

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 C₁-C₇ bond to the C₃ 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 C₇-substituent. These two reactions occurred competitively depending on the nature of the C₇ 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 dioxopyrrolone; 1*H*-pyrrole-2,3-dione; 2-azabicyclo[3.2.0]hept-2-ene; cyclobutane; thermolysis; 1,3-shift; epimerization; dihydropyridine; dihydropyridone; 2-azanorbornane

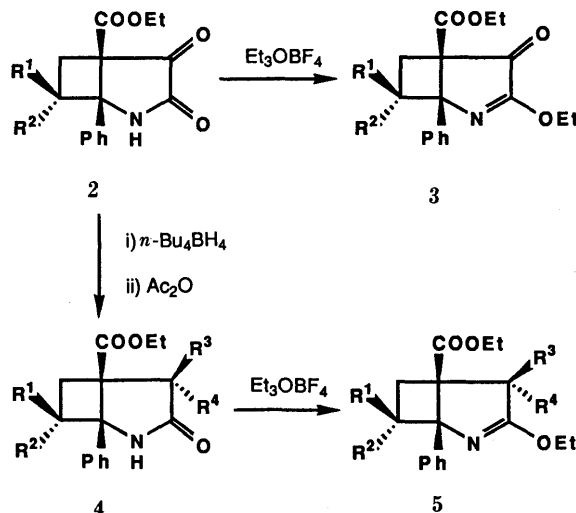
The 7-substituted 2-azabicyclo[3.2.0]heptane-3,4-diones (2), 2+2 photoadduct of olefins to 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione (1), readily undergo various skeletal rearrangements.²⁾ Recently, we reported that base treatment of the molecule caused epimerization at the C₇-substituent together with the ring expansion reaction, both reactions being due to C₁-C₅ bond fission.¹⁾ The 7-*exo*-phenyl derivative (2a) gave the dioxopyrrolone (1), a cycloreversion 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 N₂-C₃ 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 C₁-C₇ bond and another is an epimerization at the C₇-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



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

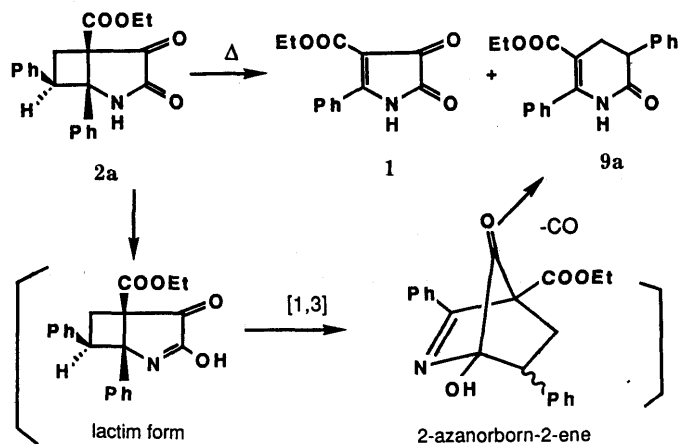


Chart 1

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 C₇-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 ¹H-nuclear magnetic resonance (¹H-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 C₁–C₇ bond followed by cheletropic loss of CO from an intermediary 2-azanorbornen-7-one (**6**).

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 C₁–C₇ bond with inversion and retention of the configuration at the migrating center (C₇), 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 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 C₂₅H₂₇NO₅ 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		Temp (°C)	Time (h)	Product	Yield (%)	Remarks
	R ¹	R ²					
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.

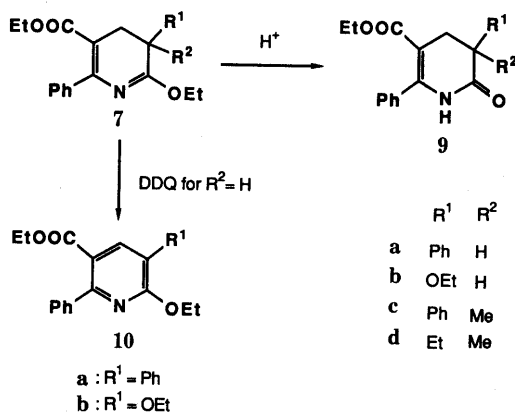
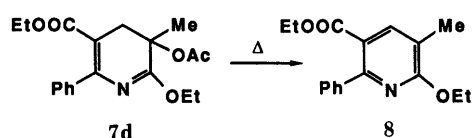
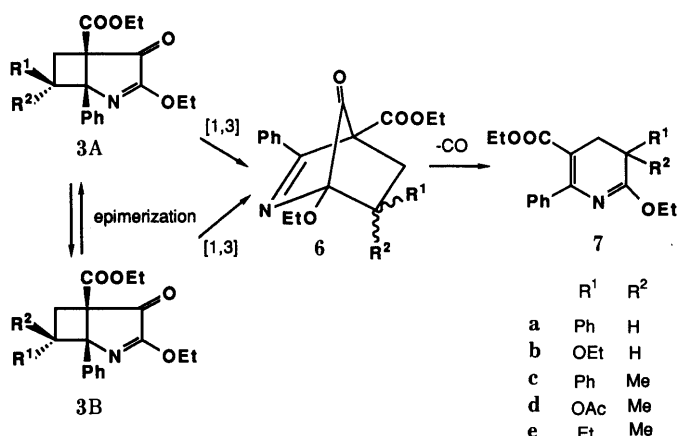


