°C under conditions of continuous extraction with refluxing 2,2,4-trimethylpentane to give after column chromatography 6-bromo-1-hexanol (**3**),[13] which was converted into the corresponding nitrile by treatment with 80% aqueous NaCN in *n*-decane under phase-transfer conditions using hexadecyltributylphosphonium bromide as catalyst at 100 °C.[14] After ether extraction of the aqueous phase and solvent evaporation, the crude oil was dissolved in tetrahydrofuran and stirred with a twofold excess of 3,4-dihydro-2*H*-pyran in the presence of a catalytic amount of dried Amberlyst H-15[15] to give **1a**: IR (film) 2240, 1130, 1110, 1070, 1030 $cm^{-1}$; NMR 4.45 (m, 1 H), 3.55 (m, 4 H), 2.3 (t, 2 H), 1.55 (m, 14 H).

**2-[5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]pentyl]-5(*Z*)-octenenitrile (1b).** **1a** was metalated according to standard procedures[16] and alkylated with (*Z*)-1-iodo-3-hexene[17] to give **1b**: IR (film) 3020, 2240, 1140, 1120, 1080, 1030, 720 $cm^{-1}$; NMR 5.3 (m, 2 H), 4.45 (m, 1 H), 3.5 (m, 4 H), 2.1 (m, 5 H), 1.5 (m, 16 H), 0.95 (t, 3 H).

**2-Ethyldecanenitrile (1c).** Alkylation[16] of butanenitrile with 1-bromooctane afforded **1c**: IR (film) 2230 $cm^{-1}$; NMR 2.4 (m, 1 H), 1.3 (m, 16 H), 0.9 (m, 6 H).

**2-Ethyl-4,4-diethoxybutanenitrile (1d).** Alkylation[16] of butanenitrile with 1,1-diethoxy-2-bromoethane afforded **1d**: IR (film) 2230, 1120, 1050, 1010 $cm^{-1}$; NMR 4.65 (t, 1 H), 3.6 (m, 4 H), 2.55 (m, 1 H), 1.4–2.2 (m, 4 H), 1–1.3 (m, 9 H).

**2-Ethyl-2-octyldecanenitrile (1e).** Dialkylation[16] of butanenitrile with 1-bromooctane afforded (**1e**): IR (film) 2230 $cm^{-1}$; NMR 1.3 (m, 30 H), 0.9 (m, 9 H).

**2,2-Dioctyl-3-butenenitrile (1f).** Dialkylation of 2-butenenitrile[8d] gave the $\beta,\gamma$-unsaturated nitrile **1f**: IR (film) 2250, 990 $cm^{-1}$; NMR 5.35 (m, 3 H), 1.3 (m, 28 H), 0.9 (t, 6 H).

**Preparation of Highly Dispersed Potassium on Alumina ($K/Al_2O_3$).** $Al_2O_3$ (3.7 g) was placed in a 100-mL two-necked flask equipped with an argon inlet and a magnetic stirring bar and heated at 150 °C (external oil bath) for 15 min under a positive argon pressure. Then potassium (0.6 g, 15 mmol) was added in small pieces. After the potassium melted, heating was stopped and the mixture was vigorously stirred to obtain a homogeneous black powder of highly dispersed metal (14% $K/Al_2O_3$).[18] Potassium/alumina is oxygen and moisture sensitive and must be handled in an inert atmosphere.

**Decyanation of 1f to 2f (General Procedure).** To a slurry of 4.3 g of potassium/alumina in 15 mL of hexane was slowly added (3 min) a solution of 0.87 g of **1f** (3.0 mmol) in 10 mL of hexane under an inert argon atmosphere. After 5 min the excess potassium was decomposed with 0.5 mL of water and the white alumina was filtered and washed with ether. After evaporation of solvent, the residue was chromatographed (silica gel, hexane) to yield 0.56 g (70%) of **2f** that was 97% pure by GLC analysis: IR (film) 820, 720 $cm^{-1}$; NMR 5.1 (q, $J$ = 7 Hz, 1 H), 1.95 (m, 4 H), 1.55 (d, $J$ = 7 Hz, 3 H), 1.25 (24 H), 0.85 (t, 6 H); mass spectrum, *m/e* ($M^+$, 266).

