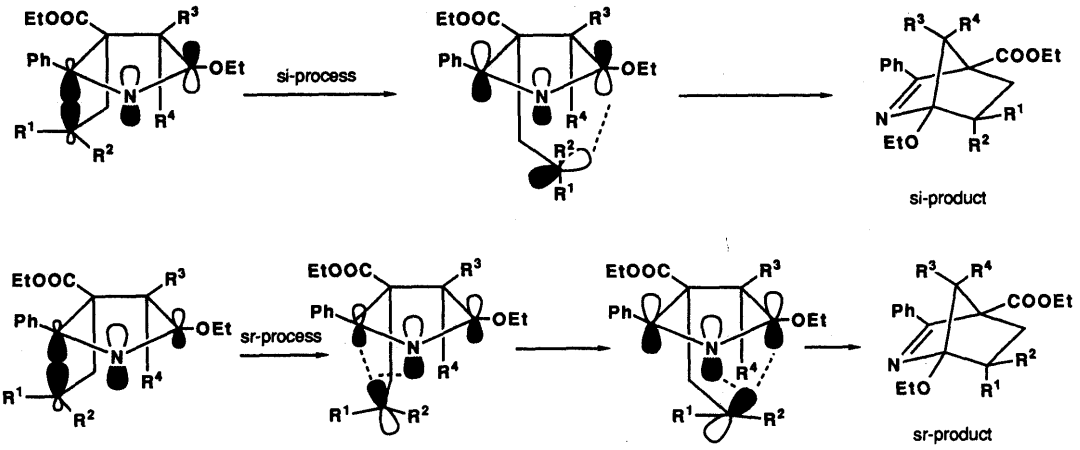


Chart 10. Thermal 1,3-Shift in 2-Azabicyclo[3.2.0]heptene System

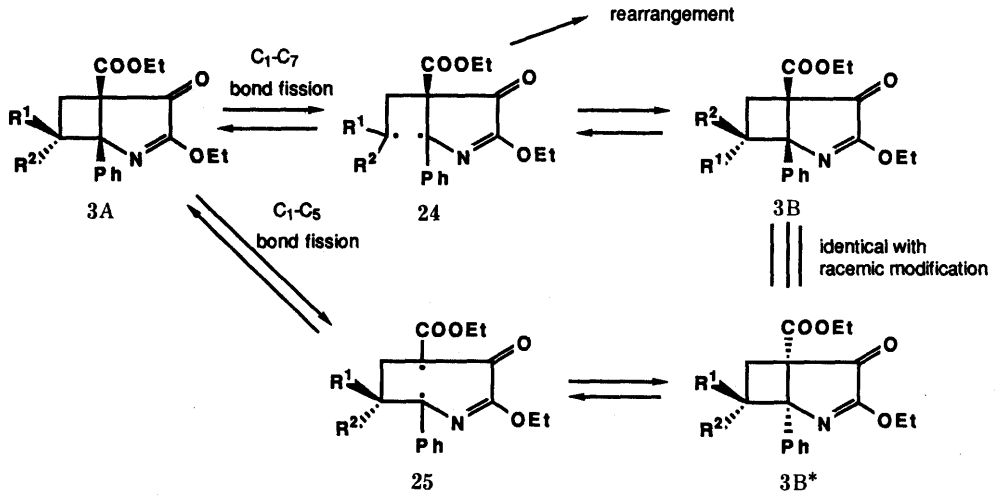


Chart 11. 7-Epimerization Reaction

must be emphasized that the epimerization in our cases was observed only for the 4-oxo derivatives, but not for the 4-acetoxy derivatives. This suggests participation of the 4-oxo group in the epimerization.

Analogous epimerization was already shown for **3a**, which epimerizes to the *endo* isomer **3b** on irradiation. This photochemical epimerization has been proved to proceed through cleavage and recombination of the C_1–C_5 bond.[1] Base catalyzed thermal epimerization of 7-*exo*-substituted 2-azabicyclo[3.2.0]heptane-3,4-dione to the *endo* isomer was also proved to proceed *via* the C_1–C_5 bond fission-recombination mechanism.[1]

Based on those facts, we consider that 7-epimerization of 4-oxo derivatives in the present thermolysis proceeds through C_1–C_5 bond fission and recombination, though there is no direct evidence to confirm this. Fission of the C_1–C_5 or C_1–C_7 bond may occur competitively for 4-oxo derivatives; the former leads to epimerization and the latter to the rearrangement.

Apart from its mechanistic interest, the above thermal rearrangement of 2-azabicyclo[3.2.0]hept-2-ene is synthetically important, because it provides a novel route to dihydropyridones and 2-azanorborn-2-enes, which are compounds with very few precedents.[14,15]

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were taken on a Yanagimoto micro hot-stage melting point apparatus, and are uncorrected. Infrared (IR) spectra were taken in Nujol mulls with a Hitachi 260-10 spectrophotometer and are given in cm^{-1}. UV spectra were taken in EtOH with a Hitachi 200-10 spectrophotometer and given in λ_{max} nm (ε). ^{1}H-NMR (100 MHz) and ^{13}C-NMR (25.0 MHz) spectra were taken in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard on a JEOL FX-100 spectrometer. HRMS were recorded on a JEOL JMS-D300 mass spectrometer. Thin layer chromatography (TLC) was performed on precoated Silica gel 60 F_{254} plates (Merck). Medium-pressure liquid chromatography (MPLC) was performed on Kusano CIC prepacked silica gel columns.

