Dioxopyrrolines. XLVII.[1] Thermal Rearrangements of 7-Vinyl Derivatives of 1-Aryl-5-ethoxycarbonyl-2-azabicyclo[3.2.0]heptane-3,4-diones and Their Imidates

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Thermolysis of the 7-vinyl derivative of 1-aryl-5-ethoxycarbonyl-2-azabicyclo[3.2.0]heptane-3,4-dione caused two different types of skeletal rearrangement depending on the stereochemistry of the 7-vinyl group. The *exo*-isomer (2) gave the hydroindole (4) by the 1,3-shift of a C_1–C_7 bond to the vinyl group (path A reaction), while the *endo*-isomer (3) gave the 7-azabicyclo[4.2.1]nonane (5) by the Cope rearrangement (path B reaction). The product on thermolysis of the corresponding imidate also depends on the stereochemistry of the 7-vinyl group. The *endo*-isomer (13) gave the Cope product (12), while the *exo*-isomer (14) gave the dihydropyridone (16), which is produced by the 1,3-shift of the C_1–C_7 bond to the C_3 position followed by cheletropic loss of CO from the intermediary 2-azanorbornene (path C reaction). The validity of path C was proved by isolation of the 2-azanorbornenes (21 and 22) formed by thermolysis of the 7-vinyl-4-acetoxy imidate (20).

Keywords dioxopyrroline; photocycloaddition; 2-azabicyclo[3.2.0]heptane; vinyl cyclobutane; thermolysis; 1,3-shift; Cope rearrangement; hydroindole; 7-azabicyclo[4.2.1]nonane; 2-azanorbornene

In previous papers[2,3] we reported that thermolysis of 7-substituted 5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]heptane-3,4-diones under basic conditions caused 7-epimerization and ring expansion to a dihydroazatropolone, both of the reactions being initiated by C_1–C_5 bond fission. The imidates, 7-substituted 3-ethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-enes underwent 1,3-shift of the C_1–C_7 bond to give 2-azanorborn-2-enes (and dihydropyridones).[1]

In this paper we describe details of the thermal reaction of 7-vinyl derivatives of 1-aryl-5-ethoxycarbonyl-2-azabicyclo[3.2.0]heptane-3,4-dione and their imidates, involving three different types of skeletal rearrangement, a 1,3-shift of the C_1–C_7 bond to the vinyl carbon (path A), a 3,3-sigmatropic rearrangement of the 7-vinyl group to the C_3-position (path B), and a 1,3-shift of the C_1–C_7 bond to the C_3-position (path C).[4]

Thermal Rearrangement of 7-Vinyl Derivatives of 1-Aryl-5-ethoxycarbonyl-2-azabicyclo[3.2.0]heptane-3,4-dione The *exo* and *endo*-7-vinyl derivatives of 1-aryl-5-ethoxycarbonyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**2** and **3**) (vinyl cyclobutanes) were prepared by photocycloaddition of 5-aryl-4-ethoxycarbonyl-1*H*-pyrrole-2,3-dione (dioxopyrroline) (**1**) to butadiene, whose stereochemistry of the vinyl group was unambigously established.[5] Heating of 7-*exo*-vinyl cyclobutane (**2a**) in toluene at 140 °C gave the hydroindole (**4a**) and the 7-azabicyclo[4.2.1]nonane (**5a**), each in 30% yield. On the other hand, thermolysis of the *endo*-vinyl isomer (**3a**), under similar conditions, gave **5a** as a sole product in 72% yield. Pyrolysis of the *exo*-vinyl (**2b**) and *endo*-vinyl (**3b**) 1-methylenedioxyphenyl analogs gave similar results; **2b** gave **4b** and **5b** in 21% and 23% yields, respectively, while **3b** gave **5b** as a sole product in 40% yield.

The hydroindole (**4**) was identical with the compound prepared by the Diels–Alder reaction of **1** and butadiene,[6] thus confirming the structure. On the other hand, the structure of **5** was elucidated from the spectral data as follow. The presence of a cis-1,2-disubstituted ethylene moiety was evidenced by the ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectra (δ 5.45 for **5a** and 5.50 for **5b**). The Ar–C=N– chromophore was indicated by the strong ultraviolet (UV) absorptions (250 nm for **5a**, and 274 and 309 nm for **5b**) and by the infrared (IR) C=N bands (1570 cm^{-1} for **5a** and 1580 cm^{-1} for **5b**). Furthermore, the IR spectra showed the presence of hydroxy and five-membered keto groups (3300, 1780 cm^{-1} for **5a**, and 3120, 1785 cm^{-1} for **5b**).

Formation of the hydroindole (**4**) was explained in terms of the 1,3-shift of the C_1–C_7 bond to the terminal carbon of

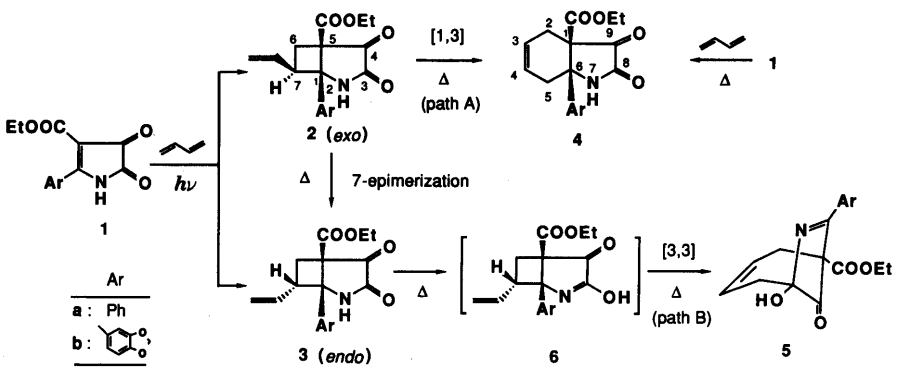


Chart 1

the vinyl group (path A). On the other hand, formation of the product (**5**) was rationalized in terms of a 3,3-sigmatropic rearrangement (Cope rearrangement) of the imino form (**6**) derived from the *endo*-isomer (**3**) (path B). Since it is sterically impossible for the *exo*-isomer (**2**) to form the Cope product (**5**), the formation of 5 from the *exo*-isomer requires the prior epimerization of the 7-vinyl group. The above results indicate that the thermolysis products of 7-vinyl cyclobutanes change depending on the stereochemistry of the 7-vinyl group.

