Syntheses and Chiroptical Properties of Optically Active Derivatives of Tricyclo[3.3.0.0^{3,7}]octane and Oxatricyclononanes[1]

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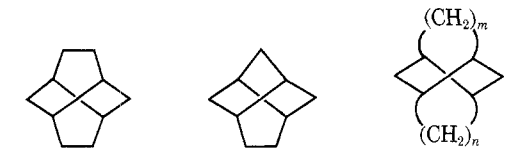
The optically active desymmetrized tricyclo[3.3.0.0^{3,7}]octane derivatives, (−)-4-methylenetricyclo[3.3.0.0^{3,7}]-octan-2-one (**20**) and (+)-4-isopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (**21**), were prepared from (−)-*endo*-2-carboxybicyclo[2.2.1]hept-5-ene (**14**) via optically active oxetane, (−)-2-methyl-3-oxatetracyclo[4.2.1.0^{2,5}.0^{4,8}]nonane (**18**) and (−)-2-isopropyl-3-oxatetracyclo[4.2.1.0^{2,5}.0^{4,8}]nonane (**24**), respectively. The syntheses established equivocally absolute configurations of these compounds, whose chiroptical properties are compared with those of tricyclo[4.4.0.0^{3,8}]decane ("twistane") and tricyclo[4.3.0.0^{3,8}]nonane ("twist-brendane") series of compounds. Oxatricyclononanes, 2-oxatricyclo[4.3.0.0^{4,8}]nonane (**7**) and 2-oxatricyclo[4.2.1.0^{4,8}]nonane (**8**), which have intrinsic chiral skeletons were also synthesized in optically active modifications.

In our preceding papers, syntheses of optically active tricyclo[4.4.0.0^{3,8}]decane[2c] ("twistane") and tricyclo-[4.3.0.0^{3,8}]nonane[3c,3d] ("twist-brendane"), together with determinations of their absolute configurations, were reported; both (+)-twistane (D_2 point group) and (+)-twist-brendane (C_2 point group) can be represented by the formulas **1** and **2**, respectively.



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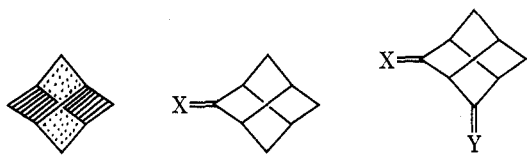
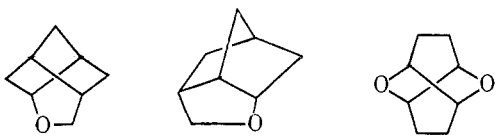


4 5 6

Collectively, these compounds can be regarded to be constructed by freezing the cyclohexane ring in a chiral twist-boat conformation by means of two short bridges $(CH_2)_m$ and $(CH_2)_n$ spanning over C_1 and C_4 as well as C_2 and C_5 carbon atoms as shown in structure **3**. When both the two bridges become methylene groups, a new situation emerges affording achiral tricyclo[3.3.0.0^{3,7}]octane[5] ("bisnoradamantane")[6] (**4**). A noteworthy feature in this molecular system (D_{2d} point group) is the condensed ring system which complies two twist-boat cyclohexanes of opposite chiralities (the hatched and the dotted ones indicated in the formula **4**). Two methylene groups in the same twist-boat cyclohexane ring system are homotopic whereas those in different cyclohexanes are enantiotopic; i.e., they form two equivalent sets of enantiotopic methylene groups. This symmetric bisnoradamantane system can be desymmetrized by converting one of the enantiotopic methylene groups into sp^2 center (X) (**5**), and desymmetrization can also be achieved by conversion of the enantiotopic methylene groups into different sp^2 centers (X, Y) to give the compound **6**.

Comparison of these desymmetrized bisnoradamantane series of compounds with twistane, twist-brendane, and their derivatives possessing intrinsic chiral structures can be expected to reveal various interesting features. In this paper, we report the syntheses of some of the optically active desymmetrized bisnoradamantane derivatives together with their chiroptical properties.

The symmetry considerations can further be extended to 2-oxatricyclo[4.3.0.0^{4,8}]nonane[7] ("2-oxa-twist-brendane") (**7**) and 2-oxatricyclo[4.2.1.0^{4,8}]nonane[8] ("2-oxabrendane") (**8**). Having an intrinsic chiral skeleton, the compound **7** keeps the original chirality upon exchange of the heteroatom with the methylene group of **7**, whereas the compound **8** changes into the enantiomeric form upon the same transformation.



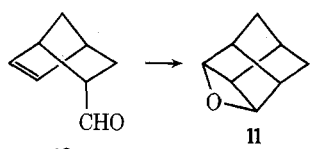
7 8 9

Besides these interesting stereochemical aspects, their syntheses in optically active forms with known absolute configurations seems appropriate to be reported here, since (−)-2,7-dioxatwistane[9] (**9**) has been the sole optically active species belonging to this type of cage-shaped compound so far prepared.

