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Synthesis and Reactions of Tricyclo[5.2.1.$0^{2,6}$]dec-2(6)-ene[1]

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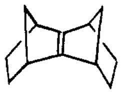
The synthesis and some addition reactions of the novel strained olefin, tricyclo[5.2.1.$0^{2,6}$]dec-2(6)-ene (**5**), are described. The stability and reactivity of **5** are discussed with regard to molecular mechanics calculations (MM2).

There is considerable current interest in the synthesis and chemistry of *syn*- and *anti*-sesquinorbornene (**1**[2,3] and **2**,[3,4] respectively) and related compounds.[5] Attention has been focused on the pyramidalization of these olefins,[6,7] which possess tricyclo[5.2.1.$0^{2,6}$]dec-2(6)-ene (**5**) carbon skeleton as a partial framework. Recently, the synthesis of **5** was independently achieved by Bartlett[8] and us.[1] It is particularly interesting to compare the chemical behavior of **5** in comparison with that of **1** and **2**. We now provide details of the preparation as well as some reactions of the olefin **5**.



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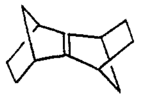

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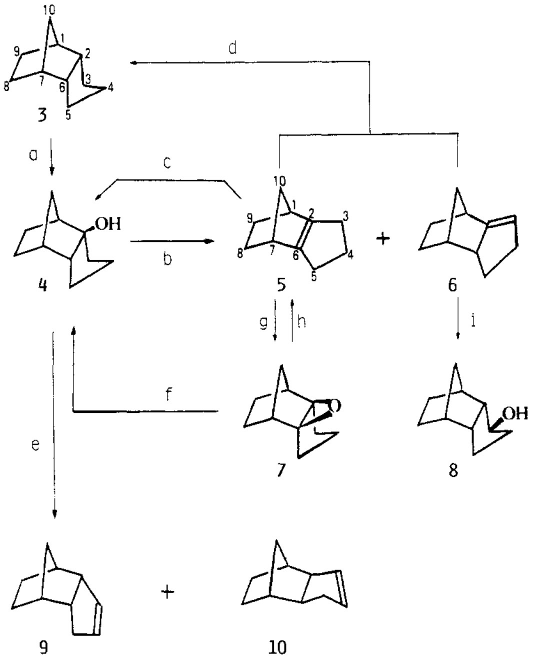
Results and Discussion

Our approach to **5** is based on the dehydration of 2-*exo*-hydroxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**4**), which can be easily obtained from the bridgehead hydroxylation of *endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**3**) with *m*-chloroperbenzoic acid (MCPBA)[9] (Scheme I). An initial attempt to dehydrate the alcohol **4** to **5** with Amberlyst-15,[10] a cation-exchange resin, was unsuccessful. Instead, *endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (**9**) and *exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (**10**), which were the products of dehydration from 8-*exo*-hydroxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]decane (**11**),[11] were obtained. Molecular mechanics calculations using the MM2 force field[12] were performed on all possible tricyclo[5.2.1.$0^{2,6}$]decene isomers. The heats of formation and strain energies are summarized in Table I. The greater stabilities of **9** and **10** relative to the other tricyclo[5.2.1.$0^{2,6}$]decenes seem to suggest that the above dehydration reaction occurred under thermodynamic control.[13]

Scheme I[a]



[a] (a) MCPBA; (b) *p*-TsCl, py; (c) B_2H_6; (d) H_2, PtO_2; (e) Amberlyst-15; (f) Li, $H_2NCH_2CH_2NH_2$; (g) MCPBA; (h) Li, THF; (i) 9-BBN.

In view of the relative instability of **5**, it seemed worthwhile to investigate the dehydration of **4** under less vigorous reaction conditions in expectation of obtaining **5**. Treatment of the alcohol **4** at ambient temperature for 40 h with *p*-toluenesulfonyl chloride and pyridine gave 68% of a 3:1 mixture of the desired olefin **5** and 6-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-2(3)-ene (**6**). These olefins were thermally stable and distilled without decomposition. Preparative GLC readily separated the mixture.

The structures of these olefins were elucidated on the basis of spectroscopic analysis as well as the structure of hydrogenation product. The ^{13}C NMR spectrum of the

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[1] A preliminary communication of part of this work has been published: Takaishi, N.; Takahashi, H.; Inamoto, Y. *Tetrahedron Lett.* **1985**, *26*, 2361.

