= F), 24523-58-8; 1 (R = Cl), 15946-43-7; 1 (R = Br), 19057-23-9; 1 (R = CF_3), 64706-20-3; 2 (R = $C(CH_3)_3$), 64706-21-4; 2 (R = $N(CH_3)_2$), 916-86-9; 2 (R = OCH_3), 64706-22-5; 2 (R = CH_3), 19059-95-1; 2 (R = F), 64706-23-6; 2 (R = Cl), 22926-90-5; 2 (R = Br), 56549-00-9; 2 (R = H), 2137-74-8; phenyl bromide, 108-86-1; 3,4-bis[*p*-(*tert*-butyl)phenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 64706-24-7; 3,4-bis[*p*-(dimethylamino)phenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 751-71-3; 3,4-bis[*p*-(dimethoxy)phenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 668-29-1; 3,4-bis[*p*-methylphenyl]2,5-diphenylcyclopentadien-2,4-one-1, 38305-61-2; 3,4-bis[*p*-fluorophenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 56805-29-9; 3,4-bis[*p*-chlorophenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 38268-08-5; 3,4-bis[*p*-bromophenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 38268-11-0; 2,3,4,5-tetraphenylcyclopentadien-2,4-one-1, 479-33-4.

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Synthesis and Absolute Configuration of (−)-D_{2d}-Bisnoradamantan-2-one (Tricyclo[3.3.0.$0^{3,7}$]octan-2-one)[1]

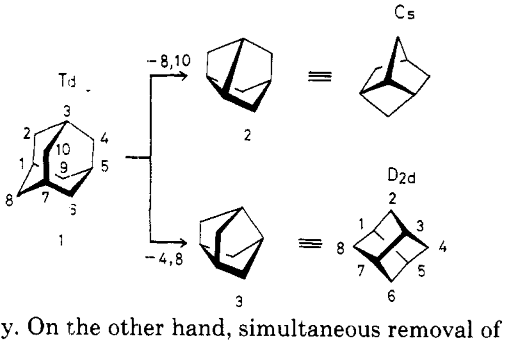
Masao Nakazaki,* Koichiro Naemura, and Nobumasa Arashiba

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, 560 Japan

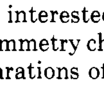
Received May 18, 1977

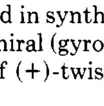
(−)-Tricyclo[3.3.0.$0^{3,7}$]octane-2-carboxylic acid (**23**) was converted into (−)-D_{2d}-bisnoradamantan-2-one (**9**), whose circular dichroism spectrum indicated the 1*R*,3*R*,5*R*,7*R* absolute configuration.

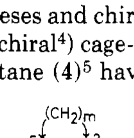
Although the high symmetry (T_d) inherent to the adamantane molecule (**1**) requires stereochemical equivalence among all of the six methylene groups, sets of two methylene groups can be classified into two different categories: the sets made of two methylene groups not situated on the same C_2 axis (e.g., 8–10) and the sets made of two methylene groups situated on the same C_2 axis (e.g., 4–8). Simultaneous removal of the two methylene groups (e.g., 8–10) belonging to the former category gives tricyclo[3.2.1.$0^{3,6}$]octane (**2**)[2] with C_s symmetry. On the other hand, simultaneous removal of the two methylene groups (e.g., 4–8) classified in the latter category will afford tricyclo[3.3.0.$0^{3,7}$]octane (**3**),[3] which belongs to the D_{2d} point group and which, for convenience, shall be referred to as D_{2d}-bisnoradamantane in this paper.



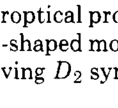
In D_{2d}-bisnoradamantane (**3**), one can discern a D_2 twist-boat cyclohexane moiety which is specified by hatching. We have been interested in syntheses and chiroptical properties of high-symmetry chiral (gyrochiral[4]) cage-shaped molecules, and preparations of (+)-twistane (**4**)[5] having D_2 symmetry and (+)-twist-brendane (**5**)[6] having C_2 symmetry, both with known absolute configurations, that have been reported from our laboratory.


