α,β-Unsaturated Carboxylic Acid Derivatives. XIV. The Synthesis and Reduction of Diels-Alder Adducts from Ethyl 3-Nitro-2-alkenoates and Cyclopentadiene[1]

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The Diels-Alder reactions of cyclopentadiene with ethyl (*E*)- and (*Z*)-3-nitrocrotonate were carried out to give only the (2+4)-nitro adduct as a mixture of three diastereomers, while that of the diene with ethyl (*Z*)-3-nitrocinnamate gave two kinds of cycloaddition products, (2+2)- and (2+4)-nitro adducts. All the nitro adducts were reduced with aluminum-amalgam to give the corresponding mono- and dihydroxyamino compounds, in which vicinal *endo*-ethoxycarbonyl-*endo*-hydroxyamino derivatives cyclized readily to give tricyclic compounds containing isoxazolidinone ring. The stereochemistry of all the new compounds were established on the basis of IR and NMR spectroscopic analyses.

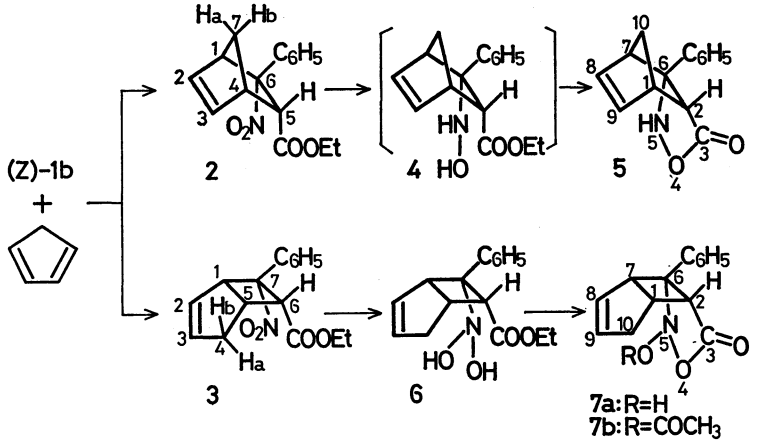
In previous papers, we reported the stereospecific formation of ethyl 3-nitro-2-alkenoate (**1**) by the elimination reaction of 2-acetoxy- or 2-chloro-3-nitroalkanoate with a base[2] and the assignment of the geometric configuration of the olefinic compounds by the photoisomerization of the (*E*)-isomer into the (*Z*)-isomer and by the their NMR analysis.[3] Although ethyl 3-nitrocinnamate (**1b**) could not be isomerized, we have recently reported on (*Z*)-geometry as a convenient configurational determination of **1b** by the application of the Diels-Alder reaction.[4]

In this paper, we wish to report further chemical proof of the configuration of ethyl (*E*)- and (*Z*)-3-nitro-2-crotonate (**1a**) by a similar method, together with a detailed description of that of (*Z*)-**1b**; *i.e.*, the cycloaddition products of **1a** with cyclopentadiene were examined to determine whether or not they form an isoxazolidinone ring between vicinal ethoxycarbonyl and hydroxyamino groups after reduction with aluminum–amalgam (Al–Hg). The structures and stereochemistry of all the new products were established on the basis of IR and NMR spectroscopic data as well as the results of elemental analyses.

Results and Discussion

Reaction of **1** *with Cyclopentadiene.* According to the method reported previously by Umezawa *et al.*,[5,6] a solution of **1b** and cyclopentadiene in benzene was heated in a sealed tube at 100 °C for 1 h to give a semi-solid substance. Its subsequent chromatographic separation on a silica gel column, using benzene and acetone as eluents, gave two kinds of cycloaddition products (**2** and **3**) in fairly good yields. Similarly, the reaction of (*Z*)-**1a** with cyclopentadiene gave an adduct (**10**) in a 75.5% yield. Furthermore, that of (*E*)-**1a** with cyclopentadiene in benzene with stirring at room temperature for 24 h was carried out to give two kinds of adducts (**8** and **9**) in 64.2 and 15.0% yields respectively. All the products were obtained as colorless crystals.

The IR spectrum of all the new cycloaddition products showed a strong band at 1720—1730 due to an ethoxycarbonyl group, strong bands at 1535—1550 and 1340—1360 due to a nitro group, and a weak band in the



Scheme 1.

