water, 5% hydrochloric acid, and water successively and dried (Na_2SO_4). Removal of the solvent and sublimation afforded the hydrocarbon 4 (95 mg, 64.1%) which was identical with the sample obtained via **21** on GLC analysis.

Acknowledgment. We are grateful to Professor Y. Hirata, Dr. K. Yamada, Mr. S. Manabe, and Mr. K. Wakamatsu (Department of Chemistry, Nagoya University) for obtaining the ^{13}C NMR spectra, and we are deeply indebted to them for their generosity. We are also grateful to Professors P. v. R. Schleyer and E. Osawa for a preprint of their manuscript (ref 3b) and the empirical force field calculation results on **1**.

Registry No.—**1**, 59014-95-8; **4**, 55638-02-3; **10a**, 50782-13-3; **13**, 41171-93-1; **13** oximino ketone, 62881-87-2; **14**, 62881-88-3; **15n**, 62881-89-4; **15n** Na salt, 62959-91-5; **15n** acid chloride, 62881-90-7; **15x**, 62959-92-6; **16n**, 62881-91-8; **17**, 62881-92-9; **18** Na salt, 62881-93-0; **19**, 62881-94-1; **20**, 62881-95-2; **20** ketene dimer, 62881-97-4; **21**, 62881-96-3; 2-adamantanecarboxaldehyde, 39750-93-1; *p*-toluenesulfonylhydrazide, 1576-35-8; isoamyl nitrite, 110-46-3; oxalyl chloride, 79-37-8; *tert*-butyl hydroperoxide, 75-91-2.

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Synthesis and Absolute Configuration of Optically Active C_2-Bishomocubane (Pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane)[1]

Masao Nakazaki* and Koichiro Naemura

Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka, Japan

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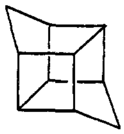
(−)-(1*S*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*)-C_2-Bishomocubane (**4**) and (+)-(1*R*,2*R*,3*S*,4*R*,5*R*,7*S*,8*S*,9*S*)-C_2-bishomocuban-6-one (**14**) were prepared by photochemical ring closure of (+)-*endo*-dicyclopentadiene-1,8-dione 8-ethylene ketal (**12**) followed by successive removal of the substituent groups. Their absolute configurations were deduced from analyses of the CD spectra of (+)-C_2-bishomocuban-6-one (**14**) as well as other synthetic intermediates.

Theoretically, there are four ways to desymmetrize the highly symmetrical cubane molecule (O_h symmetry) furnishing bishomocubanes by insertion of each of two methylene groups between its eight methine groups situated on the eight corners. Among these four types of bishomocubanes (**1**,[2] **2**,[3] **3**, **4**[4]), only pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane (**4**) (C_2 symmetry) is chiral and hereafter we shall call this species C_2-bishomocubane[5] in this communication.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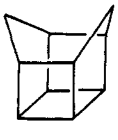
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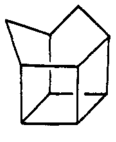
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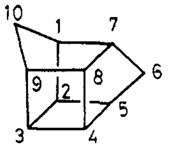

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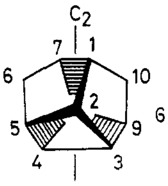
Inspection of the structure formula (**5**) of C_2-bishomocubane, which emphasizes the C_2 axis, reveals the presence of bicyclo[2.2.2]octane moiety **6** frozen in a twisted conformation, being held in position by two methylene groups and one single bond which respectively link 2–8, 3–6, and 5–7 positions of the bicyclo[2.2.2]octane. Also discernible in **5** are twist-brendane (**7**)[7] and di-twist-brendane (**8**)[8] frameworks, both of which have been prepared in the optically active forms with known absolute configurations in our laboratory.