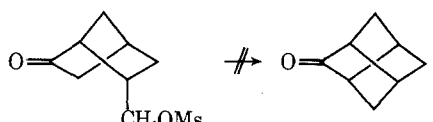
Results and Discussion

Syntheses of Optically Active Bisnoradamantane Derivatives. Although the Paterno–Büchi photocyclization[5g,5h] has been proved successful to secure various cage-shaped compounds, unfortunately this route cannot be applied to the optically active unsaturated aldehyde **10** since the expected oxetane **11** turns out to be achiral (Scheme I).

Scheme I



10 11

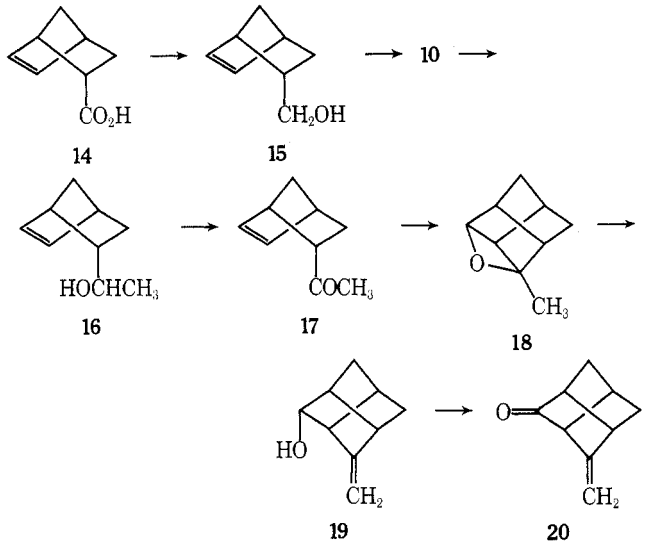


12 13

After a fruitless attempt to cyclize the mesylate **12** to tricyclo[3.3.0.0^{3,7}]octan-2-one (**13**), our efforts were directed toward the sequence illustrated in Scheme II.

(−)-*endo*-2-Carboxybicyclo[2.2.1]hept-5-ene (**14**) with known absolute configuration[10] was reduced with lithium

Scheme II

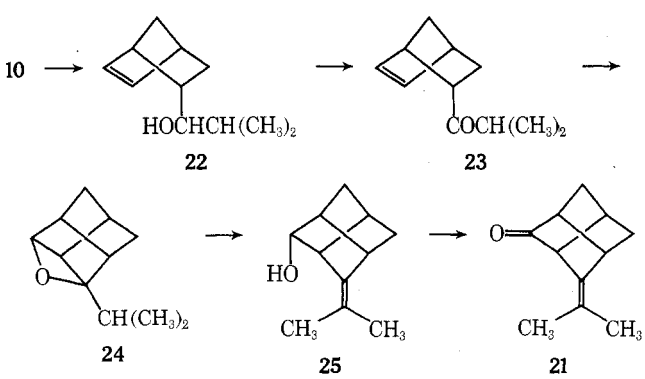


14 15 16 17 18 19 20

aluminum hydride to (−) unsaturated alcohol **15,** which was converted into the (−) unsaturated aldehyde **10** with Collins' reagent. Treatment with methylmagnesium iodide converted the (−) aldehyde **10** into the (−) alcohol **16,** which was oxidized to give (−) unsaturated methyl ketone **17.** A solution of **17** was irradiated with a medium-pressure mercury lamp to furnish (−)-2-methyl-3-oxatetracyclo-[4.2.1.$0^{2,5}$.$0^{4,8}$]nonane (**18**). Since cleavage of the oxetane ring with methanolic perchloric acid solution,[3b,3d] which has been so successful in the twist-brendane series of compound, failed, we treated **18** with hot lithium diethylamide[11] in a benzene solution to obtain alcoholic product (**19**), which was converted into 4-methylenetricyclo[3.3.0.$0^{3,7}$]-octan-2-one (**20**) upon oxidation with Collins' reagent. The structure was confirmed by infrared spectrum, exhibiting absorptions at 1765 (O=C) and at 1672, 835 cm^{-1} (H_2C=C), and NMR spectrum, which showed absorptions at δ 4.67 and 4.53 (olefinic protons).

A similar sequence of transformations as shown in Scheme III converted **10** into (+)-4-isopropylidenetricyclo[3.3.0.$0^{3,7}$]octan-2-one (**21**).