(+)-4


(+)-5



$(PMP)_2$
6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In these molecules, the $(PMP)_2$ chiral twist-boat conformation of the cyclohexane ring is frozen by means of two short bridges, $(CH_2)_m$ and $(CH_2)_n$, spanning over the C-1 and C-4 as well as C-2 and C-5 carbon atoms as shown in structure **6**. D_{2d}-Bisnoradamantane corresponds to **6** with $m = n = 1$, and the molecular model (**7**) of this compound shows that the molecule consists of two enantiomeric D_2 twist-boat cyclohexane species (the hatched and the dotted ones indicated in formula **7**) fused together as shown in **7**. This molecular geometry results in two sets of homotopic methylene groups

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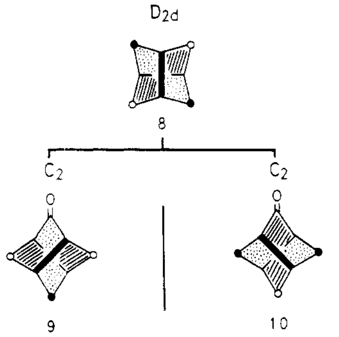
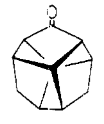
which are illustrated with the closed and the open circles in structure **8**.

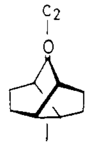


Since reflection through the planes of symmetry interchanges these sets of methylene groups (○ ⇌ ●), they are in turn enantiotopic. This symmetric D_{2d}-bisnoradamantane (**8**) can be desymmetrized by converting one of the enantiotopic methylene groups into a carbonyl group, and the chiralities of resulting D_{2d}-bisnoradamantan-2-one molecules **9** and **10** are determined by the choice of the methylene group to be converted into the carbonyl group. In a preceding paper,[7] we reported preparations of optically active D_{2d}-bisnoradamantan-2-one derivatives **16** and **17** (Scheme I) with known absolute configurations from (−)-*endo*-2-carboxybicyclo[2.2.1]hept-5-ene (**11**)[8] via the oxetanes **14** and **15**, but our efforts to convert **16** and **17** into D_{2d}-bisnoradamantan-2-one **9** with known absolute configuration have failed.

Our current research on the microbial stereo-differentiating reduction of cage-shaped ketones whose C_2 axes coincide with their carbonyl axes has indicated that *Curvularia lunata* preferentially reduces the enantiomers **18**, **19**, and **20**, all with the carbonyl group flaked by the homotopic carbon atoms with *R* configuration,[9] and the obvious extention of this study required the preparation of D_{2d}-bisnoradamantan-2-one **9** in optical active form as well as the information about its absolute configuration.



18



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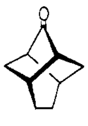

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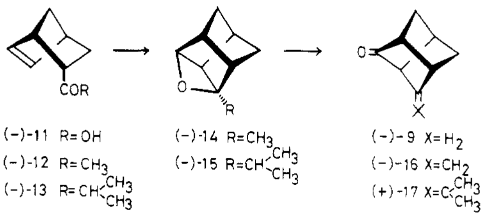
Besides its simple beauty of symmetry, D_{2d}-bisnoradamantan-2-one (**9**) ($C_8H_{10}O$) is conspicuous for being one of the simplest gyrochiral cage-shaped molecules. We report in the present paper the first successful synthesis of optically active **9** as well as its absolute configuration.

Results and Discussion

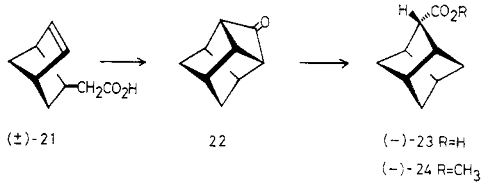
Fruitless attempts to convert (−)-**16** and (+)-**17**, both with known absolute configurations, to optically active D_{2d}-bisnoradamantan-2-one (**9**) prompted us to abandon this strategy, and our next efforts were directed toward (1) a new route to optically active **9**, (2) preparation of optically active D_{2d}-bisnoradamantan-2-one derivative **30** from an intermediate with known absolute configuration, and (3) elucidation of the absolute configuration of optically active **9** by comparing its circular dichroism (CD) spectrum with that of **30**.

