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The Synthesis and Absolute Configuration of Optically Active Tricyclo[4.3.0.0^{3,8}]nonane (Twist-brendane)

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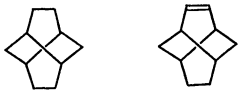
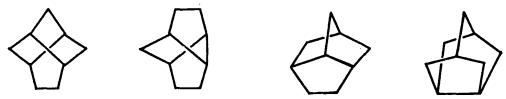
(−)-Tricyclo[4.3.0.0^{3,8}]nonane ("twist-brendane") was synthesized *via* (−)-tricyclo[4.3.0.0^{3,8}]nonan-2-one ("twist-brendan-2-one"). The absolute configuration, (1*R*,3*S*,6*S*,8*R*)-tricyclo[4.3.0.0^{3,8}]nonane was assigned to (−)-twist-brendane by correlating with (−)-*endo*-5-carboxybicyclo[2.2.1]heptane.

Of the hydrocarbons with tricyclodecane skeleton, only tricyclo[4.4.0.0^{3,8}]decane ("twistane") (**1**) and tricyclo[4.4.0.0^{3,8}]dec-4-ene ("twistene") (**2**) are known in optically active modifications, their absolute configurations having been established.[1,2]



(**1**) (**2**)

"Twist-brendane" (**3**), brexane (**4**), brendane (**5**), and noradamantane (**6**) are the members of tricyclononane,[3-8] the next lower homolog of tricyclodecane, and are free from strain. We see from their structure formula that twist-brendane (**3**) and brexane (**4**) may be called "nortwistane" retaining the chiral twist boat cyclohexane moiety of their parent compound.



(**3**) (**4**) (**5**) (**6**)

Having succeeded in the synthesis of optically active twistane (**1**) and establishment of its absolute configuration,[1] we directed our studies toward the syntheses of the chiral hydrocarbons. This paper reports the synthesis and assignment of the absolute configuration of optically active twist-brendane (**3**).

endo-5-Carboxybicyclo[2.2.1]hept-2-ene (**7a**) is convenient as starting material since the absolute configuration and the absolute rotation have been determined by Berson and his co-workers.[9,10]

Pure *endo*-carboxylic acid (**7a**) was obtained from an *endo-exo* mixture of carboxylic acid (**7a**) and **7b** by the known method.[10-12]

Since the Arndt-Eistert reaction of the unsaturated carboxylic acid (**7a**) to give the higher homolog failed, the following stepwise procedure was adopted.

Reduction of carboxylic acid (**7a**) with lithium aluminium hydride in ether afforded *endo*-5-hydroxymethylbicyclo[2.2.1]hept-2-ene (**9**) which was converted into *p*-toluenesulfonate (**10**). *endo*-5-Cyanomethylbicyclo-[2.2.1]hept-2-ene (**11**) prepared from *p*-toluenesulfonate (**10**) was hydrolyzed by heating with potassium hydroxide in ethylene glycol to yield the desired higher homologous carboxylic acid (**12**).

We next spanned the ethano-bridge between 3 and 6 positions of norbornane by using, with a slight modification, the scheme for the synthesis of optically active twistane (**1**).

Iodolactonization of the unsaturated carboxylic acid (**12**) with iodine-iodide in aqueous sodium bicarbonate solution secured iodolactone (**13**), which was heated, without further purification, with 10% aqueous sodium hydroxide to give 3-oxo-5-*endo*-carboxymethylbicyclo-[2.2.1]heptane (**14**), mp 96—97°C.[13]

After esterification of carboxylic acid (**14**) with diazomethane followed by protection of the keto group