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1630—1655 cm^{-1} region due to a ring carbon-carbon double bond. Moreover, from a comparison of the NMR spectra, it was found that the spectral pattern of **3** was considerably different from those of the other products (**2**, **8**, **9**, and **10**). The chemical shifts and coupling constants were assigned as shown in Table 3 by means of the double-resonance method. In the NMR spectrum of **3** (Table 3), the signals at δ 2.12 (d, 1H, $J_{4b,5}$=2.0 Hz), 2.66 (dd, 1H, $J_{4a,4b}$=18.0 Hz), 3.86 (d, 1H, $J_{5,6}$=8.3 Hz), 3.88 (m, 1H, 5-H) and 5.60 (d, 1H, $J_{1,5}$=8.3 Hz) are attributable to geminal protons at the 4-position and *cis*-protons at the 6-, 5-, and 1-positions respectively, while, in those of **2**, **8**—**10**, the signals of the 7- and 5-protons appeared at δ 1.42—2.08 (d, 2H, $J_{7a,7b}$=9.0—9.5 Hz) and at 3.30—4.13 (d, 1H, $J_{4,5}$=2.5—3.0 Hz) respectively. In general, (2+4)-cycloaddition products such as norbornenes and (2+2)-cycloaddition products such as bicyclo[3.2.0]heptenes can be readily distinguished from each other by means of the coupling constants between their geminal protons at the 4- and 7-positions, which have been reported to range from 8 to 10 Hz in the former adduct[5-8] and from 15 to 20 Hz in the latter.[9-11] Accordingly, **3** was identified as a (2+2)-nitro adduct. Moreover, from the *cis*-addition principle and the *endo*-rule in the Diels-Alder reaction, and the absence of any long-range coupling between the 7- and 5-protons, which are out of the *W*-letter relationship, it is reasonable to conclude that Compounds **2**, **9** and **10** are 5-*endo*-ethoxycarbonyl-6-*endo*-nitro-6-*exo*-phenylbicyclo[2.2.1]hept-2-ene, 5-*endo*-ethoxycarbonyl-6-*exo*-nitro-6-*endo*-methylbicyclo[2.2.1]-hept-2-ene, and 5-*endo*-ethoxycarbonyl-6-*endo*-nitro-*exo*-methylbicyclo[2.2.1]hept-2-ene respectively. On the other hand, from the presence of the long-range coupling (d, $J_{5,7a}$=3.0 Hz) which was collapsed by the irradiation of 5- or 7a-proton, the configuration of **8** was determined to be 5-*exo*-ethoxycarbonyl-6-*endo*-nitro-6-*exo*-methylbicyclo[2.2.1]hept-2-ene. Since the two J values between *cis* protons on cyclobutane ring are equal, Compound **3** was concluded to be 6-*endo*-ethoxycarbonyl-7-*endo*-nitro-7-*exo*-phenylbicyclo[3.2.0]hept-2-ene. These results indicate that the reaction of (*Z*)-**1b** proceeds stereospecifically to form only an *endo*-adduct and that those of (*E*)- and (*Z*)-**1a** follow the *endo*-rule unambiguously (see Table 1), because the *exo*-isomer, 5-*exo*-ethoxycarbonyl-6-*exo*-nitro-6-*endo*-methylbicyclo[2.2.1]hept-2-ene (**11**), could not be obtained.

The thermal (2+2)-cycloaddition of **1b** to diene seems to be rare, although many photochemical cycloadducts from diene and dienophiles have been reported in the literature.[9,12] However, interestingly, it was found that neither the (2+2)- nor the (2+4)-cycloaddition of **1** to the diene proceeded photochemically.

Reduction of the Nitro Adducts with Al–Hg. The *cis* stereochemistry of the nitro and ethoxycarbonyl groups of Compounds **2**, **10** (5-*endo*-6-*endo*), and **3** (6-*endo*-7-*endo* structure) were further substantiated by the facts that they were reduced to give the corresponding mono- or dihydroxyamino derivatives, which were immediately cyclized between vicinal ethoxycarbonyl and hydroxyamino groups to give tricyclic isoxazolidinone derivatives.