Chart 4

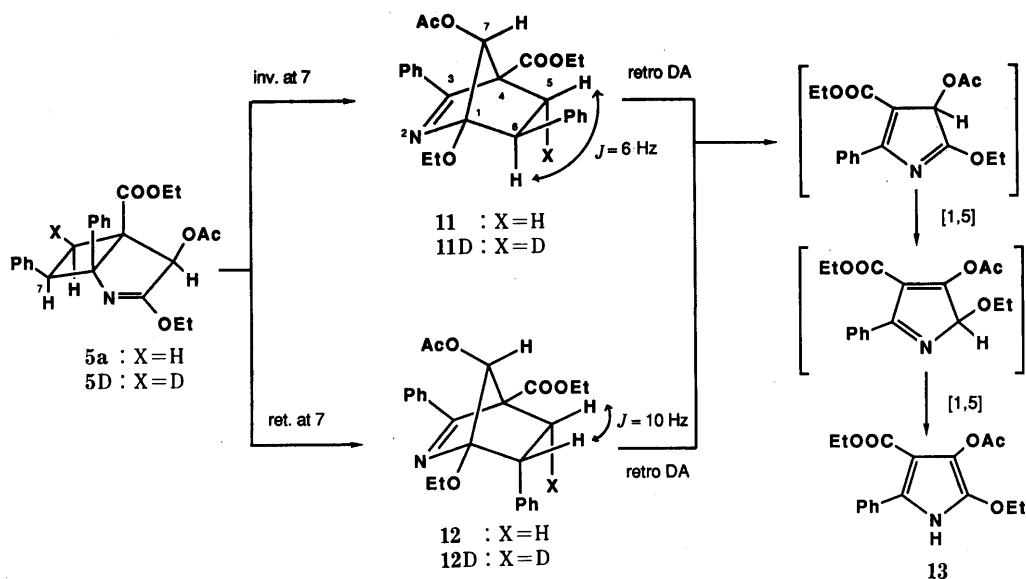


Chart 5

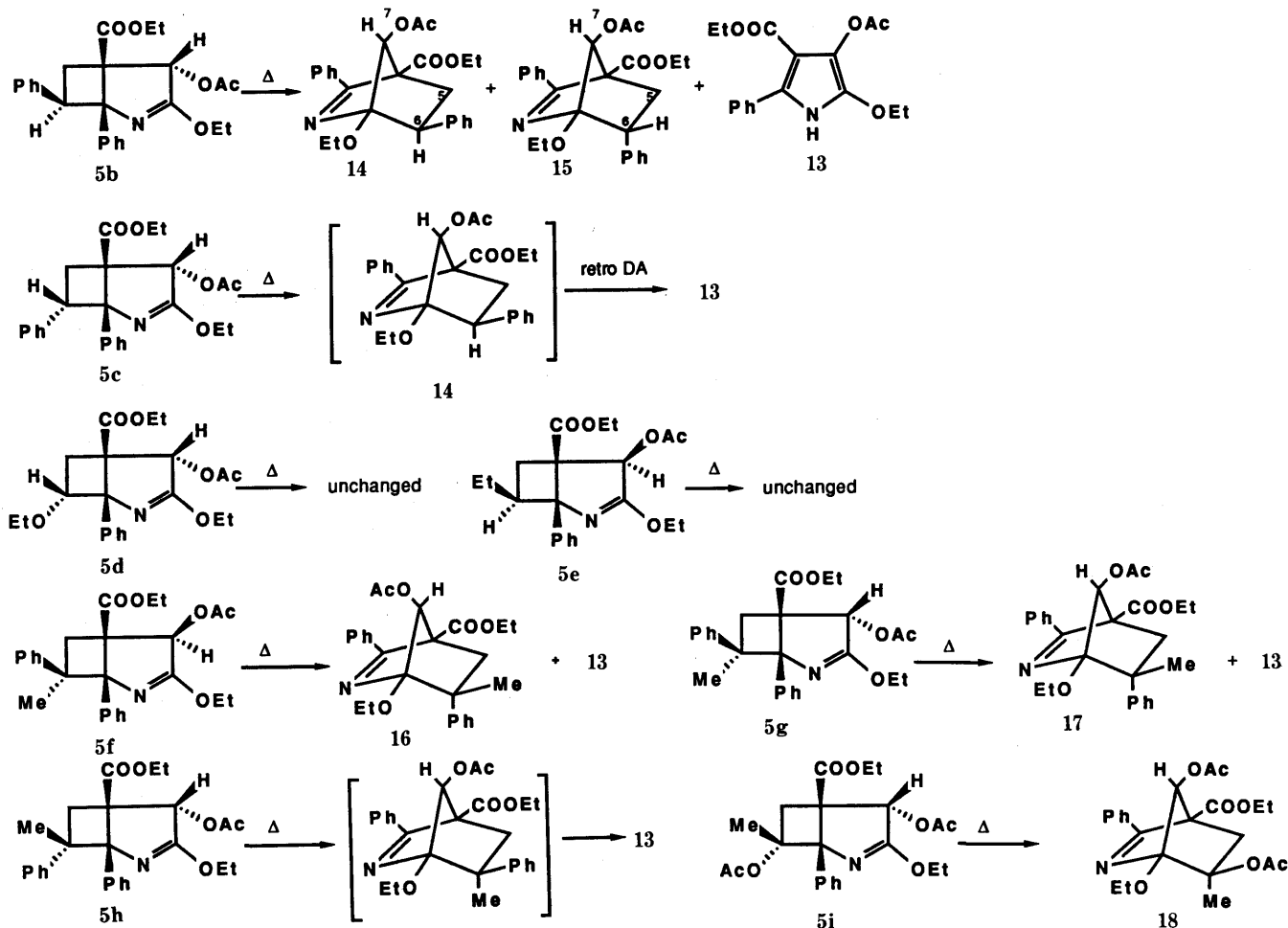


Chart 6

isomers. The stereochemistries of the C₆-phenyl group in **11** and **12** were established by analyses of the ¹H-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 C₅-*exo*-H and C₆-H was found to be 6 Hz in **11D** and 10 Hz in **12D** as shown in Chart 5, indicating that the relationship of C₅-H and C₆-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		si ^{a)}	sr ^{b)}	Product (Yield %)		si/sr
		Temp (°C)	Time (h)			py ^{c)}	rec ^{d)}	
5a <i>exo</i> -Ph	<i>exo</i>	160	8	29	23	1	—	1.2
5b <i>exo</i> -Ph	<i>endo</i>	180	8	24	47	1	—	0.5
5c <i>endo</i> -Ph	<i>endo</i>	300	5.5	—	—	21	—	—
5d <i>endo</i> -OEt	<i>endo</i>	350	5	—	—	—	80	—
5e <i>exo</i> -Et	<i>exo</i>	300	5	—	—	—	80	—
5f di ^{e)} (Ph, Me)	<i>exo</i>	180	3	—	30	35	—	(ret)
5g di (Ph, Me)	<i>endo</i>	180	18	—	25	30	30	(ret)
5h di (Me, Ph)	<i>endo</i>	250	2.5	—	—	88	—	—
5i di (Me, OAc)	<i>endo</i>	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 C₆-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 C₆ was also deduced from the ¹H-NMR spectra. Although the C₆-proton signals of **15** exhibited unresolved bands overlapped with those of the C₅-protons, **14** exhibited a W type long range coupling between C₇-H and C₆-*endo*-H (*J*=1 Hz), thus establishing that the C₆-phenyl