Preparation of the 7-*exo*-Et–*endo*-Me Derivative (2m) A solution of the cyclobutane (**2**: R^1 = vinyl, R^2 = Me)[4] (600 mg) in EtOH was hydrogenated over 5% Pd–C (600 mg) for 1 h at room temperature. After removal of the catalyst by filtration, the filtrate was concentrated to dryness. The residue in benzene was passed through a short column of SiO_2 and crystallized from CH_2Cl_2 to give *dl*-(1*R**,5*S**,7*R**)-5-ethoxycarbonyl-7-ethyl-7-methyl-1-phenyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**2m**) (535 mg, 88%). Colorless needles, mp 128—130 °C. IR: 1760, 1720, 1680. ^{1}H-NMR: 0.58 (3H, t, J=7 Hz, CH_2CH_3), 1.92 (3H, t, J=7 Hz, $COOCH_2CH_3$), 1.07 (3H, s, CH_3), 1.0—1.4 (2H, m, CH_2CH_3), 1.97 (1H, d, J=13 Hz, C_6-H), 2.93 (1H, d, J=13 Hz, C_6-H), 4.03 (2H, q, J=7 Hz, $COOCH_2CH_3$), 7.33 (5H, s, Ar-H). *Anal.* Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.35; H, 6.79; N, 4.55.

Preparation of the Imidates (3) (General Procedure) A solution of **2** (200 mg) in CH_2Cl_2 (10 ml) was treated with excess triethyloxonium fluoroborate (Et_3OBF_4) at room temperature overnight. The mixture was diluted with CH_2Cl_2 and washed with 5% $NaHCO_3$ and water. The organic extract was dried over $MgSO_4$ and evaporated. The product in benzene was passed through a short column of SiO_2 and crystallized from Et_2O–*n*-hexane.

dl-(1*R**,5*S**,7*S**)-3-Ethoxy-5-ethoxycarbonyl-1,7-diphenyl-2-azabicy-

clo[3.2.0]hept-2-en-4-one (**3a**): 173 mg, 80%. Colorless prisms, mp 133—136 °C. IR: 1760, 1740, 1640. UV: 260 sh (2000). ^{1}H-NMR: 0.67 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.20 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.38 (1H, dd, J=4, 6 Hz, C_6-H), 3.58 (1H, dd, J=4, 6 Hz, C_6-H), 3.60 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 3.78 (1H, t, J=6 Hz, C_7-H), 4.65 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.1 (10H, br s, Ar-H). *Anal.* Calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 73.43; H, 6.14; N, 3.77.

dl-(1*R**,5*S**,7*R**)-3-Ethoxy-5-ethoxycarbonyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3b**): 140 mg, 65%. Colorless prisms, mp 122—127 °C. IR: 1745, 1725, 1670, 1620. ^{1}H-NMR: 0.73 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.25 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.27 (1H, dd, J=8, 13 Hz, C_6-H), 3.47 (1H, dd, J=8, 13 Hz, C_6-H), 3.78 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.27 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.78 (1H, t, J=8 Hz, C_7-H), 7.2 (10H, m, Ar-H). *Anal.* Calcd for $C_{23}H_{23}NO_4$: C, 73.16; H, 6.14; N, 3.71. Found: C, 73.15; H, 6.11; N, 3.63.

dl-(1*R**,5*S**,7*R**)-3,7-Diethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3c**): 185 mg, 85%. Colorless prisms, mp 100—102 °C. IR: 1745, 1730, 1620. ^{1}H-NMR: 0.65 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 0.88 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.53 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.32 (1H, dd, J=8, 14 Hz, C_6-H), 3.20 (3H, m, C_6-H and $OC\underline{H}_2CH_3$), 3.69 (1H, m, C_7-H), 3.75 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.62 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.4 (5H, m, Ar-H). *Anal.* Calcd for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 65.77; H, 6.66; N, 4.12.

dl-(1*R**,5*S**,7*S**)-3,7-Diethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3d**): 194 mg, 89%. Colorless prisms, mp 68—71 °C. IR: 1770, 1760, 1735, 1630. UV: 265 sh (2100). ^{1}H-NMR: 0.67 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.10 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.54 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.93 (1H, dd, J=5, 14 Hz, C_6-H), 3.37 (2H, oct, J=2, 7 Hz, $OC\underline{H}_2CH_3$), 3.37 (1H, dd, J=8, 14 Hz, C_6-H), 3.74 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.62 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.71 (1H, dd, J=5, 8 Hz, C_7-H), 7.3 (5H, m, Ar-H). *Anal.* Calcd for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 65.77; H, 6.66; N, 4.12.

dl-(1*R**,5*S**,7*S**)-7-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3f**): 152 mg, 70%. Colorless prisms, mp 106—108 °C. IR: 1759, 1730, 1630. UV: 250 (3100). ^{1}H-NMR: 0.70 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.53 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.03 (3H, s, $OCOCH_3$), 2.05 (1H, dd, J=5, 14 Hz, C_6-H), 3.52 (1H, dd, J=9, 14 Hz, C_6-H), 3.77 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.62 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.87 (1H, dd, J=5, 9 Hz, C_7-H), 7.35 (5H, br s, Ar-H). *Anal.* Calcd for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.52; H, 5.75; N, 4.46.

dl-(1*R**,5*S**,7*R**)-3-Ethoxy-5-ethoxycarbonyl-7-ethyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3g**): 175 mg, 80%. Colorless prisms, mp 94—95 °C. IR: 1765, 1730, 1630. UV: 242 (4900). ^{1}H-NMR: 0.62 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 0.73 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.4 (2H, m, $C\underline{H}_2CH_3$), 1.50 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.08 (2H, m, C_6-H), 2.67 (1H, m, C_7-H), 3.83 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.55 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.3 (5H, m, Ar-H). *Anal.* Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.08; H, 7.05; N, 4.37.