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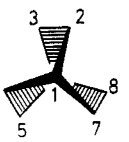

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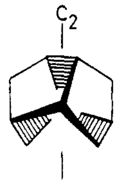

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We have been interested in the syntheses and absolute configurations of high-symmetry chiral (gyrochiral)[11] cage-shaped molecules, and previous papers from our laboratory have reported the preparations and absolute configurations of various tricyclic cage-shaped compounds; e.g., (−)-twist-brendane (**7**),[7] (−)-brexane (**9**),[11] (+)-twistane (**10**).[12]


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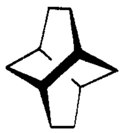
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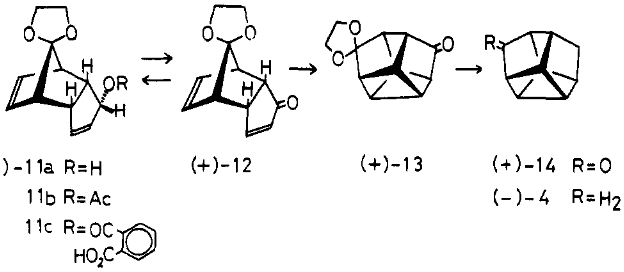
Our current interest concerning the absolute configuration determination of cage-shaped molecules by means of microbiological reduction[13] requires C_2-bishomocuban-6-one (pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one) (**14**) in the optically active form, and in this paper we report the preparations of (−)-C_2-bishomocubane (**4**) and (+)-C_2-bishomocuban-6-one (**14**) together with their chiroptical properties, which eventually established their absolute configurations.

Results and Discussion

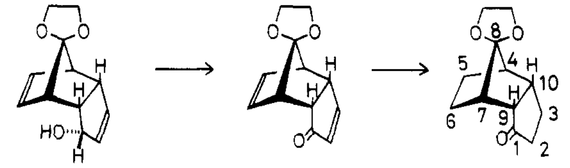
Syntheses of (+)-C_2-Bishomocuban-6-one (14) and (−)-C_2-Bishomocubane (4). Heating with sodium methoxide converted 2,5-dibromocyclopentanone ethylene ketal into *endo*-dicyclopentadiene-1,8-dione bisethylene ketal,[4] partial hydrolysis of which removed one of the protective groups to afford *endo*-dicyclopentadiene-1,8-dione 8-ethylene ketal (**12**). Photochemical ring closure[14] of this tricyclic α,β-unsaturated ketone was Chapman's[4] key strategy to secure the pentacyclic framework of C_2-bishomocubane (**13**). Of the various possible stages to accomplish the optical resolution, the stage at this compound was our choice, since we expected that the optically active unsaturated ketone **12** could be led to the *cis*-perhydroindanone derivative **15** (vide infra), whose CD spectrum could be compared with those of *cis*-perhydroindanone derivatives with known absolute configurations, furnishing informations indicative of the stereochemistry of the optically active precursor **12**.