Introduction of a methyl group at the vinyl terminus greatly affected these reactions. Thermolysis of the *exo*-(*E*)-propenyl derivative (**7**) in xylene under reflux gave the hydroindole (**8**) as a sole product, though in a low yield (29%). The other characterizable products including the C_5-stereoisomer were not isolated from the reaction mixture, suggesting that this thermal 1,3-shift proceeds in a highly stereoselective manner, although the configuration of the C_5-methyl group in this product was unclear. The *endo*-(*E*)-propenyl isomer (**9**),[5] on similar pyrolysis, gradually decomposed to give no characterizable product. On the other hand, the *exo*-(*Z*)-propenyl isomer (**10**)[5] showed different thermal behavior. When heated in xylene for 1 h, it underwent 7-epimerization to give the *endo*-isomer (**11**)[5] in 50% yield. The latter compound was thermally stable and remained unchanged on heating for 4 h (recovery 80%).

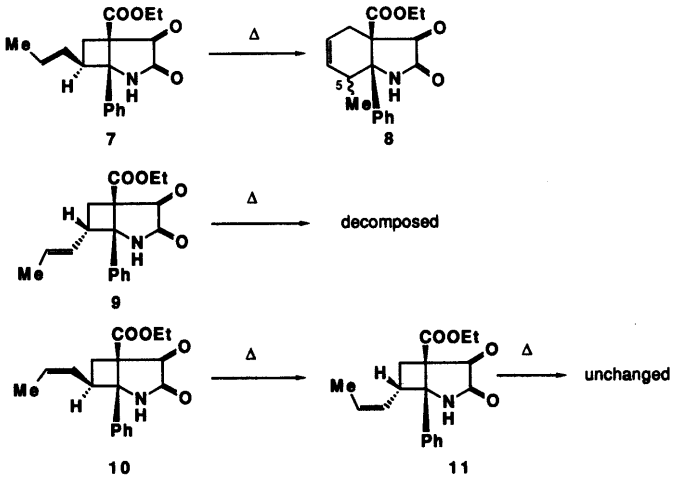


Chart 2

Thermal Rearrangements of 7-Vinyl Derivatives of 3-Ethoxy-5-ethoxycarbonyl-2-azabicyclo[3.2.0]hept-2-enes If the argument that the path B product was formed *via* the Cope rearrangement of the imino form (**6**) is correct, fixation of the double bond at N–C_3 (for example, formation of the imidate) will facilitate this rearrangement. In fact, the *endo*-isomer (**3a**), on treatment with triethyloxonium fluoroborate (Meerwein reagent) at room temperature, afforded the Cope product (**12a**) in 80% yield. Similar imidations of the *endo*-(*E*) and (*Z*)-propenyl isomers (**9** and **11**) gave stereospecifically the Cope products (**12b** and **12c**, respectively) in good yields. The spectral characteristics of these products were very similar to those of **5**, except that the products possess the OEt group instead of OH and an additional Me group, thus establishing that the compounds are the path B products formed through the intermediary imidates (**13**). The stereochemistry of the 5-methyl group in **12b** and **12c** was assigned on the basis of the mechanistic consideration that the configuration should be retained, since this rearrangement proceeds under the control of lowest unoccupied molecular orbital (LUMO)–highest occupied molecular orbital (HOMO) interaction with a boat-like conformation as the preferred transition state.

On the other hand, the *exo*-isomers (**2a**, **7**, and **10**), on treatment with the Meerwein reagent, gave the correspond-

Table I. Thermolysis of 7-*exo*-Vinyl and 7-*exo*-Propenyl Derivatives of 3-Ethoxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-ones (**14**)

Substrates	Conditions Temp. (°C)	Time (min)	Product (Yield %) **16**[a]	**12**[b]	**15**[c]
14a	120	30	60	4	10
14b	120	60	51	7	7
14c	120	60	64	8	—

a) Product of path C. *b*) Product of path B. *c*) Product of path A.

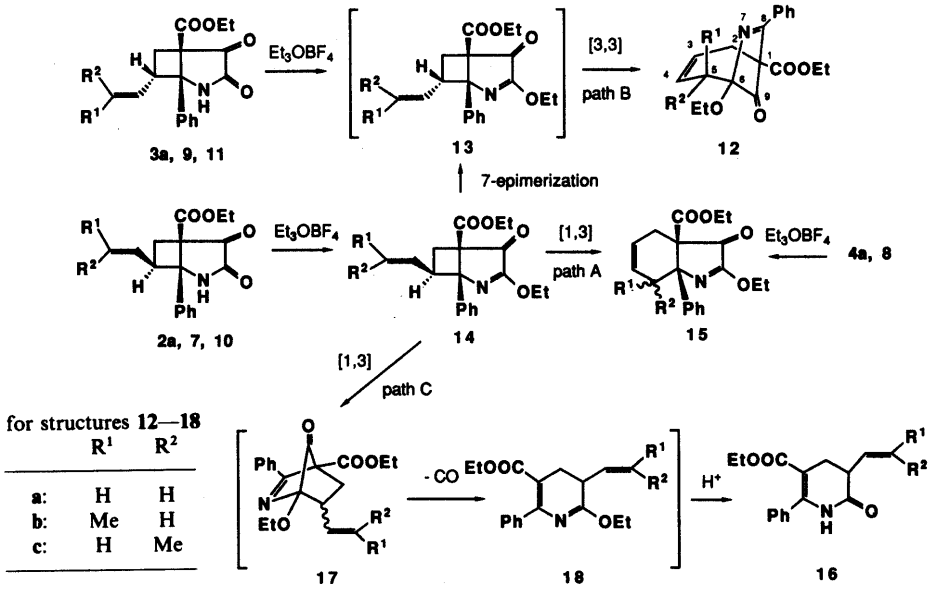
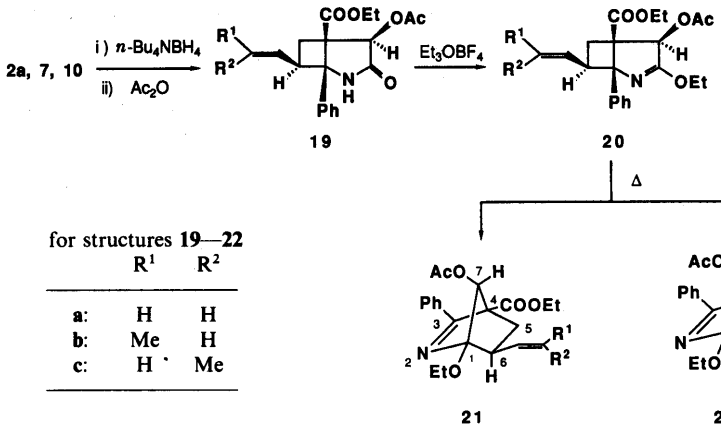