dl-(1*R**,5*S**,7*S**)-3-Ethoxy-5-ethoxycarbonyl-7-ethyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3h**): 180 mg, 82%. Colorless prisms from, mp 55—57 °C. IR: 1750, 1720, 1625. UV: 250 sh (3800). ^{1}H-NMR: 0.69 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 0.81 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.45 (2H, m, $C\underline{H}_2CH_3$), 1.53 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.56 (1H, m, C_6-H), 3.2 (2H, m, C_6-H and C_7-H), 3.73 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.58 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.31 (5H, s, Ar-H). *Anal.* Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.15; H, 7.04; N, 4.31.

dl-(1*R**,5*S**,7*S**)-3-Ethoxy-5-ethoxycarbonyl-7-methyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3i**): 204 mg, 99%. Colorless gum. IR: 1750, 1730, 1630. ^{1}H-NMR: 0.55 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.12 (3H, s, CH_3), 1.58 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.18 (1H, d, J=13 Hz, C_6-H), 3.68 (2H, oct, J=4 Hz, $COOC\underline{H}_2CH_3$), 3.74 (1H, d, J=13 Hz, C_6-H), 4.69 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.35 (3H, s, Ph), 7.8—8.1 (7H, m, Ph). HRMS *m/z*: M^+ Calcd for $C_{24}H_{25}NO_4$: 391.1784. Found: 391.1809.

dl-(1*R**,5*S**,7*R**)-3-Ethoxy-5-ethoxycarbonyl-7-methyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3j**): 163 mg from 180 mg, 84%. Colorless gum. IR: 1750, 1720, 1640. ^{1}H-NMR: 0.99 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.05 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.39 (3H, s, CH_3), 2.88 (1H, d, J=13.4 Hz, C_6-H), 3.12 (1H, d, J=13.4 Hz, C_6-H), 4.04 (4H, m, $COOC\underline{H}_2CH_3$ and $OC\underline{H}_2CH_3$), 7.0—7.4 (8H, m, Ph), 7.65 (2H, m, Ph). HRMS *m/z*: M^+ Calcd for $C_{24}H_{25}NO_4$: 391.1784. Found: 391.1760.

dl-(1*R**,5*S**,7*S**)-7-Acetoxy-3-ethoxy-5-ethoxycarbonyl-7-methyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3k**): 184 mg, 85%. Colorless prisms, mp 112—113 °C. IR: 1745, 1720, 1638. UV: 242 sh (5100). ^{1}H-NMR: 0.70 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.38 (3H, s, CH_3), 1.55 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.79 (3H, s, $OCOCH_3$), 2.25 (1H, d, J=15 Hz, C_6-H), 3.47 (1H, d, J=15 Hz, C_6-H), 3.88 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.69 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.45 (5H, m, Ar-H). *Anal.* Calcd for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21; N, 3.75. Found: C, 64.19; H, 6.22; N, 3.91.

dl-(1*R**,5*S**,7*R**)-7-Acetoxy-3-ethoxy-5-ethoxycarbonyl-7-methyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3l**): 179 mg, 83%. Colorless prisms, mp 81—83 °C. IR: 1745, 1720, 1638. UV: 242 sh (5100). ^{1}H-NMR: 0.97 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.52 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.55 (3H, s, CH_3), 1.98 (3H, s, $OCOCH_3$), 2.32 (1H, d, J=14 Hz, C_6-H), 3.20 (1H, d, J=14 Hz, C_6-H), 4.05 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.57 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.4 (5H, m, Ar-H). *Anal.* Calcd for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21; N, 3.75. Found: C, 65.10; H, 6.10; N, 3.87.

dl-(1*R**,5*S**,7*R**)-3-Ethoxy-5-ethoxycarbonyl-7-ethyl-7-methyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**3m**): 185 mg, 85%. Colorless prisms, mp 100—105 °C. IR: 1750, 1725, 1625. UV: 242 sh (5300). ^{1}H-NMR: 0.55 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 0.91 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 0.85 (3H, s, CH_3), 1.35 (2H, m, $C\underline{H}_2CH_3$), 1.48 (3H, t, J=7 Hz, $OC\underline{H}_2CH_3$), 1.69 (1H, d, J=13 Hz, C_6-H), 2.85 (1H, d, J=13 Hz, C_6-H), 4.00 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.55 (2H, q, J=7 Hz, OCH_2CH_3), 7.15—7.7 (5H, m, Ar-H). *Anal.* Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.33; N, 4.08. Found: C, 70.13; H, 7.43; N, 4.02.

Thermolysis of 4-Oxo Imidates (3) (General Procedure) A solution of **3** in toluene (10 ml) was heated in a sealed tube. After evaporation of the solvent, the product was purified by chromatography over SiO_2 using benzene as an eluent.

1) Thermolysis of **3a** (200 mg) at 120 °C for 4 h gave 2-ethoxy-5-ethoxycarbonyl-3,6-diphenyl-3,4-dihydropyridine (**7a**) (184 mg) as colorless gum. IR (CH_2Cl_2): 1750, 1700 sh, 1685, 1620, 1600. UV: 222 (13000), 293 (7800). ^{1}H-NMR: 0.90 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.27 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.00 (1H, d, J=8 Hz, C_4-H), 3.02 (1H, d, J=5 Hz, C_4-H), 3.70 (1H, dd, J=5, 8 Hz, C_3-H), 3.93 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.33 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.0—7.4 (10H, m, Ar-H). Chromatography of this gave 5-ethoxycarbonyl-3,6-diphenyl-3,4-dihydropyridin-2(1*H*)-one (**9a**) (119 mg, 70%).[4)]