1) K. Adachi, K. Naemura, and M. Nakazaki, *Tetrahedron Lett.*, **1968**, 5467.
2) M. Tichy and L. Sicher, *ibid.*, **1969**, 4609.
3) B. R. Vogt, *ibid.*, **1968**, 1579.
4) R. R. Sauers and L. A. Whittle, *J. Org. Chem.*, **34**, 3579 (1969).
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6) P. von R. Schleyer and E. Wiskott, *Tetrahedron Lett.*, **1967**, 2845.
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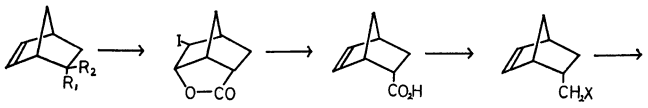
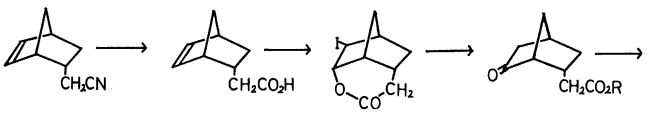
8) A. Nickon, G. D. Pandit, and R. O. Williams, *ibid.*, **1967**, 2851.
9) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Amer. Chem. Soc.*, **83**, 3986 (1961).
10) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959).
11) K. Alder, G. Stein, M. Liebmann, and E. Rolland. *Ann. Chem.*, **514**, 197 (1934). J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72**, 3116 (1959).
12) E. E. van Tamelen, and M. Shamma, *ibid.*, **77**, 2315 (1955).
13) S. Beckmann, H. Geiger, and M. Schaber-Kiechle, *Chem Ber.*, **92**, 2419 (1959). S. Beckmann and H. Geiger, *ibid.*, **92**, 2411 (1959).



(**7a**) R_1=CO_2H (**8**) (−)-(**7a**) (−)-(**9**) X=OH
R_2=H (**10**) X=OTs
(**7b**) R_1=H
R_2=CO_2H



(−)-(**11**) (−)-(**12**) (**13**) (**14**) R=H
(+)-(**15**) R=CH_3

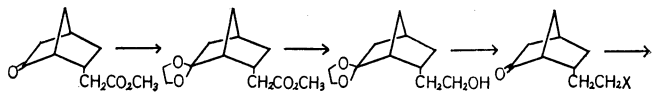
by ketal formation with ethylene glycol, the resulting ketal-ester (**16**) was treated with lithium aluminium hydride in ether to yield ketal-alcohol (**17**), hydrolysis of which with *p*-toluenesulfonic acid in acetone gave 3-oxo-5-*endo*-(2-hydroxy)ethylbicyclo[2.2.1]nonane (**18**) Since the procedure which proved satisfactory in twistane synthesis gave a very poor yield (about 2%) for intramolecular alkylation of ketomethanesulfonate (**19**),[1] the conditions were modified as follows.

Prolonged heating (22 hr) at 60°C with excess sodium hydride in dry dimethylformamide in a nitrogen atmosphere converted the methanesulfonate (**19**) into a mixture from which twist-brendan-2-one, tricyclo-[4.3.0.$0^{3,8}$]nonan-2-one (**20**), mp 174—175°C was obtained after chromatographic purification and sublimation.

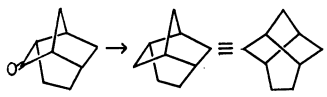
Although various evidences, including elemental analysis, mass spectrum (molecular ion peak, *m/e* 136) and infrared spectrum (1750 cm^{-1}) clearly supported the structure, conclusive proof was obtained by its conversion into the known twist-brendane.

The Wolff-Kishner reduction of the ketone (**20**) gave a product which was purified by column chromatography on neutral alumina followed by sublimation to provide a crystalline hydrocarbon, mp 159—160°C.