Scheme I



(−)-11a R=H (+)-12 (+)-13 (+)-14 R=O
11b R=Ac (−)-4 R=H$_2$
11c R=OC HO$_2$C

Scheme II



(+)-11a (−)-12 (−)-15

Actual optical resolution was accomplished by working with the unsaturated alcohol **11a** secured by lithium aluminum hydride reduction of **12**. The oily unsaturated alcohol **11a** was converted to the crystalline acetate **11b** which was purified until it exhibited a single acetyl peak in the NMR spectrum corresponding to the endo-isomer **11b**; the stereochemistry was assumed on the basis of hydride attack from the less hindered side, which has been supported by ample examples in analogous tricyclic ketones.[15] Lithium aluminum hydride reduction of the purified acetate **11b** regenerated the endo-alcohol **11a** in crystalline form, which was converted to the hydrogen phthalate **11c**. Resolution was carried out by working with (+)-2-(1-aminoethyl)naphthalene as the resolving agent. Recrystallization of the salt from acetone resulted in complete resolution, as evidenced by the specific rotations of the isolated enantiomeric alcohols **11a**: (−)-isomer, $[\alpha]^{12}{}_D$ −142.2°; (+)-isomer, $[\alpha]^{15}{}_D$ +142.5°. Collins' oxidation of the (−)-alcohol **11a** afforded the (+)-unsaturated ketone **12**,[16] which was dissolved in ether and irradiated with a medium-pressure mercury lamp for 3 h to produce an 82% yield of (+)-pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione 6-ethylene ketal (**13**): mp 60–62 °C; $[\alpha]^{14}{}_D$ +95.9°. Since attempts to hydrolyze the ketal protective group and thereby secure C_2-bishomocubane-6,10-dione (C_2 symmetry) were unsuccessful, removal of the functional groups to furnish C_2-bishomocubane was carried out in two steps. The Wolff–Kishner reduction followed by hydrolysis with 10% sulfuric acid converted the (+)-**13** into (+)-C_2-bishomocuban-6-one (**14**), $[\alpha]^{15}{}_D$ +11.0°, whose keto group was finally removed by the second Wolff–Kishner reduction to furnish (−)-C_2-bishomocubane (**4**): mp 136–138 °C; $[\alpha]^{19}{}_D$ −33.8°.

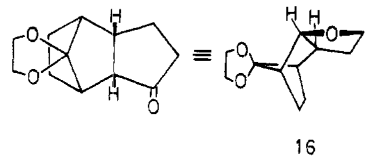
CD Spectra and Absolute Configurations. (−)-*endo*-Dicyclopentadiene-1,8-dione 8-ethylene ketal (**12**) (the enantiomer of the precursor of (−)-C_2-bishomocubane (**4**)) was prepared by Collins' oxidation of (+)-**11a**. (−)-Unsaturated ketone **12** was hydrogenated with the aid of 5% palladium-on-carbon catalyst affording the (−)-saturated ketone **15**.

A negative Cotton effect observed for the (−)-saturated tricyclic ketone **15** (Table I) is indicative of the (9*S*,10*S*) configuration for this ketone, as can be seen from the application of the octant rule to the octant projection (**16**). Furthermore, this assignment of absolute configuration was supported by the negative Cotton effects reported for *cis*-(8*R*,9*R*)-hexahydroindan-1-one (**17**)[17] and *cis*-(7*R*,8*S*)-3,3,6-trimethylbicyclo[3.3.0]octan-1-one (**18**),[18] both of which have closely related stereochemistry to the (−)-saturated tricyclic ketone **15**.

Table I. CD Spectra of (+)-C_2-Bishomocubane-6,10-dione Monoethylene Ketal (13), (+)-C_2-Bishomocuban-6-one (14), and (−)-Saturated Bicyclic Ketone (15) (in isooctane)

(+)-13[a]		(+)-14[a]		(−)-15[a]	
[θ]	nm	[θ]	nm	[θ]	nm
$+9.36 \times 10^3$ sh	297	$+1.22 \times 10^3$ sh	298	-3.70×10^3 sh	287.5
$+1.02 \times 10^4$	302	$+1.29 \times 10^3$	301.5	-5.95×10^3	296.5
$+1.00 \times 10^4$ sh	306	$+1.23 \times 10^3$ sh	304	-7.58×10^3	306.7
$+8.11 \times 10^3$ sh	312.5	$+9.48 \times 10^2$ sh	312	-6.75×10^3	318.3
				-3.10×10^3	330.5

[a] Registry no: (+)-**13**, 62928-73-8; (+)-**14**, 62928-74-9; (−)-**15**, 62851-16-5.