2) Thermolysis of **3b** (100 mg) at 200 °C for 2 h gave **7a** (92 mg) as crude gum. Chromatography of this gave **9a** (72 mg, 85%).[4)]

3) Thermolysis of **3c** (100 mg) in toluene (5 ml) at 200 °C for 2 h gave 2,3-diethoxy-5-ethoxycarbonyl-6-phenyl-3,4-dihydropyridine (**7b**) (91 mg) as a colorless gum. IR (CH_2Cl_2): 1750, 1720, 1680, 1620. UV: 228 (8800), 288 (6000). ^{1}H-NMR: 0.87 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.08 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.23 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.81 (1H, d, J=5 Hz, C_4-H), 2.91 (1H, d, J=5 Hz, C_4-H), 3.63 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 3.93 (1H, t, J=5 Hz, C_3-H), 4.00 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.36 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.1—7.4 (5H, m, Ar-H). Chromatography of this gave **9b** (63 mg, 75%).[4)]

4) Thermolysis of **3d** (200 mg) in toluene (5 ml) was carried out at 200 °C for 20 h. Evaporation of the solvent gave **7b** (182 mg) as a crude gum. This was chromatographed in benzene to give **9b** (117 mg, 70%).[4)]

5) Thermolysis of **3f** (100 mg) at 200 °C for 16 h gave a mixture of **3e** and **3f** in 1 : 2 ratio. The ratio of this mixture was determined by comparison of the ^{1}H-NMR spectrum of **3e** and **3f** mixture prepared by alkylation of a 3 : 1 mixture of **2e** and **2f**[4)] with Et_3OBF_4. After heating at 200 °C for 48 h in toluene (5 ml) this mixture was recovered unchanged. ^{1}H-NMR for **3e**: 0.66 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.53 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.78 (3H, s, $OCOCH_3$), 2.43 (1H, dd, J=8, 14 Hz, C_6-H), 3.20 (1H, dd, J=7, 14 Hz, C_6-H), 3.79 (2H, qd, J=2, 7 Hz, $COOC\underline{H}_2CH_3$), 4.63 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.80 (1H, dd, J=7, 8 Hz, C_7-H), 7.3 (5H, br s, Ar-H).

6) Thermolysis of **3g** (80 mg) at 200 °C for 2 h gave **3h** (70 mg, 88%).

The product (**3h**) (30 mg) in toluene (5 ml) was heated at 200 °C for 40 h and remained unchanged.

7) Thermolysis of **3i** (100 mg) at 120 °C for 2 h and chromatography of the product gave 2-ethoxy-4-ethoxycarbonyl-3-methyl-3,5-diphenyl-3,4-dihydropyridine (**7c**) (84 mg, 91%) as colorless prisms from Et_2O–hexane, mp 73—75 °C. IR: 1680, 1605, 1590. UV: 290 (8100). ^{1}H-NMR: 0.89 (3H, t, J=7 Hz, $COOCH_2CH_3$), 1.36 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.54 (3H, s, CH_3), 2.59 (1H, d, J=18 Hz, C_4-H), 3.38 (1H, d, J=18 Hz), 3.93 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.41 (2H, q, J=7 Hz, OCH_2CH_3), 7.3 (10H, m, Ph).

A solution of **7c** (114 mg) in tetrahydrofuran (THF) (15 ml) was treated with 10% HCl (2 drops) at room temperature for 2 h. Evaporation of the solvent and crystallization of the residue from Et_2O–hexane gave **9c** (95 mg, 91%).[4)]

8) Thermolysis of **3j** (100 mg) at 120 °C for 2 h and chromatography of the product gave **7c** (90 mg, 97%).

9) Thermolysis of **3k** (35 mg) at 200 °C for 16 h gave 2-ethoxy-5-ethoxycarbonyl-3-methyl-6-phenylpyridine (**8**) (10 mg, 34%) as a colorless gum. IR (CH_2Cl_2): 1720, 1700, 1600. UV: 281 (11000). ^{1}H-NMR: 1.05 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.41 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.25 (3H, s, CH_3), 4.12 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.50 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.2—7.6 (5H, m), 7.87 (1H, s, C_4-H). MS m/z: M^+ Calcd for $C_{17}H_{19}NO_3$ 285.1365. Found: 285.1370.

The recovered starting material (10 mg, 29%) was contaminated with the isomer (3:1 of **3k** and **3l**).

10) Thermolysis of **3l** (75 mg) at 200 °C for 16 h gave **8** (30 mg, 47%) and a 1:9 mixture of **3k** and **3l** (20 mg, 27%).

11) Thermolysis of **3m** (100 mg) at 200 °C for 20 h gave 2-ethoxy-5-ethoxycarbonyl-3-ethyl-3-methyl-6-phenyl-3,4-dihydropyridine (**7e**) (91 mg) as a colorless gum. IR (CH_2Cl_2): 1750, 1720, 1690, 1600. UV: 294 (5600). ^{1}H-NMR: 0.82 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 0.85 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.07 (3H, s, CH_3), 1.18 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.4 (2H, m, $C\underline{H}_2CH_3$), 2.37 (1H, d, J=17 Hz, C_4-H), 2.75 (1H, d, J=17 Hz, C_4-H), 3.85 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.18 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.1—7.4 (5H, m, Ar-H). Chromatography of this gave 5-ethoxycarbonyl-3-ethyl-3-methyl-6-phenyl-3,4-dihydropyridine-2(1*H*)-one (**9d**) (63 mg, 75%) colorless needles, mp 108—110 °C. IR: 1690, 1660, 1630 sh. UV: 228 (10000), 282 (10800). ^{1}H-NMR: 0.90 (6H, t, J=7 Hz, $COOCH_2C\underline{H}_3$, $CH_2C\underline{H}_3$), 1.18 (3H, s, CH_3), 1.63 (2H, brq, J=7 Hz, $C\underline{H}_2CH_3$), 2.48 (1H, d, J=18 Hz, C_4-H), 2.83 (1H, d, J=18 Hz, C_4-H), 3.92 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 7.3 (5H, brs, Ar-H). HRMS m/z: M^+ Calcd for $C_{17}H_{21}NO_3$ 287.1521. Found: 287.1526.