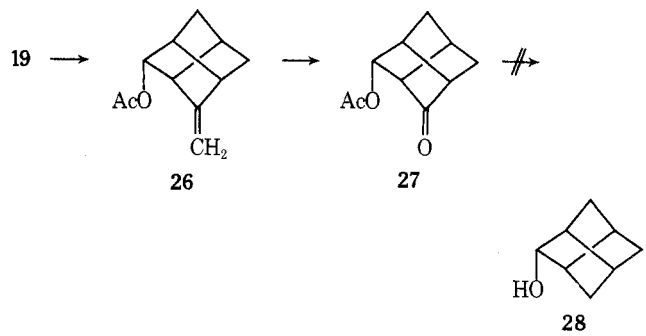
Scheme III



22 23 24 25 21

Upon treatment with isopropylmagnesium bromide, the (−) aldehyde **10** afforded the (−) alcohol **22** which was oxidized to give the (−) ketone **23.** Photocyclization of **23** gave the (−) oxetane **24,** whose oxetane ring was cleaved to yield (+)-4-isopropylidenetricyclo[3.3.0.$0^{3,7}$]octan-2-ol (**25**) on treatment with lithium diethylamide. Oxidation of **25** with Collins' reagent gave **21** which showed absorption at 1755 cm^{-1} (O=C) in the infrared spectrum and proton signals at δ 1.64 (doublet) and 1.69 (doublet) due to the nonequivalent methyl groups in the NMR spectrum. Having secured these optically active ketones with known absolute configurations, our efforts were directed toward conversion of the disubstituted derivatives into the optically active monosubstituted derivative,[12] i.e., bisnoradamantanone (**13**). An obvious route would be the one starting from the unsaturated ketone **20,** but the compound **20** was found to suffer a deep-seated decomposition on Wolff–Kishner reduction. Therefore, we made a detour illustrated in Scheme IV. The

Scheme IV



26 27 28

acetate **26** was converted into the acetate–ketone **27** by ozone cleavage at −78 °C but again its Wolff–Kishner reduction was found to cause a deep-seated decomposition affording various cleavage products.

Syntheses of Optically Active Oxatricyclononanes. Synthesis of (−)-2-oxatricyclo[4.3.0.$0^{4,8}$]nonane (**7**) is rather straightforward. According to Kropp's procedure[7] to effect diagonal ring closing, the (−) unsaturated alcohol **15** was irradiated with a medium-pressure mercury lamp, and the product was purified by chromatography and sublimation affording **7** (Scheme V). This substance has a smell

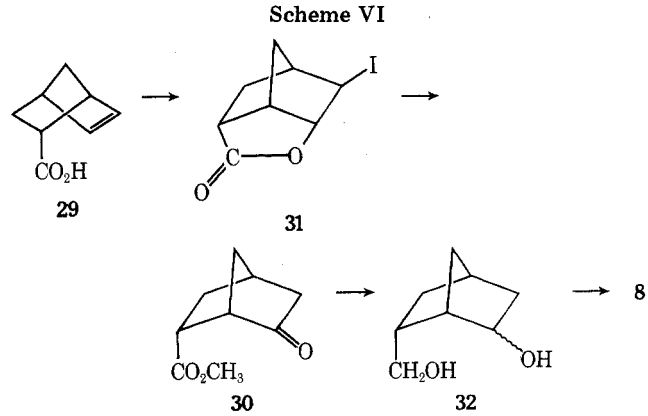
Scheme V

15 → 7

reminiscent of camphor, characteristic to cage-shaped hydrocarbons such as twistane and twist-brendane.

Our last efforts were directed toward the preparation of optically active 2-oxatricyclo[4.2.1.$0^{4,8}$]nonane (**8**) which is distinct from 2-oxa-twist-brendane (**7**) in regard to the direction of the ether bridging: diagonal in the former and transversal in the latter. Scheme VI depicts the synthetic

Scheme VI



29 31 30 32

route to (−)-2-oxabrendane (**8**) from (+)-*endo*-2-carboxybicyclo[2.2.1]hept-5-ene (**29**). The (+) carboxylic acid **29** was converted into (+)-ketocarboxylic acid methyl ester (**30**) via iodolactone **31**[13] and the (+) ester **30** was reduced with lithium aluminum hydride to furnish the (−) diol **32** which was treated with *p*-toluenesulfonyl chloride in cold pyridine solution. From the pentane-soluble fraction was isolated the oxa derivative, whose infrared spectrum and NMR spectrum exhibited absorptions at 1080 cm^{-1} (ether

Table I. Specific Rotations of Bisnoradamantane Derivatives and Twist-Brendane Derivatives

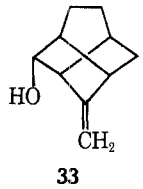
Compd	$[\alpha]_D$,[a] deg	Compd	$[\alpha]_D$,[a] deg
19	+13.2		
25	+18.3	**33**	−319
20	−36.6	**35**	−450
21	+37.6		

[a] Solvent ethanol.

linkage) and at δ 4.20–4.42 (2 H, C_1 methylene protons), 3.65–3.90 (2 H, C_3 methylene protons), respectively. Besides obvious evidence from the synthetic route, their spectroscopic evidence clearly indicates the structure of 2-oxabrendane (**8**) for this compound.