group of **14** has *exo*-configuration. Thus, **14** is the 1,3-shift product with C₇-inversion and **15** is that with C₇-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 C₇-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 C₆-C₇ bond to take an R² inside configuration at the transition

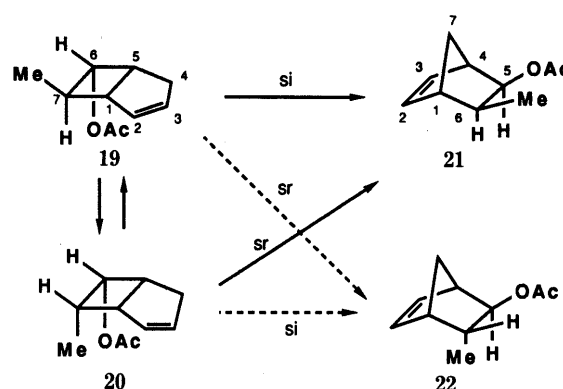


Chart 7. Thermal 1,3-Shift of 7-Substituted Bicyclo[3.2.0]heptenes (according to Berson)¹¹⁾

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 stereo-randamization 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, Fukui¹²⁾ 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 1*π* 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.

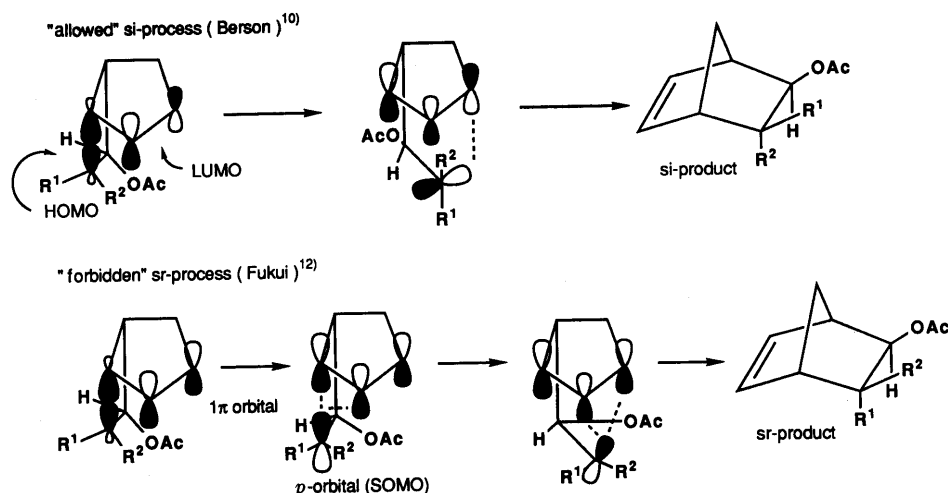


Chart 8. Proposed Mechanisms of Thermal Bicycloheptane Rearrangement

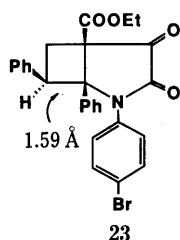


Chart 9

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 latter (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 C₁–C₇ 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 C₁–C₇ 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 is difficult or does not occur (5c and 5d). However, in 7,7-disubstituted 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 C₁–C₇ 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 examples¹⁰⁾ 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 C₁–C₇ bond cleavage. However, it