**2-(Hexyloxy)tetrahydro-2*H*-pyran (2a):** bp 125 °C (15 torr); IR (film) 1130, 1110, 1070, 1030 $cm^{-1}$; NMR 4.6 (m, 1 H), 3.5 (m, 4 H), 1.4–1.8 (m, 14 H), 0.95 (t, 3 H); identical GLC retention time with a sample obtained by acid-catalyzed tetrahydropyranylation of 1-hexanol.

**2-[(*Z*)-9-Dodecenyloxy]tetrahydro-2*H*-pyran (2b):** IR (film) 3020, 1140, 1120, 1080, 1040 $cm^{-1}$; NMR 5.2 (m, 2 H), 4.45 (m, 1 H), 3.45 (m, 4 H), 1.95 (m, 4 H), 1.1–1.6 (m, 18 H), 0.9 (t, $J$ = 7 Hz, 3 H); mass spectrum, *m/e* ($M^+$, 268).

**Undecane (2c):** bp 80 °C (15 torr); identical with an authentic sample (Merck).

**1,1-Diethoxypentane (2d):** bp 65 °C (15 torr); IR (film) 1180, 1140, 1020 $cm^{-1}$; NMR 4.4 (t, 1 H), 3.6 (m, 4 H), 1.5–1.2 (m, 6 H), 1.2 (t, 6 H), 0.9 (t, 3 H); identical GLC retention time with a sample obtained by acid-catalyzed acetalization of pentanal.

**9-Ethylheptadecane (2e):** bp 185 °C (15 torr); mass spectrum, *m/e* ($M^+$, 268).

**(*Z*)-9-Dodecenyl Acetate (4) (Sex Pheromone of *Paralobesia viteana*).** A solution of 0.54 g (2 mmol) of **2b** in 1.4 mL of acetic acid and 0.6 mL of acetyl chloride[19] was heated at 120 °C for 1 h in a sealed tube and then poured into 15 mL of saturated aqueous $NaHCO_3$ solution. The aqueous phase was extracted with ether and the concentrated organic phase was purified by column chromatography (silica gel, hexane–ether 98:2), affording 0.39 g (85%) of **4**: IR (film) 3010, 1740, 1240, 1030, 780 $cm^{-1}$; NMR 5.25 (m, 2 H), 3.9 (t, 2 H), 2.3–1.8 (m, 4 H), 1.95 (s, 3 H), 1.3 (m, 12 H), 1.05 (t, 3 H); mass spectrum, *m/e* ($M^+$, 226).

**Registry No.** **1a**, 33803-59-7; **1b**, 73804-91-8; **1c**, 73804-92-9; **1d**, 73804-93-0; **1e**, 73804-94-1; **1f**, 73804-95-2; **2a**, 1927-63-5; **2b**, 50816-22-3; **2c**, 1120-21-4; **2d**, 3658-79-5; **2e**, 73804-96-3; **2f**, 73804-97-4; **3**, 4286-55-9; **4**, 16974-11-1; potassium, 7440-09-7; alumina, 1344-28-1; 1,6-hexanediol, 629-11-8; 3,4-dihydro-2*H*-pyran, 110-87-2; (*Z*)-1-iodo-3-hexene, 21676-03-9; butanenitrile, 109-74-0; 1-bromooctane, 111-83-1; 1,1-diethoxy-2-bromoethane, 2032-35-1; 2-butenenitrile, 4786-20-3.

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[15] A. Bongini, G. Cardillo, M. Orena, and S. Sandri, *Synthesis*, 618 (1979).

[16] (a) D. S. Watt, *Tetrahedron Lett.*, 707 (1974); (b) D. Savoia, C. Trombini, and A. Umani-Ronchi, *Tetrahedron Lett.* 653 (1977).

[17] (*Z*)-1-Iodo-3-hexene was obtained through $I^-$ displacement of (*Z*)-1-tosyl-3-hexene in acetone, which was prepared from commercially available (*Z*)-3-hexenol (Aldrich, 97.3%) and tosyl chloride in pyridine.

[18] The X-ray diffraction pattern of $K/Al_2O_3$ was identical with that of $Al_2O_3$, with no observable diffractions due to the potassium.

[19] D. Warthen and M. Jacobson, *J. Med. Chem.*, 11, 1190 (1968).