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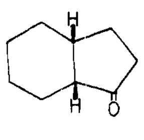

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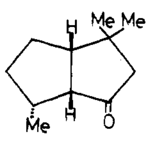

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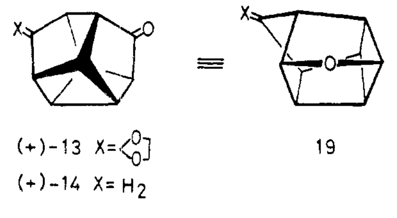
These conclusions suggest (1*R*,2*R*,3*R*,4*R*,5*S*,7*R*,8*R*,9*S*) and (1*R*,2*R*,3*S*,4*R*,5*R*,7*S*,8*S*,9*S*) configurations, respectively, to the pentacyclic intermediates, (+)-**13** and (+)-**14**, and this eventually assigns the (1*S*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*) configuration to (−)-C_2-bishomocubane (**4**). Table I also records the Cotton effects of (+)-C_2-bishomocubane-6,10-dione monoethylene ketal (**13**) and (+)-C_2-bishomocuban-6-one (**14**). Examination of the octant projectons (**19**) given with the stereochemical representations of these pentacyclic ketones reveals that the groups (X) which should influence the Cotton effect fall in the positive octant region, predicting positive Cotton effects of these ketones. Observed positive Cotton effects (Table I) consistent with the octant projection (**19**) confirm our previous assignments of absolute configurations based on the CD spectrum of the tricyclic ketone **15**.



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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-DPI-SL automatic polarimeter. Circular dichroism data were measured on a JASCO-J-40 spectropolarimeter. Elemental analyses were performed on a Yanagimoto CHN-Corder type II. All melting points and boiling points are uncorrected.

***endo*-Dicyclopentadiene-1,8-dione 8-Ethylene Ketal (12).** A mixture of *endo*-dicyclopentadiene-1,8-dione bisethylene ketal[4] (mp 90–92 °C) (35.0 g, 0.141 mol), 35 mL of hydrochloric acid, and 350 mL of tetrahydrofuran was stirred for 1 h at room temperature and then diluted with 1.5 L of ether. The ethereal solution was washed with water, saturated sodium bicarbonate solution, and water, and dried over magnesium sulfate. Evaporation of the solvent gave a solid which was recrystallized from ethanol to yield 22.1 g of **12** (yield 77%): mp 94–95 °C (lit.[4] mp 93–94 °C).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.36; H, 5.90.

***endo*-1-Acetoxydicyclopentadien-8-one Ethylene Ketal (11b).** A solution of **12** (9.52 g, 0.0467 mol) in 200 mL of dry ether was added dropwise to a suspension of lithium aluminum hydride (1.20 g, 0.0316 mol) in 50 mL of dry ether, and the mixture was gently refluxed for 3 h. Saturated ammonium chloride solution was carefully added to the chilled reaction mixture. After an inorganic solid was filtered off, the filtrate was dried over magnesium sulfate. Evaporation of the solvent gave 9.00 g of an oily residue which was acetylated with 9.00 g of acetic anhydride and 25 mL of dry pyridine. The reaction mixture was stirred for 6 h at 0–5 °C, and then allowed to stand overnight at room temperature. The mixture was poured onto ice and the separated solid was collected. This was recrystallized from hexane to give 6.01 g of **11b** (yield 52% based on **12**): mp 72–73 °C; IR (KBr) 3025, 1725, 1298, 1245, 1090, 1038, 785, and 770 cm^{-1}; NMR ($CDCl_3$) δ 1.4–1.7 (m, 1 H), 2.04 (s, 3 H), 2.49–2.80 (m, 2 H), 2.90–3.46 (m, 2 H), 3.75–3.90 (m, 4 H), and 5.40–6.20 (m, 4 H).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.50; H, 6.59.

***endo*-1-Hydroxydicyclopentadiene-8-one Ethylene Ketal (11a).** A solution of **11b** (8.36 g, 0.0337 mol) in 200 mL of dry ether was added dropwise to a suspension of lithium aluminum hydride (2.00 g, 0.0526 mol) in 100 mL of dry ether, and the mixture was refluxed for 5 h. The reaction mixture was cooled with ice, and saturated ammonium chloride solution was added carefully to the chilled mixture. The precipitated inorganic solid was filtered, and the filtrate was dried over magnesium sulfate. Evaporation of the solvent gave a solid which was recrystallized from ether to yield 5.14 g of **11a** (yield 74%): mp 95–97 °C; IR (KBr) 3510, 3040, 1280, 1118, 1100, 1082, 1045, 1020, 1005, 785, and 770 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.85; H, 6.81.