Its mass spectrum showed peaks at *m/e* 122, 93, 81, 80, 79, 67, 41, and 39. The NMR spectrum exhibited two broad singlets at τ 7.75 and 8.16 and a poorly resolved multiplet around 8.30—8.90. These spectra are found to be in line with those reported for twist-brendane (**3**) by Vogt.[3]



(+)-(**15**) (+)-(**16**) (**17**) (+)-(**18**) X=OH
(**19**) X=OMs

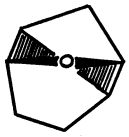


(−)-(**20**) (−)-(**3**)

The same reaction scheme outlined above provided optically active twist-brendan-2-one (**20**), mp 169—171°C, $[\alpha]_D^{21}$ −240° and twist-brendane (**3**), mp 157.5—159°C, $[\alpha]_D^{18}$ −235° from (−)-*endo*-5-carboxybicyclo-[2.2.1]hept-2-ene (**7a**), $[\alpha]_D^{20}$ −119° (82% optical purity), which was obtained by optical resolution of racemate *via* cinchonidine salt.

Since the absolute configuration of (−)-unsaturated carboxylic acid (**7a**) has been established by correlating with (−)-fenchone, (−)-twist-brendan-2-one (**20**) and (−)-twist-brendane (**3**) should be (−)-(1*R*,3*R*,6*S*,8*R*)-tricyclo[4.3.0.$0^{3,8}$]nonan-2-one and (−)-(1*R*,3*S*,6*S*,8*R*)-tricyclo[4.3.0.$0^{3,8}$]nonane, respectively.

The cyclohexanone moiety of twist-brendan-2-one which is indicated by the shaded past in the projection formula (**21**) has a "right-handed" twist boat form according to the definition of Djerassi and Klyne who drew the general conclusion that the twist boat form of this type exhibits a strong positive CD curve around 300 mμ.[15]



(**21**)

Contrary to expectation, (−)-twist-brendan-2-one (**20**) shows a negative maximum ($[\theta]$ 1.50×10^4) at 289 mμ (Fig. 1).

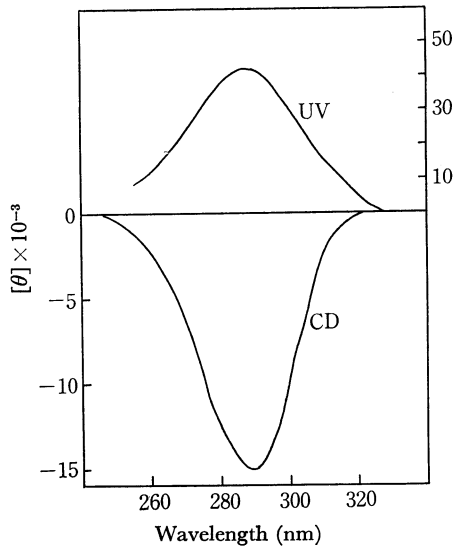


Fig. 6. UV and CD spectra.

This suggests that proper caution should be paid in applying this rule, which has been proved valid in steroid, to this type of cage compound.

Experimental[16]

(±)-endo-5-Hydroxymethylbicyclo[2.2.1]hept-2-ene (9) and Its Tosylate (10). *endo*-5-Carboxybicyclo[2.2.1]hept-2-ene

14) The structure formula indicated refers to the enantiomers which eventually give (−)-twist-brendane.

15) C. Djerassi and W. Klyne, *Proc. Nat. Acad. Sci. U.S.*, **48**, 1093 (1962).

16) Melting points and boiling points are uncorrected. NMR measurements were carried out on a JEOLC-60 H. Optical rotations were measured with a JASCO DIP-SL automatic polarimeter. Mass spectra were measured with a Hitachi RMS-4 spectrometer.

(**7a**) (35.6 g), which was prepared by the method of Berson,[10] was refluxed for 4.5 hr with 9.8 g of lithium aluminium hydride in 300 ml of dry ether. After addition of aqueous sodium sulfate, a separated solid was filtered off and the filtrate was washed with saturated aqueous sodium carbonate, saturated aqueous sodium chloride and dried. After removal of the solvent, the residue was distilled to give 28.3 g of *endo*-5-hydroxymethylbicyclo[2.2.1]hept-2-ene (**9**), bp 100—104°C/18 mmHg, n_D^{18} 1.5000.

