(7) E. E. Schweizer, W. S. Creasy, J. G. Liecher, M. E. Jenkins, and P. L. Dalrymple, *J. Org. Chem.*, **35**, 601 (1970).
(8) I. Kawamoto, T. Hata, Y. Kishida, and C. Tamura, *Tetrahedron Lett.*, 1611 (1972).
(9) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 1 (1967).
(10) The stability of pentasubstituted phosphorus interemediates is well known and has been reviewed; see R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Thieme Verlag, Stuttgart, 1973.
(11) N. J. De'Ath and D. B. Denney, *Chem. Commun.*, 395 (1972); C. D. Hall, J. D. Bramblett, and F. F. S. Liu, *J. Am. Chem. Soc.*, **94**, 9264 (1972).
(12) A. Gastaminza, T.-R. Modro, J. H. Ridd, and J. H. P. Utley, *J. Chem. Soc. B*, 534 (1968), and references cited therein.
(13) J. M. Conia and M. L. Leriverend, *Bull. Soc. Chim. Fr.*, 2992 (1970); M. Simalty and L. Van Chau, *Tetrahedron Lett.*, 4371 (1970).

Oxymercuration–Demercuration and Hydroboration–Oxidation of *endo*-Tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene. Stereospecific Oxymercuration Leading to the 4-*exo*-Hydroxy Derivative

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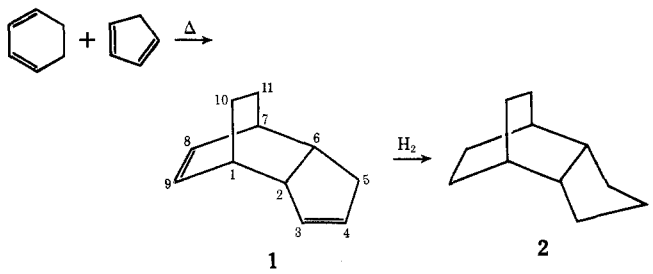
Oxymercuration–sodium borohydride reduction of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (1) was found to proceed highly regioselectively and stereospecifically, giving 4-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (3). Saturation of the 8,9 ethylenic bond in 1 resulted in a great reduction in the reactivity as well as the stereoselectivity. In contrast to this, hydroboration of 1 proceeded stereospecifically but not regiospecifically, to give three *exo*-hydroxytricycloundecene isomers. The result suggests a trans addition mechanism for the oxymercuration of 1 with the attack of mercuric ion from the endo side of the diene, the transition state being stabilized with the coordination of the 8,9 ethylenic bond to the mercuric ion.

In a series of the studies on biological activities of substituted polycycloalkanes,[1] we have been interested in the plant-hormonal properties of hydroxypolycycloalkanes. After some hydroxynorbornanes and -adamantanes as well as 3-[2] and other hydroxy derivatives of 4-homoisotwistane (tricyclo[5.3.1.0^{3,8}]undecane) had been tested,[3] examination of the activity of tricyclo[5.2.2.0^{2,6}]undecane (2) with hydroxy substituents was planned. The hydrocarbon 2 was prepared for the first time by us[4–6] through hydrogenation of the Diels–Alder adduct (1)[7] of cyclohexa-1,3-diene and cyclopentadiene. Although adamantane rearrangement of 2 under the catalysis of Lewis[4,5] and Bronsted[5,6,8] acids was studied, no functionalization reaction has been attempted to date. In this paper, oxymercuration–demercuration and hydroboration–oxidation of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (1) giving a variety of hydroxy compounds related to 2 are described.