Chiroptical Properties. As can be seen from Table I, which compared specific rotations of corresponding bisnoradamantane and twist-brendane series of compounds,[3c,3d] the bisnoradamantane series without intrinsic skeletal chirality always shows much smaller optical rotations. This is in harmony with our previously advanced explanation that a "twist" of the carbon skeleton mainly contributes to their optical rotation in these cage-shaped molecules.

In their circular dichroism curves, (−)-bisnoradamantanone with methylene group (**20**) exhibits maxima at 199.5 ([θ], +9.8 × 10^4), 301 (−1.79 × 10^4), and 307 nm (sh) (−1.65 × 10^4); (+)-bisnoradamantanone with isopropylidene group (**21**) shows maxima at 214 ([θ], +3.26 × 10^4), 298.5 (−1.37 × 10^4), and 304 nm (sh) (−1.34 × 10^4). The negative Cotton effect due to n–π* transition observed at around 300 nm can be explained just as in the case of twistanone and twist-brendanone: application of the octant rule to the projection formula **34** in which the carbonyl group is placed at the "point of twist".[14] In a previous paper,[3d] we indicat-



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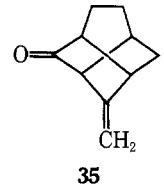

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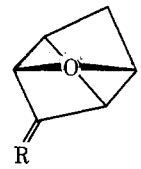

R = CH_2 or $C(CH_3)_2$

34

ed that the exocyclic methylene group in the twist-brendane derivative (**35**) exerts negligible effect on the sign and shape of the circular dichroism curve due to n–π* transition and this seems also to hold in the bisnoradamantane derivatives **20** and **21**.

Turning to the optical rotatory power of 2-oxa-twist-brendane (**7**) and 2-oxabrendane (**8**), we notice that 2-oxa-twist-brendane (**7**) derived from the intrinsically chiral parent compound shows lager optical rotation. Comparison within the twist-brendane series, however, shows that 2-oxa-twist-brendane (**7**) has a smaller rotation than the parent hydrocarbon, twist-brendane. The same tendency was observed by Ganter[9] when comparison was made between the optical rotatory power of twistane and that of dioxatwistane (**9**).

Experimental Section

Infrared spectral data were obtained from a Hitachi EPI-S2 spectrophotometer. Nuclear magnetic resonance spectra were obtained from a JNM-MH-100 spectrometer. Ultraviolet spectra were recorded on a Beckman DB spectrometer. Optical rotations were measured with a JASCO-DIP-SL automatic polarimeter. Circular dichroism (CD) data were measured on a JASCO J-20 spectropolarimeter with CD attachment. Elemental analyses were determined by Yanagimoto CHN-Corder type I. All the melting points and the boiling points are uncorrected.

(−)-*endo*-2-Carboxybicyclo[2.2.1]hept-5-ene (14). The levorotatory carboxylic acid **14** was prepared from the levorotatory salt of the carboxylic acid with cinchonidine by the same procedure previously reported:[3c,10a] bp 112–114 °C (6 mm); $[\alpha]^{24}D$ −112.4° (*c* 0.61, ethanol).[15]

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.47; H, 7.32.

(+)-*endo*-2-Carboxybicyclo[2.2.1]hept-5-ene (29). The dextrorotatory carboxylic acid **29** was prepared from the salt which was obtained from the combined mother liquors: bp 112–113.5 °C (6 mm); $[\alpha]^{25}D$ +73.1° (*c* 0.65, ethanol).

Anal. Calcd for $C_8H_{10}C_2$: C, 69.54; H, 7.30. Found: C, 69.49; H, 7.34.

(−)-*endo*-2-Hydroxymethylbicyclo[2.2.1]hept-5-ene (15). A solution of 17.2 g of **14** in 150 ml of dry ether was added to a suspension of 6.9 g of lithium aluminum hydride in 200 ml of dry ether at room temperature. The mixture was then refluxed for 4 h. After cooling with ice, to the chilled reaction mixture was added a saturated aqueous ammonium chloride solution and a solid was filtered off. A filtrate was washed with water and dried over magnesium sulfate. After evaporation of the solvent, the residue was distilled to give 15.1 g of **15** (97%): bp 85–87 °C (11 mm); $[\alpha]^{25}D$ −66.6° (*c* 0.60, ethanol).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.29; H, 9.77.

(−)-*endo*-2-Formylbicyclo[2.2.1]hept-5-ene (10). To a mixture of 96.0 g of dry pyridine and 1.4 l. of dry methylene chloride was added 60.0 g of chromium trioxide and the mixture was then stirred for 15 min at room temperature.[16] A solution of 12.2 g of (−) alcohol **15** in 10 ml of dry methylene chloride was added to the reagent and then the reaction mixture was stirred for a further 15 min at room temperature. After the organic layer was separated, the residue was rinsed with the same solvent. Combined organic solutions were washed with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, and water, and dried over magnesium sulfate. After removal of the solvent, the residue was distilled to yield 8.54 g of **10** (71%): bp 97–100 °C (66 mm); $[\alpha]^{26}D$ −69.6° (*c* 1.07, ethanol); ir (film) 3020, 2720, 1715, 1335, and 720 cm^{-1}.