Chart 3



for structures **19**—**22**

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

Chart 4

ing imidates (**14**). The *exo*-vinyl (**14a**) and propenyl imidates (**14b** and **14c**), on heating in toluene under reflux followed by silica gel chromatography of the pyrolysates, afforded three products, the dihydropyridone (**16**), the hydroindole (**15**), and the Cope product (**12**). The results (Table I) showed that the 1,3-shift leading to dihydropyridone (path C) is a major and the 1,3-shift forming hydroindole (path A) is a minor path in the reaction of imidates. In the case of **14c** the hydroindole (**15c**) was not isolated. The structures (**16a**—**c**) were elucidated by means of elementary analyses and by comparison of the spectral data with those of the known dihydropyridones.[1,5] The hydroindoles (**15a** and **15b**) were identical with the compounds obtained by imidation of **4a** and **8**, respectively.

The path C reaction, as discussed in the preceding paper,[1] involves the 1,3-shift of the C_1–C_7 bond to C_3 followed by cheletropic loss of CO from the intermediary 2-azanorborn-2-en-7-one (**17**). Apparently fixation of the double bond at N–C_3 facilitates this rearrangement from the *exo*-isomer. Formation of the Cope product (path B) from this isomer apparently requires the prior epimerization of the 7-vinyl or the propenyl group as described above.

In order to clarify the reaction pathway of path C we carried out thermolyses of 4-acetoxy imidates, where the 2-azanorborn-2-enes are expected to be isolated as discussed in the preceding paper.[1] The substrates (**20a**—**c**) were prepared from the lactams (**2a**, **7**, and **10**) by reduction with tetra-*n*-butyl ammonium borohydride, acetylation, and imidation (Chart 4). The stereochemistry of the 4-acetoxy group was elucidated from the observation of γ-effect in the ^{13}C-NMR spectra as described in the previous paper.[2]

Thermolysis of the imidates (**20a**—**c**) caused the path C reaction to give exclusively two stereoisomeric 2-azanorbornenes (**21a**—**c** and **22a**—**c**). The structures of 2-azanorborn-2-enes including the stereochemistry of the 6-vinyl or the 6-propenyl groups were deduced by comparisons of the spectral data with those of the 6-phenyl derivatives.[1] In particular, the presence of a strong UV absorption band around 240 nm due to the –N=C–Ph chromophore and the signal patterns of the C_5 and C_6-ring protons in the ^{1}H-NMR spectra supported this asignment. The 2-azanorborn-2-enes (**21** and **22**) are the products of C_7-inversion (*si*-product) and of C_7-retention (*sr*-product), respectively. The product ratios (*si*/*sr*=1.2 for **20a**, 1.7 for **20b**, and 1.0 for **20c**) are very similar to the case of the 7-*exo*-phenyl analog (*si*/*sr*=1.2),[1] indicating that this 1,3-shift proceeds with slight preference of the symmetry-allowed *si*-process, as discussed in the preceding paper.[1]

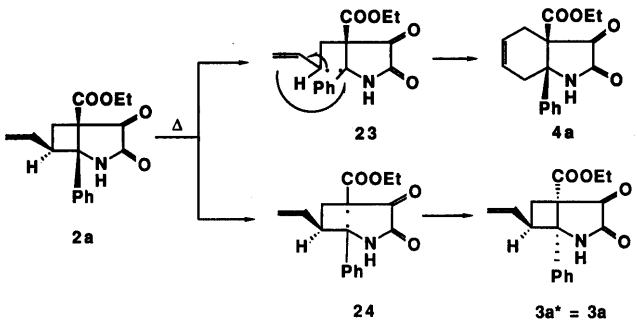


Chart 5

Finally, we will briefly discuss the mechanisms of path A rearrangement and 7-epimerization. We consider that these two reactions would proceed *via* a biradical, but probably different species. The 1,3-shift of path A reaction should occur from the biradical (**23**) formed by fission of the C_1–C_7 bond, while the 7-epimerization would proceed *via* the biradical (**24**) formed by C_1–C_5 bond fission (Chart 5) as discussed in the previous paper.[2]

It is noteworthy that the above results suggest that the dioxopyrroline-butadiene photoannulation followed by thermolysis of the resulting vinyl cyclobutanes provides a potential new route to hydroindole, whose skeleton appears in various natural alkaloids.

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. IR spectra were taken in Nujol mulls with a Hitachi 260-10 spectrophotometer and are given in cm^{-1}. UV spectra were recorded with a Hitachi 200-10 spectrophotometer and are given in λ_{max} nm (ε). ^{1}H-NMR (100 MHz) and ^{13}C-NMR (25.0 MHz) spectra were taken in a $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard on a JEOL FX-100 spectrometer. Chemical shifts are reported in δ, and signals are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). High resolution mass spectra (HRMS) were recorded on a JEOL JMS-D300 mass spectrometer. Chromatography was carried out on silica gel (Wako-gel C-200). Thin layer chromatography (TLC) was performed on Merck precoated Silica gel 60 F_{254} plates. Medium pressure liquid chromatography (MPLC) was performed on Kusano CIG prepacked silica gel columns. The photolysis was done by internal irradiation using a 300 W high pressure mercury lamp (Eikosha

Halos PIH 300) with a Pyrex filter. The preparation of the vinyl cyclobutanes **2a**, **3a**, **7**, **9**, **10**, and **11** has been reported.[5]