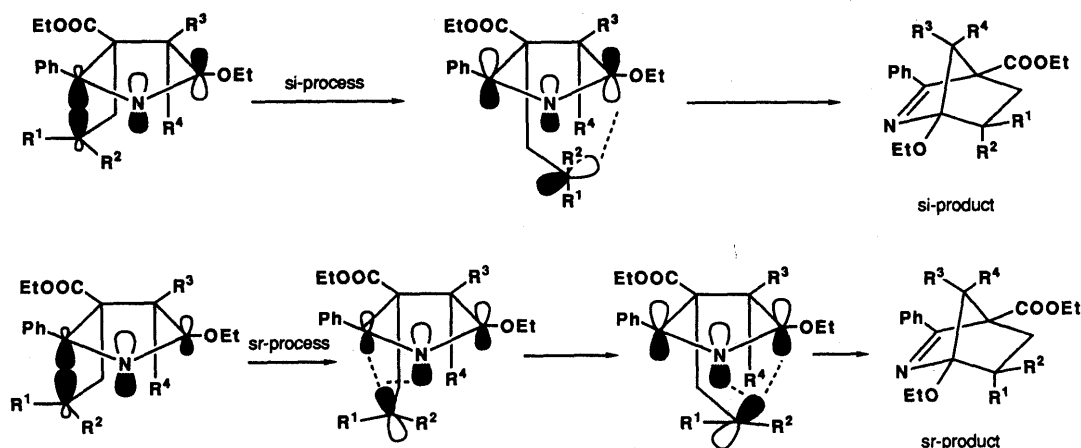


Chart 10. Thermal 1,3-Shift in 2-Azabicyclo[3.2.0]heptene System

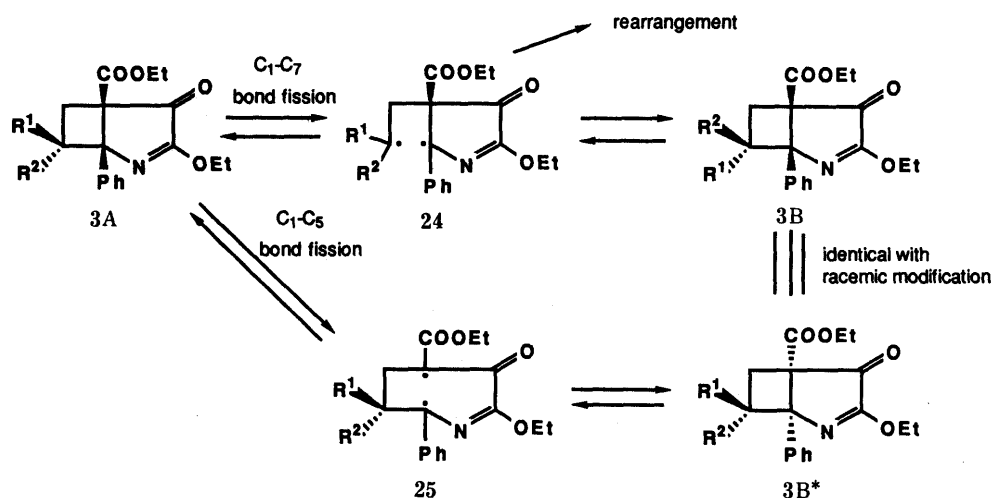


Chart 11. 7-Epimerization Reaction

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 C₁–C₅ 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 C₁–C₅ bond fission-recombination mechanism.¹⁾

Based on those facts, we consider that 7-epimerization of 4-oxo derivatives in the present thermolysis proceeds through C₁–C₅ bond fission and recombination, though there is no direct evidence to confirm this. Fission of the C₁–C₅ or C₁–C₇ 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). ¹H-NMR (100 MHz) and ¹³C-NMR (25.0 MHz) spectra were taken in CDCl₃ 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 F₂₅₄ plates (Merck). Medium-pressure liquid chromatography (MPLC) was performed on Kusano CIC preppacked silica gel columns.

Preparation of the 7-*exo*-Et-*endo*-Me Derivative (2m) A solution of the cyclobutane (2: R¹ = vinyl, R² = 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 SiO₂ and crystallized from CH₂Cl₂ 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. ¹H-NMR: 0.58 (3H, t, *J* = 7 Hz, CH₂CH₃), 1.92 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.07 (3H, s, CH₃), 1.0–1.4 (2H, m, CH₂CH₃), 1.97 (1H, d, *J* = 13 Hz, C₆-H), 2.93 (1H, d, *J* = 13 Hz, C₆-H), 4.03 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 7.33 (5H, s, Ar-H). *Anal.* Calcd for C₁₈H₂₁NO₄: 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 CH₂Cl₂ (10 ml) was treated with excess triethyloxonium fluoroborate (Et₃OBF₄) at room temperature overnight. The mixture was diluted with CH₂Cl₂ and washed with 5% NaHCO₃ and water. The organic extract was dried over MgSO₄ and evaporated. The product in benzene was passed through a short column of SiO₂ and crystallized from Et₂O–*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). ¹H-NMR: 0.67 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.20 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.38 (1H, dd, *J* = 4, 6 Hz, C₆-H), 3.58 (1H, dd, *J* = 4, 6 Hz, C₆-H), 3.60 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 3.78 (1H, t, *J* = 6 Hz, C₇-H), 4.65 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.1 (10H, brs, Ar-H). *Anal.* Calcd for C₂₃H₂₃NO₄: 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. ¹H-NMR: 0.73 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.25 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.27 (1H, dd, *J* = 8, 13 Hz, C₆-H), 3.47 (1H, dd, *J* = 8, 13 Hz, C₆-H), 3.78 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.27 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.78 (1H, t, *J* = 8 Hz, C₇-H), 7.2 (10H, m, Ar-H). *Anal.* Calcd for C₂₃H₂₃NO₄: 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. ¹H-NMR: 0.65 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 0.88 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.53 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.32 (1H, dd, *J* = 8, 14 Hz, C₆-H), 3.20 (3H, m, C₆-H and OCH₂CH₃), 3.69 (1H, m, C₇-H), 3.75 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.62 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.4 (5H, m, Ar-H). *Anal.* Calcd for C₁₉H₂₃NO₆: 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). ¹H-NMR: 0.67 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.10 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.54 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.93 (1H, dd, *J* = 5, 14 Hz, C₆-H), 3.37 (2H, oct, *J* = 2, 7 Hz, OCH₂CH₃), 3.37 (1H, dd, *J* = 8, 14 Hz, C₆-H), 3.74 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.62 (2H, q, *J* = 7 Hz, OCH₂CH₃), 4.71 (1H, dd, *J* = 5, 8 Hz, C₇-H), 7.3 (5H, m, Ar-H). *Anal.* Calcd for C₁₉H₂₃NO₆: 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). ¹H-NMR: 0.60 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.53 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.03 (3H, s, OCOCH₃), 2.05 (1H, dd, *J* = 5, 14 Hz, C₆-H), 3.52 (1H, dd, *J* = 9, 14 Hz, C₆-H), 3.77 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.62 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.87 (1H, dd, *J* = 5, 9 Hz, C₇-H), 7.35 (5H, brs, Ar-H). *Anal.* Calcd for C₁₉H₂₁NO₆: 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). ¹H-NMR: 0.62 (3H, t, *J* = 7 Hz, CH₂CH₃), 0.73 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.4 (2H, m, CH₂CH₃), 1.50 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.08 (2H, m, C₆-H), 2.67 (1H, m, C₇-H), 3.83 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.55 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.3 (5H, m, Ar-H). *Anal.* Calcd for C₁₉H₂₃NO₄: 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). ¹H-NMR: 0.69 (3H, t, *J* = 7 Hz, CH₂CH₃), 0.81 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.45 (2H, m, CH₂CH₃), 1.53 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.56 (1H, m, C₆-H), 3.2 (2H, m, C₆-H and C₇-H), 3.73 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.58 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.31 (5H, s, Ar-H). *Anal.* Calcd for C₁₉H₂₃NO₄: 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. ¹H-NMR: 0.55 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.12 (3H, s, CH₃), 1.58 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.18 (1H, d, *J* = 13 Hz, C₆-H), 3.68 (2H, oct, *J* = 4 Hz, COOCH₂CH₃), 3.74 (1H, d, *J* = 13 Hz, C₆-H), 4.69 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.35 (3H, s, Ph), 7.8–8.1 (7H, m, Ph). HRMS *m/z*: M⁺ Calcd for C₂₄H₂₅NO₄: 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. ¹H-NMR: 0.99 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.05 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.39 (3H, s, CH₃), 2.88 (1H, d, *J* = 13.4 Hz, C₆-H), 3.12 (1H, d, *J* = 13.4 Hz, C₆-H), 4.04 (4H, m, COOCH₂CH₃ and OCH₂CH₃), 7.0–7.4 (8H, m, Ph), 7.65 (2H, m, Ph). HRMS *m/z*: M⁺ Calcd for C₂₄H₂₅NO₄: 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). ¹H-NMR: 0.70 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.38 (3H, s, CH₃), 1.55 (3H, t,