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.84; H, 8.23.

Photocyclization of 10. A solution of 1.14 g of the (−) aldehyde **10** in 200 ml of benzene was irradiated for 12 h with a mercury lamp (SHL-100UV, Toshiba). The crude oxetane was obtained by evaporation of the benzene at reduced pressure. Sublimation gave 650 mg of the oxetane **11** (57%): mp 136–137 °C (in a sealed tube) (lit.[5g] 136–137.5 °C); $[\alpha]^{20}D$ 0° (*c* 0.90, ethanol).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.87; H, 8.22.

(−)-*endo*-2-(1-Hydroxyethyl)bicyclo[2.2.1]hept-5-ene (16). A solution of 8.54 g of (−) aldehyde **10** in 100 ml of dry ether was added at room temperature to methylmagnesium bromide which was prepared from a large excess of methyl bromide and 4.25 g of magnesium in 100 ml of dry ether. The mixture was refluxed for 2 h and then cooled with ice. Saturated aqueous ammonium chloride solution was added to the chilled mixture. The organic layer was washed with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, and water, and dried over magnesium sulfate. After evaporation of the solvent, the residue was distilled to yield 8.81 g of **16** (91%): bp 104–106 °C (28 mm); $[\alpha]^{27}D$ −48.3° (*c* 0.47, ethanol); ir (film) 3350, 3020, 1100, and 720 cm^{-1}.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.27.

(−)-*endo*-2-Acetylbicyclo[2.2.1]hept-5-ene (17). A solution of 6.60 g of (−) alcohol **16** in 10 ml of dry methylene chloride was added to Collins' reagent which was prepared from 29.0 g of chromium trioxide, 45.0 g of dry pyridine, and 660 ml of dry methylene chloride. The reaction mixture was then stirred for 15 min at room temperature. The organic layer was separated and the residue was rinsed with the same solvent. Combined organic solutions were

worked up by the same manner described above. The solvent was evaporated and the residue was distilled to yield 5.42 g of **17** (83%): bp 83 °C (15 mm); $[\alpha]^{22}D$ −93.6° (*c* 1.23, ethanol); ir (film) 3080, 1705, 1355, 1185, 1175, and 720 cm^{-1}.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.57; H, 8.95.

(−)-2-Methyl-3-oxatetracyclo[4.2.1.0^{2,5}.0^{4,8}]nonane (18). A solution of 5.10 g of (−) ketone **17** in 300 ml of benzene was irradiated for 51 h with a mercury lamp (SHL-100UV, Toshiba) under a nitrogen atmosphere. After evaporation of benzene, the residue was chromatographed on silica gel. Fractions eluted with pentane–ether (9:1 volume) were distilled to give 2.87 g of **18** (56%): bp 101–105 °C (80 mm); $[\alpha]^{22}D$ −12.0° (*c* 0.88, ethanol); ir (film) 1105, 980, 858, 845, and 835 cm^{-1}; NMR (CCl_4) δ 1.34 (s, 3 H), 1.47–1.65 (m, 4 H), 1.70–2.20 (m, 2 H), 2.45–2.70 (m, 2 H), and 4.37–4.46 (m, 1 H).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.44; H, 8.95.

(+)-4-Methylenetricyclo[3.3.0.0^{3,7}]octan-2-ol (19). To a solution of 6.0 g of diethylamine in 40 ml of dry benzene was added 42 ml of a 15% solution of butyllithium in hexane with ice cooling under a nitrogen atmosphere. After the reaction mixture was warmed to room temperature, a solution of 3.30 g of (−) oxetane **18** in 40 ml of dry benzene was added to the mixture. After refluxing for 32 h under a nitrogen atmosphere, it was poured onto ice and extracted with benzene. The extract was washed with saturated aqueous ammonium chloride and water, and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on neutral alumina (Woelm activity III) and fractions eluted with pentane–ether (4:1 volume) were distilled to give 876 mg of **19** (27%): bp 104 °C (45 mm); $[\alpha]^{26}D$ +13.2° (*c* 0.60, ethanol); ir (film) 3450, 3050, 1670, 1410, 1265, 1110, 1080, 1065, 880, and 815 cm^{-1}.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.09; H, 8.94.