Synthesis of (−)-D_{2d}-Bisnoradamantan-2-one (9). Alkaline ring fission of the tetracyclic ketone **22**, prepared from (±)-*endo*-carboxylic acid **21** following Sauers' procedure,[3e] furnished (±)-tricyclo[3.3.0.0^{3,7}]octane-2-carboxylic acid (**23**), whose optical resolution was accomplished using (+)-2-(1-aminoethyl)naphthalene as the resolving agent.

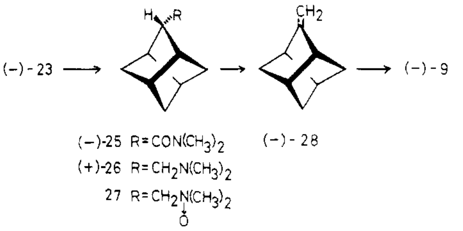
Scheme I



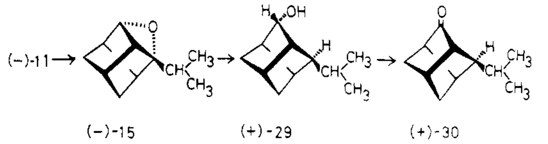
Scheme II



Scheme III



Scheme IV



Although recrystallization of the salt from acetone appeared to result in fairly good resolution, as evidenced by the similar optical rotations of the isolated acids, $[\alpha]_D$ −22.5° and +22.1°, an optical purity measurement with the tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) [Eu(facam)$_3$][10] chiral NMR shift reagent indicated 70% optical purity for the (+)-methyl ester (**24**), $[\alpha]_D$ +14.5°, prepared from the (+)-acid (**23**), $[\alpha]_D$ +22.1°. The (−)-acid (**23**), $[\alpha]_D$ −22.5°, was converted into the (−)-dimethylamide (**25**, Scheme III), $[\alpha]_D$ −3.2°, whose $LiAlH_4$ reduction afforded the (+)-dimethylamine (**26**), $[\alpha]_D$ +5.7°. Oxidation with 30% hydrogen peroxide followed by pyrolysis[11] of the resulting amine oxide (**27**) at 160 °C yielded an oily product (59%), $[\alpha]_D$ −32.1°, whose NMR spectrum exhibited a sharp singlet of olefinic protons centered at δ 4.09, indicating C_2 symmetrical structure **28** for this olefin. Ozonization of (−)-**28** in methylene chloride at −78 °C[12] and reductive cleavage of the ozonide with zinc and acetic acid completed the synthesis of (−)-D_{2d}-bisnoradamantan-2-one (**9**): mp 103–105 °C; $[\alpha]_D$ −55.9°. Because of its extreme volatility, elemental analysis could not be performed, but the identity of (−)-**9** was established by comparison of its NMR and mass spectrum and VPC and TLC results with a racemic specimen prepared by Sauers' procedure.[3f]

Synthesis of (+)-4-Isopropyltricyclo[3.3.0.0^{3,7}]octan-2-one (30). Elucidation of the absolute configuration of (−)-**9** by means of CD spectral analysis required an optically active D_{2d}-bisnoradamantan-2-one derivative as a reference substance, and Scheme IV illustrates the preparation of the (+)-(4*S*)-isopropyl derivative (**30**) from (−)-*endo*-2-carboxybicyclo[2.2.1]hept-5-ene (**11**)[8] with known absolute configuration.