Optical Resolution of 11a. Phthalic anhydride (22.6 g, 0.153 mol) was added to a chilled solution of **11a** (31.5 g, 0.153 mol) in 50 mL of pyridine, and the mixture was stirred for 5 h in an ice bath. After standing overnight at room temperature, the reaction mixture was poured onto ice. It was acidified with hydrochloric acid and extracted with ether. The extract was washed with water and dried over magnesium sulfate. Evaporation of the solvent gave a viscous oily product which, without further purification, was dissolved in 700 mL of acetone. To the solution was added (+)-2-(1-aminoethyl)naphthalene (24.0 g, 0.151 mol) with stirring at room temperature and then this mixture was boiled for 3 h. Standing overnight at room temperature deposited a solid which was collected to yield 56.5 g of the hydrogen phthalate salt: $[\alpha]^{13}_{D}$ +3.3° (*c* 0.144, $CHCl_3$). Fractional recrystallization of the salt from acetone (six times) yielded 30.2 g of the levorotatory salt; $[\alpha]^{12}_{D}$ −57.7° (*c* 0.147, $CHCl_3$). After this salt (29.0 g) was mixed with 300 mL of 5% aqueous potassium hydroxide solution, the mixture was stirred for 24 h at room temperature, and then extracted with ether. The extract was washed with 5% hydrochloric acid and water successively and dried over magnesium sulfate. Evaporation of the solvent gave 7.49 g of (−)-**11a** (yield 65%); $[\alpha]^{13}_{D}$ −123° (*c* 0.499, $CHCl_3$). Recrystallization of this from ether yielded 4.11 g of (−)-**11a**: mp 135–136 °C; $[\alpha]^{12}_{D}$ − 142.2° (*c* 0.449, $CHCl_3$). The specific rotation did not change with further recrystallization.

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.68; H, 6.75.

Concentration of the combined mother liquors precipitated the dextrorotatory salt (8.91 g), $[\alpha]^{12}_{D}$ +61.3° (*c* 0.400, $CHCl_3$), which was treated with 5% aqueous potassium hydroxide solution. The same procedure described above for the enantiomer yielded 1.50 g of (+)-**11a** (yield 43%): $[\alpha]^{13}_{D}$ +139.4° (*c* 0.160, $CHCl_3$). Recrystallization of this from acetone afforded 1.37 g of (+)-**11a**: mp 135.5–136 °C; $[\alpha]^{15}_{D}$ +142.5° (*c* 0.175, $CHCl_3$).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.73; H, 6.81.

(+)-*endo*-Dicyclopentadiene-1,8-dione 8-Ethylene Ketal (12). A solution of (−)-**11a** (1.51 g, 7.40 mmol), $[\alpha]^{12}_{\mathrm{D}}$ −142.2°, in 15 mL of dry methylene chloride was added to Collins' reagent, which was prepared from chromium trioxide (4.40 g, 44.0 mmol), dry pyridine (6.95 g, 87.9 mmol), and 140 mL of dry methylene chloride by the usual method.[19] After the mixture was stirred for 20 min at room temperature, the organic layer was separated by decantation. The residue was rinsed with methylene chloride. The combined methylene chloride solutions were washed successively with diluted hydrochloric acid, saturated sodium bicarbonate, and water. After drying over magnesium sulfate, the solvent was evaporated to give a solid which was recrystallized from ether to yield 1.33 g of **12** (yield 89%): mp 44.5–45.5 °C; $[\alpha]^{14}_{\mathrm{D}}$ +117.6° (*c* 0.407, $CHCl_3$); IR (KBr) 3050, 1695, 1580, 1300, 1232, 1105, 1070, 795, and 780 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.34; H, 5.92.