(−)-4-Methylenetricyclo[3.3.0.0^{3,7}]octan-2-one (20). A solution of 850 mg of (+) alcohol **19** in 2 ml of dry methylene chloride was added to Collins' reagent from 4.4 g of chromium trioxide, 6.9 g of dry pyridine, and 110 ml of dry methylene chloride. The mixture was agitated for 20 min at room temperature. After working up by the same method described above, the solvent was evaporated. The residue was chromatographed on neutral alumina (Woelm activity III) and fractions eluted with pentane were distilled to yield 531 mg of **20** (63%): bp 123 °C (65 mm); $[\alpha]^{25}D$ −36.6° (*c* 1.24, ethanol); ir (film) 3080, 1765, 1672, 1110, 880, and 835 cm^{-1}; NMR (CCl_4) δ 1.64–1.77 (m, 4 H), 2.34–2.42 (m, 1 H), 2.45–2.57 (m, 1 H), 2.65–2.75 (m, 1 H), 2.80–2.90 (m, 1 H), 4.53 (s, 1 H), and 4.67 (s, 1 H); uv max (isooctane) 292 nm sh (ε 383), 298 sh (410), 300.5 (445), 306.5 sh (367); CD (*c* 1.87 × 10^{-2}, isooctane) [θ] (nm) +4.3 × 10^4 (190), +9.8 × 10^4 (199.5), 0 (224), 0 (245), −1.79 × 10^4 (301), −1.65 × 10^4 sh (307), 0 (335).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.83; H, 7.57.

(−)-*endo*-2-(1-Hydroxy-2-methylpropyl)bicyclo[2.2.1]hept-5-ene (22). A solution of 6.70 g of (−) aldehyde **10** in 60 ml of dry ether was added to isopropylmagnesium bromide which was prepared from 12.3 g of isopropyl bromide and 2.43 g of magnesium in 40 ml of dry ether. The reaction mixture was gently refluxed for 4 h. To the chilled mixture was added saturated aqueous ammonium chloride solution and the inorganic solid was filtered off. The filtrate was washed with water and dried over magnesium sulfate. Removal of the solvent gave a solid, which was washed with cold hexane to yield 5.29 g of **22** (58%): mp 85–87 °C; $[\alpha]^{20}D$ −31.6° (*c* 0.47, ethanol); ir (KBr) 3330, 3050, 1390, 1370, 1000, and 720 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.19; H, 10.84.

(−)-*endo*-2-(1-Oxo-2-methylpropyl)bicyclo[2.2.1]hept-5-ene (23). A solution of 5.13 g of (−) alcohol **22** in 5 ml of dry methylene chloride was added to Collins' reagent from 18.5 g of chromium trioxide, 31.2 g of dry pyridine, and 460 ml of dry methylene chloride. The reaction mixture was then stirred for 20 min at room temperature. After working up as usual, the solvent was evaporated and the residue was distilled to give 4.47 g of **23** (88%): bp 111–112 °C (20 mm); $[\alpha]^{19}D$ −71.9° (*c* 0.42, ethanol); ir (film) 3080, 1705, 1380, 1355, and 720 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.23; H, 9.83.

(−)-2-Isopropyl-3-oxatetracyclo[4.2.1.0^{2,5}.0^{4,8}]nonane (24). A solution of 4.40 g of (−) ketone **23** in 600 ml of benzene was irradiated with a mercury lamp (SHL-100UV, Toshiba) for 35 h. After evaporation of the benzene, the residue was chromatographed on silica gel and fractions eluted with pentane were distilled to give 3.58 g of **24** (81%): bp 101–104 °C (20 mm); $[\alpha]^{20}D$ −5.78° (*c* 0.47, ethanol); ir (film) 1383, 1365, 1110, 990, and 910 cm^{-1}; NMR (CCl_4) δ 0.90 (d, 3 H, *J* = 7 Hz), 1.00 (d, 3 H, *J* = 7 Hz), 1.40–1.80 (m, 5 H), 1.87–2.00 (m, 1 H), 2.25–2.38 (m, 1 H), 2.52–2.70 (m, 1 H), 2.77–2.90 (m, 1 H), and 4.42–4.50 (m, 1 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.19; H, 9.81.

(+)-4-Isopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-ol (25). A solution of 1.83 g of (−) oxetane **24** in 15 ml of dry benzene was added to lithium diethylamide which was prepared from 3.43 g of diethylamine, 25 ml of a 15% solution of butyllithium in hexane, and 23 ml of dry benzene. The reaction mixture was refluxed for 130 h under a nitrogen atmosphere. After usual working up, the solvent was evaporated and the residue was chromatographed on silica gel. Fractions eluted with pentane gave 0.45 g of **24** (24%) and succeeding fractions eluted with the same solvent afforded an alcoholic product which was distilled to yield 0.44 g of **25** (24%): bp 120–122 °C (20 mm); $[\alpha]^{17}D$ +18.3° (*c* 0.43, ethanol); ir (film) 3500, 1412, 1265, 1205, 1112, 1100, 1080, and 1065 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.44; H, 9.74.