Photocycloaddition of 1b to Butadiene A solution of **1b** (1.0 g) and butadiene (10 ml) in dimethoxyethane (150 ml) was irradiated at 0 °C for 1 h. After evaporation of the solvent, the residue was chromatographed. Elution with CH_2Cl_2 gave a mixture of **2b** and **3b** (1 : 1) (580 mg, 49%) as colorless crystals. This was separated by fractional crystallizations. The Et_2O insoluble fractions gave *dl*-(1*R**,4*S**,7*S**)-5-ethoxycarbonyl-1-(3′,4′-methylenedioxyphenyl)-7-vinyl-2-azabicyclo[3.2.0]-heptane-3,4-dione (**2b**) as colorless prisms from MeOH, mp 175—177 °C. IR: 1775, 1770, 1740, 1700. ^{1}H-NMR: 0.82 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.44 (1H, dd, J=9, 12 Hz, C_6-H), 3.09 (1H, t, J=12 Hz, C_6-H), 3.3 (1H, m, C_7-H), 3.98 (2H, m, $COOC\underline{H}_2CH_3$), 5.13 (1H, d, J=18 Hz, olefinic H), 5.18 (1H, d, J=10 Hz, olefinic H), 5.60—5.83 (1H, m, olefinic H), 5.97 (1H, s, OCH_2O), 6.83 (3H, br s, ArH). *Anal.* Calcd for $C_{18}H_{17}NO_6$: C, 62.97; H, 4.99; N, 4.08. Found: C, 62.98; H, 5.15; N, 3.73.

The Et_2O soluble fractions gave *dl*-(1*R**,5*S**,7*R**)-5-ethoxycarbonyl-1-(3′,4′-methylenedioxyphenyl)-7-vinyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**3b**) as colorless prisms from Et_2O–hexane, mp 172—177 °C. IR: 1775, 1745, 1730. ^{1}H-NMR: 0.89 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.17 (1H, dd, J=9, 13 Hz, C_6-H), 3.16 (1H, dd, J=9, 13 Hz, C_6-H), 3.90 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.08 (1H, m, C_7-H), 5.19 (1H, d, J=17 Hz, olefinic H), 5.32 (1H, d, J=9 Hz, olefinic H), 5.90 (1H, m, olefinic H), 5.98 (2H, s, OCH_2O), 6.82 (3H, m, ArH). *Anal.* Calcd for $C_{18}H_{17}NO_6$: C, 62.97; H, 4.99; N, 4.08. Found: C, 63.06; H, 5.02; N, 3.79.

Pyrolysis of 7-Vinyl (2 and 3) and 7-Propenyl Cyclobutanes (7 and 10) (General Procedure) A solution of **2**, **3**, **7** or **10** (100—200 mg) in toluene (10 ml) was heated in a sealed tube. After removal of the solvent *in vacuo*, the residue was chromatographed and eluted with benzene–CH_2Cl_2 (1 : 1) to give the products. Each product was crystallized from CH_2Cl_2–Et_2O, unless otherwise stated.

1) Pyrolysis of **2a** (200 mg) at 140 °C for 4 h gave **4a** (60 mg, 30%) and **5a** (60 mg, 30%). *dl*-(1*R**,6*S**)-1-Ethoxycarbonyl-6-phenyl-7-azabicyclo[4.3.0]non-3-ene-8,9-dione (**4a**), colorless prisms, mp 228—230 °C. Compound **4a** was identical with an authentic sample.[6] *dl*-(1*R**,6*R**)-1-Ethoxycarbonyl-6-hydroxy-8-phenyl-7-azabicyclo-[4.2.1]nona-3,7-dien-9-one (**5a**). Colorless prisms, mp 150—155 °C. IR: 3100, 1780, 1735, 1600. UV: 250 (14800), 330 (3200). ^{1}H-NMR: 0.98 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.7—3.0 (4H, m, C_2-H and C_5-H), 4.10 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.15 (1H, br s, OH), 5.45 (2H, m, olefinic H), 7.4 (3H, m, ArH), 7.7 (2H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{17}H_{17}NO_4$ 299.1184. Found: 299.1187.

2) Pyrolysis of **3a** (180 mg) at 160 °C for 5 h gave **5a** (130 mg, 72%).

3) Pyrolysis of **2b** (100 mg) at 140 °C for 4 h gave **4b** (25 mg, 25%) and **5b** (23 mg, 23%). *dl*-(1*R**,6*S**)-1-Ethoxycarbonyl-6-(3′,4′-methylenedioxyphenyl)-7-azabicyclo[4.3.0]non-3-ene-8,9-dione (**4b**), colorless prisms, mp 222—224 °C. Compound **4b** was identical with an authentic sample.[6] *dl*-(1*R**,6*R**)-1-Ethoxycarbonyl-6-hydroxy-8-(3′,4′-methylenedioxyphenyl)-7-azabicyclo[4.2.1]nona-3,7-dien-9-one (**5b**). Colorless prisms, mp 178—183 °C. IR: 3120, 1785, 1740, 1580. UV: 228 (12900), 274 (7600), 309 (8500). ^{1}H-NMR: 1.07 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.50—2.95 (4H, m, C_2-H and C_5-H), 4.15 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.49 (2H, m, olefinic H), 6.02 (2H, s, OCH_2O), 6.80 (1H, d, J=8 Hz, ArH), 7.17 (1H, dd, J=2, 8 Hz, ArH), 7.49 (1H, d, J=2 Hz, ArH). *Anal.* Calcd for $C_{18}H_{17}NO_6$: C, 62.97; H, 4.99; N, 4.08. Found: 62.98; H, 5.17; N, 3.82.

4) Pyrolysis of **3b** (200 mg) at 140 °C for 1.5 h gave **5b** (120 mg, 60%).

5) Pyrolysis of **7** (105 mg) at 140 °C for 5 h gave *dl*-(1*R**,6*S**)-1-ethoxycarbonyl-5-methyl-6-phenyl-7-azabicyclo[4.3.0]non-3-ene-8,9-dione (**8**) (30 mg, 29%) as colorless prisms, mp 284—286 °C. IR: 3170, 1780, 1722, 1700. ^{1}H-NMR: 0.71 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 0.95 (3H, d, J=7 Hz, CH_3), 2.96 (3H, m, C_2-H and C_5-H), 3.50 (2H, m, $COOC\underline{H}_2CH_3$), 5.50—6.20 (2H, m, olefinic H), 7.40 (5H, br s, ArH). *Anal.* Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.60; H, 6.18; N, 4.20.