Although Compounds **8** and **9** were treated with Al–Hg in ether to give the corresponding 6-hydroxyamino derivatives (**12** and **13** respectively), a similar reduction of **2** and **10** readily gave 6-*exo*-phenyl- and methyl-*endo*-4-oxa-5-azatricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-one (**5** and **15**) respectively *via* unstable intermediates, the corresponding 6-*endo*-hydroxyamino derivatives (**4** and **14**), in which **4** could not be isolated purely. Moreover, the treatment of **14** with *N*-bromosuccinimide (NBS) in chloroform gave the *N*-bromo derivative of **15** (**16**), which could not be derived from **15** and NBS. Surprisingly, the similar reduction of **3** gave stable colorless

Table 1. Physical data and IR spectra of bicyclo[2.2.1]- and [3.2.0]heptene derivatives

Compd No.	Yield (%)	Mp, °C (Bp, °C/mmHg)	Formula	Found (Calcd), %			IR spectrum, cm^{-1} in KBr			
				C	H	N	NHOH (OH)	COOEt	C=C	NO_2
2	47.3[a]	84—85	$C_{16}H_{17}NO_4$	66.63 (66.88)	5.93 (5.96)	4.78 (4.88)		1725,	1640,	1540, 1360
3	31.5[a]	90—91	$C_{16}H_{17}NO_4$	66.92 (66.88)	5.95 (5.96)	4.86 (4.88)		1735,	1620,	1550, 1350
6	48.8[b]	97—98	$C_{16}H_{19}NO_4$	66.35 (66.42)	6.63 (6.62)	4.78 (4.84)	(3450), (3225),	1738,	1640	
8	64.2[c]	98—99	$C_{11}H_{15}NO_4$	58.65 (58.67)	6.71 (6.67)	6.20 (6.22)		1720,	1650,	1540, 1350
9	15.0[d]	41—43 (92—98/0.2)	$C_{11}H_{15}NO_4$	58.39 (58.67)	6.69 (6.67)	6.31 (6.22)		1725,	1655,	1535, 1355
10	75.5[d]	38—40 ((98—99/0.2)	$C_{11}H_{15}NO_4$	58.76 (58.67)	6.77 (6.67)	6.30 (6.22)		1735,	1635,	1535, 1355
12	74.7[a]	133—134	$C_{11}H_{17}NO_3$	62.54 (62.54)	7.98 (8.11)	6.25 (6.63)	3250,	1730,	1640	
13	22.0[e]	137—138	$C_{11}H_{17}NO_3$	62.62 (62.54)	7.99 (8.11)	6.58 (6.63)	3250,	1730,	1630	
14	15.0[f]	137—138	$C_{11}H_{17}NO_3$	62.70 (62.54)	8.18 (8.11)	6.63 (6.63)	3250,	1725,	1630	

a) Colorless needles from ethanol. b) Colorless fibers from benzene. c) Colorless prisms from ethanol. d) Colorless needles from hexane. e) Colorless needles from cyclohexane–ethanol. f) Colorless needles from carbon tetrachloride.

Table 2. Physical data and IR spectra of tricyclo[5.2.1.$0^{2,6}$]- and [5.3.0.$0^{2,6}$]decene derivatives

Compd No.	Yield (%)	Mp °C	Formula	Found (Calcd), % C	H	N	IR spectrum, cm^{-1} in KBr NH (OH)	Lactone	C=C
5	31.6[a]	112—113	$C_{14}H_{13}NO_2$	73.89 (73.99	5.82 5.77	6.14 6.16)	3240,	1765,	1640
7	52.5[b]	118—119	$C_{14}H_{13}NO_3$	68.72 (69.12	5.39 5.39	5.75 5.76)	(3340),	1745,	1620
7b	48.5[c]	107—108	$C_{16}H_{15}NO_4$	67.33 (67.36	5.11 5.30	5.03 4.91)	1775, acetyl	1755,	1630
15	24.0[d]	95—96	$C_9H_{11}NO_2$	65.77 (65.44	6.75 6.71	8.45 8.48)	3250,	1760,	1660
16	43.0[a]	102—103	$C_9H_{10}NO_2Br$	44.42 (44.28	4.21 4.13	5.61 5.74)		1640,	1620

a) Colorless needles from ethanol. b) Colorless prisms from hexane. c) Colorless prisms from ethanol. d) Pink prisms from carbon tetrachloride.