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# Asymmetric Synthesis of Optically Active Trans Doubly Bridged Ethylene. (−)-($R$)-$D_2$-Bicyclo[8.8.0]octadec-1(10)-ene

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Ultraviolet irradiation of the "cis" bicyclic $\alpha,\beta$-unsaturated ketone **9** in diethyl $\text{L}_g$-(+)-tartrate afforded a 1:7 mixture of *cis*-**9** and trans ketone **10** enriched in the (−)-enantiomer, whose Wolff–Kishner reduction yielded (−)-$D_2$-bicyclo[8.8.0]octadec-1(10)-ene (**3**; optical purity 0.5–1.0%) with the $R$ configuration.

Our continuing interests in twisted gyrochiral[1] $\pi$-electron systems have led us to study the preparation, stereochemistry, and chiroptical properties of [$n$]-chochines (**1**,[2] see Chart I), [$m$][$n$]paracyclophanes (**2**),[3] and (−)-($S$)-bicyclo[3.3.1]non-1-ene (**12**),[4] the first optically active

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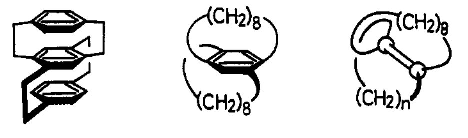
[1] M. Nakazaki, K. Naemura, and S. Harita, *Bull. Chem. Soc. Jpn.*, 48, 1907 (1975).

[2] M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki, K. Yamamoto, S. Tanaka, and H. Kametani, *J. Org. Chem.*, 42, 287 (1977).

0022-3263/80/1945-3229$01.00/0

Chart I

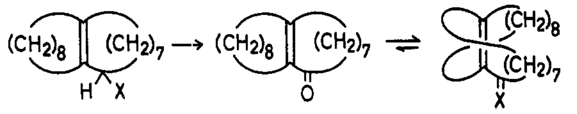


(−)(R)-[3]chochine (1)

(+)(S)-[8][8] paracyclophane (2)

(R)-(3) n = 8
(R)-(4) n = 10

Scheme I



(5) X = H
(6) X = Br
(7) X = OAc
(8) X = OH

(9)

(−)-(10) X = O
(−)(R)-(3) X = H2

anti-Bredt rule compound with known absolute configuration.

Recently, we have achieved the syntheses of "trans" [8][8] (**3**) and "trans" [8][10] doubly bridged ethylenes (**4**),[5] ethylene analogues of [*m*][*n*]paracyclophane, via cis–trans photoisomerization of their "cis" precursors, and this prompted us to attempt the optical resolution of "trans" [8][8] doubly bridged ethylene (**3**).

Since "trans" [8][8] doubly bridged ethylene (**3**) with $D_2$ symmetry can be regarded to be constructed by "fusing" two *trans*-cyclodecenes ($C_2$ symmetry) with the same chirality, to secure **3** in an optically active modification should offer the counterpart to Cope's classical optical resolution of *trans*-cyclooctene (**11**).[6]

An obvious device will be the use of a chiral Pt complex as the resolving agent which has been proved effective in the case of *trans*-cyclooctene (**11**).[6] We feared, however, that the reported buried nature of the unsaturated center in **3** would prevent its forming the complex. To circumvent this difficulty, our effort was directed toward functionalization of **3** to provide a "handle" for optical resolution.

In this paper, we report the preparation of *cis*-2-oxo derivative **10**[7] whose chiral solvent-induced asymmetric cis–trans photoisomerization eventually led to $D_2$-bicyclo[8.8.0]octadec-1(10)-ene (**3**) enriched in the (−)-enantiomer.

## Results and Discussion

**Synthesis of 2-Oxo-$D_{2h}$-bicyclo[8.8.0]octadec-1(10)-ene (9).** The sequence of steps[8] leading to the 2-oxo derivative **9** from the "cis" [8][8] doubly bridged ethylene **5** is encompassed in Scheme I. Bromination of **5** with 0.5 equiv of *N*-bromosuccinimide gave the 2-bromide **6**, which was treated with silver acetate to provide the acetate **7**. The unsaturated alcohol **8**, mp 94–95 °C, secured from the acetate **7** by alkaline hydrolysis, was oxidized with Jones reagent to afford the cis [8][8] $\alpha,\beta$-unsaturated ketone **9** (52% overall yield from the bromide **6**), mp 125–126 °C, whose conjugated nature was clearly exhibited in its spectral data[9] (IR 1674 cm$^{-1}$; UV $\lambda_{max}$ 240 nm ($\epsilon$ 7950), 315 (80)).