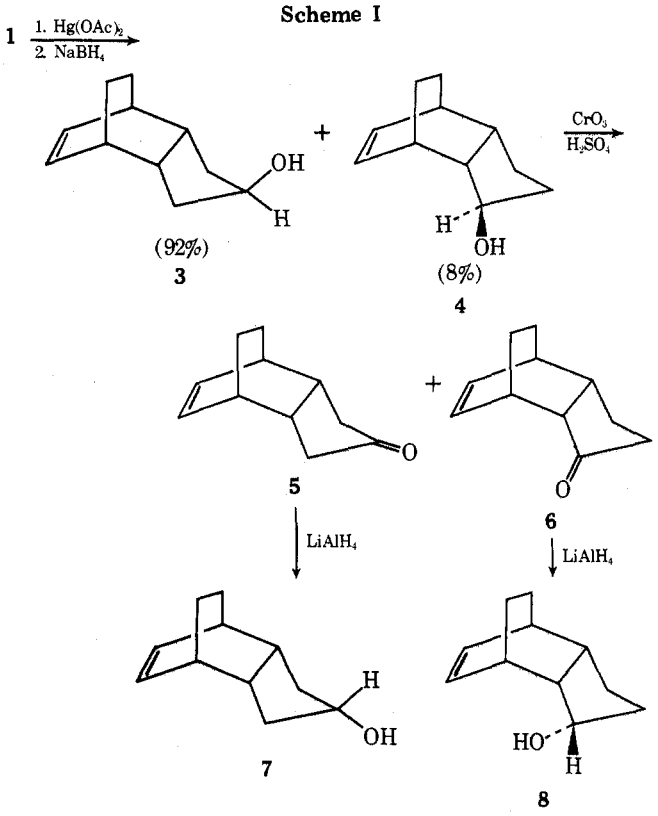


Results

Oxymercuration–sodium borohydride reduction[9,10] of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (1) in aqueous tetrahydrofuran at ambient temperature for 1 hr gave in 96% yield a mixture of 92% 4-*exo*-hydroxy (3) and 8% 3-*exo*-hydroxy (4) derivatives of *endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (13) (Scheme I). The ratio of the two isomeric alcohols in the product was determined on a Golay GC–MS, since conventional VPC could not separate them. However, a pure sample of 3 could be isolated by repeated recrystallizations.

The structure of the alcohol 3 was established as follows.

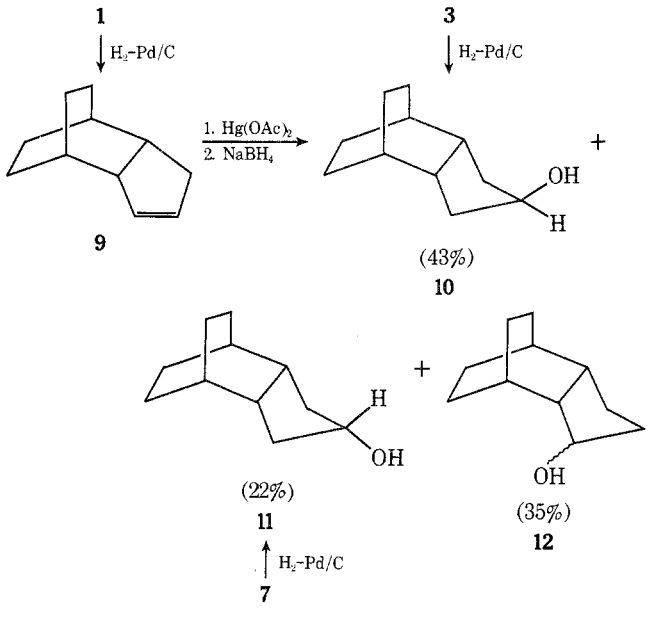
Scheme I



The ^{13}C NMR spectrum indicated that the molecule had a C_s symmetry, showing a correct chemical shift,[11] fine structure, and relative intensity of the signal for the hydroxy-substituted 4-carbon atom. The structure assignment was supported by the ^{1}H NMR spectrum, which had a olefinic proton signal corresponding to that of bicyclo[2.2.2]oct-2-ene,[12] and in which no resonance similar to that of the olefinic protons of 3,4-dimethylcyclopentene[13] was observed.

Jones oxidation[14] of the above oxymercuration–demercuration product from 1 gave a mixture of *endo*-tricy-

Scheme II



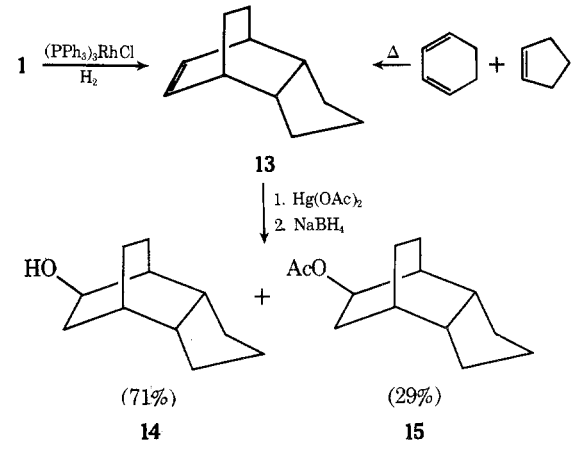
clo[5.2.2.0^{2,6}]undec-8-en-4-one (**5**) and -3-one (**6**) (Scheme I), which could be separated on preparative VPC. The ketone **5** gave endo[15-17] alcohols **7** on lithium aluminum hydride reduction (Scheme I), which was found different from the original alcohol **3**. The exo configuration of the 4-hydroxy group of **3** was thus established.

^{1}H NMR of the ketone **6** showed the presence of intact 8,9-ethylenic bond in the molecule. Since the endo alcohol **8** obtained on lithium aluminum hydride reduction of **6** (Scheme I) was different from **4**, the original alcohol **4** should have an exo configuration.