Table 3. Chemical shifts (δ) and coupling constants (Hz) of bicyclo[2.2.1]- and [3.2.0]heptenes

Compound No.	H^1	H^2	H^3	H^4	H^5	H^6	C_6H_5 [CH_3]	H^{7a} [H^{4a}]	H^{7b} H^{4b}]	OH [NHOH]
2	4.07(bs)	6.10(dd) $J_{2,3}$=5.7 $J_{1,2}$=3.0	6.73(dd) $J_{3,4}$=3.0	3.18(bs)	3.62(d) $J_{4,5}$=3.0		7.40— 7.85(m)	1.67(d) $J_{7a,7b}$=9.2	1.46(dd) $J_{1,7b}$=2.0 $J_{4,7b}$=2.0	
3	5.60(d) $J_{1,5}$=8.3	5.95(dd) $J_{2,3}$=5.7	6.08(dd)		3.88(m)	3.86(d) $J_{5,6}$=8.3	7.30— 7.94(m)	[2.66(dd) $J_{4a,4b}$=18.0	2.12(d)] $J_{4b,5}$=2.0	
6	5.66(d) $J_{1,5}$=8.0	5.88(dd) $J_{2,3}$=6.0	6.04(dd) $J_{3,4}$=3.0		3.46(m)	3.64(d) $J_{5,6}$=8.0	7.40(m)	[2.77(dd) $J_{4a,4b}$=17.5	2.41(dd)] $J_{4b,5}$=2.0	2.05—3.00 7.20—7.70
8	3.21(dd) $J_{1,2}$=3.0	6.05(dd) $J_{2,3}$=6.0	6.34(dd) $J_{3,4}$=3.0	3.09(bs)	3.35(d) $J_{4,5}$=3.0 $J_{5,7a}$=3.0		[1.85(s)]	2.80(d) $J_{7a,7b}$=9.5	1.69(d)	
9	3.46(dd) $J_{1,2}$=3.0	6.15(dd) $J_{2,3}$=6.0	6.66(dd) $J_{3,4}$=3.0	3.18(bs)	4.13(d) $J_{4,5}$=3.0		[1.51(s)]	1.54(d) $J_{7a,7b}$=9.0	1.42(d)	
10	3.14(bs) $J_{1,2}$=2.5	6.03(dd) $J_{2,3}$=6.0	6.55(dd) $J_{3,4}$=2.5	3.14(bs)	3.30(d) $J_{4,5}$=2.5		[2.03(s)]	1.67(bd) $J_{7a,7b}$=9.5	2.03(bd)	
12	2.80(bs)	6.31(bs)		2.97(bs)	1.83(d) $J_{4,5}$=3.0 $J_{5,7a}$=3.0		[1.40(s)]	2.30(dd) $J_{7a,7b}$=9.5	1.82(d)	[5.50(bs)]
13	2.80(bs)	6.01—6.34(m)		2.94(bs)	2.61(d) $J_{4,5}$=3.0		[1.11(s)]	1.76(d) $J_{7a,7b}$=9.0	1.44(d)	[5.62(bs)]

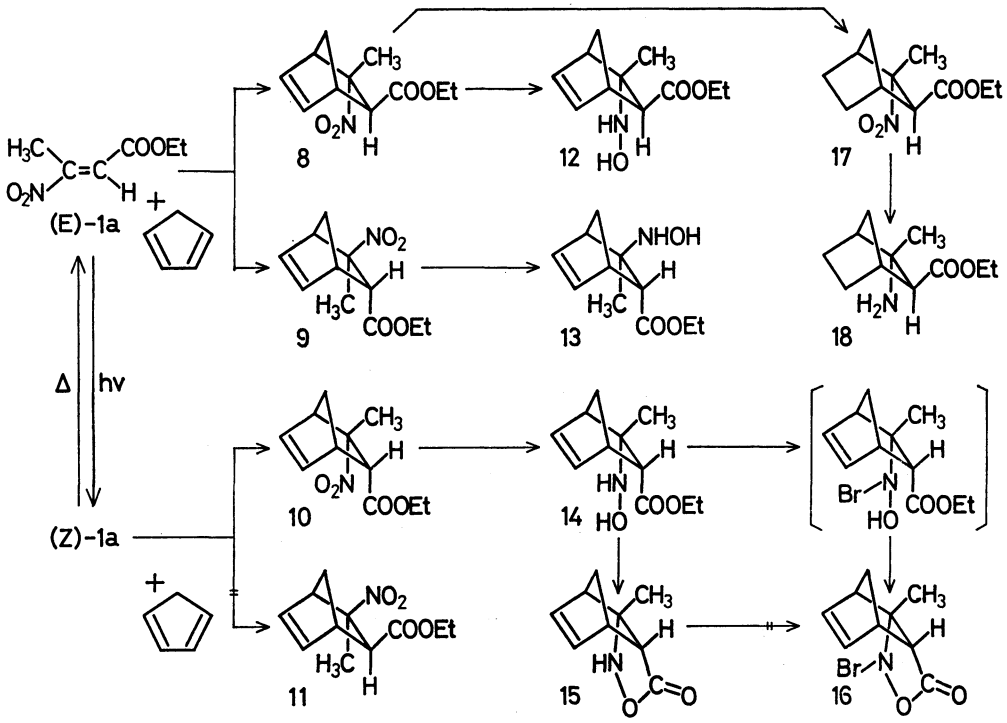
Measured in $CDCl_3$.