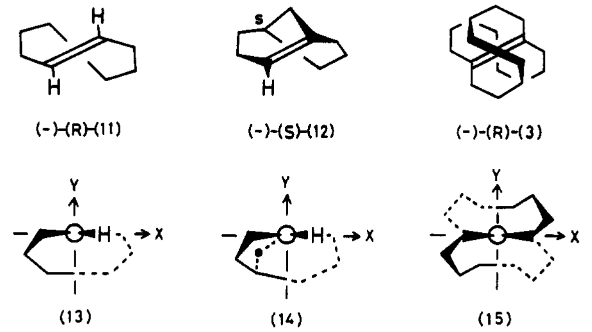


Figure 1. Octant projections of (−)-(*R*)-*trans*-cyclooctene (**11**), (−)-(*S*)-bicyclo[3.3.1]non-1(12)-ene (**12**), and (−)-(*R*)-$D_2$-bicyclo[8.8.0]octadec-1(10)-ene (**3**).

**Asymmetric Cis–Trans Photoisomerization of *cis*-2-Oxo-[8][8] Doubly Bridged Ethylene (9).** Contrary to our experience in the photoisomerization[5] of *cis*-**5** $\rightleftharpoons$ *trans*-**3** which could only be achieved by irradiation with a low-pressure mercury lamp to give an unfavorable conversion ratio (cis:trans = 9:1), our preliminary experiment with the cis $\alpha,\beta$-unsaturated ketone **9** showed that irradiation in hexane with a common medium-pressure lamp was found sufficient to provide a 1:5.5[10] equilibrium mixture of *cis*-**9** and *trans*-**10**. Separation of the isomers was accomplished by preparative GLC which gave a 30% yield of the trans isomer **10** as the faster moving zone, parallel to the GLC behavior observed in their parent unsaturated hydrocarbons **5** and **3**.[5]

Inspection of a molecular model reveals that the rigid stereochemistry of the trans unsaturated ketone **10** should destroy the conjugated system typical of common $\alpha,\beta$-unsaturated ketones, and this is born out by its carbonyl absorption band (1725 cm$^{-1}$)[9] in the infrared spectrum as well as its UV spectrum ($\lambda_{max}$ 307 nm ($\epsilon$ 60)[9]) lacking the $\pi \rightarrow \pi^*$ band (240 nm) observed in the cis precursor **9**.

The favorable high conversion ratio together with the observed longer wavelength of radiation which give rise to the photoisomerization prompted us to examine a chiral-solvent-induced asymmetric conversion of **9** into **10**. After a preliminary experiment which showed that 3 h of irradiation of **9** in diethyl $\text{L}_g$-tartrate[11] gave a 1:7 optimal mixture of **9** and **10**, a preparative-scale run was tried which produced a 38% yield of **10** enriched in the (−)-enantiomer, $[\alpha]^{24}_{D}$ −13° (hexane) and $[\theta]_{307\text{nm}}$ $-2.2 \times 10^3$ (hexane).

**Preparation of $D_2$-Bicyclo[8.8.0]octadec-1(10)-ene (3) Enriched in the (−)-Enantiomer.** Guided by our previous finding that a discriminating reaction of di-

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[3] M. Nakazaki, K. Yamamoto, and M. Itoh, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Org. Chem.*, **41**, 4081 (1976); M. Nakazaki, K. Yamamoto, M. Itoh, and S. Tanaka, *ibid.*, **42**, 3466 (1977).

[4] M. Nakazaki, K. Naemura, and S. Nakahara, *J. Chem. Soc., Chem. Commun.*, 82 (1979); M. Nakazaki, K. Naemura, and S. Nakahara, *J. Org. Chem.*, **44**, 2438 (1979).

[5] M. Nakazaki, K. Yamamoto, and J. Yanagi, *J. Chem. Soc., Chem. Commun.*, 346 (1977). M. Nakazaki, K. Yamamoto, and J. Yanagi, *J. Am. Chem. Soc.*, **101**, 147 (1979). For another synthesis, see J. A. Marshall and M. Lewellyn, *ibid.*, **99**, 3508 (1977). J. A. Marshall and K. Chung, *J. Org. Chem.*, **44**, 1566 (1979).

[6] A. C. Cope, C. R. Ganellin, and H. W. Johnson, Jr., *J. Am. Chem. Soc.*, **84**, 3191 (1962); A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., and T. V. van Auken, *ibid.*, **85**, 3276 (1963).