6) Pyrolysis of **10** (208 mg) at 140 °C for 1 h gave **11** (104 mg, 50%) as colorless prisms from acetone–hexane, mp 152—154 °C.[5]

Treatment of the *endo*-Vinyl (3a) and Propenyl Cyclobutanes (9 and 11) with Triethyloxonium Fluoroborate (General Procedure) A solution of **3a**, **9**, or **11** (100 mg) and an excess of Et_3OBF_4 in CH_2Cl_2 (10 ml) was stirred at room temperature overnight. The raction mixture was washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated. Chromatography of the residue and elution with benzene gave the Cope rearrangement product (**12**), which was crystallized from Et_2O–hexane.

dl-(1*R**,6*R**)-6-Ethoxyl-1-ethoxycarbonyl-8-phenyl-7-azabicyclo[4.2.1]-nona-3,7-dien-9-one (**12a**): 76.5 mg, 70%. Colorless prisms, mp 95—97 °C. IR: 1780, 1730, 1600. UV: 250 (12200). ^{1}H-NMR: 1.05 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.28 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.4—2.9 (4H, m, C_2-H and C_5-H), 3.56 (2H, m, $COOC\underline{H}_2CH_3$), 4.18 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.31 (2H, m, olefinic H), 7.5 (3H, m, ArH), 7.8 (2H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{19}H_{21}NO_4$ 327.1471. Found: 327.1503.

dl-(1*R**,5*S**,6*R**)-6-Ethoxy-1-ethoxycarbonyl-5-methyl-8-phenyl-7-azabicyclo[4.2.1]nona-3,7-dien-9-one (**12b**): 82 mg, 75%. Colorless prisms, mp 86 °C. IR: 1780, 1740, 1735, 1600. UV: 250 (14700). ^{1}H-NMR: 1.07 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.27 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.37 (3H, d, J=8 Hz, CH_3), 2.6—3.0 (3H, m, C_2-H and C_5-H), 3.53 (2H, quint, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.18 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.31 (2H, m, olefinic H), 7.5 (3H, m, ArH), 7.8 (2H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{20}H_{23}NO_4$ 341.1626. Found: 341.1611.

dl-(1*R**,5*R**,6*R**)-6-Ethoxy-1-ethoxycarbonyl-5-methyl-8-phenyl-7-azabicyclo[4.2.1]nona-3,7-dien-9-one (**12c**): 78 mg, 72%. Colorless prisms, mp 90—91 °C. IR: 1780, 1745, 1600. UV: 250 (15000). ^{1}H-NMR: 1.05 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.13 (3H, d, J=7 Hz, CH_3), 1.28 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.9 (3H, m, C_2-H and C_5-H), 3.60 (2H, quint, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.20 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.45 (2H, m, olefinic H), 7.5 (3H, m, ArH), 7.8 (2H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{20}H_{23}NO_4$ 341.1625. Found: 341.1625.

Imidation of the *exo*-Vinyl (2a) and Propenyl Cyclobutanes (7 and 10) with Triethyloxonium Fluoroborate (General Procedure) A solution of **2a**, **7**, or **10** (200 mg) and an excess of Et_3OBF_4 in CH_2Cl_2 (30 ml) was allowed to stand at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2, washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated. The product was crystallized from Et_2O–hexane to give the imidate (**14**).

dl-(1*R**,5*S**,7*S**)-3-Ethoxy-5-ethoxycarbonyl-1-phenyl-7-vinyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**14a**): 180 mg, 82%. Colorless prisms, mp 96—97 °C. IR: 1760, 1730, 1630. ^{1}H-NMR: 0.67 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.52 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.15—2.45 (1H, m, C_6-H), 2.7—3.0 (2H, m, C_6 and C_7-H), 3.79 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.59 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.8—5.2 (2H, m, olefinic H), 5.45—5.85 (1H, m, olefinic H), 7.3 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{19}H_{21}NO_4$ 327.1470. Found: 327.1490.

dl-(1*R**,5*S**,7*S**)-3-Ethoxy-5-ethoxycarbonyl-1-phenyl-7-(*E*)-propenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**14b**): 157 mg, 72%. Colorless prisms, mp 104—106 °C. IR: 1760, 1730, 1630. ^{1}H-NMR: 0.67 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.48 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.53 (3H, d, J=5 Hz, CH_3), 2.1 (1H, m, C_6-H), 2.6—3.2 (2H, m, C_6 and C_7-H), 3.75 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.53 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.3 (2H, m, olefinic H), 7.2 (5H, m, ArH). *Anal.* Calcd for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.33; H, 6.87; N, 3.99.

dl-(1*R**,5*S**,7*S**)-3-Ethoxy-5-ethoxycarbonyl-1-phenyl-7-(*Z*)-propenyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**14c**): 211 mg, 97%. Colorless prisms, mp 108—111 °C. IR: 1750, 1720, 1630. ^{1}H-NMR: 0.67 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.43 (3H, d, J=3 Hz, CH_3), 1.50 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.25 (1H, m, C_6-H), 2.7—3.28 (2H, m, C_6 and C_7-H), 3.83 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 3.97 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.4 (2H, m, olefinic H), 7.3 (5H, m, ArH). *Anal.* Calcd for $C_{20}H_{23}NO_4$: C, 70.36, H, 6.79; N, 4.10. Found: C, 70.30; H, 6.83; N, 4.01.

Pyrolysis of the 4-Keto Imidates (14) (General Procedure) A solution of **15** (100 mg) in toluene (5 ml) was heated in a sealed tube. Chromatography of the products and elution with benzene gave a mixture of **12** and **14** which was separated by preparative TLC (developed with CH_2Cl_2). Further elution with CH_2Cl_2 gave **16**. The products (**12a**—**c** and **16a**) were identical with the compounds obtaind from the *endo*-derivatives and the reported dihydropyridone,[5] respectively.