DDQ Oxidation of 7a A solution of **7a** (100 mg) and DDQ (100 mg) in benzene (10 ml) was heated in a sealed tube at 100 °C for 30 min. The reaction mixture was diluted with CH_2Cl_2 and washed with 5% $NaHCO_3$ and water. The extract was dried over $MgSO_4$ and evaporated. The residue in benzene was chromatographed over SiO_2 to give 2-ethoxy-5-ethoxycarbonyl-3,6-diphenylpyridine (**10a**) (77 mg, 84%) as colorless needles from Et_2O–hexane, mp 102—103.5 °C. IR: 1700, 1590. UV: 300 (17900). ^{1}H-NMR: 1.09 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.40 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 4.18 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.57 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.4—7.7 (10H, m, Ar-H), 8.13 (1H, s, C_4-H). HRMS m/z: M^+ Calcd for $C_{22}H_{21}NO_3$ 347.1520. Found: 347.1511.

DDQ Oxidation of 7b A solution of **7b** (100 mg) and DDQ (100 mg) in benzene was heated at 120 °C for 1 h. Similar work-up gave 2,3-diethoxy-5-ethoxycarbonyl-6-phenylpyridine (**10b**) (64 mg, 71%) as colorless prisms from Et_2O–hexane, 65—66 °C. IR: 1685, 1580. UV: 288 (12700). ^{1}H-NMR: 1.03 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.43 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.50 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 4.13 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.20 (3H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.60 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.30 (1H, s, C_4-H), 7.4—7.6 (5H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{18}H_{21}NO_4$ 315.1471. Found: 315.1476.

Preparation of 4-Acetoxy Imidates (5) (General Procedure) A solution of a 4-acetoxy lactam (**4**) (100 mg) in dry CH_2Cl_2 (5 ml) was treated with excess Et_2OBF_4 at room temperature for 6 h. The mixture was diluted with CH_2Cl_2 and washed with 5% $NaHCO_3$ and water, then dried over $MgSO_4$. Evaporation of the solvent gave the residue which was purified with SiO_2 chromatography to give the corresponding 4-acetoxy imidate (**5**). The product was recrystallized from Et_2O–hexane.

dl-(1*R**,4*S**,5*S**,7*S**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-ene (**5a**): 81 mg, 76%. Colorless prisms, mp 127—128 °C. IR: 1740, 1710, 1650. UV: 260 sh (4600). ^{1}H-NMR: 0.75 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.47 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.07 (3H, $OCOCH_3$), 2.67 (1H, dd, J=10, 12 Hz, C_6-H), 3.27 (1H, dd, J=11, 12 Hz, C_6-H), 3.68 (1H, dd, J=10, 11 Hz, C_7-H), 3.68 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.54 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.02 (1H, s, C_4-H), 6.9—7.25 (10H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{25}H_{27}NO_5$ 421.1890. Found: 421.1912.

dl-(1*R**,4*R**,5*S**,7*S**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-ene (**5b**): 56 mg, 53%. Colorless needles, mp 109—109.5 °C. IR: 1745, 1730, 1640. UV: 270 (3100). ^{1}H-NMR: 0.74 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.50 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.22 (3H, s, $OCOCH_3$), 2.40 (1H, dd, J=10, 13 Hz, C_4-H), 3.29 (1H, dd, J=10.5, 13 Hz, C_4-H), 3.73 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 3.76 (1H, dd, J=10, 10.5 Hz, C_7-H), 4.56 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.02 (1H, s, C_4-H), 6.9—7.25 (10H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{25}H_{27}NO_5$ 421.1890. Found: 421.1910.

dl-(1*R**,4*R**,5*S**,7*R**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-ene (**5c**): 94 mg, 88%. Colorless gum. IR (CH_2Cl_2): 1740, 1715, 1640. ^{1}H-NMR: 0.83 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.26 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.16 (3H, s, $OCOCH_3$), 2.51 (1H, dd, J=10, 12 Hz, C_4-H), 2.89 (1H, dd, J=10, 12 Hz, C_4-H), 3.81 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.23 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.70 (1H, t, J=10 Hz, C_7-H), 6.30 (1H, s, C_4-H), 7.05—7.5 (10H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{25}H_{27}NO_5$ 421.1890. Found: 421.1911.

dl-(1*R**,4*R**,5*S**,7*S**)-4-Acetoxy-3,7-diethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-ene (**5d**): 105 mg, 97%. Colorless gum. IR (CH_2Cl_2): 1745, 1720, 1650. ^{1}H-NMR: 0.79 (1H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.13 (2H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.44 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.10 (3H, s, $OCOCH_3$), 2.18 (1H, dd, J=8, 13 Hz, C_6-H), 2.89 (1H, dd, J=8, 13 Hz, C_6-H), 3.52 (2H, m, $COOC\underline{H}_2CH_3$), 3.79 (2H, m, $OC\underline{H}_2CH_3$), 4.50 (2H, m, $OC\underline{H}_2CH_3$), 4.79 (1H, t, J=8 Hz, C_7-H), 6.22 (1H, s, C_4-H), 7.29 (5H, brs, Ar-H). HRMS m/z: M^+ Calcd for $C_{21}H_{27}NO_6$ 389.1837. Found: 389.1827.