[2] (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Paquette, L. A.; Ohkata, K.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 3303. (c) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553. (d) Paquette, L. A.; DeLucca, G.; Ohkata, K.; Gallucci, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1015.

[3] (a) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520. (b) Brown, R. S.; Bushek, J. M.; Kopecky, K. R.; Miller, A. J. *J. Org. Chem.* **1983**, *48*, 3692. (c) Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J. *J. Org. Chem.* **1984**, *49*, 1875. (d) Roof, A. A. M.; Winter, W. J.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 4093.

[4] (a) Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383. (b) Kopecky, K. R.; Miller, A. J. *Can. J. Chem.* **1984**, *62*, 1840. (c) Gajhede, M.; Jorgensen, F. S.; Kopecky, K. R.; Watson, W. H.; Kashyap, R. P. *J. Org. Chem.* **1985**, *50*, 4395.

[5] Watson, W. H., Ed. *Stereochemistry and Reactivity of Systems Containing π Electrons*; Verlag Chemie: Deerfield Beach, FL, 1983.

[6] Norbornenes: (a) Wipff, G.; Morokuma, K. *Chem. Phys. Lett.* **1980**, *74*, 400. Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1980**, *21*, 4445. (b) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436. (c) Burkert, U. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 572. (d) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, *23*, 2435.

[7] Sesquinorbornenes: (a) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022. (b) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, *23*, 927. (c) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *39*, 3345. (d) Jorgensen, F. S. *Tetrahedron Lett.* **1983**, *24*, 5289. (e) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmayer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. (f) Johnson, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1135. (g) Ermer, O.; Bodecker, C.-D. *Helv. Chim. Acta* **1983**, *66*, 943. (h) Ginsburg, D. *Tetrahedron* **1983**, *39*, 2095.

[8] Wu, C.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 733.

[9] Takaishi, N.; Fujikura, Y.; Inamoto, Y. *Synthesis* **1983**, 293.

[10] Takaishi, N.; Inamoto, Y.; Aigami, K. *J. Org. Chem.* **1980**, *45*, 2254.

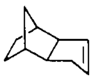
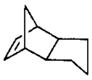
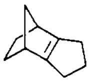
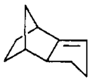
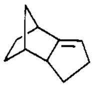
[11] (a) Schleyer, P. v. R.; Donaldson, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 5702. (b) Wilder, P., Jr.; Youngblood, G. T. *J. Am. Chem. Soc.* **1956**, *78*, 5706. (c) Wilder, P., Jr.; Cash, D. J.; Wheland, R. C.; Wright, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 791. (d) Gates, M.; Zabriskie, J. L., Jr. *J. Org. Chem.* **1974**, *39*, 222.

[12] (a) Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *12*, 395. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982; ACS Monogr. No. 177.

[13] For the use of force field calculations on the prediction of olefin distribution under thermodynamic control, see: Honig, N.; Allinger, N. L. *J. Org. Chem.* **1977**, *42*, 2330.

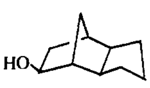
0022-3263/86/1951-4862$01.50/0

Table I. Calculated Enthalpies and Strain Energies for Tricyclo[5.2.1.0^{2,6}]decenes (kcal/mol, 25 °C, Gas)[a]

name	structure	$\Delta H_f°$	strain energy
2-exo,6-exo 3-ene (**10**)		10.21	24.68
2-endo,6-endo 3-ene (**9**)		12.11	26.59
2-exo,6-exo 8-ene		15.92	30.39
2-endo,6-endo 8-ene		16.65	31.12
2(6)-ene (**5**)		17.36	35.63
6-exo 2(3)-ene (**13**)		18.60	34.97
6-endo 2(3)-ene (**6**)		19.14	35.51

[a] Calculations based on the MM2 force field described in ref 12.

minor product **6** showed two sp^2 carbon signals [δ 159.0 (s) and 114.7 (d)], characteristic of trisubstituted olefin functionality. The surprizing low field absorption of the unsaturated bridgehead carbon atom in **6** may be a reflection of the strain in this compound incorporating the bicyclo[3.3.0]oct-1(2)-ene carbon skeleton.[14] The stereochemistry of C-6 in olefin **6** was deduced from the result that catalytic hydrogenation[15] of **6** over platinum oxide at room temperature led quantitatively to **3** without any trace of the isomeric *exo*-tricyclo[5.2.1.0^{2,6}]decane (**12**), which might be derived from 6-*exo*-tricyclo[5.2.1.0^{2,6}]dec-2-ene (**13**). On the other hand, no isomerization of either **3** or **12** was observed under these reaction conditions.[16]