1) Pyrolysis of **14a** at 120 °C for 30 min gave **12a** (4 mg, 4%), **15a** (10 mg, 10%), and **16a** (50 mg, 60%). *dl*-(1*R**,6*S**)-8-Ethoxy-1-ethoxycarbonyl-6-phenyl-7-azabicyclo[4.3.0]nona-3,7-dien-9-one (**15a**): Colorless prisms, mp 94—96 °C. IR: 1750, 1730, 1630. ^{1}H-NMR: 0.57 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.42 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.60—2.78 (4H, m, C_2-H and C_5-H), 3.42 (2H, quint, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.45 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.63—5.84 (2H, m, olefinic H), 7.12—7.50 (5H, m, ArH). *Anal.* Calcd for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.47; N, 4.28. Found: C, 69.64; H, 6.47; N, 4.34.

2) Pyrolysis of **14b** at 120 °C for 1 h gave **12b** (7 mg, 7%), **15b** (7 mg, 7%), and **16b** (50 mg, 51%). *dl*-(1*R**,6*S**)-8-Ethoxy-1-ethoxycarbonyl-5-methyl-6-phenyl-7-azabicyclo[4.3.0]nona-3,7-dien-9-one (**15b**): Colorless prisms, mp 112—114 °C. IR: 1755, 1725, 1640. ^{1}H-NMR: 0.60 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 0.98 (3H, d, J=7 Hz, CH_3), 1.47 (3H, t, J=7 Hz. $OCH_2C\underline{H}_3$), 2.9 (3H, m, C_2-H and C_5-H), 3.39 (2H, m, $COOC\underline{H}_2CH_3$), 4.55 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.5 (1H, m,

olefinic H), 5.8 (1H, m, olefinic H), 7.3 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{20}H_{23}NO_4$ 341.1626. Found: 341.1615. 5-Ethoxycarbonyl-6-phenyl-3-(*E*)-propenyl-3,4-dihydropyridin-2(1*H*)-one (**16b**): Colorless needles, mp. 111—112 °C. IR: 3350, 3300, 1710, 1660, 1640, 1600. UV: 227 (9200), 285 (9750). ^{1}H-NMR: 0.93 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.72 (3H, d, J=5 Hz, CH_3), 2.67—2.90 (2H, m, C_4-H), 3.2 (1H, m, C_3-H), 3.93 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.67 (2H, m, olefinic H), 7.35 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{17}H_{19}NO_3$ 285.1365. Found: 275.1362.

3) Pyrolysis of **14c** at 120 °C for 1 h gave **12c** (8 mg, 8%) and **16c** (53 mg, 64%). 5-Ethoxycarbonyl-6-phenyl-3-(*Z*)-propenyl-3,4-dihydropyridin-2(1*H*)-one (**16c**): Colorless needles, mp 121—122 °C. IR: 3200, 3100, 1695, 1680, 1635, 1600. UV: 225 (9800), 284 (9800). ^{1}H-NMR: 0.90 (3H, t, J=7 Hz, $COOCH_2CH_3$), 1.68 (3H, d, J=7 Hz, CH_3), 2.53 (1H, dd, J=12, 16 Hz, C_4-H), 2.93 (1H, dd, J=7, 16 Hz, C_4-H), 3.30—3.73 (1H, m, C_3-H), 3.90 (2H, q, J=7 Hz, $COOCH_2CH_3$), 5.23—6.00 (2H, m, olefinic H), 7.2 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{17}H_{19}NO_3$ 285.1365. Found: 285.1410.

Imidation of the Hydroindole (4a and 8) with Triethyloxonium Fluoroborate A solution of **4a** and **8** (20 mg) in CH_2Cl_2 (5 ml) was treated with an excess of Et_3OBF_4 at room temperature for 6 h, and worked up as usual to give the products **15a** (18 mg, 82%) and **15b** (17 mg, 80%), which were identical with the hydroindoles (**15a** and **15b**) described above, respectively.

Preparation of 4-Acetoxy Lactams (19) (General Procedure) A solution of **2a**, **7**, or **10** (100 mg) in CH_2Cl_2 (30 ml) was treated with *n*-$(C_4H_9)_4NBH_4$ (0.5 mol eq) at 0 °C for 30 min. The mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated. The residue was acetylated with Ac_2O (1 ml) and pyridine (2 ml) at room temperature overnight. Chromatography of the product, elution with benzene, and recrystallization from CH_2Cl_2–Et_2O gave the acetate (**19**).

dl-(1*R**,4*S**,5*S**,7*S**)-4-Acetoxy-5-ethoxycarbonyl-1-phenyl-7-vinyl-2-azabicyclo[3.2.0]heptan-3-one (**19a**): 65 mg, 57%. Colorless prisms, mp 179—182 °C. IR: 1755, 1720. UV: 258sh (1700). ^{1}H-NMR: 0.83 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.13 (3H, s, OAc), 2.5—2.9 (2H, m, C_6-H), 3.2—3.5 (1H, m, C_7-H), 3.82 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.05 (1H, d, J=10 Hz, olefinic H), 5.07 (1H, d, J=17 Hz, olefinic H), 5.73 (1H, ddd, J=6.5, 10, 17 Hz, olefinic H), 5.80 (1H, s, C_4-H), 7.1—7.3 (5H, m, ArH), 7.81 (1H, br s, NH). ^{13}C-NMR: 13.6 (q, $COOCH_2\underline{C}H_3$), 20.4 (q, $OCO\underline{C}H_3$), 31.1 (t, C_6), 50.5 (d, C_7), 56.1 (s, C_5), 60.6 (t, $COO\underline{C}H_2CH_3$), 70.3 (s, C_1), 76.4 (d, C_4), 116.5 (t, $CH=\underline{C}H_2$), 125.9 (d, 2C, $CH=\underline{C}H_2$), 127.6 (d, Ph), 128.0 (d, 2C, Ph), 136.3 (d, Ph), 136.3 (s, Ph), 168.4 (s, C_3), 169.4 (s, $\underline{C}OOCH_2CH_3$), 172.6 (s, $O\underline{C}OCH_3$). *Anal.* Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. HRMS *m/z*: 343.1419. Found: C, 66.34; H, 6.16; N, 3.84. HRMS *m/z*: 343.1424.