IR (neat film): 3320, 1030, and 720 cm^{-1}.

NMR (CCl_4): τ 3.88—4.20 (2H, s), 6.00 (1H, s), 6.55—7.00 (2H, m), 7.05—7.35 (2H, m), 7.50—8.00 (1H, m), 8.00—8.50 (1H, m), 8.55—8.90 (2H, m), 9.40—9.70 (1H, m).[17]

A solution of 25.1 g of unsaturated alcohol (**9**) and 42.4 g of *p*-toluenesulfonyl chloride in 80 ml of dry pyridine was kept at room temperature for 24 hr. The reaction mixture was poured into chilled hydrochloric acid and extracted with ether. The extract was washed with dilute hydrochloric acid, aqueous sodium bicarbonate, saturated aqueous sodium chloride and dried. After removal of the solvent, crude *p*-toluenesulfonate (**10**) was recrystallized from *n*-hexane to give needles (50.4 g), mp 47—48°C.

Found: C, 64.47; H, 6.45; S, 11.64%. Calcd for $C_{15}H_{18}O_3S$: C, 64.73; H, 6.52; S, 11.50%.

(±)-endo-5-Cyanomethylbicyclo[2.2.1]hept-2-ene (11). A mixture of 55.9 g of *p*-toluenesulfonate (**10**) and 29.7 g of sodium cyanide in 330 ml of dry dimethylformamide was heated at 110—120°C for 2 hr and then at 130—140°C for further 8 hr. After cooling, a solid was filtered off and the filtrate was concentrated under reduced pressure. The residue was poured into chilled water and extracted with ether. The extract was washed with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, saturated aqueous sodium chloride and dried over magnesium sulfate. After filtration and removal of the solvent, distillation gave *endo*-5-cyanomethylbicyclo[2.2.1]hept-2-ene (**11**) (20.7 g), bp 106—107°C/19 mmHg, n_D^{18} 1.4864.

IR (neat film): 2250 and 720 cm^{-1}.

Found: C, 80.75; H, 8.38; N, 10.32%. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.33; N, 10.52%.

(±)-endo-5-Carboxymethylbicyclo[2.2.1]hept-2-ene (12). A mixture of 19.5 g of *endo*-5-cyanomethylbicyclo[2.2.1]hept-2-ene (**11**), 25.0 g of potassium hydroxide and 200 ml of ethylene glycol was heated at 130—140°C for 1 hr and then at 150—160°C for further 6 hr. After cooling, the reaction mixture was diluted with water and washed with ether. The aqueous solution was then acidified and extracted with ether. The extract was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. After removal of the solvent, distillation gave 20.5 g of *endo*-5-carboxymethylbicyclo[2.2.1]hept-2-ene (**12**), bp 118—119°C/3 mmHg, n_D^{18} 1.4970.

IR (neat film): 1700 and 720 cm^{-1}.

Found: C, 70.74; H, 8.01%. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95%.

(±)-3-Oxo-5-endo-carboxymethylbicyclo[2.2.1]heptane (14). To a solution of 19.7 g of *endo*-5-carboxymethylbicyclo[2.2.1]-hept-2-ene (**12**) in 860 ml of 0.5N aqueous sodium bicarbonate was added a solution of 40 g of iodine and 158 g of potassium iodide in 470 ml of water and the mixture was kept for 24 hr in a dark place. A dark oil was separated by decantation and dissolved in chloroform and the water layer was extracted with chloroform. A combined chloroform solution was washed with aqueous sodium thiosulfate, saturated aqueous sodium bicarbonate, saturated aqueous sodium chloride and dried over magnesium sulfate. After filtration, the solvent was removed to give a crystalline iodolactone (**13**), which, without purification, was dissolved in 10% aqueous sodium hydroxide (800 ml). The mixture was heated at 100°C for 1 hr and then washed with ether. The alkaline solution was acidified and extracted with ether. The extract was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. Filtration and removal of the solvent afforded a crystalline substance which was recrystallized from *n*-hexane–benzene to give 16.5 g of 3-oxo-5-*endo*-carboxymethylbicyclo-[2.2.1]heptane (**14**), mp 96—97°C.