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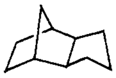
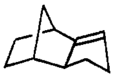


12



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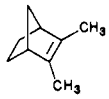
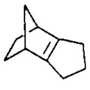
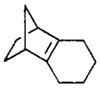
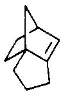
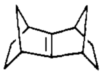
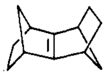
The ^{1}H NMR spectrum of the major olefin **5** showed no olefinic proton, and the ^{13}C NMR spectrum [25.7 (t, 2 C), 27.6 (t), 28.0 (t, 2 C), 41.9 (d, 2 C), 49.6 (t), 149.8 (s, 2 C) ppm] was especially informative on the C_s symmetry of the molecule and the presence of two quarternary carbon atoms. The chemical shift (149.8 ppm) of the trigonal carbon atoms in **5** appeared between that found in **1** (151.6 ppm)[2c] or **2** (153.9 ppm)[4a] and that in bicyclo[3.3.0]oct-1-(5)-ene (146.0 ppm),[14a,b] the olefin devoid of the ethano bridge (C-8 and C-9) from **5**. The result shows that addition of an ethano bridge causes in the lower field shift of tetrasubstituted annulated olefin carbon signals owing to the strain increase in the resulting molecules.[17]

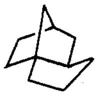
Table II. Calculated Out-of-Plane Bending Angles for Seven Relevant molecules[a]

structure	out-of-plane bending angle, deg
	1.7[b]
	3.6[b]
 **5**	21.3[c]
	7.9[c]
 **14**	3.8[c]
 **1**	17.8,[d] 18[e]
 **2**[f]	27.3,[d] 26[e]

[a] Calculations based on the MM2 force field described in ref 12. [b] Reference 6c. [c] This work. [d] Reference 7f. [e] Reference 7d. [f] Small pyramidalization (0.2°) has been calculated in ref 7e by eliminating tortional contributions.

The structure of **5** was further confirmed by hydrogenation which gave the endo hydrocarbon **3**. The hydrogen addition occurred stereoselectively from the exo side of the molecule to give the less stable hydrocarbon **3**,[18] whereas **1** was inert to the catalytic hydrogenation owing to the steric congestion on both sides of molecule.[2c] The reactivity of **5** is in contrast to that of the similarly strained 1,2-trimethylenenorborn-2-ene (**14**) ($\Delta H_f°$ = 20.67 kcal/mol; strain energy = 38.01 kcal/mol), where the hydrogenation of double bond took place from the endo side to yield thermodynamically more stable 1,2-*exo*-trimethylenenorbornane (**15**).[19]

14



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The preferred exo stereoselectivity observed in the addition reaction to norbornene derivatives has been discussed in view of out-of-plane deformation for the double bond.[6,7] The calculated out-of-plane bending angles for seven relevant molecules are shown in Table II. The

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(14) (a) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 68. (b) Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878. (c) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (d) Agosta, W. C.; Wolff, S. *J. Org. Chem.* **1975**, *40*, 1699.

(15) Hydrogenation of bicyclo[3.3.0]oct-1(2)-ene to bicyclo[3.3.0]octane has been reported: Ketley, A. D.; McClanahan, J. L. *J. Org. Chem.* **1965**, *30*, 940.

(16) (a) Schleyer, P. v. R.; Donaldson, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 4645. (b) Quinn, H. A.; McKervey, M. A.; Jackson, W. R.; Rooney, J. J. *Ibid.* **1970**, *92*, 2922. (c) Inamoto, Y.; Kadono, T., Kao Soap Co., Ltd., Japan Kokai 73-78155; *Chem. Abstr.* **1974**, *80*, P70449d.

(17) The ^{13}C chemical shift of the trigonal carbons in tricyclo-[6.3.0.0^{2,6}]undec-1(8)-ene [2,3-trimethylenebicyclo[3.3.0]oct-1(5)-ene], not so strained as **5**, appears at 144.4 and 148.2 ppm: Kakiuchi, K.; Takeuchi, H.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1613.