Tricyclo[5.2.2.0^{2,6}]undec-3-ene (**9**), prepared by partial hydrogenation of the diene **1** over palladium catalyst (Scheme II) was found to react quite sluggishly with mercuric acetate at ambient temperature. The decrease in the reactant **9** was only 33% at the end of 1 week, as monitored by VPC. Golay GC–MS showed that the product consisted of 43% 4-*exo*-hydroxy (**10**), 22% 4-*endo*-hydroxy (**11**), and 35% 3-hydroxy (**12**) derivatives of *endo*-tricyclo[5.2.2.0^{2,6}]undecane (**2**) (Scheme II). The configurations of the 4-hydroxy groups in **10** and **11** were determined unequivocally by comparison of the VPC retention time and mass spectrum with those of authentic specimens prepared by the hydrogenation of the corresponding unsaturated alcohols, **3**, and **7**, obtained above (cf. Scheme II). The structure of **12**[18] was proven by Jones oxidation of the mixture of **10**, **11**, and **12** obtained above, whereby **12** was converted to tricyclo[5.2.2.0^{2,6}]undecan-3-one (**22**) which was identical with the specimens prepared by hydroboration–sodium dichromate oxidation of **9** (Scheme IV) as well as by hydrogenation of **6**.

Oxymercuration of *endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (**13**), prepared either by partial hydrogenation of the diene **1** in the presence of Wilkinson complex [$(PPh_3)_3RhCl$][19] (Scheme III) or by Diels–Alder addition of cyclohexa-1,3-diene and cyclopentene, proceeded also fairly slowly, 33% of the reactant **13** having disappeared in 24 hr at ambient temperature. The products were 71% 8-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**14**) and 29% of its acetate (**15**) (Scheme III). The structures of **14** and **15** were unambiguously established by comparison of VPC retention time and mass spectrum with those of authentic specimens prepared by hydroboration–oxidation of the olefin **13** and subsequent acetylation, as described below (Scheme IV).

Scheme III



Hydroboration–hydrogen peroxide oxidation[20] of the diene **1** gave three hydroxytricycloundecenes, **3**, **4**, and a compound of unknown structure, in the ratio of 30, 67, and 3%, respectively. The alcohols **3** and **4** obtained in this reaction were in complete agreement on examination by Golay GC–MS with the **3** and **4** formed in the oxymercuration–demercuration of the diene **1** (Scheme I). The third component in the product mixture was identified as 8-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-3-ene (**16**)[21] by the following reactions (Scheme IV). Jones oxidation of the above hydroboration product gave a mixture of ketones, **5**, **6**, and *endo*-tricyclo[5.2.2.0^{2,6}]undec-3-en-8-one (**17**),[21] from which **17** could be separated on preparative VPC. The ketone **17** gave on reduction with lithium aluminum hydride followed by hydrogenation over palladium catalyst 8-*endo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**19**) which was identical with the specimen prepared from **13** through hydroboration, Jones oxidation, and lithium aluminum hydride reduction (Scheme IV).

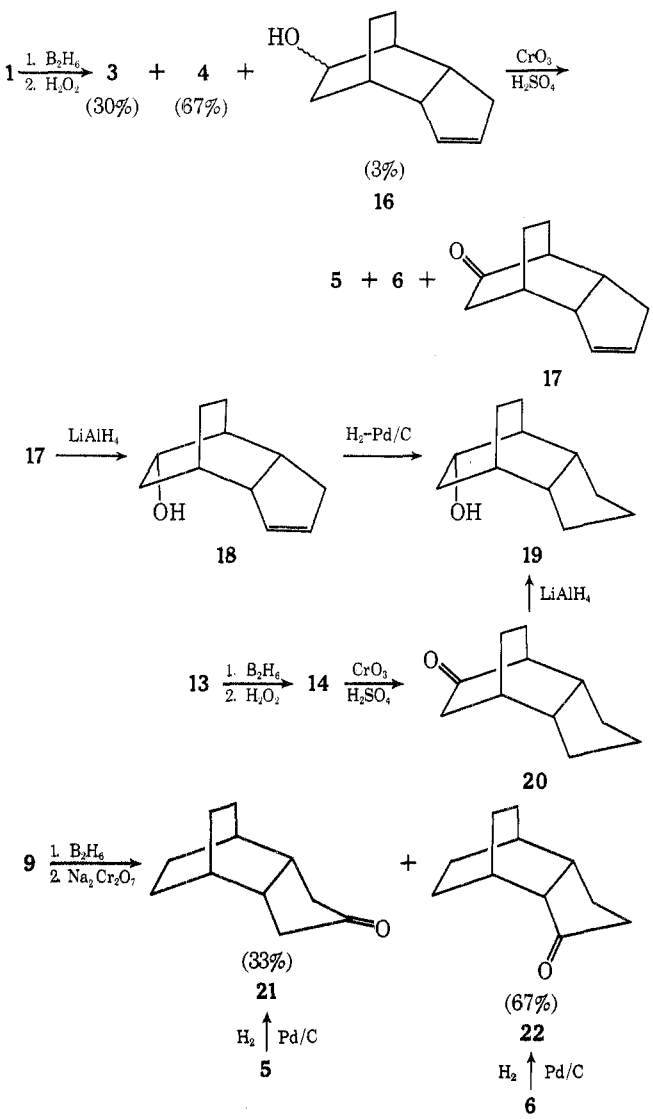
Hydroboration–sodium dichromate oxidation[20] of tricyclo[5.2.2.0^{2,6}]undec-3-ene (**9**) gave two ketones, tricyclo[5.2.2.0^{2,6}]undecan-4-one (**21**) and -3-one (**22**), in 33:67 ratio (Scheme IV), that was almost the same as that of **3** to **4** (30:67) in the hydroboration of the diene **1**. The 4-one **21** separated on preparative VPC exhibited a correct ^{13C} NMR spectrum corresponding to the structure. Structures of the ketones **21** and **22** were unambiguously established by comparison with authentic specimens prepared by hydrogenation of unsaturated ketones **5** and **6**, respectively.