IR (nujol): 1730 and 1700 cm^{-1}.

Found: C, 64.62; H, 7.23%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

(±)-3-Oxo-5-endo-methoxycarbonylmethylbicyclo[2.2.1]heptane (15). To a solution of 8.40 g of 3-oxo-5-*endo*-carboxymethylbicyclo[2.2.1]heptane (**14**) in ether was added a solution of diazomethane in ether at 5—0°C and the mixture was stirred for 2 hr at the same temperature. The solvent and excess diazomethane were then removed under reduced pressure and the residue was distilled to give 8.36 g of the methyl ester (**15**), bp 128—129°C/5 mmHg, n_D^{18} 1.4787.

IR (neat film): 1740 cm^{-1}.

NMR (CCl_4): τ 6.40 (3H, s), 7.3—7.6 (3H, m), 7.7—7.8 (2H, d), 8.0—8.1 (2H, d), 8.2—8.3 (3H, m), 8.85—9.20 (1H, d).

2,4-Dinitrophenylhydrazone: mp 95—96°C.

Found: C, 53.14; H, 5.02; N, 15.37%. Calcd for $C_{16}H_{18}O_6N_4$: C, 53.03; H, 5.01; N, 15.46%.

(±)-3-Ethylenedioxy-5-endo-methoxycarbonylbicyclo[2.2.1]heptane (16). A mixture of 32.6 g of 3-oxo-5-*endo*-methoxycarbonylmethylbicyclo[2.2.1]heptane (**15**), 560 ml of ethylene glycol, 2.10 g of *p*-toluenesulfonic acid and 2.5 l of benzene was refluxed for 21 hr. During this period the water generated was separated as benzene azeotrope from the reaction mixture. After cooling, the benzene layer was separated from ethylene glycol layer, which was poured into water and extracted with benzene. A combined benzene solution was washed with saturated aqueous sodium bicarbonate, saturated aqueous sodium chloride and dried over magnesium sulfate. After removal of the solvent, distillation gave 30.7 g of 3-ethylenedioxy-5-*endo*-methoxycarbonylmethylbicyclo[2.2.1]heptane (**15**), bp 127—131°C/4 mmHg, n_D^{18} 1.4829.

IR (neat film): 1735, 1175, 1100, and 1020 cm^{-1}.

Found: C, 63.51; H, 7.97%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

(±)-3-Oxo-5-endo-(2-hydroxy)ethylbicyclo[2.2.1]heptane (18). A solution of 30.5 g of 3-ethylenedioxy-5-*endo*-methoxycarbonylbicyclo[2.2.1]heptane (**16**) in 240 ml of dry ether was added to a suspension of 7.6 g of lithium aluminium hydride on 240 ml of dry ether and the mixture was refluxed for 4.5 hr. Saturated aqueous sodium sulfate was added to the chilled reaction mixture and a solid was filtered off. The filtrate was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. After filtration, the solvent was removed to give ketalalcohol (**17**), which was stirred at room temperature for 5 hr with *p*-toluenesulfonic acid (4.4 g) in 1.8 l of acetone. After neutralization with sodium bicarbonate the acetone was removed and then a residue was diluted with ether. The resulting mixture was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. After removal of the solvent, distillation gave 3-oxo-5-*endo*-(2-hydroxy)ethylbicyclo[2.2.1]-heptane (**18**) (14.1 g), bp 118—120°C/1.5 mmHg, n_D^{18} 1.4968.

IR (neat film): 3400, 1735, and 1050 cm^{-1}.