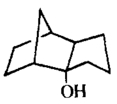
(18) Molecular mechanics calculation has indicated that the exo isomer **11** is 4.5 kcal/mol more stable than the endo isomer **3**: Engler, E. M.; Farcasiu, M.; Sevin, A.; Cense, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 5769.

(19) Jaggi, F. J.; Ganter, C. *Helv. Chim. Acta* **1980**, *63*, 866.

double bond in **5** is pyramidalized to the extent of 21.3°, which is comparable in magnitude to an 18° deviation from planarity calculated for **1**. This phenomenon in **5** has been predicted by Houk.[7e] The same property may also be responsible for the high exo reactivity of **5** even in the hydrogenation giving thermodynamically unstable hydrocarbon **3**. Comparison of **5** with norbornene (1.7°), 2,3-dimethylnorbornene (3.6°), and **14** (3.8°) reveals that the introduction of 2,3-trimethylene bridge causes a significant puckering of the molecule as compared to that of 1,2-trimethylene bridge. The small bending in **14** may be related to the preferential endo attack in hydrogenation.

Epoxidation of **5** with MCPBA, like hydrogenation, also proceeded exclusively from the exo side to give 2,6-*exo*-epoxytricyclo[5.2.1.$0^{2,6}$]decane (**7**), which is the same steric pattern of reaction as in *syn*-sesquinorbornene **1**.[2d] In contrast to **1**,[2c] but similarly as other hindered olefins,[20] olefin **5** showed a high reactivity toward atmospheric oxygen[21] at ambient temperature, giving **7** as the sole characterizable product. The configurational assignment in **7** is made on the basis of the long-range shielding effects of epoxide ring on the ^{13}C chemical shift of the methano bridge carbon signal. The signal for C-10 in **7** (34.9 ppm) appeared at a higher field than that in the corresponding hydrocarbon **3** (43.3 ppm).[22] The similar effect of the epoxide ring on the ^{13}C chemical shift of remote carbon atoms in norbornane derivatives has been reported.[23] The exo stereochemical assignment to **7** was further confirmed by the reduction[2d,3c,24] with lithium in ethylenediamine to the exo alcohol **4**. The molecule did not react with lithium aluminum hydride which was effective for 1,5-epoxybicyclo[3.3.0]octane,[25] a partial structure of **7**. Facile deoxygenation to **5** was observed when **7** was treated with lithium in tetrahydrofuran.[26]

Since hydrogenation and epoxidation occurred from the exo side of **5**, hydroboration is also expected to take place from this side. Treatment of **5** with diborane in tetrahydrofuran followed by oxidation with alkaline hydrogen peroxide produced 99.8% of the exo alcohol **4** and 0.2% of 2-*endo*-hydroxy-*exo*-tricyclo[5.2.1.$0^{2,6}$]decane (**16**).[27]



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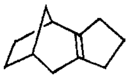

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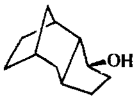

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The structure of **16** was established by the identity of its GLC retention time and mass spectrum with those of an authentic sample prepared from **12** with bridgehead hydroxylation by MCPBA.[9] The hydroboration of tricyclo[6.2.1.$0^{2,6}$]undec-2(6)-ene (**17**), the next higher homologue of tetrasubstituted annulated olefin **5**, has been found to afford rearranged secondary alcohol **18** due to the exceptionally facile isomerization of the organoborane intermediate.[28] In the present investigation, however, such rearranged secondary alcohols were not obtained even when the reaction temperature was raised up to 160 °C.[29] These results can be rationalized in terms of the difference in steric crowding of the initially formed organoborane intermediates.[31]

Extremely low reactivity of tetrasubstituted olefin **5** toward hydroboration with 9-borabicyclo[3.3.1]nonane (9-BBN)[32] permitted a facile separation of **5** from **6**. Treatment of a 3:1 mixture of **5** and **6** with 9-BBN followed by hydrogen peroxide oxidation resulted in a selective reaction of **6** to give 3-*exo*-hydroxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**8**), which was identical with the major product of hydroboration of **9**.[33] The olefin **5** was finally obtained in a purity of over 99% by vacuum fractional distillation of the product mixture.[34]

In summary, dehydration of 2-*exo*-hydroxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**4**) with *p*-toluenesulfonyl chloride and pyridine yielded 68% of a 3:1 mixture of tricyclo[5.2.1.$0^{2,6}$]dec-2(6)-ene (**5**) and 6-*endo*-tricyclo[5.2.1.$0^{2,6}$]-dec-2(3)-ene (**6**), from which **5** was readily separated upon treatment with 9-BBN. The tetrasubstituted annulated olefin **5** exhibited high reactivities characteristic of the strained olefin. The hydrogenation, epoxidation, and hydroboration of **5** took place exclusively with attack of reagent from the exo side of the molecule.