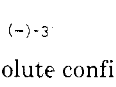
Preparation of (−)-isopropyl ketone **13** from the (−)-*endo*-carboxylic acid **11** and its subsequent Paterno-Buchi

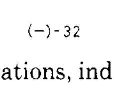
Table I. CD Spectra of (−)-Bisnoradamantan-2-one (9) and (+)-4-Isopropylbisnoradamantan-2-one (30) (in Isooctane)

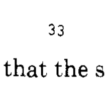
(−)-9		(+)-30	
$[\theta]$, deg cm^2/dmol	λ_{max}, nm	$[\theta]$, deg cm^2/dmol	λ_{max}, nm
-9.71×10^3 sh	281.6	-2.48×10^3	299.5
-1.05×10^4	286.3	-2.43×10^3 sh	304.0
-9.91×10^3 sh	290.4		
-7.77×10^3 sh	296.2		

photocyclization to (−)-isopropyl oxetane **15** were reported in our preceding paper.[7] Heating (−)-**15**, $[\alpha]_D$ −5.8°, with $LiAlH_4$ in *N*-methylmorpholine[3f] gave a (+)-alcohol (59%), $[\alpha]_D$ +2.8°, to which the stereochemistry (**29**) was assigned from the analogy to the methyl derivative.[13] Jones oxidation converted (+)-**29** to the requisite ketone **30**, and the configurational relations outlined in Schemes I and IV are indicative of its 1*R*,3*R*,4*S*,5*R*,7*R* absolute configuration.

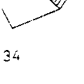
Absolute Configurations and Chiroptical Properties. Table I lists CD spectral data of (+)-(1*R*,3*R*,4*S*,5*R*,7*R*)-4-isopropyltricyclo[3.3.0.0^{3,7}]octan-2-one (**30**) and (−)-D_{2d}-bisnoradamantan-2-one (**9**), and a comparison of their Cotton effects indicates the 1*R*,3*R*,5*R*,7*R* absolute configuration for (−)-**9**. Circular dichroism spectra of various tricyclic ketones (e.g., (−)-**31**[5a] and (−)-**32**[6a]), prepared from intermediates of known absolute configurations, indicate that the sign of the CD curve due to the n → π* transition around 300 nm can be predicted by applying the octant rule to the "outer ring"[14] in the projection formula **33** which holds the carbonyl group at the "point of twist."[15]


(−)-3


(−)-32


33

Applying this generalization to the projection formula **34** of (−)-**9** with a negative Cotton effect (Table I), we again obtain the 1*R*,3*R*,5*R*,7*R* absolute configuration for this ketone. It appears pertinent to point out here that, although our assignment of the 4*S* configuration to (+)-isopropyl derivative **30** was made by mere analogy, this does not affect the sign of the Cotton effect, as can be seen from the projection formula **35**.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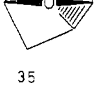
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Experimental Section

Infrared spectral data were obtained with a Hitachi EPI-S2 spectrophotometer. Nuclear magnetic resonance spectra were obtained with 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 data were measured on a JASCO J-40 spectropolarimeter. Elemental analyses were determined on a Yanagimoto CHN-Corder type II. All melting points and boiling points are uncorrected.

(±)-Tricyclo[3.3.0.0^{3,7}]octane-2-carboxylic acid (23) was prepared as described by Sauers and Kelly,[3e] mp 99–100.5 °C (lit.[3e] mp 99–100.5 °C).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.85; H, 8.01.

Optical Resolution of Tricyclo[3.3.0.0^{3,7}]octane-2-carboxylic Acid (23). To a solution of (±)-**23** (34.9 g, 0.230 mol) in acetone (1.9 L) was added a solution of (+)-2-(1-aminoethyl)naphthalene (39.2 g, 0.230 mol) in acetone (300 mL) with stirring. The mixture was heated under reflux for 5 h, and 1 L of acetone was then distilled away. The salt solution was allowed to stand overnight at room temperature, and the deposited solid was collected by filtration (the filtrate was reserved for isolation of (+)-**23**) to give 57.2 g of dextrorotatory salt, $[\alpha]^{16}_D$ +12.4° (*c* 0.305, $CHCl_3$). Several fractional recrystallizations of the (+)-salt from acetone afforded 24.5 g of salt with $[\alpha]^{14}_D$ +5.3° (*c* 0.311, $CHCl_3$), mp 181–183 °C.