[7] Although the stereochemistry of the bicyclic olefins **3** and **5** cannot be specified by the conventional *E,Z* system, this system functions satisfactorily to distinguish their 2-substituted derivatives.

[8] Adapted with a slight modification from Cope's procedure for preparation of *cis*-2-cyclooctenol from *cis*-cyclooctene. A. C. Cope and L. L. Ester, *J. Am. Chem. Soc.*, **72**, 1129 (1950); A. C. Cope, M. R. Kinter, and R. T. Keller, *ibid.*, **76**, 2757 (1954).

[9] IR and UV spectral data of our *cis*-**9** and *trans*-**10** are found to be parallel to those reported for *cis*-2-cyclooctenone (IR, 1675 cm$^{-1}$; UV $\lambda_{max}$ 223 nm ($\epsilon$ 7600), 321 (70)) and *trans*-2-cyclooctenone (IR 1727 cm$^{-1}$; UV $\lambda_{max}$ 283 nm ($\epsilon$ 60)). P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **86**, 2087 (1964).

[10] Eaton and Lin[9] reported photochemical isomerization of *cis*-2-cyclooctenone to give a 1:4 mixture of cis and trans isomers.

[11] An asymmetric photosynthesis of hexahelicene (1.1% optical purity) in diethyl $\text{L}_g$-(+)-tartrate was reported: W. H. Laarhoven and Th. J. H. Cuppeen, *J. Chem. Soc., Chem. Commun.*, 47 (1977).

chlorocarbene toward the "cis" olefin **5** provides a convenient preparative way to isolate the "trans" isomer **3** from a cis-trans reaction mixture, our preparation of optically active "trans" [8][8] doubly bridged ethylene **3** was incepted by conversion of the crude mixture of the cis and trans $\alpha,\beta$-unsaturated ketones slightly enriched in the (-)-enantiomer into a mixture of the "cis" and "trans" olefins **5** and **3**. Wolff-Kishner reduction of the crude mixture of **9** and **10** gave a mixture of **3** and **5** (84% yield) which was treated with 50% aqueous NaOH, $CHCl_3$, and cetyltrimethylammonium chloride.[12] On preparative silica gel chromatography of the product, elution with hexane afforded a 64% yield (from the cis ketone **9**) of the "trans"-[8][8] doubly bridged ethylene **10**, enriched in the (-)-enantiomer, $[\alpha]^{24}{}_D$ -2.3° (isooctane), $[\theta]_{222.5nm}$ $-1.8 \times 10^3$ (isooctane), whose identity was established by comparison with an authentic specimen[5] (GLC, IR, UV, and mass spectra).

**Chiroptical Property.** The reported $\pi \rightarrow \pi^*$ electronic absorption[5] centered at 222.5 nm ($\epsilon$ 5400) of the "trans"-[8][8] doubly bridged ethylene (**3**) clearly indicates that the $\pi \rightarrow \pi^*$ optically active transition of a dissymmetrically perturbed ethylene chromophore is responsible for this (-)-Cotton effect observed in the same region. In Figure 1, **13** and **14** illustrate Scott's octant projections of closely related chiral *trans*-cycloolefins with established absolute configuration, (-)-($R$)-*trans*-cyclooctene (**11**)[13] ($[\theta]_{196nm}$ $-1.41 \times 10^5$ (cyclohexane)) and (-)-($S$)-bicyclo[3.3.1]non-1(2)-ene (**12**)[4] [$(\theta]_{213nm}$ $-13.6 \times 10^5$ (isooctane)), both exhibiting (-)-Cotton curves. Comparison with these compounds should reasonably suggest that the (-)-*trans*-[8][8] doubly bridged ethylene (**3**) possesses the planar $R$ structure, whose Scott's octant projection[14] (**15**) with all ring methylene groups located either in the (-)-front octants or in the (-)-rear octants predicts the observed (-)-Cotton curve.

Finally, as for the optical purity of our (-) specimen, currently we have nothing definite to say but only suggest an approximate 0.5-1.0% optical purity for our specimen with $[\alpha]_D$ -2.3°, on an assumption that the "trans" [8][8] doubly bridged ethylene (**3**) could be expected to show a rotatory strength comparable to that of *trans*-cyclooctene (**11**).