dl-(1*R**,4*S**,5*S**,7*S**)-4-Acetoxy-5-ethoxycarbonyl-1-phenyl-7-(*E*)-propenyl-2-azabicyclo[3.2.0]heptan-3-one (**19b**): 60 mg, 52%. Colorless prisms, mp 193—194 °C. IR: 1750, 1725, 1720sh, 1710. UV: 260sh (300). ^{1}H-NMR: 0.83 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.58 (3H, d, J=5 Hz, CH_3), 2.12 (3H, s, OAc), 2.66 (1H, d, J=10 Hz, C_6-H), 2.70 (1H, d, J=10 Hz, C_6-H), 3.16—3.3 (1H, m, C_7-H), 3.81 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.2—5.6 (2H, m, olefinic H), 5.79 (1H, s, C_4-H), 7.24—7.33 (5H, m, Ar-H), 7.64 (1H, s, NH). ^{13}C-NMR: 13.6 (q, $COOCH_2\underline{C}H_3$), 17.8 (q, CH_3), 20.5 (q, $OCO\underline{C}H_3$), 31.6 (t, C_6), 49.8 (d, C_7), 56.0 (s, C_5), 60.6 (t, $COO\underline{C}H_2CH_3$), 70.7 (s, C_1), 76.6 (d, C_4), 125.9 (d, 2C, Ph), 127.5 (d, $CH=\underline{C}H$), 127.7 (d, $CH=\underline{C}H$), 128.0 (d, 2C, Ph), 128.9 (d, Ph), 136.4 (s, Ph), 168.6 (s, C_3), 169.6 (s, $\underline{C}OOCH_2CH_3$), 172.8 (s, $O\underline{C}OCH_3$). HRMS *m/z*: M^+ Calcd for $C_{20}H_{23}NO_5$ 357.1575. Found: 357.1560.

dl-(1*R**,4*S**,5*S**7*S**)-4-Acetoxy-5-ethoxycarbonyl-1-phenyl-7-(*Z*)-propenyl-2-azabicyclo[3.2.0]heptan-3-one (**19c**): 74 mg, 65%. Colorless prisms, mp. 166—170 °C. IR: 1760, 1730, 1710. UV: 260sh (200). ^{1}H-NMR: 0.84 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.53 (3H, d, J=5 Hz, CH_3), 2.13 (3H, s, OAc), 2.69 (1H, d, J=10 Hz, C_6-H), 2.70 (1H, d, J=10 Hz, C_6-H), 3.4—3.6 (1H, m, C_7-H), 3.84 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.35—5.45 (2H, m, olefinic H), 5.84 (1H, s, C_4-H), 7.2—7.4 (5H, m, Ar-H), 7.51 (1H, s, NH). ^{13}C-NMR: 13.6 (q, $COOCH_2\underline{C}H_3$), 13.8 (q, CH_3), 20.5 (q, $OCO\underline{C}H_3$), 33.0 (t, C_6), 44.8 (d, C_7), 56.3 (s, C_5), 60.7 (t, $COO\underline{C}H_2CH_3$), 71.4 (s, C_1), 76.6 (d, C_4), 125.8 (d, 2C, Ph), 126.9 (d, $CH=\underline{C}H$), 127.5 (d, $CH=\underline{C}H$), 128.0 (d, 2C, Ph), 128.8 (d, Ph), 136.4 (s, Ph), 168.6 (s, C_3), 169.6 (s, $\underline{C}OOCH_2CH_3$), 172.8 (s, $O\underline{C}OCH_3$). *Anal.* Calcd for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49; N, 3.92. HRMS *m/z*: 357.1575. Found: C, 67.00; H, 6.49; N, 3.72. HRMS *m/z*: 357.1560.

Preparation of 4-Acetoxy Imidates (20) (General Procedure) A solution of 4-acetoxy lactam (**19**) (100 mg) in CH_2Cl_2 (5 ml) was treated with an excess of Et_3OBF_4 at room temperature for 6 h. The mixture was diluted with CH_2Cl_2 (30 ml), washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated. The residue in benzene was passed through a short column of SiO_2 to give the 4-acetoxy imidate (**20**).

dl-(1*R**,4*S**,5*S**,7*S**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1-phenyl-7-vinyl-2-azabicyclo[3.2.0]hept-2-ene (**20a**): 94 mg, 87%. Colorless needles, mp 82—86 °C. IR: 1755, 1720, 1645, 1630. ^{1}H-NMR: 0.84 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.39 (3H, t, J=7 Hz, OCH_2CH_3), 2.07 (3H, s, OAc), 2.2—2.5 (1H, m, C_6-H), 2.6—2.9 (1H, m, C_6-H), 2.9—3.2 (1H, m, C_7-H), 3.81 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.41 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.01 (1H, d, J=11 Hz, olefinic H), 5.03 (1H, d, J=17 Hz, olefinic H), 5.83 (1H, ddd, J=6, 11, 17 Hz, olefinic H), 5.88 (1H, s, C_4-H), 7.1—7.4 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{21}H_{25}NO_5$ 371.1733. Found: 371.1734.

dl-(1*R**,4*S**,5*S**,7*S**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1-phenyl-7-(*E*)-propenyl-2-azabicyclo[3.2.0]hept-2-ene (**20b**): 101 mg, 90%. Colorless gum. IR (CH_2Cl_2): 1740, 1720, 1640. ^{1}H-NMR: 0.83 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.39 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.57 (3H, d, J=4 Hz, CH_3), 2.08 (3H, s, OAc), 2.36 (1H, dd, J=9, 12 Hz, C_6-H), 2.73 (1H, dd, J=9, 12 Hz, C_6-H), 2.85—3.0 (1H, m, C_7-H), 3.73 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.40 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.4—5.5 (2H, m, olefinic H), 5.86 (1H, s, C_4-H), 7.15—7.45 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{22}H_{27}NO_5$ 385.1890. Found: 385.1902.

dl-(1*R**,4*S**,5*S**7*S**)-4-Acetoxy-3-ethoxy-5-ethoxycarbonyl-1-phenyl-7-(*Z*)-propenyl-2-azabicyclo[3.2.0]hept-2-ene (**20c**): 104 mg, 93%. Colorless gum. IR (CH_2Cl_2): 1750, 1720, 1650. ^{1}H-NMR: 0.85 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.39 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.51 (3H, d, J=5 Hz, CH_3), 2.09 (3H, s, OAc), 2.43 (1H, dd, J=9.5, 13 Hz, C_6-H), 2.65 (1H, dd, J=8, 13 Hz, C_6-H), 3.1—3.0 (1H, m, C_7-H), 3.83 (1H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.42 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.3—5.6 (2H, m, olefinic H), 5.90 (1H, s, C_4-H), 7.15—7.4 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{22}H_{27}NO_5$ 385.1889. Found: 385.1920.