Discussion

Oxymercuration of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (**1**) was found to proceed highly regioselectively (92%) and stereospecifically (practically 100%). The high stereospecificity as well as the high reactivity of **1**, as compared to those of tricyclo[5.2.2.0^{2,6}]undec-3-ene (**9**) and -8-ene (**13**), could be interpreted most reasonably in terms of trans addition of mercuric ion and nucleophile with the attack of the mercuric ion from the more hindered, endo side of the diene molecule. Although this assumption might apparently be inconsistent with the established cis addition on the exo side in bicyclic olefins,[15,22-25] no better alternative seems to be at hand, as will be discussed below, for the explanation of the whole experimental results presented here.

Oxymercuration of the monoolefin **9** progressed quite slowly (33% completion in a week) with a loss in regio- and stereoselectivity (Scheme II).[26] It would be rational, in accordance with the preferential exo attack of mercuric ion in oxymercuration of bi- and polycyclic olefins,[15,22-25,27] to presume also the exo attack for the monoolefin **9**. If this is

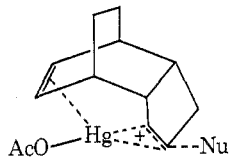
Scheme IV



the case, predominant formation of **10** (Scheme II) would be explained, based on the above exo attack of mercuric ion, by cis addition, and that of **11** by trans addition, of the reagents. The slow formation of **10** then could be attributed to a high activation energy associated with cis addition,[28] while an unusually low trans addition rate for the formation of **11** might be a result of steric hindrance to the approach of the nucleophile from endo side. An exo cis addition mechanism also in the oxymercuration of **13** (Scheme III) is indicated by its low reactivity (33% completion in 24 hr) and exclusive formation of the exo products (**14** and **15**), especially that of the exo acetate[23,24] **15.**

Contrary to the monoolefins **9** and **13,** the diene **1** shows high reactivity and selectivity in oxymercuration. It would be apparent that this cannot be explained by a mechanism involving exo attack of mercuric ion. If exo attack occurred, the high reactivity and selectivity of the diene **1,** as compared to the monoolefin **9,** has to be attributed to the presence of the 8,9-ethylenic bond in the former compound. However, it is quite improbable that the 8,9-unsaturated bond exerts such a large influence on the reactivity and selectivity of the remote 3,4 bond. Furthermore, exo attack of mercuric ion on **1** should give a 8- (and/or 9-) substituted derivative(s), since the 8,9-ethylenic bond would be more reactive than the 3,4 bond, as is shown in the reactivity difference between the model compound **9** and **13.** This is also contrary to the experimental results.

On the other hand, a supposition of the transition state **23,** that corresponds to a trans addition mechanism involv-



23

ing endo attack of mercuric ion with some stabilization by coordination of the 8,9-ethylenic bond to the mercury atom (chelate effect), seems to best explain the whole experimental results. A high rate of reaction for **1** would be a characteristic of the trans addition, while the high stereospecificity is a result of an exclusive approach of nucleophile from the exo side.

No definite explanation can be given to the orientation of nucleophile to the 3,4-, rather than the 8,9-, ethylenic bond to give **23.** The orientation of nucleophile should be interpreted in terms of the relative reactivity for trans oxymercuration of the two ethylenic bonds in **1.** However, it seems difficult to estimate this because no appropriate model is available at present.[29] Steric hindrance might be a predominating factor to control the orientation of the nucleophile, which attacks the less hindered 3,4 bond. Selection between the 3 and the 4 position (8 and 92%, respectively) within the bond by the nucleophile seems to be determined, as in ordinary Markownikoff additions, mainly by the charge distribution on the mercury-bridged 3,4 bond.[30]

Stabilization of the transition state of oxymercuration reaction by coordination of a p orbital to the mercury atom has some precedents.[31-33] Thus coordination of hydroxyl,[31] cyano,[31] carboxyl,[32] and carbamate[33] groups determined the regio- and stereoselectivity of the reaction in these examples. It would be probable, therefore, to assume a similar role of the 8,9-ethylenic bond in the oxymercuration of **1** which leads to a more or less stabilization of the transition state **23.** This stabilization would also contribute to a counterbalance to nonbonded repulsions between endo hydrogens and the mercury atom.[34]