NMR (CCl_4): τ 6.23 (1H, s), 6.51 (2H, m), 7.50 (1H, s),

17) R. G. Foster and M. C. McIvor, *Chem. Commun.*, **1967**, 280.

7.8—9.1 (10H, m).

2,4-Dinitrophenylhydrazone: mp 124.5—125°C.

Found: C, 53.76; H, 5.35; N, 16.64%. Calcd for $C_{15}H_{18}O_5N_4$: C, 53.88; H, 5.43; N, 16.76%.

(±)-Tricyclo[4.3.0.0^{3,8}]nonan-2-one (20). To a solution of 4.34 g of 3-oxo-5-*endo*-(2-hydroxy)ethylbicyclo[2.2.1]heptane (**18**) in 16 ml of dry pyridine was added 6.9 g of methanesulfonyl chloride at 5—0°C. After stirring at the same temperature for 2 hr, the reaction mixture was kept at room temperature for 24 hr and then poured into chilled hydrochloric acid. The mixture was extracted with ether and the extract was washed with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, saturated aqueous sodium chloride and dried over magnesium sulfate. After filtration, the solvent was removed to give methanesulfonate (**19**), which, without purification, was dissolved in 50 ml of dry dimethylformamide. The solution was added to a suspension of 4.00 g of sodium hydride on 100 ml of dry dimethylformamide and the mixture was heated at 60°C for 21.5 hr under a nitrogen atmosphere. The reaction mixture was poured into chilled water and extracted with ether. The extract was washed with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, saturated aqueous sodium chloride and dried over magnesium sulfate. After removal of the solvent, the residue was chromatographed on neutral alumina (activity III). An elution with *n*-pentane gave a semisolid which was sublimed to yield 0.89 g of tricyclo[4.3.0.0^{3,8}]nonan-2-one (**20**), mp 174—175°C (in a sealed tube).

IR (CCl_4 solution): 1750 cm^{-1}.

NMR (CCl_4): τ 7.37 (1H, m), 7.60 (2H, s), 7.85 (1H, m), 8.0—8.6 (8H, m).

Mass spectrum: *m/e* 136, 93, 80, 79, 67, 66, 58, 54, 41, and 39.

Found: C, 79.38; H, 9.00%. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88%.

2,4-Dinitrophenylhydrazone: mp 137—139°C.

Found: C, 56.81; H, 5.00; N, 17.61%. Calcd for $C_{15}H_{16}O_4N_4$: C, 56.96; H, 5.10; N, 17.71%.

(±)-Tricyclo[4.3.0.0^{3,8}]nonane (3). A solution of 220 mg of tricyclo[4.3.0.0^{3,8}]nonan-2-one (**20**), 0.13 g of potassium hydroxide and 0.22 ml of 80% hydrazine hydrate in 2 ml of triethylene glycol was heated at reflux for 1.5 hr. Water was then allowed to boil out of the mixture as the temperature approached 200°C. The resulting mixture was heated at reflux for further 4 hr during which time a white solid collected in the condenser. After cooling, the solid was rinsed out with *n*-hexane and the triethylene glycol solution was extracted with *n*-pentane. A combined solution was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. After filtration, removal of the solvent gave a solid which was chromatographed on neutral alumina (activity III). Sublimation of a solid eluted with *n*-pentane gave 85 mg of tricyclo[4.3.0.0^{3,8}]nonane (**3**), mp 159—160°C (in a sealed tube) (lit, mp 165—166°C,[3] 140°C[4]).

NMR (CCl_4): τ 7.75 (2H, s), 8.16 (2H, s), 8.30—8.90 (10H, m).

Mass spectrum: *m/e* 122, 93, 81, 80, 79, 67, 41, and 39.

Found: C, 87.68; H, 11.48%. Calcd for C_9H_{14}: C, 88.45; H, 11.55%.