Experimental Section

All melting and boiling points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi 260-50 spectrometer as liquid films unless otherwise stated. Mass (GLC–mass) spectra were performed on a JEOL JMS-D 300 mass spectrometer equipped with a JEOL JGC-20 KP gas chromatograph and with a JMA-2000 data analyzer system. ^{1}H NMR spectra were taken on a Varian EM 360L spectrometer, and ^{13}C NMR spectra were obtained on a JEOL JNM PS/PFT-100 spectrometer. Chemical shifts were reported in parts per million (δ) relative to Me_4Si as an internal standard in $CDCl_3$. Analytical GLC was carried out on a Shimadzu GC-4CM with a 10% FFAP column or a 20% SE-30 column. Column chromatography was performed on silica gel from Wako Pure Chemical Industries (Wakogel C-200, 100–200 mesh). 2-*exo*-Hydroxytricyclo[5.2.1.$0^{2,6}$]decane (**4**) was prepared by bridgehead hydroxylation of *endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**3**) with *m*-chloroperbenzoic acid (MCPBA) as described previously.[9]

Dehydration of 4 with Amberlyst-15.[10] A solution of **4** (1.0 g, 6.6 mmol) in toluene (10 mL) was heated under reflux with Amberlyst-15 (0.5 g) for 6 h. The resin was filtered off from the cooled reaction mixture and washed with petroleum ether. The combined filtrates were washed with saturated $NaHCO_3$ solution and water and dried over Na_2SO_4. After removal of the solvent the residue was distilled by Kugelrohr at 80–90 °C (20 mm) to afford 0.23 g of a mixture consisting of **3**, *endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (**9**), and *exo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (**10**) in a ratio of 1:1:2 (estimated from GLC analysis). These products

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had ^{13}C NMR[22] and mass spectra identical with those of authentic samples prepared by the reported methods.[11]

Tricyclo[5.2.1.0^{2,6}]dec-2(6)-ene (5) and 6-*endo*-Tricyclo[5.2.1.0^{2,6}]dec-2(3)-ene (6). To a solution of 4 (1.52 g, 10 mmol) in pyridine (10 mL) kept cooled in an ice bath was added portionwise with stirring *p*-toluenesulfonyl chloride (2.86 g, 15 mmol). The reaction mixture was stirred for 0.5 h at 5 °C and for another 40 h at ambient temperature. The mixture was poured onto ice-water (100 g) and extracted with ether (40 mL × 3). The combined organic extracts were washed successively with 10% HCl, saturated $NaHCO_3$ solution, and water and then dried over Na_2SO_4. The solvent was evaporated, and the residue was fractionally distilled to give 0.91 g (68%) of a 3:1 mixture of **5** and **6** [bp 52–55 °C (7 mm)].

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.78; H, 10.23.

The mixture was further separated by GLC (20% SE-30, 80 °C) to provide analytically pure **5** (t_R 23.6 min) and **6** (26.2 min). Compound **5**: IR 2955, 2870, 2845, 1450, 1280, 1120, 1035, 950, 870, 800, 765 cm^{-1}; ^{1}H NMR δ 0.7–2.8 (complex m); ^{13}C NMR δ 25.7 (t, 2 C), 27.55 (t), 28.0 (t, 2 C), 41.9 (d, 2 C), 49.6 (t), 149.8 (s, 2 C); mass spectrum, *m/e* (relative intensity) 134 (M$^+$, 23), 107 (10), 106 (100), 105 (17), 91 (44), 79 (9), 78 (26), 77 (10), 65 (6). Compound **6**: IR 3055, 2950, 2870, 2845, 1655, 1450, 1280, 1095, 1040, 960, 790, 775 cm^{-1}; ^{1}H NMR δ 1.0–3.1 (complex m, 13 H), 5.0–5.3 (m, 1 H); ^{13}C NMR δ 20.6 (t), 27.6 (t), 35.3 (t), 37.1 (t), 38.9 (d), 39.3 (d), 44.6 (t), 57.6 (d), 114.7 (d), 159.0 (s); mass spectrum, *m/e* (relative intensity) 134 (M$^+$, 53), 119 (42), 106 (57), 105 (39), 93 (67), 92 (43), 91 (100), 78 (23), 77 (35), 66 (29).