Table 4. Chemical shifts (δ) and coupling constants (Hz) of tricyclo[5.2.1.$0^{2,6}$]- and [5.3.0.$0^{2,6}$]decenes

Compound No.	H^1	H^2	5-NH[OH]	6-C_6H_5[CH_3]	H^7	H^8	H^9	H^{10a}	H^{10b}
5	3.76(m)	3.76(d) $J_{1,2}$=4.0	6.14(bs)	7.43(m)	3.48(m)	6.43(dd) $J_{8,9}$=5.5	6.56(dd) $J_{1,9}$=3.0	1.70(d) $J_{10a,10b}$=9.0	1.54(dd) $J_{1,10b}$=2.0 $J_{7,10b}$=2.0
7a	3.43(m)	3.74(d) $J_{1,2}$=8.0	[7.20—7.70]	7.40(m)	5.64(d) $J_{1,7}$=8.0	5.79(dd) $J_{7,8}$=3.0 $J_{8,9}$=6.0	6.12(dd) $J_{9,10}$=3.0	2.74(dd) $J_{10a,10b}$=18.0 $J_{1,10a}$=8.0	2.38(d) $J_{1,10b}$=2.5
7b	3.40(m)	3.85(d) $J_{1,2}$=8.1		7.45—7.69(m)	5.73(d) $J_{1,7}$=8.1	5.95(dd) $J_{7,8}$=3.5	6.12(dd) $J_{9,10}$=3.0	2.80(dd) $J_{10a,10b}$=17.8 $J_{1,10a}$=8.1	2.46(d) $J_{1,10b}$=2.0
15	2.86(bs)	3.02(d) $J_{1,2}$=5.0	3.33(bs)	[1.58(s)]	2.86(bs)	6.31(dd) $J_{7,8}$=2.5 $J_{8,9}$=6.0	6.45(dd) $J_{9,10}$=2.5	1.77(d) $J_{10a,10b}$=9.5 $J_{1,10b}$=2.5	1.62(d) $J_{1,10b}$=2.5

Measured in $CDCl_3$.

crystals of unexpected 6-*endo*-ethoxycarbonyl-7-*endo*-dihydroxyamino-7-*exo*-phenylbicyclo[3.2.0]hept-2-ene (**6**), which was subsequently heated in dry benzene at 50 °C to give the expected 5-hydroxy-6-*exo*-phenyl-*cis*-*cisoid*-*cis*-4-oxa-5-azatricyclo[5.3.0.$0^{2,6}$]dec-8-en-3-one (**7a**) in a 52.5% yield. In order to prove the presence of the hydroxy group, **7a** was acetylated by the usual procedure, using acetic anhydride and pyridine at room temperature, to give the corresponding 5-acetoxy derivative (**7b**) in a 48.5% yield.



Scheme 2.

The structures of all the new reduction products and tricyclic compounds were characterized spectroscopically (see Tables 3 and 4) and gave satisfactory elemental analyses (see Tables 1 and 2), although the attempt at the measurement of the NMR spectrum of **14** was unsuccessful.

On the other hand, the catalytic reduction of **8** with Raney-nickel in ethanol at room temperature was carried out to give the corresponding 6-nitronorbornene (**17**) in the initial step; the further reduction of **17** gave the corresponding 6-aminonorbornene (**18**) in an almost quantitative yield.