(+)-4-Isopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (21). A solution of 265 mg of (+) alcohol **25** in 5 ml of dry methylene chloride was added to Collins' reagent from 1.0 g of chromium trioxide, 1.6 g of dry pyridine, and 25 ml of dry methylene chloride, and the solution was stirred for 20 min at room temperature. After usual working up, the solvent was evaporated and the residue was chromatographed on silica gel. Fractions eluted with pentane–ether (1:1 volume) were distilled to yield 220 mg of **21** (84%): bp 150–155 °C (20 mm); $[\alpha]^{20}D$ +37.6° (*c* 0.61, ethanol); ir (film) 1755, 1440, 1365, 1275, 1140, 1115, and 820 cm^{-1}; NMR (CCl_4) δ 1.12–1.20 (m, 2 H), 1.5–1.6 (m, 2 H), 1.64 (s, 3 H), 1.69 (s, 3 H), 2.22–2.40 (m, 1 H), 2.63–2.75 (m, 2 H), and 2.90–3.10 (m, 1 H); uv max (isooctane) 290 nm sh (ε 521), 296 sh (607), 298 (616), 304 sh (538); CD (*c* 2.88 × 10^{-4}, isooctane) [θ] (nm) +3.26 × 10^4 (214), 0 (242), 0 (260), −1.37 × 10^4 (298.5), −1.34 × 10^4 sh (304), 0 (320).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.30; H, 8.76.

(±)-2-Acetoxy-4-methylenetricyclo[3.3.0.0^{3,7}]octane (26). A solution of 2.45 g of (±) alcohol **19** in 30 ml of pyridine was mixed with 10.0 g of acetic anhydride. After stirring for 3 h at 0–5 °C, the solution was kept overnight at room temperature and then poured onto ice. It was worked up as usual and the solvent was evaporated. The residue was distilled to give 1.94 g of **26** (60%): bp 125 °C (20 mm); ir (film) 3080, 1735, 1675, 1360, 1050, and 870 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.41; H, 8.02.

(±)-2-Acetoxytricyclo[3.3.0.0^{3,7}]octan-4-one (27). A solution of 1.94 g of (±) acetate **26** in 75 ml of chloroform was cooled to −78 °C and then treated with ozone until an intense blue color persisted. The solution was allowed to warm to room temperature and the excess ozone was purged by passing nitrogen through the solution. The reaction mixture was added to a mixture of 3.0 g of zinc dust, 5 ml of acetic acid, 125 ml of chloroform, and 500 ml of water, and the mixture was agitated for 8 h at room temperature. After the organic layer was separated and washed with saturated aqueous sodium carbonate and water, it was dried over magnesium sulfate. Evaporation of the solvent gave an oily product, which was distilled to give 0.89 g of **27** (45%): bp 150 °C (10 mm); ir (film) 1770, 1740, 1370, 1270, 1230, 1200, and 1045 cm^{-1}; NMR (CCl_4) δ 1.65–1.90 (m, 4 H), 1.97 (s, 3 H), 2.16–2.33 (m, 2 H), 2.55–2.77 (m, 2 H), and 4.54–4.65 (m, 1 H).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.34; H, 6.72.

(−)-2-Oxatricyclo[4.3.0.0^{4,8}]nonane (7). A solution of 4.00 g of (−) alcohol **15** in 300 ml of benzene was irradiated with a mercury lamp (SHL-100UV, Toshiba) for 49 h. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel. Fractions eluted with pentane gave a solid which was sublimed to yield 850 mg of **7** (21%): mp 121–124 °C (in a sealed tube); $[\alpha]^{15}D$ −142° (*c* 0.70, ethanol); ir (Nujol) 1025, 945, 850, and 825 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.6 (m, 4 H), 1.7–1.9 (m, 1 H), 2.0–2.3 (m, 2 H), 2.43–2.58 (m, 1 H), 2.63–2.80 (m, 1 H), 3.5–3.7 (d, d, 1 H, *J* = 9, 3 Hz), 3.85–4.00 (d, d, 1 H, *J* = 9, 1.5 Hz), and 4.1–4.2 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.56; H, 9.69.

(+)-*endo*-6-Methoxycarbonylbicyclo[2.2.1]heptan-2-one (30). A solution of 29 g of iodine and 112 g of potassium iodide in 340 ml of water was added to a solution of 15.0 g of (+) carboxylic acid **29** in 680 ml of 0.5 N aqueous sodium bicarbonate solution. The mixture was kept overnight at room temperature and then extracted with chloroform. The extract was washed with aqueous sodium thiosulfate, aqueous sodium bicarbonate, and water, and was dried over magnesium sulfate. Evaporation of the solvent gave 25.0 g of **31** (86%), to which 500 ml of 10% aqueous sodium hydroxide solution was added. The mixture was boiled for 1 h and then cooled with ice. After extraction with chloroform, the extract was washed with aqueous sodium thiosulfate and water, and was dried over magnesium sulfate. After evaporation of the solvent, the residue was distilled to give 4.40 g of *endo*-6-carboxybicyclo[2.2.1]heptan-2-one: bp 170–172 °C (5 mm); $[\alpha]^{13}D$ +16.2° (*c* 0.63, ethanol). The carboxylic acid was treated with a solution of diazomethane in ether by the usual manner. Distillation of the product yielded 4.40 g of **30** (24%): bp 144–146 °C (20 mm); $[\alpha]^{15}D$ +14.1° (*c* 1.15, ethanol); ir (film) 1750, 1735, 1220, 1195, and 1175 cm^{-1}.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.27.