Pyrolysis of 4-Acetoxy Imidates (20) (General Procedure) A solution of **20** in toluene (5 ml) was heated in a sealed tube. After evaporation of the solvent, the residue was chromatographed with benzene as an eluent to give a mixture of **21** and **22**, which was separated by preparative MPLC eluting with AcOEt–hexane (1 : 3).

1) Pyrolysis of **20a** (50 mg) at 180 °C for 2 h gave **21a** (21 mg, 42%) and **22a** (18 mg, 36%). *dl*-(1*R**,4*R**,6*S**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3-phenyl-6-vinyl-2-azabicyclo[2.2.1]hept-2-ene (**21a**): Colorless gum. IR (CH_2Cl_2): 1745, 1725, 1650. UV: 249 (10300). ^{1}H-NMR: 1.07 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.29 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.01 (1H, dd, J=10, 13 Hz, C_5*endo*-H), 2.03 (3H, s, OAc), 2.29 (1H, dd, J=5, 13 Hz, C_5*exo*-H), 2.5—2.7 (1H, m, C_6*endo*-H), 3.55—4.46 (2H, m, $COOC\underline{H}_2CH_3$), 4.07 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.18—5.35 (1H, m, olefinic H), 5.26 (1H, s, C_7-H), 5.85—6.20 (2H, m, olefinic H), 7.2—7.7 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{21}H_{25}NO_5$ 371.1731. Found: 371.1723. *dl*-(1*R**,4*R**,6*R**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3-phenyl-6-vinyl-2-azabicyclo[2.2.1]hept-2-ene (**22a**): Colorless gum. IR (CH_2Cl_2): 1745, 1730. UV: 249 (12000). ^{1}H-NMR: 1.09 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.29 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.56 (1H, dd, J=4, 13 Hz, C_5*endo*-H), 2.04 (3H, s, OAc), 2.74 (1H, dd, J=10, 13 Hz, C_5*exo*-H), 2.9—3.2 (1H, m, C_6*exo*-H), 4.06 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.09 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.96—5.16 (1H, m, olefinic H), 5.22 (1H, s, C_7-H), 5.4—6.0 (2H, m, olefinic H), 7.2—7.8 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{21}H_{25}NO_5$ 371.1733. Found: 371.1745.

2) Pyrolysis of **20b** (50 mg) at 180 °C for 1 h gave **21b** (20 mg, 40%) and **22b** (11.5 mg, 23%). *dl*-(1*R**,4*R**,6*S**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3-phenyl-6-(*E*)-propenyl-2-azabicyclo[2.2.1]hept-2-ene (**21b**): Colorless gum. IR (CH_2Cl_2): 1750, 1730. UV: 248 (13700). ^{1}H-NMR: 1.07 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.29 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.73 (3H, d, J=5 Hz, CH_3), 2.04 (3H, s, OAc), 2.05 (1H, dd, J=9, 13 Hz, C_5*endo*-H), 2.24 (1H, dd, J=5, 13 Hz, C_5*exo*-H), 2.4—2.6 (1H, m, C_6*endo*-H), 4.07 (4H, q, J=7 Hz, $COOC\underline{H}_2CH_3$, $OC\underline{H}_2CH_3$), 5.26 (1H, s, C_7-H), 5.42—5.62 (2H, m, olefinic H), 7.22—7.61 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{22}H_{27}NO_5$ 385.1888. Found: 385.1908. *dl*-(1*R**,4*R**,6*R**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3-phenyl-6-(*E*)-propenyl-2-azabicyclo[2.2.1]hept-2-ene (**22b**): Colorless gum. IR (CH_2Cl_2): 1750, 1730. UV: 248 (11400). ^{1}H-NMR: 1.08 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.28 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.48 (1H, dd, J=4, 13 Hz, C_5*endo*-H), 1.60 (3H, d, J=7 Hz, CH_3), 2.03 (3H, s, OAc), 2.73 (1H, dd, J=10, 13 Hz, C_5*exo*-H), 2.9—3.2 (1H, m, C_6*exo*-H), 3.99 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.08 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.19 (1H, s, C_7-H), 5.2—5.6 (2H, m, olefinic H), 7.2—7.7 (5H, m, ArH). HRMS *m/z*: M^+ Calcd for $C_{22}H_{27}NO_5$ 385.1888. Found: 385.1888.

3) Pyrolysis of **20c** (50 mg) at 180 °C for 2 h gave **21c** and **22c** (38

mg, 78%) as a 1:1 mixture. An attempt to separate the mixture by preparative TLC failed. *dl*-(1*R**,4*R**,6*S**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3-phenyl-6-(*Z*)-propenyl-2-azabicyclo[2.2.1]hept-2-ene (**21c**) and *dl*-(1*R**,4*R**,6*R**,7*R**)-7-Acetoxy-1-ethoxy-4-ethoxycarbonyl-3-phenyl-6-(*Z*)-propenyl-2-azabicyclo[2.2.1]hept-2-ene (**22c**): The spectral data of the mixture: IR (CH_2Cl_2): 1735, 1720. UV: 248 (11500). ^{1}H-NMR: 1.07 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.09 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.27 (3H, t, J=7 Hz, $OC\underline{H}_2CH_3$), 1.28 (3H, t, J=7 Hz, $OC\underline{H}_2CH_3$), 1.45 (1H, m, C_6-H), 1.63 (3H, d, J=5 Hz, CH_3), 1.68 (3H, d, J=7 Hz, CH_3), 2.03 (3H, s, OAc), 2.04 (3H, s, OAc), 2.11 (1H, m, C_6-H), 2.6—3.0 (3H, m, C_6 and C_7-H), 3.4 (1H, m, C_7-H), 4.0 (4H, m, 2×$OC\underline{H}_2CH_3$), 4.07 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.08 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.1—5.8 (4H, m, olefinic H), 5.24 (1H, s, C_4-H), 5.30 (1H, s, C_4-H), 7.26—7.80 (10H, m, 2×Ar).

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