The oxymercuration of the diene **1** can be contrasted to that of *endo*-dicyclopentadiene, a lower homolog of **1.** *endo*-Dicyclopentadiene gave a mixture of 8- and 9-*exo*-hydroxy-*endo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene as sole products.[22,26,27] The result is in complete agreement with what is expected from the oxymercuration reaction of norbornene.[25,28] Norbornene has been shown to undergo oxymercuration quite rapidly, yet with exo cis addition mechanism. This exceptional reactivity was ascribed to a high strain of the molecule with steric congestion on the endo side.[28] The 8,9-ethylenic bond of **1** is not so strained as the corresponding bonds in *endo*-dicyclopentadiene and norbornene.[35] Therefore, the same, exo cis addition mechanism must be unfavorable for the reaction of the 8,9 bond of **1,** and the activation energy for the transition state **23** is possibly smaller than that for the exo cis attack to the 8,9 bond.

In contrast to oxymercuration, hydroboration of the diene **1** proceeded with a loss in regiospecificity (Scheme IV). However, stereospecificity of the reaction was high, giving predominantly exo alcohols (**3** and **4**). Prevalent formation of **3** and **4,** in turn, may indicate a smaller steric congestion around the 3,4 bond as compared to that around the 8,9 bond. This result, coupled with those for the monoolefins **9** and **13,** confirmed the preference to exo attack by diborane that had been demonstrated in many other bi- and polycyclic systems.[16,17,19,36,37] The loss of regioselectiv-

ity in hydroboration was observed also for *endo*-dicyclopentadiene,[22,27] in spite of the large difference in the reactivities between the two ethylenic bonds in the molecule.

Experimental Section

All melting and boiling points are uncorrected. Ir spectra were obtained for neat samples on a Hitachi 215 spectrophotometer. ^{1}H NMR spectra were obtained on a Varian T-60 instrument, and ^{13}C NMR spectra were measured at 15.03 MHz on a Jeol JNM FX-60 spectrometer, both using deuteriochloroform as solvent. Chemical shifts are reported in δ for protons and in parts per million downfield from the internal Me_4Si standard for ^{13}C nuclei. Golay column GC–MS measurements were done with a combination of a Jeol JGC-20-KP gas chromatograph and a JMS-D-100 mass spectrometer. Capillary columns used were of the dimension of 0.01 in. × 150 ft, packed with Apiezon L or silicone SE-30, and the VPC was run at 60–70°. A Varian Aerograph 700 instrument was used for the preparative VPC. Preparation of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (**1**) is described in the previous work.[5,7]

Tricyclo[5.2.2.0^{2,6}]undec-3-ene (9). A mixture of 29.2 g (0.2 mol) of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (**1**), 300 ml of ethyl ether, and 1.5 g of palladium on charcoal catalyst (containing 5% metal) was placed in a 500-ml autoclave. After being flushed thoroughly with hydrogen, the vessel was charged with 10 kg/cm^2 of hydrogen. Hydrogenation was done at room temperature with efficient stirring until about 0.2 mol of hydrogen had been absorbed. The catalyst was filtered off, and the filtrate was concentrated to give 23.8 g of a mixture consisting of 48% tricyclo[5.2.2.0^{2,6}]undec-3-ene (**9**) and 52% tricyclo[5.2.2.0^{2,6}]undecane (**2**). Purification on a preparative VPC gave a pure sample of **9**: ir 3040 cm^{-1}; ^{1}H NMR δ 1.0–3.0 (m, 14), 5.63 (s, 2); mass spectrum *m/e* (rel intensity) 148 (51, M$^+$), 120 (46), 105 (41), 92 (46), 91 (78), 81 (49), 80 (90), 79 (88), 67 (65), 66 (100).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.03; H, 10.59.

***endo*-Tricyclo[5.2.2.0^{2,6}]undec-8-ene (13). A. Partial Hydrogenation of *endo*-Tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (2) in the Presence of Wilkinson Complex.** A mixture of 43.8 g (0.3 mol) of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (**1**), 20 ml of benzene, and 0.2 g of tris(triphenylphosphine)chlororhodium(I) in a 500-ml autoclave was hydrogenated with efficient stirring at 50° under 50 kg/cm^2 of hydrogen, until the calculated amount (0.3 mol) of hydrogen had been absorbed. The reaction mixture was concentrated to remove benzene, and the residue was chromatographed with *n*-hexane through a column packed with alumina containing 10% silver nitrate, whereby any unreacted **1** and the catalyst were separated. The eluent was concentrated to give 39.4 g of a mixture consisting of 52% **13** and 48% **2**. Separation on a preparative VPC gave a pure sample of **13**: ir 3060 cm^{-1}; ^{1}H NMR δ 0.7–2.75 (m, 14), 6.13 (t, 2); mass spectrum *m/e* (rel intensity) 148 (7, M$^+$), 120 (4), 92 (6), 91 (12), 81 (9), 80 (100), 79 (20), 78 (6), 77 (8), 67 (4), 51 (5), 41 (8), 39 (9).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.86; H, 10.87.