dl-(1*R**,4*S**,5*S**,7*S**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-7-ethyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-ene (**5e**): 102 mg, 94%. Colorless gum. IR (CH_2Cl_2): 1740, 1715, 1650. ^{1}H-NMR: 0.65 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 0.82 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.31 (2H, quint, J=7 Hz, $C\underline{H}_2CH_3$), 1.40 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.05 (3H, s, $OCOCH_3$), 2.17—2.50 (3H, m, C_6 and C_7-H), 3.81 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.42 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.89 (1H, s, C_4-H), 7.18—7.48 (5H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{21}H_{27}NO_5$ 373.1890. Found: 435.2025.

dl-(1*R**,4*S**,5*S**,7*S**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-7-methyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-ene (**5f**): 104 mg, 97%. Colorless prisms, mp 137—141 °C. IR (CH_2Cl_2): 1740, 1715, 1650 sh, 1640. ^{1}H-NMR: 0.67 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.26 (3H, s, CH_3), 1.49 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.04 (3H, s, $OCOCH_3$), 2.34 (1H, d, J=13 Hz, C_6-H), 3.61 (2H, m, $COOC\underline{H}_2CH_3$), 3.67 (1H, d, J=13 Hz, C_6-H), 4.59 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.98 (1H, s, C_4-H), 6.75—7.25 (10H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{26}H_{29}NO_5$ 435.2045. Found: 435.2025.

dl-(1*R**,4*R**,5*R**,7*S**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-7-methyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-ene (**5g**): 104.5 mg, 95%. Colorless prisms, mp 104—107 °C. IR: 1750, 1730, 1650. ^{1}H-NMR: 0.71 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.32 (3H, s, CH_3), 1.52 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.00 (1H, d, J=12 Hz, C_6-H), 2.23 (3H, s, $OCOCH_3$), 3.56 (1H, d, J=12 Hz, C_6-H), 3.67 (2H, m, $COOC\underline{H}_2CH_3$), 4.59 (2H, q, $OC\underline{H}_2CH_3$), 5.93 (1H, s, C_4-H), 6.8—7.12 (10H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{26}H_{29}NO_5$ 435.2045. Found: 435.2040.

dl-(1*R**,4*R**,5*S**,7*R**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-7-methyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-ene (**5h**): 104 mg, 97%. Colorless gum. IR (CH_2Cl_2): 1735, 1710, 1655. ^{1}H-NMR: 1.02 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.15 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.45 (3H, s, CH_3), 2.15 (3H, s, $OCOCH_3$), 2.76 (2H, s, C_6-H), 3.99 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.19 (2H, m, $OC\underline{H}_2CH_3$), 6.12 (1H, s, C_4-H), 7.1—7.7 (10H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{26}H_{29}NO_5$ 435.2045. Found: 435.2025.

dl-(1*R**,4*R**,5*S**,7*S**)-4,7-Diacetoxy-3-ethoxy-5-ethoxycarbonyl-7-methyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-ene (**5i**): 99 mg, 92.6%. Colorless gum. IR (CH_2Cl_2): 1745, 1725, 1660. ^{1}H-NMR: 1.09 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.40 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.64 (3H, s, CH_3), 2.02 (3H, s, $OCOCH_3$), 2.13 (3H, s, $OCOCH_3$), 2.54 (1H, d, J=14 Hz, C_6-H), 2.85 (1H, d, J=14 Hz, C_6-H), 4.12 (2H, m, $COOC\underline{H}_2CH_3$), 4.41 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.25 (1H, s, C_4-H), 7.2—7.5 (5H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{22}H_{27}NO_7$ 417.1786. Found: 417.1785.

dl-(1*R**,4*S**,5*S**,6*S**,7*S**)-4-Acetoxy-6-deuterio-3-ethoxy-5-ethoxycarbonyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-ene (**5D**): 97 mg, 91%. Colorless prisms, mp 132—136 °C. IR: 1750, 1715, 1680. ^{1}H-NMR: 0.71 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.45 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.05 (3H, s, $OCOCH_3$), 2.63 (1H, d, J=9 Hz, C_6-H), 3.67 (1H, d, J=9 Hz, C_7-H), 3.67 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.53 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.01 (1H, s, C_4-H), 6.9—7.2 (10H, m, Ar-H). HRMS m/z: M^+ Calcd for $C_{25}H_{26}DNO_5$ 422.0950. Found: 422.1949.

Thermolysis of 4-Acetoxy Imidates (5) (General Procedure) A solution of **5** in a hydrocarbon solvent (5 ml) (below 200 °C in toluene, 250—300 °C in xylene, and 350 °C in cymene) was heated in a sealed tube. After evaporation of the solvent *in vacuo*, the residue was purified with MPLC using EtOAc–hexane (1:3) as an eluent to give the products.

1) Thermolysis of **5a** (80 mg) at 160 °C for 8 h gave **11** (23 mg, 29%), **12** (18 mg, 23%) and **13** (1 mg, 1.7%).

dl-(1*R**,4*R**,6*S**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (**11**): Colorless prisms from Et_2O–CH_2Cl_2, mp 119—120 °C. IR: 1740, 1725. UV: 249 (15400). ^{1}H-NMR: 1.06 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.09 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.06 (3H, s, $OCOCH_3$), 2.28 (1H, dd, J=10, 13 Hz, C_5*endo*-H), 2.54 (1H, dd, J=6, 13 Hz, C_5*exo*-H), 3.07 (1H, dd, J=6, 10 Hz, C_6*endo*-H), 3.78 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.10 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.68

(1H, s, C_7-H), 7.2—7.7 (10H, m, Ar-H). HRMS *m/z*: M^+ Calcd for $C_{25}H_{27}NO_5$ 421.1889. Found: 421.1874.