Anal. Calcd for $C_{21}H_{25}O_2N$: C, 77.98; H, 7.79; N, 4.33. Found: C, 77.69; H, 7.74; N, 4.19.

To this dextrorotatory salt (13.5 g, 0.0420 mol) was added 5% NaOH aqueous solution (160 mL), and the mixture was stirred for 3 h at room temperature. The reaction mixture was extracted with ether to remove the amine and then made acidic with HCl. The acidic solution was extracted with ether, and the extract was washed with water and dried over $MgSO_4$. Evaporation of the solvent gave 6.22 g of a white solid, $[\alpha]^{15}_D$ −16.2° (*c* 0.576, $CHCl_3$), which was recrystallized from *n*-hexane to yield 3.30 g of (−)-**23:** $[\alpha]^{15}_D$ −22.5° (*c* 0.800, $CHCl_3$); mp 85–86 °C (in a sealed tube).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.81; H, 7.95.

The filtrate that separated from the salt of (−)-**23** was concentrated to give a crystalline material which was recrystallized from acetone to afford 5.8 g of the dextrorotatory salt, $[\alpha]^{18}_D$ +24.8° (*c* 0.320, $CHCl_3$). This salt (5.50 g) was treated with 5% NaOH aqueous solution (70 mL), and the same workup described for (−)-**23** gave 2.30 g of (+)-**23,** $[\alpha]^{18}_D$ +19.1° (*c* 0.305, $CHCl_3$). Several recrystallizations of the (+)-carboxylic acid from *n*-hexane afforded 850 mg of (+)-**23:** $[\alpha]^{18}_D$ +22.1° (*c* 0.581, $CHCl_3$); mp 80–84 °C.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.81; H, 7.96.

(+)-Methyl Tricyclo[3.3.0.0^{3,7}]octane-2-carboxylate (24). To a solution of (+)-**23** (600 mg, 3.94 mmol), $[\alpha]^{18}_D$ +22.1°, in ether (20 mL) was added an excess of diazomethane in ether with ice cooling, and the mixture was stirred for 2 h at room temperature. After decomposition of excess diazomethane with acetic acid, the solution was washed successively with a saturated $NaHCO_3$ solution and water and dried over $MgSO_4$. Evaporation of the solvent gave 0.63 g of an oily product, which was distilled to yield 490 mg of (+)-**24** (75% yield): bp 83–84 °C (4 mm); $[\alpha]^{17}_D$ +14.5° (*c* 1.05, $CHCl_3$); IR (neat film) 1735, 1443, 1365, 1043 cm^{-1}; NMR (CCl_4) δ 1.39 (br s, 6 H), 2.42 (br s, 4 H), 2.55 (br s, 1 H), 3.55 (s, 3 H); NMR (CCl_4; Eu(facam)$_3$/(+)-**24** = 0.188 molar ratio) δ 5.92 and 6.01 (anisochronous CO_2CH_3 signals).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.34. Found: C, 71.91; H, 8.38.

(−)-*N,N*-Dimethyltricyclo[3.3.0.0^{3,7}]octane-2-carboxamide (25). To a solution of (−)-**23** (5.50 g, 0.0362 mol) in dry benzene (55 mL) was slowly added thionyl chloride (7.50 g, 0.0630 mol) with ice cooling. After stirring for 3 days at room temperature, the reaction mixture was concentrated under reduced pressure to give 7.45 g of acid chloride, which was used without further purification. A solution of the acid chloride (7.45 g) in dry benzene (35 mL) was added dropwise to a solution of dimethylamine (8.5 mL) in dry benzene (30 mL) with ice cooling. After stirring for 9 h at room temperature, the reaction mixture was poured into ice water and made acidic with HCl. The mixture was extracted with ether, and the extract was washed with saturated $NaHCO_3$ solution and water and dried over $MgSO_4$. Removal of the solvent gave 5.61 g of **25** as a white solid (87% yield): $[\alpha]^{18}_D$ −3.2° (*c* 0.702, $CHCl_3$); mp 82–84 °C (in a sealed tube); IR (KBr) 1625, 1419, 1398, 1169, 1155 cm^{-1}.