B. Diels–Alder Addition of Cyclohexa-1,3-diene and Cyclopentene. Diels–Alder reaction of cyclohexa-1,3-diene and cyclopentene, similar to cyclopentadiene and cyclopentene,[38] was found to undergo endo addition to give *endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (**13**). In a 500-ml autoclave were placed 20 g (0.25 mol) of cyclohexa-1,3-diene, 79.3 g (1.17 mol) of cyclopentene, and 50 mg of hydroquinone. After being flushed thoroughly with nitrogen, the vessel was closed and heated to 200° for 6 hr with efficient stirring. The reaction mixture was filtered to separate undissolved hydroquinone, and the filtrate was fractionated in vacuo through a 1-ft Vigreux column to give 5.2 g (14% yield) of **13**. Ir, ^{1}H NMR, and mass spectra of a VPC-purified sample of the **13** thus obtained agreed completely with those of the sample described in the preceding paragraph.

Oxymercuration–Sodium Borohydride Reduction of *endo*-Tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (1). To a yellow solution of 127.4 g (0.4 mol) of mercuric acetate in 200 ml of water and 200 ml of tetrahydrofuran was added with efficient stirring at ambient temperature 58.4 g (0.4 mol) of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (**1**) in 20 min. The yellow color of the solution disappeared in a few minutes after the completion of the addition of **1**. The reaction solution was then stirred for an additional 1 hr. The reaction mixture was cooled down to −10°, to which was added 400 ml of 3 *N* sodium hydroxide solution followed by a solution of 7.56 g (0.2 mol) of sodium borohydride in 400 ml of 3 *N* sodium hydroxide solution. After precipitated mercury was filtered off, the organic layer was separated from the filtrate, and the aqueous layer was extracted once with ether. The combined organic layer and ether extract were dried over anhydrous magnesium sulfate and concentrated. The solidified residue amounted to 62.9 g (96% yield), which was found on Golay GC–MS to consist of 92% 4-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (**3**) and 8% 3-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (**4**). Three recrystallizations of a sample of the crude product from *n*-hexane gave a pure sample of **3**: mp 98–99°; ir 3290, 3050, 2920, 2860, 1610, 1460, 1370, 1330, 1280, 1210, 1170, 1020, 940, 860, 720 cm^{-1}; ^{1}H NMR δ 1.0–2.6 (m, 12), 2.02 (s, 1, OH), 4.18 (m, 1, CHOH), 6.12 (t, 2, CH=CH); ^{13}C NMR (multiplicity, rel intensity) 25.3 (t, 2), 34.4 (d, 2), 40.8 (t, 2), 42.5 (d, 2), 73.6 (d, 1), 133.7 ppm (d, 2); mass spectrum *m/e* (rel intensity) 164 (50, M$^+$), 121 (18), 108 (17), 92 (13), 91 (19), 83 (55), 82 (31), 80 (100), 79 (43), 77 (13).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.15; H, 9.93.

The mass spectrum of **4** was taken on the Golay GC–MS: *m/e* (rel intensity) 164 (26, M$^+$), 92 (14), 91 (20), 83 (64), 82 (27), 80 (100), 79 (49), 77 (15), 41 (14), 39 (17).

***endo*-Tricyclo[5.2.2.0^{2,6}]undec-8-en-4-one (5) and *endo*-Tricyclo[5.2.2.0^{2,6}]undec-8-en-3-one (6).** The crude product of the oxymercuration–demercuration of **1** was converted to a mixture of *endo*-tricyclo[5.2.2.0^{2,6}]undec-8-en-4-one (**5**) and -3-one (**6**) by Jones oxidation. A solution of 32.8 g (0.2 mol) of the crude product obtained above in 200 ml of acetone was kept at 0–5°, while an oxidizing agent prepared from 14 g (0.14 mol) of chromium trioxide, 20 ml of 95% sulfuric acid, and 60 ml of water was added with efficient stirring in a period of 5 hr. The reaction mixture was stirred for an additional 4 hr at ambient temperature. Any excess chromium trioxide in the reaction mixture was destroyed by the addition of a sodium bisulfite solution, and the mixture was extracted with two 100-ml portions of ether. The combined extracts were washed with water and dried over anhydrous sodium sulfate. Evaporation of the ether left a solid, crude product which contained **5** and **6** in 93:7 ratio.