(−)-endo-5-Carboxybicyclo[2.2.1]hept-2-ene (7a). To a boiling mixture of 50.0 g of cinchonidine in 3 l of acetone was added 24.0 g of pure *endo*-5-carboxybicyclo[2.2.1]hept-2-ene (**7a**). Cooling of the clear solution produced a salt $[\alpha]_D^{20}$ −84.8° (*c* 1.1, 99% ethanol), (47.0 g). Recrystallization six times from acetone gave the salt $[\alpha]_D^{19}$ −122° (*c* 1.2, 99% ethanol), (11.7 g). The salt was treated with 10% aqueous sodium hydroxide at room temperature. After acidification, the solution was extracted with ether and the extract was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. After filtration and evaporation of the solvent, the residue was distilled to give 2.64 g of (−)-*endo*-5-carboxybicyclo[2.2.1]hept-2-ene (**7a**), bp 139—140°C/20 mmHg, $[\alpha]_D^{20}$ −119° (*c* 1.4, 95% ethanol), (lit, $[\alpha]_D^{26}$ −70.4°, *c* 1.4, 95% ethanol[10]).

Found: C, 69.45; H, 7.37%. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30%.

(−)-endo-5-Hydroxymethylbicyclo[2.2.1]hept-2-ene (9). (−)-*endo*-5-Carboxybicyclo[2.2.1]hept-2-ene (**7a**) (23.7 g) was reduced with lithium aluminium hydride in ether by the same procedure as described for the racemate to give 20.1 g of (−)-*endo*-5-hydroxymethylbicyclo[2.2.1]hept-2-ene (**9**), bp 92—96°C/14 mmHg, $[\alpha]_D^{23}$ −70.0° (*c* 1.0, 99% ethanol), n_D^{18} 1.4999.

Found: C, 77.27; H, 9.74%. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74%.

(−)-endo-5-Cyanomethylbicyclo[2.2.1]hept-2-ene (11). (−)-*endo*-5-Hydroxymethylbicyclo[2.2.1]hept-2-ene (**9**) (20.0 g) was treated with 34.4 g of *p*-toluenesulfonylchloride and 65 ml of dry pyridine to give *p*-toluenesulfonate (**10**), which, without purification, was heated with 27.0 g of sodium cyanide in 300 ml of dry dimethylformamide at 130—140°C for 12 hr to give 16.5 g of (−)-*endo*-5-cyanomethylbicyclo-[2.2.1]hept-2-ene (**11**), bp 100—102°C/15 mmHg, $[\alpha]_D^{18}$ −92.1° (*c* 0.75, 99% ethanol), n_D^{18} 1.4869.

Found: C, 80.69; H, 8.36; N, 10.30%. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.33; N, 10.52%.

(−)-endo-5-Carboxymethylbicyclo[2.2.1]hept-2-ene (12). Hydrolysis of 16.5 g of (−)-*endo*-5-cyanomethylbicyclo[2.2.1]-hept-2-ene (**11**) with potassium hydroxide in ethylene glycol gave 18.7 g of (−)-*endo*-5-carboxymethylbicyclo[2.2.1]hept-2-ene (**12**), bp 102—105°C/1 mmHg, $[\alpha]_D^{24}$ −61.5° (*c* 0.68, 99% ethanol), n_D^{18} 1.4911.

Found: C, 70.69; H, 8.00%. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95%.

(+)-3-Oxo-5-endo-methoxycarbonylmethylbicyclo[2.2.1]heptane (15). Iodolactone (**13**) which was prepared from 18.5 g of (−)-*endo*-5-carboxymethylbicyclo[2.2.1]hept-2-ene (**12**) by the same procedure as described for racemate was, without purification, treated with 10% aqueous sodium hydroxide at 100°C for 1 hr to give 32.3 g of 3-oxo-5-*endo*-carboxymethylbicyclo[2.2.1]heptane (**15**). Without purification, the ketocarboxylic acid (**14**) was treated with diazomethane in ether to give 17.9 g of (+)-3-oxo-5-*endo*-methoxycarbonylbicyclo[2.2.1]heptane (**15**), bp 106—108°C/2 mmHg, $[\alpha]_D^{14}$ +16.5° (*c* 1.2, 99% ethanol), n_D^{18} 1.4790.