## Experimental Section

IR spectra were recorded on a Hitachi EPI-S2 spectrophotometer. NMR spectra were determined on a JNM-MH-100 spectrometer. UV spectra were obtained on a Hitachi EPS-3T spectrometer. Circular dichroism (CD) spectra were determined on a JASCO-J-40 spectropolarimeter. Mass spectra were taken on a Hitachi RMS-4 spectrometer. GLC analyses were performed on a JGC-20K equipped with FID, using a 2-m column of 15% DC QF-1 (188 °C) on Chromosorb W. Preparative GLC was carried out with a JGC-20K with a 2 m × 3 mm stainless-steel column of 15% DC QF-1 (180 °C) on Chromosorb W. Elemental analyses were performed with a Yanagimoto CHN-Corder type II. All melting points and boiling points are uncorrected.

**2-Bromo-$D_{2h}$-bicyclo[8.8.0]octadec-1(10)-ene (6).** A mixture of $D_{2h}$-bicyclo[8.8.0]octadec-1(10)-ene (**5**;[5] 2 g, 8 mmol), carbon tetrachloride (40 mL), NBS (0.7 g, 4 mmol), and benzoyl peroxide (5 mg) was heated to reflux for 45 min in a nitrogen atmosphere. After the deposited succinimide was removed by filtration, the filtrate was washed with 3% $NaHCO_3$ solution and water and dried over $MgSO_4$. Upon cooling in an ice bath, the solution deposited the unreacted olefin **5** (1.1 g, 55% yield) which was separated by filtration. The filtrate was concentrated under vacuum to yield an oily product which was distilled in vacuum as rapdily as possible to prevent decomposition. The distillate, an oil, weighed 0.7 g (59% yield based on the consumed olefin): bp 124-127 °C (0.1 mm); $n^{22}{}_D$ 1.5685.

Anal. Calcd for $C_{18}H_{31}Br$: C, 66.04; H, 9.55; Br, 24.41. Found: C, 66.26; H, 9.63; Br, 24.31.

**2-Hydroxy-$D_{2h}$-bicyclo[8.8.0]octadec-1(10)-ene (8).** To a stirred solution of silver acetate (1.0 g, 6 mmol) in acetic acid (7 mL) was added dropwise a solution of **6** (0.65 g, 2 mmol) in acetic acid (10 mL) and benzene (2 mL) at room temperature. The mixture was allowed to stand overnight and then was filtered to separate the silver bromide, which was washed with acetic acid (15 mL). After concentration of the combined filtrates, the residue was chromatographed on silica gel (30 g) with ether-hexane (1:2) as the eluant to give **7**, a pale yellow oil (0.5 g): IR (neat) 1738 cm$^{-1}$ (C=O); mass spectrum, $m/e$ 306 ($M^+$).

The acetate (**7**, 0.5 g, 1.63 mmol) was added to a solution of 7% methanolic KOH (10 mL), and the solution was refluxed for 3 h. The reaction mixture was diluted with water (30 mL) and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and concentrated, and the residual solid was recrystallized from hexane to give **8** (0.32 g, 61% yield from **6**): mp 94-95 °C; IR (KBr) 3450 cm$^{-1}$ (OH); NMR ($CDCl_3$) $\delta$ 0.9-1.6 (m, 22 H), 1.6-2.3 (m, 6 H), 2.3-2.9 (m, 3 H), 5.10 (d of d, $J$ = 3, 4 Hz, 1 H).

Anal. Calcd for $C_{18}H_{32}O$: C, 81.75; H, 12.20. Found: C, 81.63; H, 12.23.

**2-Oxo-$D_{2h}$-bicyclo[8.8.0]octadec-1(10)-ene (9).** To a chilled solution of **8** (0.3 g, 1.1 mmol) in acetone (30 mL) was added an excess amount of Jones reagent prepared from $CrO_3$ (2.6 g), concentrated $H_2SO_4$ (2.3 mL), and water (10 mL), and the mixture was stirred for 1 h with ice cooling. The reaction mixture was diluted with water and extracted with ether. The extract was washed with 3% $NaHCO_3$ solution and water and dried ($MgSO_4$). Removal of the solvent afforded a solid which was recrystallized from ethanol-water to give **9** (0.25 g, 85% yield): mp 125-126 °C; IR (KBr) 1674 cm$^{-1}$ (C=O); UV (hexane) $\lambda_{max}$ 240, 315 nm ($\epsilon$ 9750, 80); NMR ($CDCl_3$) $\delta$ 0.9-2.0 (m, 22 H), 2.05-2.74 (m, 8 H); mass spectrum, $m/e$ 262 ($M^+$).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.45; H, 11.48.