Three recrystallizations of the above crude product mixture from *n*-hexane gave a pure sample of **5**: mp 38–39°; ir 3040, 2950, 2910, 2870, 1730 cm^{-1}; ^{1}H NMR δ 1.0–2.8 (m, 12), 6.30 (t, 2, CH=CH); mass spectrum *m/e* (rel intensity) 162 (8, M$^+$), 92 (7), 91 (9), 81 (8), 80 (100), 79 (20), 77 (7), 39 (10), 27 (9), 18 (19).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.18; H, 8.75.

Fractionation of the above crude product mixture on preparative VPC gave a pure sample of **6**: ir 3050, 2950, 2870, 1740 cm^{-1}; ^{1}H NMR δ 1.0–3.2 (m, 12), 6.22 (t, 2, CH=CH); mass spectrum *m/e* (rel intensity) 162 (13, M$^+$), 92 (20), 91 (16), 83 (22), 80 (100), 79 (28), 78 (21).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.53; H, 8.90.

4-*endo*-Hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (7) and 3-*endo*-Hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (8). To a suspension of 1.0 g (0.026 mol) of lithium aluminum hydride in 50 ml of dry ether was added dropwise under gentle reflux with efficient stirring a solution of 5.8 g (0.036 mol) of *endo*-tricyclo[5.2.2.0^{2,6}]undec-8-en-4-one (**5**) in 30 ml of ether. The reaction was then refluxed for an additional 2 hr and worked up in the usual manner to give 5.4 g (92% yield) of solid crude **7**. Purification on preparative VPC gave a pure material: mp 101–102°; ir 3280, 3040, 2920, 2860, 1610, 1460, 1440, 1370, 1350, 1290, 1080, 1020, 840, 710 cm^{-1}; ^{1}H NMR δ 0.8–2.8 (m, 13), 3.8 (m, 1, CHOH), 6.17 (t, 2, CH=CH); mass spectrum *m/e* (rel intensity) 164 (3, M$^+$), 92 (5), 91 (6), 81 (8), 80 (100), 79 (15), 77 (5), 67 (3), 44 (3).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.23; H, 9.90.

A sample (2.9 g, 0.018 mol) of *endo*-tricyclo[5.2.2.0^{2,6}]undec-8-en-3-one (**6**) was reduced in ether with 0.5 g (0.013 mol) of lithium aluminum hydride with the same procedure as above. Crude **8** obtained (2.6 g, 88% yield) was purified on preparative VPC to give a pure sample: ir 3400, 3050, 2930, 2870, 1620, 1460, 1440, 1370, 1090, 1050, 1020, 960, 900, 870, 850, 820, 710 cm^{-1}; mass spectrum *m/e* (rel intensity) 164 (5, M$^+$), 92 (14) 91 (11), 80 (100), 79 (27), 68 (24), 67 (10).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.68; H, 9.79.

4-*exo*-Hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (10) and 4-*endo*-Hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (11). Authentic specimens of 4-*exo*- and -*endo*-hydroxy-*endo*-tricyclo [5.2.2.0^{2,6}]undecane (**10** and **11**) were prepared by catalytic hydro-

genation of 4-*exo* and -*endo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]-undec-8-ene (**3** and **7**), respectively. A mixture of 10 g (0.061 mol) of **3**, 50 ml of ethanol, and 0.5 g of the palladium on charcoal catalyst was stirred at room temperature in a 100-ml autoclave with repeatedly charged hydrogen (pressure below 10 kg/cm^2), until pressure drop was no longer observed (30 min). The catalyst was filtered off, and the filtrate was concentrated. Recrystallization of the residue from *n*-hexane gave 8.6 g (85% yield) of pure **10**: mp 98–99°; mmp with **3** 65–68°; ir 3250, 1060, 1020 cm^{-1}; ^{1}H NMR δ 1.0–2.5 (m, 16), 2.17 (s, 1, OH), 4.4 (m, 1, CHOH); mass spectrum *m/e* (rel intensity) 166 (3, M$^+$), 148 (71), 120 (35), 119 (27), 107 (33), 94 (54), 93 (30), 81 (41), 80 (100), 79 (50), 67 (38).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.26; H, 10.98.

Hydrogenation in the same procedure of 1.7 g (0.01 mol) of the crude **7** obtained above gave 1.3 g (75% yield) of the crude crystals of **11**. Purification on preparative VPC gave a pure sample: mp 87–88°; ir 3250, 1090, 1060, 1040 cm^{-1}; ^{1}H NMR δ 1.0–2.6 (m, 16), 2.63 (s, 1, OH), 4.13 (m, 1, CHOH); mass spectrum *m/e* (rel intensity) 166 (1, M$^+$), 148 (32), 107 (29), 81 (33), 80 (100), 79 (47), 67 (40), 66 (35), 41 (35).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.88; H, 10.73.