In the IR spectrum, all the hydroxyamino and the tricyclic compounds showed a weak band in the 1630—1640 cm^{-1} region due to a ring double bond. Particularly, the IR spectra of **6** and **7a** showed the strong absorption bands of hydroxyl groups at 3450 and 3225, and 3340 cm^{-1}, respectively. The disappearance of the hydroxyl absorption and the appearance of a carbonyl band at 1775 cm^{-1} upon the acetylation of **7a**, and the presence of a molecular peak (*m/e* 244 (M^+)) in the mass spectrum of **7a**, supported the presence of an *N*-hydroxyisoxazolidinone ring in **7a**.

In the NMR spectra of **12** and **13**, the signals of the two protons at δ 5.50 and 5.62 are both attributable to the hydroxyamino group, while, in that of **6**, the broad signals of two protons of dihydroxyamino groups appeared in the δ 2.05—3.00 and 7.20—7.70 regions. It seemed that the chemical shift in the lower field is due to a hydrogen bond between one of the hydroxyl groups and the ethoxycarbonyl groups.

In conclusion, the cycloaddition reaction and reduction sequences are generalized for the chemical determination of the configurations of β-nitro olefinic acids.

Experimental

All the boiling and melting points are uncorrected. The IR spectra were recorded with a Hitachi EPI-G3 Spectrometer. The NMR spectra were measured with a JNM-PS 100 Spectrometer (Japan Electron Optics Laboratory Co., Ltd.), using tetramethylsilane as the internal standard.

Starting Materials. The (*E*)- and (*Z*)-isomers of **1a** and the (*Z*)-isomer of **1b** were prepared and confirmed by a method previously reported.[2-4]

Preparation of 2 and 3. A solution of (*Z*)-**1b** (2.9 g, 9 mmol) and cyclopentadiene (0.9 g, 14 mmol) in dry benzene (20 ml) was heated in a sealed tube at 100 °C for 1 h. After the removal of the benzene under reduced pressure, the residual semi-solid thus obtained was chromatographed on a silica gel column, using benzene–acetone (50: 1, V/V) as the eluent, to give two fractions. After each of the fractions had been concentrated under reduced pressure, the first one gave **2** and the second one gave **3** both as colorless crystals.

Preparation of 10. In an analogous manner, a reaction mixture of (*Z*)-**1a** (8.0 g, 50 mmol) and cyclopentadiene (4.0 g, 60 mmol) in benzene (100 ml) was worked up to give a viscous syrup, which gradually solidified to give only colorless crystalline **10**.

Preparation of 8 and 9. A solution of (*E*)-**1a** (8.0 g, 50 mmol) and cyclopentadiene (4.0 g, 60 mmol) in dry benzene (100 ml) was stirred overnight at room temperature. After the removal of the benzene under reduced pressure, a pale yellow semi-solid was obtained. The residue was recrystallized from ethanol to give colorless crystalline **8**. Subsequently, the mother liquor was evaporated to give a residual syrup. The yellowish residue was distilled under reduced pressure to give a viscous syrup, which gradually solidified to give colorless crystalline **9**.

Preparation of 5. A solution of **2** (2.9 g, 10 mmol) in ether (10 ml) was vigorously stirred into a suspension of Al–Hg (made from Al (1.5 g) and $HgCl_2$ (1.5 g))[13] in ether (50 ml)

at room temperature. After a few minutes, the ether began to reflux. During the addition of the above solution, a few drops of water were added at 20-min intervals to maintain refluxing. After the addition of the solution of **2** had been completed, the stirring was continued for 4 h. The mixture was then extracted thoroughly several times with ether (200 ml) and finally twice with ethyl acetate (60 ml). The combined extracts were dried over anhydrous magnesium sulfate and then evaporated to give colorless crystalline **5**.

Preparation of ***6***. In an analogous manner, a reaction mixture of **3** (1.5 g, 5 mmol) with Al–Hg (from Al (1.0 g) and $HgCl_2$ (1.0 g)) in ether (30 ml) was worked-up to give colorless crystalline **6**, after stirring for 3 h.

Preparation of ***12***. A mixture of **8** (4.5 g, 20 mmol) and Al–Hg (from Al (4 g) and $HgCl_2$ (4 g)) in ether (100 ml) was stirred for 6 h; there after a similar work-up gave **12**, 5-*exo*-ethoxycarbonyl-6-*endo*-hydroxyamino-6-*exo*-methylbicyclo-[2.2.1]hept-2-ene, as colorless crystals.