Hydrogenation of a Mixture of 5 and 6. A solution of **5** and **6** [3:1 mixture, 134 mg (10 mmol)] in ethyl acetate (10 mL) was mixed with platinum oxide (10 mg) and subjected to atmospheric pressure hydrogenation. After reaction for 2 h at ambient temperature, the catalyst was filtrated off and the filtrate was evaporated to provide 130 mg (96 %) of **3**. No trace of the isomeric *exo*-tricyclo[5.2.1.0^{2,6}]decane (**12**) was detected by GLC and ^{13}C NMR analysis.

Epoxidation of 5 with MCPBA. To a stirred solution of **5** (1.34 g, 10 mmol) in $CHCl_3$ (25 mL) kept at 0–5 °C was added dropwise over a period of 1 h a solution of MCPBA (2.2g, 11 mmol) in $CHCl_3$ (15 mL). After the reaction was completed, the mixture was shaken with 1 N NaOH solution (15 mL × 2) and water. The organic layer was separated, dried over Na_2SO_4, and concentrated. Column chromatography of the residue using ether as eluent gave 1.16 g (77 %) of 2,6-*exo*-epoxytricyclo[5.2.1.0^{2,6}]decane (**7**): bp 102–103 °C (22 mm); IR 2955, 1385, 1295, 1128, 950, 908, 865, 815 cm^{-1}; ^{1}H NMR δ 0.75–1.0 (m, 1 H), 1.3–1.5 (m, 4 H), 1.6–2.0 (m, 7 H), 2.2–2.5 (m, 2 H); ^{13}C NMR δ 23.0 (t, 2 C), 24.9 (t, 2 C), 27.9 (t), 34.9 (t), 38.5 (d, 2 C), 69.2 (s, 2 C); mass spectrum, *m/e* (relative intensity) 150 (M$^+$, 25), 121 (48), 107 (29), 94 (46), 93 (40), 91 (37), 84 (47), 80 (44), 79 (100), 67 (46).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.27; H, 9.18.

Autoxidation of 5. A sample of **5** (134 mg, 1 mmol) was allowed to stand for 1 month in contact with atmospheric oxygen at ambient temperature. GLC analysis indicated the presence of 14% epoxide **7** (selectivity 61%), which showed the ^{13}C NMR and mass spectra identical with those of an authentic sample obtained above.

2-*endo*-Hydroxy-*exo*-tricyclo[5.2.1.0^{2,6}]decane (16).[27] A stirred mixture of **12** (1.36 g, 10 mmol) and MCPBA (2.0 g, 10 mmol) in 1,2-dichloroethane (15 mL) was heated at 65 °C for 32 h. The reaction mixture was cooled to ambient temperature, diluted with 1,2-dichloroethane (35 mL), and poured onto 1 N NaOH solution (15 mL). The organic layer was separated, washed with 1 N NaOH solution (10 mL) and then with water (10 mL × 2), dried over Na_2SO_4, and concentrated. Purification of the residue by column chromatography using petroleum ether–ether (3:1) as eluent gave 0.20 g (13%) of **16** as colorless crystals: mp 60–61 °C; IR (Nujol) 3330, 1185, 1120, 1060, 990, 975 cm^{-1}; ^{13}C NMR δ 21.7 (t), 25.3 (t), 28.4 (t), 33.3 (t), 35.5 (t), 41.3 (t and d), 45.7 (d), 56.7 (d), 89.2 (s); mass spectrum, *m/e* (relative intensity) 152 (M$^+$, 1), 110 (8), 95 (9), 85 (11), 84 (100), 83 (19), 67 (26), 66 (14), 55 (13).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.62; H, 10.69.

Reduction of 7 with Li and Ethylenediamine.[24] Lithium wire cuts (0.21 g, 30 mg atm) were added with vigorous stirring under a nitrogen atmosphere to a solution of **7** (0.75 g, 5 mmol) in anhydrous ethelenediamine (10 mL) at room temperature. The reaction mixture was stirred at 50 °C for 1 h, cooled, and treated with water (10 mL). The mixture was extracted with tetrahydrofuran (50 mL × 2). The extracts were dried over Na_2SO_4 and concentrated in vacuo to give 0.71 g (93 %) of exo alcohol **4**. No trace of endo alcohol **16** was detected by GLC analysis.