J = 7 Hz, OCH₂CH₃), 1.79 (3H, s, OCOCH₃), 2.25 (1H, d, *J* = 15 Hz, C₆-H), 3.47 (1H, d, *J* = 15 Hz, C₆-H), 3.88 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.69 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.45 (5H, m, Ar-H). *Anal.* Calcd for C₂₀H₂₃NO₆: 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). ¹H-NMR: 0.97 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.52 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.55 (3H, s, CH₃), 1.98 (3H, s, OCOCH₃), 2.32 (1H, d, *J* = 14 Hz, C₆-H), 3.20 (1H, d, *J* = 14 Hz, C₆-H), 4.05 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.57 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.4 (5H, m, Ar-H). *Anal.* Calcd for C₂₀H₂₃NO₆: C, 64.33; H, 6.21; N, 3.75. Found: C, 65.10; H, 6.50; N, 3.87.

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 (**3m**): 185 mg, 85%. Colorless prisms, mp 100–105 °C. IR: 1750, 1725, 1625. UV: 242 sh (5300). ¹H-NMR: 0.55 (3H, t, *J* = 7 Hz, CH₂CH₃), 0.91 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 0.85 (3H, s, CH₃), 1.35 (2H, m, CH₂CH₃), 1.48 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.69 (1H, d, *J* = 13 Hz, C₆-H), 2.85 (1H, d, *J* = 13 Hz, C₆-H), 4.00 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.55 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.15–7.7 (5H, m, Ar-H). *Anal.* Calcd for C₂₀H₂₃NO₄: 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 SiO₂ 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 (CH₂Cl₂): 1750, 1700 sh, 1685, 1620, 1600. UV: 222 (13000), 293 (7800). ¹H-NMR: 0.90 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.27 (3H, t, *J* = 7 Hz, OCH₂CH₃), 3.00 (1H, d, *J* = 8 Hz, C₄-H), 3.02 (1H, d, *J* = 5 Hz, C₄-H), 3.70 (1H, dd, *J* = 5, 8 Hz, C₃-H), 3.93 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.33 (2H, q, *J* = 7 Hz, OCH₂CH₃), 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 (CH₂Cl₂): 1750, 1720, 1680, 1620. UV: 228 (8800), 288 (6000). ¹H-NMR: 0.87 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.08 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.23 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.81 (1H, d, *J* = 5 Hz, C₄-H), 2.91 (1H, d, *J* = 5 Hz, C₄-H), 3.63 (2H, q, *J* = 7 Hz, OCH₂CH₃), 3.93 (1H, t, *J* = 5 Hz, C₃-H), 4.00 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.36 (2H, q, *J* = 7 Hz, OCH₂CH₃), 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 ¹H-NMR spectrum of **3e** and **3f** mixture prepared by alkylation of a 3 : 1 mixture of **2e** and **2f**⁴⁾ with Et₃OBf₄. After heating at 200 °C for 48 h in toluene (5 ml) this mixture was recovered unchanged. ¹H-NMR for **3e**: 0.66 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.53 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.78 (3H, s, OCOCH₃), 2.43 (1H, dd, *J* = 8, 14 Hz, C₆-H), 3.20 (1H, dd, *J* = 7, 14 Hz, C₆-H), 3.79 (2H, qd, *J* = 2, 7 Hz, COOCH₂CH₃), 4.63 (2H, q, *J* = 7 Hz, OCH₂CH₃), 4.80 (1H, dd, *J* = 7, 8 Hz, C₇-H), 7.3 (5H, brs, 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 Et₂O–hexane, mp 73–75 °C. IR: 1680, 1605, 1590. UV: 290 (8100). ¹H-NMR: 0.89 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.36 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.54 (3H, s, CH₃), 2.59 (1H, d, *J* = 18 Hz, C₄-H), 3.38 (1H, d, *J* = 18 Hz), 3.93 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.41 (2H, q, *J* = 7 Hz, OCH₂CH₃), 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 Et₂O–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 (CH₂Cl₂): 1720, 1700, 1600. UV: 281 (11000). ¹H-NMR: 1.05 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.41 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.25 (3H, s, CH₃), 4.12 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.50 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.2–7.6 (5H, m), 7.87 (1H, s, C₄-H). MS *m/z*: M⁺ Calcd for C₁₇H₁₉NO₃ 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 (CH₂Cl₂): 1750, 1720, 1690, 1600. UV: 294 (5600). ¹H-NMR: 0.82 (3H, t, *J* = 7 Hz, CH₂CH₃), 0.85 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.07 (3H, s, CH₃), 1.18 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.4 (2H, m, CH₂CH₃), 2.37 (1H, d, *J* = 17 Hz, C₄-H), 2.75 (1H, d, *J* = 17 Hz, C₄-H), 3.85 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.18 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.1–7.4 (5H, m, Ar-H). Chromatography of this gave 5-ethoxycarbonyl-3-ethyl-3-methyl-6-phenyl-3,4-dihydropyridine-2(1H)-one (**9d**) (63 mg, 75%) colorless needles, mp 108–110 °C. IR: 1690, 1660, 1630 sh. UV: 228 (10000), 282 (10800). ¹H-NMR: 0.90 (6H, t, *J* = 7 Hz, COOCH₂CH₃, CH₂CH₃), 1.18 (3H, s, CH₃), 1.63 (2H, br q, *J* = 7 Hz, CH₂CH₃), 2.48 (1H, d, *J* = 18 Hz, C₄-H), 2.83 (1H, d, *J* = 18 Hz, C₄-H), 3.92 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 7.3 (5H, brs, Ar-H). HRMS *m/z*: M⁺ Calcd for C₁₇H₂₁NO₃ 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 CH₂Cl₂ and washed with 5% NaHCO₃ and water. The extract was dried over MgSO₄ and evaporated. The residue in benzene was chromatographed over SiO₂ to give 2-ethoxy-5-ethoxycarbonyl-3,6-diphenylpyridine (**10a**) (77 mg, 84%) as colorless needles from Et₂O–hexane, mp 102–103.5 °C. IR: 1700, 1590. UV: 300 (17900). ¹H-NMR: 1.09 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.40 (3H, t, *J* = 7 Hz, OCH₂CH₃), 4.18 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.57 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.4–7.7 (10H, m, Ar-H), 8.13 (1H, s, C₄-H). HRMS *m/z*: M⁺ Calcd for C₂₂H₂₁NO₃ 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 Et₂O–hexane, 65–66 °C. IR: 1685, 1580. UV: 288 (12700). ¹H-NMR: 1.03 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.43 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.50 (3H, t, *J* = 7 Hz, OCH₂CH₃), 4.13 (2H, q, *J* = 7 Hz, OCH₂CH₃), 4.20 (3H, q, *J* = 7 Hz, COOCH₂CH₃), 4.60 (2H, q, *J* = 7 Hz, OCH₂CH₃), 7.30 (1H, s, C₄-H), 7.4–7.6 (5H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₁₈H₂₁NO₄ 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 CH₂Cl₂ (5 ml) was treated with excess Et₂OBF₄ at room temperature for 6 h. The mixture was diluted with CH₂Cl₂ and washed with 5% NaHCO₃ and water, then dried over MgSO₄. Evaporation of the solvent gave the residue which was purified with SiO₂ chromatography to give the corresponding 4-acetoxy imidate (**5**). The product was recrystallized from Et₂O–hexane.

dl-(1R*,4R*,5S*,7S*)-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). ¹H-NMR: 0.75 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.47 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.07 (3H, OCOCH₃), 2.67 (1H, dd, *J* = 10, 12 Hz, C₆-H), 3.27 (1H, dd, *J* = 11, 12 Hz, C₆-H), 3.68 (1H, dd, *J* = 10, 11 Hz, C₇-H), 3.68 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.54 (2H, q, *J* = 7 Hz, OCH₂CH₃), 6.02 (1H, s, C₄-H), 6.9–7.25 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₇NO₅ 421.1890. Found: 421.1912.

dl-(1R*,4R*,5S*,7S*)-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). ¹H-NMR: 0.74 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.50 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.22 (3H, s, OCOCH₃), 2.40 (1H, dd, *J* = 10, 13 Hz, C₄-H), 3.29 (1H, dd, *J* = 10.5, 13 Hz, C₄-H), 3.73 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 3.76 (1H, dd, *J* = 10, 10.5 Hz, C₇-H), 4.56 (2H, q, *J* = 7 Hz, OCH₂CH₃), 6.02 (1H, s, C₄-H), 6.9–7.25 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₇NO₅ 421.1890. Found: 421.1910.

dl-(1R*,4R*,5S*,7R*)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-2-ene (**5c**): 94 mg, 88%. Colorless gum. IR (CH₂Cl₂): 1740, 1715, 1640. ¹H-NMR: 0.83 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.26 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.16 (3H, s, OCOCH₃),

2.51 (1H, dd, *J* = 10, 12 Hz, C₄-H), 2.89 (1H, dd, *J* = 10, 12 Hz, C₄-H), 3.81 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.23 (2H, q, *J* = 7 Hz, OCH₂CH₃), 4.70 (1H, t, *J* = 10 Hz, C₇-H), 6.30 (1H, s, C₄-H), 7.05–7.5 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₇NO₅ 421.1890. Found: 421.1911.