**(±)-2-Oxo-$D_2$-bicyclo[8.8.0]octadec-1(10)-ene (10).** A solution of **9** (10 mg) in hexane (10 mL) was placed in a photolysis tube (Pyrex glass), and a slow, fine stream of nitrogen was passed through the solution during the reaction. After 1 h of irradiation with a medium-pressure mercury lamp (Toshiba, SHL-100UV), the solvent was removed in vacuo, leaving an oil whose GLC analysis (nitrogen, 188 °C, 1.9 kg/cm$^2$) revealed a 1:5.5 ratio of the cis (retention time 5.5 min) and the trans isomer (retention time 5.0 min). For isolation of the trans isomer, five irradiation aliquots were combined and processed by preparative GLC to give trans $\alpha,\beta$-unsaturated ketone **10** as an oil (15 mg, 30% yield): mass spectrum, $m/e$ 262 ($M^+$); IR (neat) 1725 cm$^{-1}$ (C=O); UV (hexane) $\lambda_{max}$ 307 nm ($\epsilon$ 60).

**(-)-2-Oxo-$D_2$-bicyclo[8.8.0]octadec-1(10)-ene (10).** The cis $\alpha,\beta$-unsaturated ketone **9** (200 mg) was dissolved in 100 mL of diethyl $L_g$-(+)-tartrate, and ten 10-mL aliquots were irradiated with a medium-pressure mercury lamp for 3 h as described above. The reaction mixture was analyzed by GLC to reveal a 1:7 ratio of the cis and trans isomers, which was observed to drop to 1:6.5 after 4 h of irradiation. The combined aliquots were diluted with water (500 mL) and extracted with hexane. The extract was washed with water, dried ($MgSO_4$), and concentrated to afford a light yellow oil, which was purified by column chromatography ($SiO_2$ (10 g), elution with hexane) to give a mixture of *cis*-**9** and *trans*-**10** isomers (190 mg). Preparative GLC of a 50-mg portion of the product gave trans unsaturated ketone (-)-**10** as an oil (20 mg, 38% yield from **9**): $[\alpha]^{24}{}_D$ -13° ($c$ 0.46, hexane); IR (neat) 1725 cm$^{-1}$ (C=O); UV (hexane) $\lambda_{max}$ 307 nm ($\epsilon$ 60); NMR ($CCl_4$) $\delta$ 0.7-1.55 (m, 22 H), 1.55-2.65 (m, 8 H); CD (hexane) $[\theta]_{307nm}$ $-2.2 \times 10^3$; mass spectrum, $m/e$ 262 ($M^+$).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.11; H, 11.42.

**(-)-$D_2$-Bicyclo[8.8.0]octadec-1(10)-ene (3).** A mixture (100 mg) of the crude cis and trans unsaturated ketones, freed from diethyl tartrate and chromatographed over silica gel, was mixed with KOH (0.5 g), 100% hydrazine hydrate (0.5 mL), and di-

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ethylene glycol (15 mL). A slow stream of nitrogen was passed over the reaction mixture, and volatile materials were collected in a chilled trap. After the mixture was heated at 140 °C for 1 h, the reaction temperature was gradually raised to 200 °C and kept at this temperature for 3 h. After dilution with water, the mixture was extracted with hexane, and the extract was combined with the hexane solution of an oily product collected in the trap. The combined hexane extracts were washed with 3% HCl solution, 3% $NaHCO_3$ solution, and water and dried over $MgSO_4$. Evaporation of the solvent left an oily product which was stirred with 50% NaOH solution (0.8 mL), $CHCl_3$ (1 mL), and cetyltrimethylammonium chloride (5 mg) at 50 °C for 1 h. After dilution with water, the mixture was extracted with chloroform, and the extract was washed with water and dried over $MgSO_4$. Evaporation of the solvent afforded a residue which on preparative TLC on silicic acid (elution with hexane) gave (−)-**3** (64 mg, 64% yield from **9**): bp 126–128 °C (0.1 mm); $[\alpha]^{24}{}_D$ −2.3° (*c* 0.60, isooctane); CD (isooctane) $[\theta]_{222.5nm}$ $-1.8 \times 10^3$; mass spectrum, *m/e* 248 ($M^+$).