Deoxygenation of 7 with Li.[26] To a solution of **7** (1.50 g, 10 mmol) in tetrahydrofuran (15 mL) were added lithium wire cuts (0.15 g, 22 mmol) at room temperature under a nitrogen atmosphere. The reaction mixture was heated under reflux for 16 days. After cooling, excess lithium and lithium oxide were removed by filtration and were washed with ether. The filtrate was concentrated in vacuo and the residue was fractionally distilled to give 0.77 g (57 %) of the olefin, which showed identical IR, MS, and ^{13}C NMR spectra with those of **5**.

Hydroboration of 5 with Diborane. To a solution of **5** (134 mg, 1 mmol) in tetrahydrofuran (2 mL) was added at 5 °C under nitrogen atmosphere a 1 M diborane–tetrahydrofuran solution (2 mL). The reaction mixture was stirred at ambient temperature for 1 h. The excess borane was destroyed by a careful addition of water (0.2 mL). The organoboranes were oxidized with 3 N NaOH solution (0.6 mL) and 30% hydrogen peroxide (0.6 mL) at 40 °C for 1 h. The organic layer was separated, and the aqueous layer was extracted with ether (10 mL × 2). The combined organic layers were washed with saturated NaCl solution and dried over Na_2SO_4. Evaporation of the solvent gave 140 mg (92%) of the crude product which comprised of exo alcohol **4** and endo alcohol **16** in 99.8:0.2 ratio (GLC).

Hydroboration of a Mixture of 5 and 6 with 9-BBN.[32] To a cooled mixture of **5** and **6** [3:1 mixture, 1.31 g (9.8 mmol)] in tetrahydrofuran (10 mL) was added dropwise a 0.54 M 9-BBN–tetrahydrofuran solution (9 mL, 4.86 mmol). The reaction temperature was maintained at room temperature for 7 h. To the reaction mixture were added successively ethanol (4 mL), 3 N NaOH solution (6 mL), and 30% hydrogen peroxide (6 mL). After heated at 60 °C for 1 h the reaction mixture was cooled to room temperature and extracted with ether. Evaporation of the solvent gave 1.38 g of a mixture of **5**, **4**, and 3-*exo*-hydroxy-*endo*-tricyclo[5.2.1.0^{2,6}]decane (**8**) in a ratio of 80:1:19 on the basis of ^{13}C NMR and GLC analyses. Fractional distillation [109–111 °C (85 mm)] readily afforded 0.87 g (89%) of unreacted **5**. The residue was purified by preparative GLC to give **8**: ^{13}C NMR δ 22.7 (t), 23.9 (t), 24.3 (t), 37.7 (t), 39.8 (d), 41.7 (d), 42.7 (t), 44.5 (d), 55.5 (d), 74.9 (d).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.77; H, 10.80.

Hydroboration of 9.[34] To a stirred suspension of sodium borohydride (0.38 g, 10 mol) and **9** (1.34 g, 10 mmol) in tetrahydrofuran (15 mL) was added boron trifluoride etherate (1.8 g, 13 mmol) dropwise over a period of 15 min, and the mixture was stirred at room temperature for additional 1 h. After successive addition of water (2 mL), 3 N NaOH solution (6 mL), and 30% hydrogen peroxide (6 mL), the organic layer was separated, and the aqueous layer was extracted with ether (30 mL × 2). The combined organic layers were washed with water and dried over Na_2SO_4. Evaporation of the solvent afforded two alcohols [1.14 g (75 %), 3:2]. The ^{13}C NMR spectrum of the major product was identical with that of the alcohol **8** obtained above.

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Registry No. **3**, 2825-83-4; **4**, 86594-77-6; **5**, 87238-75-3; **6**, 99872-98-7; **7**, 87238-74-2; **8**, 10271-46-2; **9**, 2825-86-7; **10**, 3129-29-1; **12**, 2825-82-3; **13**, 105018-79-9; **14**, 74836-08-1; **16**, 84276-17-5; 2-*exo*,6-*exo*-tricyclo[5.2.1.0^{2,6}]dec-8-ene, 10466-50-9; 2-*endo*,6-*endo*-tricyclo[5.2.1.0^{2,6}]dec-8-ene, 2826-19-9; tricyclo[6.2.1.0^{2,7}]-undec-2(7)-ene, 96543-34-9.