Anal. Calcd for $C_{11}H_{17}ON$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.85; H, 9.50; N, 7.78.

(+)-2-*N,N*-Dimethylaminomethyltricyclo[3.3.0.0^{3,7}]octane (26). To a suspension of $LiAlH_4$ (1.20 g, 0.0316 mol) in dry ether (40 mL) was added dropwise a solution of (−)-amide **25** (5.60 g, 0.0313 mol) in dry ether (70 mL), and the mixture was refluxed gently for 20 h. Excessive reducing agent and the reaction complex were decomposed by successive addition of 3 mL of water and a solution of NaOH (67 g) in water (170 mL) to the chilled reaction mixture. Distillation of the reaction mixture gave about 250 mL of the distillate containing the resulting amine (**26**), which was extracted with ether. The ethereal extract was washed successively with saturated $NaHCO_3$ solution and water and dried over NaOH. Evaporation of the solvent gave an oily product, which was distilled to yield 4.50 g of **26** (87% yield): bp 102–103 °C (20 mm); $[\alpha]^{18}_D$ +5.7° (*c* 1.38, $CHCl_3$); IR (neat film) 2980, 2870, 2850, 2830, 2795, 2705, 1460, 1295, 1046, 1027, 850 cm^{-1}.

Anal. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59; N, 8.48. Found: C, 79.70; H, 11.74; N, 8.40.

(−)-2-Methylenetricyclo[3.3.0.0^{3,7}]octane (28). After a 30% hydrogen peroxide solution (3.1 g) was slowly added to a solution of (+)-**26** (4.40 g, 0.0267 mol) in methanol (7 mL) chilled in an ice–salt bath, the mixture was gradually warmed to room temperature with stirring. After stirring for 24 h, the mixture was chilled in an ice–salt bath. Additional 30% hydrogen peroxide (3.1 g) was added to the reaction mixture which was further stirred for 30 h at room temperature. The remaining hydrogen peroxide was destroyed by stirring with 5% Pd-on-carbon (20 mg) for 24 h; the catalyst was removed by filtration, and the filtrate was condensed to give amine oxide **27** as a waxy product. The amine oxide (**27**) was heated at 20 mm in a small distilling flask connected to a trap which was cooled in a dry ice–acetone bath. Decomposition of the amine oxide began at 160 °C and was complete after 1 h. The distillate was dissolved in 200 mL of ether, and the ethereal solution was washed successively with 10% HCl, saturated $NaHCO_3$ solution, and water and dried over $MgSO_4$. Evaporation of the solvent gave an oily product, which was distilled to yield 1.90 g of **28** (59% yield based on **26**): bp 92–93 °C (120 mm); $[\alpha]^{18}{}_{\mathrm{D}}$ −32.1° (c 1.68, EtOH); NMR (CCl_4) δ 1.42 (s, 6 H), 2.38 (m, 4 H), 4.09 (s, 2 H); IR (neat film) 3060, 1683, 860 cm^{-1}; CD (c 1.88×10^{-4}, isooctane) $[\theta]$ -6.96×10^4 (192 nm).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.87; H, 10.11.