dl-(1R*,4R*,5S*,7S*)-4-Acetoxy-3,7-diethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-ene (**5d**): 105 mg, 97%. Colorless gum. IR (CH₂Cl₂): 1745, 1720, 1650. ¹H-NMR: 0.79 (1H, t, *J* = 7 Hz, COOCH₂CH₃), 1.13 (2H, t, *J* = 7 Hz, OCH₂CH₃), 1.44 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.10 (3H, s, OCOCH₃), 2.18 (1H, dd, *J* = 8, 13 Hz, C₆-H), 2.89 (1H, dd, *J* = 8, 13 Hz, C₆-H), 3.52 (2H, m, COOCH₂CH₃), 3.79 (2H, m, OCH₂CH₃), 4.50 (2H, m, OCH₂CH₃), 4.79 (1H, t, *J* = 8 Hz, C₇-H), 6.22 (1H, s, C₄-H), 7.29 (5H, brs, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₁H₂₇NO₆ 389.1837. Found: 389.1827.

dl-(1R*,4S*,5S*,7S*)-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 (CH₂Cl₂): 1740, 1715, 1650. ¹H-NMR: 0.65 (3H, t, *J* = 7 Hz, CH₂CH₃), 0.82 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.31 (2H, quint, *J* = 7 Hz, CH₂CH₃), 1.40 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.05 (3H, s, OCOCH₃), 2.17–2.50 (3H, m, C₆ and C₇-H), 3.81 (2H, q, *J* = 7 Hz, OCH₂CH₃), 4.42 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 5.89 (1H, s, C₄-H), 7.18–7.48 (5H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₁H₂₇NO₅ 373.1890. Found: 435.2025.

dl-(1R*,4S*,5S*,7S*)-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 (CH₂Cl₂): 1740, 1715, 1650 sh, 1640. ¹H-NMR: 0.67 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.26 (3H, s, CH₃), 1.49 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.04 (3H, s, OCOCH₃), 2.34 (1H, d, *J* = 13 Hz, C₆-H), 3.61 (2H, m, COOCH₂CH₃), 3.67 (1H, d, *J* = 13 Hz, C₆-H), 4.59 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.98 (1H, s, C₄-H), 6.75–7.25 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₆H₂₉NO₅ 435.2045. Found: 435.2025.

dl-(1R*,4R*,5R*,7S*)-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. ¹H-NMR: 0.71 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.32 (3H, s, CH₃), 1.52 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.00 (1H, d, *J* = 12 Hz, C₆-H), 2.23 (3H, s, OCOCH₃), 3.56 (1H, d, *J* = 12 Hz, C₆-H), 3.67 (2H, m, COOCH₂CH₃), 4.59 (2H, q, OCH₂CH₃), 5.93 (1H, s, C₄-H), 6.8–7.12 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₆H₂₉NO₅ 435.2045. Found: 435.2040.

dl-(1R*,4R*,5S*,7R*)-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 (CH₂Cl₂): 1735, 1710, 1655. ¹H-NMR: 1.02 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.15 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.45 (3H, s, CH₃), 2.15 (3H, s, OCOCH₃), 2.76 (2H, s, C₆-H), 3.99 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.19 (2H, m, OCH₂CH₃), 6.12 (1H, s, C₄-H), 7.1–7.7 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₆H₂₉NO₅ 435.2045. Found: 435.2025.

dl-(1R*,4R*,5S*,7S*)-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 (CH₂Cl₂): 1745, 1725, 1660. ¹H-NMR: 1.09 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.40 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.64 (3H, s, CH₃), 2.02 (3H, s, OCOCH₃), 2.13 (3H, s, OCOCH₃), 2.54 (1H, d, *J* = 14 Hz, C₆-H), 2.85 (1H, d, *J* = 14 Hz, C₆-H), 4.12 (2H, m, COOCH₂CH₃), 4.41 (2H, q, *J* = 7 Hz, OCH₂CH₃), 6.25 (1H, s, C₄-H), 7.2–7.5 (5H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₂H₂₇NO₆ 417.1786. Found: 417.1785.

dl-(1R*,4S*,5S*,6S*,7S*)-4-Acetoxy-6-deutero-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. ¹H-NMR: 0.71 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.45 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.05 (3H, s, OCOCH₃), 2.63 (1H, d, *J* = 9 Hz, C₆-H), 3.67 (1H, d, *J* = 9 Hz, C₇-H), 3.67 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.53 (2H, q, *J* = 7 Hz, OCH₂CH₃), 6.01 (1H, s, C₄-H), 6.9–7.2 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₆DNO₅ 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-(1R*,4R*,6S*,7R*)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (**11**): Colorless prisms from Et₂O–CH₂Cl₂, mp 119–120 °C. IR: 1740, 1725. UV: 249 (15400). ¹H-NMR: 1.06 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.09 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.06 (3H, s, OCOCH₃), 2.28 (1H, dd, *J* = 10, 13 Hz, C₅*endo*-H), 2.54 (1H, dd, *J* = 6, 13 Hz, C₅*exo*-H), 3.07 (1H, dd, *J* = 6, 10 Hz, C₆*endo*-H), 3.78 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.10 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.68

(1H, s, C₇-H), 7.2–7.7 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₇NO₅, 421.1889. Found: 421.1874.

dl-(1R*,4R*,6R*,7R*)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (12): Colorless prisms from Et₂O-CH₂Cl₂, mp 116–118°C. IR: 1740, 1710. UV: 249 (11900). ¹H-NMR: 1.11 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.20 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.98 (1H, dd, *J* = 5, 13 Hz, C₅*endo*-H), 2.05 (3H, s, OCOCH₃), 2.98 (1H, dd, *J* = 10, 13 Hz, C₅*exo*-H), 3.67 (1H, dd, *J* = 5, 10 Hz, C₆*exo*-H), 3.90 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.13 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.37 (1H, s, C₇-H), 6.95–7.7 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₇NO₅, 421.1887. Found: 421.1861.