Anal. Calcd for $C_{18}H_{32}$: C, 87.02; H, 12.98. Found: C, 86.78; H, 13.15.

**Registry No.** (*R*)-**3**, 74080-15-2; **5**, 69416-63-3; **6**, 73986-32-0; **7**, 73986-33-1; **8**, 73986-34-2; **9**, 73986-35-3; (±)-**10**, 73986-36-4; (−)-**10**, 73986-37-5.

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# Syntheses and Chiroptical Properties of $C_2$-Bissecocubane (Tricyclo[4.2.0.0$^{3,6}$]octane) Derivatives

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(+)-2,6-Dioxotricyclo[3.3.2.0$^{3,7}$]decane-1,5-dicarboxylic acid (**18**) was converted into the dibromo diketone (−)-**10**, whose double Favorskii ring contraction afforded (−)-$C_2$-bissecocubane-3,6-dicarboxylic acid (**12**). Circular dichroism (CD) spectral comparison of the (−)-diketone **20**, derived from (−)-**10**, with (+)-(1*S*,3*R*,6*R*,8*S*)-homoadamantane-2,7-dione (**31**) assigned the (1*S*,3*R*,5*S*,7*R*) configuration to (−)-**20**, indicating the presence of a $D_3$-twisted bicyclo[2.2.2]octane moiety with *M*-helicity in (−)-**12**, common to (−)-twistane (**2**) and (−)-*twist*-brendane (**3**).

Diagonal bridging between C(2) and C(5) positions desymmetrizes bicyclo[2.2.2]octane (**1**) to yield a group of tricyclic cage-shaped compounds, (−)-twistane (**2**),[1] (−)-*twist*-brendane (**3**),[2] and tricyclo[4.2.0.0$^{3,6}$]octane (**4**),[3] all possessing the $D_3$-twisted bicyclo[2.2.2]octane moiety with *M*-helicity as a common structural unit (see Chart I).

The same (*M*)-$D_3$-twisted structural feature (**1**) can be found in another group of pentacyclic cage-shaped compounds, (−)-$C_2$-bismethanotwistane (**6**),[4] (−)-$D_3$-trishomocubane (**7**),[5] and (−)-$C_2$-bishomocubane (**8**),[6] all conceptually built by dissymmetrical homologation of cubane molecule ($O_h$ symmetry; **5**), which in turn can be conceived to be constructed by interlocking two $D_3$-twisted bicyclo[2.2.2]octane units with opposite helicities (see Chart II).

Preparation of these gyrochiral cage-shaped rigid compounds in an optically active modification as well as their absolute configuration determination has been accomplished in our laboratory, except for **4** (see Chart III), which is conspicuous in the following two stereochemical features: (a) this is the only chiral compound among the four possible tricyclic hydrocarbons attainable by two bond fission ("$C_2$-bissecocubane")[7] of cubane (**5**), and (b) this is the next higher gyrochiral homologue of tricyclo[3.2.0.0$^{3,7}$]heptane (**9**), the smallest gyrochiral tricyclic hydrocarbon resulting from the diagonal methylene bridging of bicyclo[2.2.0]hexane (the shaped part).

Chart I

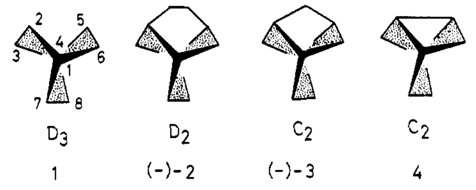


Chart II

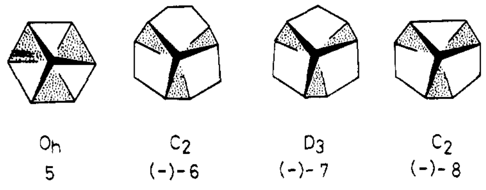
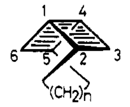
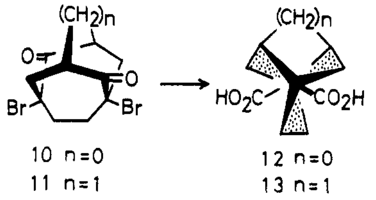


Chart III



4 n = 2
9 n = 1

Scheme I



Our continuing interests in gyrochiral cage-shaped molecules prompted us to prepare the $C_2$-bissecocubane (**4**) derivatives in optically active modification with known

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