(−)-*endo*-6-Hydroxymethylbicyclo[2.2.1]heptan-2-ol (32). A solution of 3.97 g of (+) keto ester **30** in 50 ml of dry ether was added to a suspension of 0.95 g of lithium aluminum hydride in 50 ml of dry ether, and the mixture was refluxed for 4 h. After cooling with ice, saturated aqueous ammonium chloride solution was added to the chilled mixture and inorganic solid was filtered off. The filtrate was washed with water and dried over magnesium sulfate. After removal of the solvent, the residue was distilled to give 2.51 g of **32** (75%): bp 147 °C (5 mm); $[\alpha]^{15}D$ −1.05° (*c* 0.72, ethanol); ir (film) 3300, 1120, 1045, and 1030 cm^{-1}.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.58; H, 10.05.

(−)-2-Oxatricyclo[4.2.1.$0^{4,8}$]nonane (8). A solution of 1.02 g of (−) diol **32** in 5 ml of dry pyridine was mixed with 1.36 g of *p*-toluenesulfonyl chloride at 0–5 °C. After stirring for 2 h at this temperature and keeping overnight at room temperature, the solution was poured onto ice and acidified with hydrochloric acid. After extraction with ether, the extract was washed with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, and water, and was dried over magnesium sulfate. Removal of the solvent gave an oily product on which pentane was added. After an immiscible substance was discarded, the solution was concentrated to give a wax. This was sublimed at 70–80 °C (5 mm) to yield 220 mg of **8** (25%): mp 117–119 °C (in a sealed tube); $[\alpha]^{15}D$ −31.7° (*c* 1.15, ethanol); ir (Nujol) 1145, 1130, 1080, 1040, 1005, 990, 948, 888, and 800 cm^{-1}; NMR ($CDCl_3$) δ 1.0–1.5 (m, 4 H), 1.5–2.0 (m, 2 H), 2.05–2.40 (m, 2 H), 2.50–2.70 (m, 1 H), 3.65–3.90 (m, 2 H), and 4.20–4.42 (m, 1 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.66; H, 9.65.

Registry No.—**7**, 58001-92-6; **8**, 58001-93-7; **10**, 58001-94-8; **11**, 22398-42-1; **14**, 20507-53-3; **15**, 42070-82-6; **16**, 13307-34-1; **17**, 58001-95-9; **18**, 58001-96-0; **19**, 57969-19-4; **20**, 57969-20-7; **21**, 57969-21-8; **22**, 13307-39-6; **23**, 58001-97-1; **24**, 58001-98-2; **25**, 57969-22-9; **26**, 57969-23-0; **27**, 57969-24-1; **29**, 58001-99-3; **30**, 57969-25-2; **32**, 933-91-5; *endo*-6-carboxybicyclo[2.2.1]heptan-2-one, 58002-00-9.

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Thermal Rearrangements of *trans*-1-Trimethylsiloxy-1-vinylcyclotridec-3-ene

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The thermal rearrangement of *trans*-1-trimethylsiloxy-1-vinylcyclotridec-3-ene (**13t**), followed by hydrolysis of the enol ethers, gives two products in comparable amounts: the [1,3] shift ring-expanded ketone, *trans*-cyclopentadec-5-en-1-one (**15t**), and the [3,3] shift product, 4-vinylcyclotridecanone (**14**). Unlike the earlier medium-sized systems, the ratio of [1,3] shift to [3,3] shift product varies with temperature. The activation parameters for the [1,3] shift compare reasonably with similar systems while those for the [3,3] shift are intermediate between the medium-sized ring cases and open-chain systems.

Previous papers in this series[1-3] have described the thermal rearrangements of a set of compounds exemplified by structure **10t**. The major pathway (>70%) for **10t** and for two analogues, the cis isomer, **10c**, and for the cis nine-membered-ring case, **9c**, is a [1,3] sigmatropic shift ring expansion with retention of the ring double bond stereochemistry (e.g., **1**). The [3,3] shift product (e.g., **3**) and the [1,3] shift product with double bond isomerization (e.g., **2**) are formed in minor amounts. The cis eight-membered case, **8c**, is more complex, in that the kinetically preferred pathway is a [1,3] sigmatropic shift ring contraction leading to 1-trimethylsiloxy-1,2-divinylcyclohexane which can then