Preparation of ***13***. Similarly, Compound **9** was treated with Al–Hg in ether to give **13**, 5-*endo*-ethoxycarbonyl-6-*exo*-hydroxyamino-6-*endo*-methylbicyclo[2.2.1]hept-2-ene, as colorless crystals.

Preparation of ***14*** *and* ***15***. Similarly, Compound **10** was treated with Al–Hg in ether, giving colorless crystals (**14**), 5-*endo*-ethoxycarbonyl-6-*endo*-hydroxyamino-6-*exo*-methylbicyclo[2.2.1]hept-2-ene. The crystals obtained were gradually converted to **15** by refluxing in carbon tetrachloride for 1 h.

Preparation of ***16***. Into a solution of **14** (1.1 g, 5 mmol) in chloroform (20 ml) we stirred NBS (0.7 g, 5 mmol), portion by portion below 10 °C. After stirring for 1 h, the resulting solution was washed once with water and then dried over anhydrous magnesium sulfate. The solution was evaporated to give **16**, 5-bromo-6-*exo*-methyl-4-oxa-5-azatricyclo[5.2.1.$0^{2,6}$]-dec-8-en-3-one, as colorless crystals.

Preparation of ***7a***. A solution of **6** (0.3 g, 1 mmol) in dry benzene (10 ml) was refluxed for 5 min. After the removal of the benzene under reduced pressure, a residual syrup was obtained. The syrup was dissolved in hexane (5 ml), and then the hexane solution was allowed to stand at room temperature to give colorless crystalline **7a**.

Preparation of ***7b***. The acetylation of **7a** (0.12 g, 0.5 mmol) was carried out by the usual procedure using acetic anhydride (10 ml) and pyridine (3 ml) at room temperature; it gave colorless crystalline **7b**, 5-acetoxy-6-*exo*-phenyl-*cis*-*oid*-*cis*-4-oxa-5-azatricyclo[5.3.0.$0^{2,6}$]dec-8-en-3-one.

Preparation of ***17***. To a suspension of a Raney-nickel catalyst (3 ml) in ethanol (200 ml) we added **8** (6 g, 26.7 mmol). The mixture was shaken under a hydrogen atmosphere at room temperature for 24 h. After the removal of the catalyst by filtration, the resulting solution was evaporated under reduced pressure to give a residue. The residual syrup was distilled under reduced pressure to a colorless oil, which gradually crystallized to give **17**, 5-*exo*-ethoxycarbonyl-6-*endo*-nitro-6-*exo*-methylbicyclo[2.2.1]heptane, as colorless crystals. Yield, 5.7 g (97.4%); bp 118—120 °C/1 mmHg, mp 34.5—36.5 °C. NMR ($CDCl_3$): δ 1.25—2.25 (6H, m, 2-, 3- and 7-H), 1.66 (3H, s, 6-CH_3), 2.60 (2H, m, 1- and 4-H), 3.64 (1H, d, $J_{5,7b}$=2.8 Hz, 5-H). IR (KBr): 1745 (ester), 1550 and 1360 (NO_2) cm^{-1}. Found: C, 57.99; H, 7.56; N, 6.12%. Calcd for $C_{11}H_{17}NO_4$: C, 58.13; H, 7.54; N, 6.61%.

Preparation of ***18***. In an analogous manner, a mixture of **17** (5.7 g, 26.0 mmol) and Raney-nickel (3 ml) in ethanol (200 ml) was worked-up to give a colorless oil, 6-*endo*-amino-5-*exo*-ethoxycarbonyl-6-*exo*-methylbicyclo[2.2.1]heptane (**18**). Yield, 4.9 g (95.7%); bp 90—91 °C/0.7 mmHg. NMR ($CDCl_3$): δ 1.16 (2H, s, 6-NH_2), 1.25—2.25 (6H, m, 2-, 3- and 7-H), 1.54 (3H, s, 6-CH_3), 1.90 (1H, m, 4-H), 2.03 (1H, d, $J_{5,7b}$=2.3 Hz, 5-H), 2.40 (1H, m, 1-H). IR (KBr): 3350 (NH_2), 1735 (ester) cm^{-1}. Found: C, 66.78; H, 9.67; N, 7.10%. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10%.

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