(−)-*endo*-Dicyclopentadiene-1,8-dione 8-Ethylene Ketal (12). Oxidation of (+)-**11a** (1.00 g, 5.21 mmol), $[\alpha]^{12}_{\mathrm{D}}$ −125.2°, was carried out by the same procedure described above and yielded 0.55 g of (−)-**12** (yield 55%): bp 130–133 °C (0.4 mm); $[\alpha]^{12}_{\mathrm{D}}$ −102.7° (*c* 1.25, $CHCl_3$); CD (*c* 1.18×10^{-2}, isooctane) $[\theta]$ (nm) $+3.97 \times 10^4$ (213), 0 (265), -1.29×10^3 sh (304), -1.78×10^3 sh (310), -3.09×10^3 (323), -3.94×10^3 (347.5), -3.48×10^3 (353.5), -1.41×10^3 (372), and 0 (390).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.32; H, 5.91.

(−)-*endo*-Tetrahydrodicyclopentadiene-1,8-dione 8-Ethylene Ketal (15). A solution of (−)-**12** (500 mg, 2.45 mmol), $[\alpha]^{12}_{\mathrm{D}}$ −102.7°, in 25 mL of ethyl acetate was shaken at room temperature in a hydrogenation flask with 80 mg of 5% palladium-on-carbon at 1 atm of hydrogen. After the hydrogen absorption had ceased, the catalyst was removed by filtration. The filtrate was condensed and the residue was distilled to give 450 mg of **15** (yield 89%): bp 115–118 °C (0.35 mm); $[\alpha]^{15}_{\mathrm{D}}$ −189° (*c* 0.441, $CHCl_3$); IR (neat film) 1725, 1323, 1128, 1075, 1048, 1023, 1012, and 953 cm^{-1}; CD (*c* 1.00×10^{-2}, isooctane) $[\theta]$ (nm) 0 (235), -3.70×10^3 sh (287.5), -5.95×10^3 (296.5), -7.58×10^3 (306.7), -6.75×10^3 (318.3), -3.10×10^3 (330.5), and 0 (348).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.09; H, 7.71.

(+)-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione 6-Ethylene Ketal (13). A solution of (+)-ketone ketal **12** (1.00 g, 4.90 mmol), $[\alpha]^{14}_{\mathrm{D}}$ +117.6°, in 200 mL of dry ether was irradiated with a medium pressure mercury lamp (SHL-100UV, Toshiba) for 3 h at 5–6 °C. The ether was removed under reduced pressure, and the residue was chromatographed on neutral alumina (Woelm, activity III). Combined fractions eluted with benzene gave a solid, which was recrystallized from ether. Cooling at −78 °C furnished 817 mg of **13** (yield 82%): mp 60–62 °C (lit.[4] racemate, mp 58–60 °C); $[\alpha]^{14}_{\mathrm{D}}$ +95.9° (*c* 0.323, $CHCl_3$); IR (KBr) 1755, 1720, 1325, 1105, 1090, 1055, 1010, and 945 cm^{-1}; CD (*c* 5.62×10^{-3}, isooctane) $[\theta]$ (nm) 0 (242), $+9.36 \times 10^3$ sh (297), $+1.02 \times 10^4$ (302), $+1.00 \times 10^4$ sh (306), $+8.11 \times 10^3$ sh (312.5), and 0 (340); λ_{max} (isooctane) 298 sh (ϵ 24.7), 302 (25.5), 306.5 sh (24.2), and 314 nm sh (18.6).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.42; H, 5.93.