Found: C, 65.45; H, 7.67%. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74%.

(+)-3-Ethylenedioxy-5-endo-methoxycarbonylmethylbicyclo-[2.2.1]heptane (16). Treatment of 17.5 g of (+)-3-oxo-5-*endo*-methoxycarbonylmethylbicyclo[2.2.1]heptane (**15**) with 300 ml of ethylene glycol and 1.38 g of *p*-toluenesulfonic acid in 1.34 l of benzene gave 18.7 g of (+)-3-ethylenedioxy-5-*endo*-methoxycarbonylmethylbicyclo[2.2.1]heptane (**16**), bp 112—115°C/1 mmHg, $[\alpha]_D^{23}$ +22.1° (*c* 1.1, 99% ethanol), n_D^{18} 1.4833.

Found: C, 63.28; H, 7.88%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

(+)-3-Oxo-5-endo-(2-hydroxy)ethylbicyclo[2.2.1]heptane (18). Reduction of 18.6 g of (+)-3-ethylenedioxy-5-*endo*-methoxycarbonylmethylbicyclo[2.2.1]heptane (**16**) with lithium aluminium hydride in ether gave 3-ethylenedioxy-5-*endo*-(2-hydroxy)ethylbicyclo[2.2.1]heptane (**17**), which, without purification, was treated with *p*-toluenesulfonic acid in acetone to

give 8.79 g of (+)-3-oxo-5-*endo*-(2-hydroxy)ethylbicyclo-[2.2.1]heptane (**18**), bp 122—123°C/1.5 mmHg, $[\alpha]_D^{22}$ +17.2° (*c* 1.1, 99% ethanol), n_D^{18} 1.5007. The substance was very hygroscopic.

Found: C, 69.22; H, 8.20%. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

(−)-Tricyclo[4.3.0.0^{3,8}]nonan-2-one (20). Methanesulfonate (**19**), prepared from 4.26 g of (+)-3-oxo-5-*endo*-(2-hydroxyethyl)bicyclo[2.2.1]heptane (**18**), was heated at 60°C for 25 hr with 4.00 g of sodium hydride in 150 ml of dry dimethylformamide. The product was chromatographed on neutral alumina (activity III) and a semisolid eluted with *n*-pentane was sublimed to yield 789 mg of (−)-tricyclo-[4.3.0.0^{3,8}]nonan-2-one (**20**), mp 169—171°C (in a sealed tube), $[\alpha]_D^{21}$ −240° (*c* 0.58, 99% ethanol).

UV: λ_{max}^{MeOH} 289 mμ (ε 43).

CD (*c* 3.03×10^{-3}, methanol): $[\theta]_{320}$ 0, $[\theta]_{289}$ -150×10^2, $[\theta]_{245}$ 0.

Found: C, 78.72; H, 8.92%. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88%.

(−)-Tricyclo[4.3.0.0^{3,8}]nonane (3). The Wolff-Kishner reduction of 450 mg of (−)-tricyclo[4.3.0.0^{3,8}]nonan-2-one (**20**) was carried out by the same procedure as described for racemate. The product was purified by chromatography and sublimation to give 208 mg of (−)-tricyclo[4.3.0.0^{3,8}]-nonane (**3**), mp 157.5—159°C (in a sealed tube), $[\alpha]_D^{18}$ −235°, $[\alpha]_{436}^{20}$ −483° (*c* 0.52, 99% ethanol).

Found: C, 87.76; H, 11.49%. Calcd for C_9H_{14}: C, 88.45; H, 11.55%.

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