dl-(1*R**,4*R**,6*R**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (**12**): Colorless prisms from Et_2O–CH_2Cl_2, mp 116—118 °C. IR: 1740, 1710. UV: 249 (11900). ^{1}H-NMR: 1.11 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.20 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.98 (1H, dd, J=5, 13 Hz, C_5*endo*-H), 2.05 (3H, s, $OCOCH_3$), 2.98 (1H, dd, J=10, 13 Hz, C_5*exo*-H), 3.67 (1H, dd, J=5, 10 Hz, C_6*exo*-H), 3.90 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.13 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.37 (1H, s, C_7-H), 6.95—7.7 (10H, m, Ar-H). HRMS *m/z*: M^+ Calcd for $C_{25}H_{27}NO_5$ 421.1887. Found: 421.1861.

3-Acetoxy-2-ethoxy-4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole (**13**): Colorless plates from hexane, mp 126—130 °C. IR (CH_2Cl_2): 3440, 1765, 1700, 1635. UV: 304 (8800). ^{1}H-NMR: 1.17 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.34 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.31 (3H, s, $OCOCH_3$), 4.14 (4H, q, J=7 Hz, $COOC\underline{H}_2CH_3$, $OC\underline{H}_2CH_3$), 7.25—7.55 (5H, m, Ar-H), 7.95 (1H, brs, NH). HRMS *m/z*: M^+ Calcd for $C_{17}H_{19}NO_5$ 317.1261. Found: 317.1239.

2) Thermolysis of **5D** (60 mg) at 160 °C for 8 h gave **11D** (22 mg, 37%) and **12D** (13 mg, 21%).

dl-(1*R**,4*R**,5*R**,6*R**,7*R**)-7-Acetoxy-5-deuterio-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (**11D**): Colorless needles from CH_2Cl_2–hexane, mp 117—120 °C. IR: 1765, 1720. UV: 249 (14200). ^{1}H-NMR: 1.06 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.09 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.06 (3H, s, $OCOCH_3$), 2.51 (1H, d, J=6 Hz, C_5*exo*-H), 3.06 (1H, d, J=6 Hz, C_6*endo*-H), 3.78 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.10 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.68 (1H, s, C_7-H), 7.25—7.7 (10H, m, Ar-H). HRMS *m/z*: M^+ Calcd for $C_{25}H_{26}DNO_5$ 422.1951. Found: 422.1931.

dl-(1*R**,4*R**,5*R**,6*S**,7*R**)-7-Acetoxy-5-deuterio-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (**12D**): Colorless needles from CH_2Cl_2–hexane, mp 122—127 °C. IR: 1765, 1715. UV: 249 (10400). ^{1}H-NMR: 1.12 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.19 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.05 (3H, s, $OCOCH_3$), 2.95 (1H, d, J=10 Hz, C_5*exo*-H), 3.66 (1H, d, J=10 Hz, C_6*exo*-H), 3.90 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.10 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.37 (1H, s, C_7-H), 7.0—7.75 (10H, m, Ar-H). HRMS *m/z*: M^+ Calcd for $C_{25}H_{26}DNO_5$ 422.1950. Found: 422.1922.

3) Thermolysis of **5b** (40 mg) at 180 °C for 8 h gave **14** (10 mg, 25%) and **15** (19 mg, 48%), and **13** (1 mg, 1.7%).

dl-(1*R**,4*R**,6*S**,7*S**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (**14**): Colorless gum. IR (CH_2Cl_2): 1750, 1730. UV: 247 (12200). ^{1}H-NMR: 1.08 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.21 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.07 (1H, dd, J=10, 13 Hz, C_5*endo*-H), 2.18 (3H, s, $OCOCH_3$), 3.07 (1H, dd, J=5, 13 Hz, C_5*exo*-H), 3.6—3.9 (2H, m, $COOC\underline{H}_2CH_3$), 3.84 (1H, ddd, J=1, 5, 10 Hz, C_6*endo*-H), 4.16 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.44 (1H, d, J=1 Hz, C_7-H), 7.0—7.2 (5H, m, Ar-H), 7.25—7.7 (5H, m, Ar-H). HRMS *m/z*: M^+ Calcd for $C_{25}H_{27}NO_5$ 421.1889. Found:421.1935.

dl-(1*R**,4*R**,6*R**,7*S**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1] hept-2-ene (**15**): Colorless gum. IR (CH_2Cl_2): 1750, 1725. UV: 248 (15200). ^{1}H-NMR: 1.07 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.18 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.96 (3H, s, $OCOCH_3$), 2.15—2.41 (1H, m, C_5*endo*-H), 2.9—3.2 (2H, m, C_5*exo*-H, C_6*exo*-H), 3.83 (2H, m, $COOC\underline{H}_2CH_3$), 4.15 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.43 (1H, s, C_7-H), 7.25—7.7 (5H, m, Ar-H). HRMS *m/z*: M^+ Calcd for $C_{25}H_{27}NO_5$ 421.1889. Found: 421.1909.

4) Thermolysis of **5c** (80 mg) at 300 °C for 5.5 h gave **13** (13 mg, 21%).

5) Thermolysis of **5f** (50 mg) at 180 °C for 3 h gave **16** (15 mg, 30%) and **13** (13 mg, 35%).

dl-(1*R**,4*R**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-6-methyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (**16**): Colorless gum. IR (CH_2Cl_2): 1745, 1725. UV: 249 (6800). ^{1}H-NMR: 1.10 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.34 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.65 (3H, s, CH_3), 2.05 (3H, s, $OCOCH_3$), 2.52 (2H, s, C_5-H), 3.9—4.4 (2H, m, $COOC\underline{H}_2CH_3$), 4.10 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.65 (1H, s, C_7-H), 6.85—7.5 (10H, m, Ar-H). HRMS *m/z*: M^+ Calcd for $C_{26}H_{29}NO_5$ 435.2045. Found: 435.2055.