(+)-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (14). To a mixture of potassium hydroxide (0.42 g), 85% hydrazine hydrate, and triethylene glycol (7.4 mL) was added (+)-**13** (1.00 g, 4.90 mmol), $[\alpha]^{14}_{\mathrm{D}}$ +95.9°, and the mixture was heated in an oil bath. When the bath temperature was raised to ca. 70 °C, the mixture gave a clear solution, which was stirred for 1.5 h at 150–160 °C and then for an additional 3 h at 200 °C. After cooling to room temperature, it was diluted with 10 mL of water and extracted with ether. The extract was washed successively with diluted hydrochloric acid, saturated sodium bicarbonate solution, and water. After drying over magnesium sulfate, the solvent was evaporated to give the residue, which was mixed with 10% sulfuric acid and stirred for 2 days at room temperature. The mixture was extracted with ether, and the extract was washed with saturated sodium bicarbonate solution and water and dried over magnesium sulfate. The solvent was evaporated and the residue was chromatographed on neutral alumina (Woelm, activity III). Elution with pentane yielded a solid, which was sublimed at 5 mmHg (60–70 °C bath temperature) to give 510 mg of **14** (yield 71%): mp 123–124 °C (in a sealed tube) (lit.[20] racemate, mp 111–112 °C); $[\alpha]^{15}_{\mathrm{D}}$ +11°0 (*c* 0.519, $CHCl_3$); CD (*c* 4.89×10^{-2}, isooctane) $[\theta]$ (nm) 0 (256), $+1.22 \times 10^3$ sh (298), $+1.29 \times 10^3$ (301.5), $+1.23 \times 10^3$ sh (304), $+9.48 \times 10^2$ sh (312), and 0 (326); λ_{max} (isooctane) 292 sh (ϵ 13.1), 296 (13.8), 300 sh (13.6), and 306 nm sh (12.5).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.92; H, 6.93.

(−)-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (4). To a mixture of potassium hydroxide (0.17 g), 80% hydrazine hydrate (0.3 mL), and triethylene glycol (3 mL) was added (+)-monoketone **14** (400 mg, 2.74 mmol), $[\alpha]^{15}_{\mathrm{D}}$ +11.0°, and the mixture was heated in an oil bath. During 1.5 h, the bath temperature was gradually raised to 190 °C. When the temperature reached ca. 160 °C, a solid was observed to condense on the inner wall of the condenser. After cooling, this was washed with pentane, and the reaction mixture was diluted with water followed by extraction with pentane. Combined pentane solutions were washed with water and dried over magnesium sulfate. After evaporation of the solvent, the residue was sublimed at 70 °C (20 mm) to yield 240 mg of **4** (yield 64%): mp 136–138 °C (in a sealed tube) (lit.[4] racemate, mp 139–141 °C); $[\alpha]^{19}_{\mathrm{D}}$ −33.8° (*c* 0.621, $CHCl_3$); IR (KBr) 1298, 1272, 1262, 948, 838, and 770 cm^{-1}; NMR ($CDCl_3$) δ 2.40–2.85 (m, 8 H), 1.64 (d, J = 10.5 Hz, 2 H), and 1.21 (d, J = 10.5 Hz, 2 H).

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.53; H, 9.05.

Registry No.—(−)-**4,** 62928-75-0; *endo*-**11a,** 62851-17-6; (−)-**11a,** 62928-76-1; (+)-**11a,** 62928-77-2; *endo*-**11b,** 62851,18,7; (−)-**11c**(+)-2-(1-aminoethyl)naphthalene, 62928-78-3; (+)-**11c** (+)-2-(1-aminoethyl)naphthalene, 62928-72-7; *endo*-**12,** 62929-25-3; (+)-**12,** 62928-79-4; (−)-**12,** 62928-80-7; *endo*-dicyclopentadiene-1,8-dione bisethylene ketal, 62929-26-4; (+)-2-(1-aminoethyl)naphthalene, 3906-16-9.

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(16) Collins' oxidation of (+)-alcohol **11a,** $[\alpha]^{12}_{\mathrm{D}}$ +142°, afforded (−)-ketone **12,** $[\alpha]^{23}_{\mathrm{D}}$ −116° (71% yield), whose lithium aluminum hydride reduction gave back a 95% yield of (+)-alcohol **11a** with $[\alpha]^{23}_{\mathrm{D}}$ +130°. This means the Collins' oxidation proceeded virtually with no racemization, ruling out the possibility of intervention of a symmetric allylic cation or radical intermediate.

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