(−)-Tricyclo[3.3.0.0^{3,7}]octan-2-one (9). A stream of oxygen containing about 7% ozone was passed into a chilled solution (−78 °C) of (−)-**28** (520 mg, 4.33 mmol) in methylene chloride (20 mL) until an intense blue color persisted. The solution was allowed to warm to room temperature, and excess ozone was purged by passing a stream of nitrogen through the solution. The reaction mixture was poured into a mixture of zinc powder (1.2 g), acetic acid (1 mL), and water (100 mL) and stirred for 6 h at room temperature. The organic layer was separated, washed with saturated $NaHCO_3$ solution and water, and dried over $MgSO_4$. The solvent was carefully evaporated through a short distillation column to give a solid, which was chromatographed on neutral alumina (Woelm, activity II). Fractions eluted with pentane gave 174 mg of **9** (33% yield), which was further purified by sublimation at 65 °C in a nitrogen atmosphere to give a pure sample: mp 103–105 °C (in a sealed tube) (lit.[3f] racemate, mp 106–110 °C); $[\alpha]^{13}{}_{\mathrm{D}}$ −55.9° (c 0.347, EtOH); IR (KBr) 1770 cm^{-1}; CD (c 1.17×10^{-2}, isooctane) $[\theta]$ 0 (237 nm), -9.71×10^3 sh (281.6), -1.05×10^4 (286.3), -9.91×10^3 sh (290.4), -7.77×10^3 sh (296.2), 0 (320.5); UV max (isooctane) 282 nm (ϵ 25.3); NMR (CCl_4) δ 1.62 (brd s, 6 H), 2.20 (m, 2 H), 2.57 (m, 2 H); mass spectrum m/e 122 (M^+).

Because of its high volatility, elemental analysis could not be performed.

(+)-4-Isopropyltricyclo[3.3.0.0^{3,7}]octan-2-ol (29). To a refluxing slurry of $LiAlH_4$ (1.52 g, 0.0400 mol) in N-methylmorpholine (50 mL) a solution of (−)-oxetane (**15**),[7] $]\alpha]^{20}{}_{\mathrm{D}}$ −5.78° (820 mg, 5.00 mmol), in N-methylmorpholine (15 mL) was added over 1 h, and refluxing with stirring was continued for 5 days. The excess hydride was decomposed by dropwise addition of methanol, and the reaction mixture was poured into dilute HCl. The resulting mixture was extracted with ether, and the extract was washed with saturated $NaHCO_3$ solution and water and dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel. Earlier fractions eluted with pentane gave 80 mg of the starting material, and later fractions eluted with ether–pentane (1:1 volume) afforded 0.88 g of **29**, which was distilled to yield 492 mg of **29** (59% yield): bp 119–122 °C (25 mm); $[\alpha]^{20}{}_{\mathrm{D}}$ +2.8° (c 0.568, EtOH); IR (neat film) 3450, 1065 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.29; H, 10.80.

(+)-4-Isopropyltricyclo[3.3.0.0^{3,7}]octan-2-one (30). To a solution of (+)-**29** (300 mg, 1.81 mmol) in acetone (5 mL) was added an excess of Jones reagent[16] at 0–5 °C, and the mixture was stirred for 3 h at this temperature. The reaction mixture was diluted with water and extracted with ether. The extract was washed with saturated $NaHCO_3$ solution and water and dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel, and fractions eluted with pentane–ether (4:1 volume) gave 0.11 g of an oily product, which was distilled to afford 90 mg of **30** (30% yield): bp 125 °C [bath temperature (20 mm)]; $[\alpha]^{23}{}_{\mathrm{D}}$ +18.2° (c 0.665, EtOH); IR (neat film) 1760 cm^{-1}; CD (c 2.10×10^{-2}, isooctane) $[\theta]$ 0 (250 nm), -2.48×10^3 (299.5), -2.43×10^3 sh (304), 0 (327).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.18; H, 9.77.

Registry No.—(−)-**9**, 61826-77-5; (−)-**15**, 58001-98-2; (±)-**23**, 61775-75-5; (+)-**23** (+)-2-(1-aminoethyl), naphthalene salt, 64783-62-6; (+)-**23**, 64753-43-1; (−)-**23** (+)-2-(1-aminoethyl)naphthalene salt, 64753-44-2; (−)-**23**, 61826-78-6; (−)-**23** acid chloride, 64715-14-6; (+)-**24**, 64715-15-7; (−)-**25**, 61775-76-6; (+)-**26**, 61775-77-7; **27**, 61775-79-9; (−)-**28**, 61775-80-2; (+)-**29**, 61775-78-8; (+)-**30**, 61775-81-3; (+)-2-(1-aminoethyl)naphthalene, 3906-16-9; thionyl chloride, 7719-09-7; dimethylamine, 124-40-3.

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