6) Thermolysis of **5g** (50 mg) at 180 °C for 18 h gave a 1 : 1 mixture of **17** and **13** (20 mg, yield for **17** and **13** was 28%) and the starting material (**5g**) (15 mg, 30%).

dl-(1*R**,4*R**,7*S**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-6-methyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (**17**) was isolated as a mixture with **13**. ^{1}H-NMR for **17**: 1.07 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.37 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.66 (3H, s, CH_3), 2.15 (3H, s, $OCOCH_3$), 2.72 (2H, s, C_5-H), 3.73 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.13 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.53 (1H, s, C_7-H), 7.0—7.5 (10H, m, Ar-H).

7) Thermolysis of **5h** (50 mg) at 250 °C for 2.5 h gave **13** (32 mg, 88%).

8) Thermolysis of **5i** (50 mg) at 350 °C for 1 h gave **18** (4.5 mg, 9%) and the starting material (**5i**) (34 mg, 67%).

dl-(1*R**,4*R**,7*S**)-6,7-Diacetoxy-1-ethoxy-4-ethoxycarbonyl-6-methyl-3-phenyl-2-azabicyclo[2.2.1]hept-2-ene (**18**): Colorless gum. IR (CH_2Cl_2): 1750 sh, 1730. UV: 247 (12200). ^{1}H-NMR: 1.07 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.34 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.41 (3H, s, CH_3), 2.08 (3H, s, $OCOCH_3$), 2.09 (3H, s, $OCOCH_3$), 2.24 (1H, dd, J=1.5, 14.5 Hz, C_5*endo*-H), 3.10 (1H, d, J=14.5 Hz, C_5*exo*-H), 3.91 (2H, m, $COOC\underline{H}_2CH_3$), 4.13 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.46 (1H, d, J=1.5 Hz, C_7-H), 7.25—7.65 (5H, m, Ar-H). HRMS *m/z*: M^+ Calcd for $C_{22}H_{27}NO_7$ 417.1788. Found: 417.1815.

Thermolysis of 2-Azanorbornenes (11 and 12) A solution of **11** or **12** (15 mg) in xylene (5 ml) was heated in a sealed tube at 300 °C for 2 h. After evaporation of the solvent *in vacuo*, the residue in benzene was chromatographed over SiO_2 to give **13** (11 mg, 99% from **11** and 10 mg, 95% from **12**).

References and Notes

1) Part XLII: T. Sano, Y. Horiguchi, K. Tanaka, K. Abe, and Y. Tsuda, *Chem. Pharm. Bull.*, **37**, 652 (1989); Part XLIII: K. Isobe, C. Mohri, H. Sano, K. Mohri, H. Enomoto, T. Sano, and Y. Tsuda, *ibid.*, **37**, 3236 (1989).
2) T. Sano, *Yuki Gosei Kagaku Kyokaishi*, **42**, 340 (1980).
3) T. Sano, Y. Horiguchi, and Y. Tsuda, unpublished results.
4) T. Sano, Y. Horiguchi, Y. Tsuda, K. Furuhata, H. Takayanagi, and H. Ogura, *Chem. Pharm. Bull.*, **35**, 9 (1987).
5) Preliminary communications: *a*) T. Sano, Y. Horiguchi, and Y. Tsuda, *Heterocycles*, **16**, 889 (1981); *b*) T. Sano, K. Tanaka, Y. Horiguchi, and Y. Tsuda, *ibid.*, **23**, 813 (1985).
6) *a*) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963); *b*) S. McLean and R. Haynes, *Tetrahedron Lett.*, **1964**, 2385; *c*) W. R. Roth, *ibid.*, **1964**, 1009.
7) T. Sano, Y. Horiguchi, and Y. Tsuda, *Chem. Pharm. Bull.*, **35**, 23 (1987).
8) A. P. Marchand, "Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems," Verlag Chemie International Inc., Florida, 1982, p. 59.
9) For definition of *exo* and *endo* in this ring system, see the text: M. Orchin, F. Kaplan, R. S. Macomber, R. M. Wilson, and H. Zimmer, "The Vocabulary of Organic Chemistry," Wiley and Sons, Inc., New York, 1980, p. 141.
10) J. A. Berson, *Acc. Chem. Res.*, **5**, 406 (1972).
11) J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **92**, 1096 (1970).
12) K. Fukui, "Kagaku Hanno To Denshi No Kido," Maruzen Inc., Tokyo, 1976, p. 196.
13) A referee suggested that this bond elongation may originate from the through bond interaction between C_1-Ph and C_7-*exo*-Ph groups arranged in face-to-face orientation and that this electronic effect may enhance the reactivity of the 7-*exo*-phenyl derivative.
14) 2-Azanorborn-2-enes were previously prepared by intramolecular Diels–Alder reactions of sulfonyl cyanides and cyclopentadient: J. C. Jagt and A. M. van Leusen, *J. Org. Chem.*, **39**, 564 (1974); and of olefins and pentachloro-1-azapentadiene: M. E. Jung and J. J. Sharpiro, *J. Am. Chem. Soc.*, **102**, 7862 (1980); B. K. Ramash, C. M. Gladstone, and J. L. Wong, *J. Org. Chem.*, **46**, 3036 (1981).
15) Preparations and chemical properties of azanorbornanes have beeh reviewed; D. Blondet and C. Morin, *Heterocycles*, **19**, 2155 (1982).