3-Acetoxy-2-ethoxy-4-ethoxycarbonyl-5-phenyl-1H-pyrrole (13): Colorless plates from hexane, mp 126–130°C. IR (CH₂Cl₂): 3440, 1765, 1700, 1635. UV: 304 (8800). ¹H-NMR: 1.17 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.34 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.31 (3H, s, OCOCH₃), 4.14 (4H, q, *J* = 7 Hz, COOCH₂CH₃, OCH₂CH₃), 7.25–7.55 (5H, m, Ar-H), 7.95 (1H, brs, NH). HRMS *m/z*: M⁺ Calcd for C₁₇H₁₉NO₅, 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-(1R*,4R*,5R*,6R*,7R*)-7-Acetoxy-5-deuterio-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (11D): Colorless needles from CH₂Cl₂-hexane, mp 117–120°C. IR: 1765, 1720. UV: 249 (14200). ¹H-NMR: 1.06 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.09 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.06 (3H, s, OCOCH₃), 2.51 (1H, d, *J* = 6 Hz, C₅*exo*-H), 3.06 (1H, d, *J* = 6 Hz, C₆*endo*-H), 3.78 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.10 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.68 (1H, s, C₇-H), 7.25–7.7 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₆DNO₅, 422.1951. Found: 422.1931.

dl-(1R*,4R*,5R*,6S*,7R*)-7-Acetoxy-5-deuterio-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (12D): Colorless needles from CH₂Cl₂-hexane, mp 122–127°C. IR: 1765, 1715. UV: 249 (10400). ¹H-NMR: 1.12 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.19 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.05 (3H, s, OCOCH₃), 2.95 (1H, d, *J* = 10 Hz, C₅*exo*-H), 3.66 (1H, d, *J* = 10 Hz, C₆*exo*-H), 3.90 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.10 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.37 (1H, s, C₇-H), 7.0–7.75 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₆DNO₅, 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-(1R*,4R*,6S*,7S*)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (14): Colorless gum. IR (CH₂Cl₂): 1750, 1730. UV: 247 (12200). ¹H-NMR: 1.08 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.21 (3H, t, *J* = 7 Hz, OCH₂CH₃), 2.07 (1H, dd, *J* = 10, 13 Hz, C₅*endo*-H), 2.18 (3H, s, OCOCH₃), 3.07 (1H, dd, *J* = 5, 13 Hz, C₅*exo*-H), 3.6–3.9 (2H, m, COOCH₂CH₃), 3.84 (1H, ddd, *J* = 1, 5, 10 Hz, C₆*endo*-H), 4.16 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.44 (1H, d, *J* = 1 Hz, C₇-H), 7.0–7.2 (5H, m, Ar-H), 7.25–7.7 (5H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₇NO₅, 421.1889. Found: 421.1935.

dl-(1R*,4R*,6R*,7S*)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (15): Colorless gum. IR (CH₂Cl₂): 1750, 1725. UV: 248 (15200). ¹H-NMR: 1.07 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.18 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.96 (3H, s, OCOCH₃), 2.15–2.41 (1H, m, C₅*endo*-H), 2.9–3.2 (2H, m, C₅*exo*-H, C₆*exo*-H), 3.83 (2H, m, COOCH₂CH₃), 4.15 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.43 (1H, s, C₇-H), 7.25–7.7 (5H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₅H₂₇NO₅, 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-(1R*,4R*,7R*)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-6-methyl-3,6-diphenyl-2-azabicyclo[2.2.1]hept-2-ene (16): Colorless gum. IR (CH₂Cl₂): 1745, 1725. UV: 249 (6800). ¹H-NMR: 1.10 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.34 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.65 (3H, s, CH₃), 2.05 (3H, s, OCOCH₃), 2.52 (2H, s, C₅-H), 3.9–4.4 (2H, m, COOCH₂CH₃), 4.10 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.65 (1H, s, C₇-H), 6.85–7.5 (10H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₆H₂₉NO₅, 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-(1R*,4R*,7S*)-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. ¹H-NMR for 17: 1.07 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.37 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.66 (3H, s, CH₃), 2.15 (3H, s, OCOCH₃), 2.72 (2H, s, C₅-H), 3.73 (2H, q, *J* = 7 Hz, COOCH₂CH₃), 4.13 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.53 (1H, s, C₇-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-(1R*,4R*,7S*)-6,7-Diacetoxy-1-ethoxy-4-ethoxycarbonyl-6-methyl-3-phenyl-2-azabicyclo[2.2.1]hept-2-ene (18): Colorless gum. IR (CH₂Cl₂): 1750 sh, 1730. UV: 247 (12200). ¹H-NMR: 1.07 (3H, t, *J* = 7 Hz, COOCH₂CH₃), 1.34 (3H, t, *J* = 7 Hz, OCH₂CH₃), 1.41 (3H, s, CH₃), 2.08 (3H, s, OCOCH₃), 2.09 (3H, s, OCOCH₃), 2.24 (1H, dd, *J* = 1.5, 14.5 Hz, C₅*endo*-H), 3.10 (1H, d, *J* = 14.5 Hz, C₅*exo*-H), 3.91 (2H, m, COOCH₂CH₃), 4.13 (2H, q, *J* = 7 Hz, OCH₂CH₃), 5.46 (1H, d, *J* = 1.5 Hz, C₇-H), 7.25–7.65 (5H, m, Ar-H). HRMS *m/z*: M⁺ Calcd for C₂₂H₂₇NO₇, 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 SiO₂ to give 13 (11 mg, 99% from 11 and 10 mg, 95% from 12).

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- 13) A referee suggested that this bond elongation may originate from the through bond interaction between C₁-Ph and C₇-*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 cyclopentadiene: 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 azanorbornenes have been reviewed; D. Blondet and C. Morin, *Heterocycles*, **19**, 2155 (1982).