Oxymercuration–Sodium Borohydride Reduction of Tricyclo[5.2.2.0^{2,6}]undec-3-ene (9). A sample (1.48 g, 0.01 mol) of tricyclo[5.2.2.0^{2,6}]undec-3-ene (**9**) was stirred at ambient temperature with a solution of 3.19 g (0.01 mol) of mercuric acetate in 20 ml of 50% aqueous tetrahydrofuran. After 1 week, the reaction mixture was treated at −10° with 10 ml of 3 *N* sodium hydroxide solution and then with 0.19 g (0.005 mol) of sodium borohydride in 10 ml of 3 *N* sodium hydroxide solution. After being saturated with sodium chloride the mixture was extracted with three 10-ml portions of ether. The combined ether extracts were dried over sodium sulfate and concentrated to give 0.9 g of residue. The residue was found by Golay GC–MS to consist of 67% unreacted **9**, 14% 4-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**10**), 7% 4-*endo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**11**), and 12% a tricycloundecanol of undetermined structure. This compound was identified as 3-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**12**)[18] since Jones oxidation of the above oxymercuration–demercuration product gave a mixture comprising 65% unreacted **9**, 22% tricyclo[5.2.2.0^{2,6}]undecan-4-one (**21**), and 13% tricyclo[5.2.2.0^{2,6}]undecan-3-one (**22**). Identification of **10**, **11**, **21**, and **22** was made by comparison on Golay GC–MS with authentic materials.

Oxymercuration–Sodium Borohydride Reduction of *endo*-Tricyclo[5.2.2.0^{2,6}]undec-8-ene (13). *endo*-Tricyclo[5.2.2.0^{2,6}]undec-8-ene (**13**, 1.48 g, 0.01 mol) was treated with 3.19 g (0.01 mol) of mercuric acetate in 20 ml of 50% aqueous tetrahydrofuran for 24 hr at ambient temperature. The reaction mixture was reduced with 0.19 g (0.005 mol) of sodium borohydride in sodium hydroxide solution. The reaction product consisted of 67% unreacted **13**, 23% 8-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**14**), and 10% 8-*exo*-acetoxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**15**). Identification of **14** and **15** was made on Golay GC–MS by comparison with the authentic specimens prepared in the following paragraph.

8-*exo*-Hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (14) and Its Acetate (15). Tricyclo[5.2.2.0^{2,6}]undec-8-ene (**13**) gave 8-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**14**) on hydroboration–hydrogen peroxide oxidation. To a suspension of 4.44 g (0.03 mol) of **13** and 0.57 g (0.015 mol) of sodium borohydride in 15 ml of tetrahydrofuran was dropped under nitrogen stream at ambient temperature with efficient stirring a solution of 2.84 g (0.02 mol) of boron trifluoride etherate in 5 ml of tetrahydrofuran in a period of 45 min. The reaction mixture was then stirred overnight, allowed to react with hydrogen peroxide, and worked up in the usual way to give 4.55 g (91% yield) of crude **14**. Purification on preparative VPC gave a pure sample: mp 66–67°; ir 3300, 2930, 2870, 1470, 1360, 1310, 1090, 1070, 1020, 980, 910, 810, 720 cm^{-1}; ^{1}H NMR δ 1.0–2.4 (m, 16), 2.13 (s, 1, OH), 4.07 (m, 1, CHOH); mass spectrum *m/e* (rel intensity) 166 (12, M$^+$), 148 (67), 122 (44), 93 (44), 81 (55), 80 (100), 79 (88), 78 (53), 67 (61).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.18; H, 11.07.

Acetylation of **14** with acetic anhydride in pyridine at reflux gave 8-*exo*-acetoxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**15**). Purification on preparative VPC gave a pure sample: ir 1730 cm^{-1}; mass spectrum *m/e* (rel intensity) 148 (56), 120 (58), 119 (47), 91 (37), 80 (100), 79 (55), 77 (20), 67 (36), 43 (77), 41 (38).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.10; H, 9.89.

***endo*-Tricyclo[5.2.2.0^{2,6}]undecan-8-one (20).** Jones oxidation of 1.66 g (0.01 mol) of 8-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**14**) with 0.7 g (0.007 mol) of chromium trioxide in 1 ml of 95% sulfuric acid and 3 ml of water gave 1.31 g (81% yield) a crude *endo*-tricyclo[5.2.2.0^{2,6}]undecan-8-one (**20**). Purification on preparative VPC gave a pure sample: ir 1720 cm^{-1}; ^{1}H NMR δ 1.0–2.6 (m); mass spectrum *m/e* (rel intensity) 164 (30, M$^+$), 120 (46), 106 (100), 95 (30), 80 (30), 79 (41), 67 (46), 41 (44), 39 (39).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.19; H, 9.90.

8-*endo*-Hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (19). Reduction of 0.66 g (0.004 mol) of *endo*-tricyclo[5.2.2.0^{2,6}]undecan-8-one (**20**) with 0.15 g (0.004 mol) of lithium aluminum hydride in 7 ml of ether gave 0.6 g (92% yield) of crude 8-*endo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**19**), which was purified on preparative VPC to afford a pure sample: mp 92–93°; ir 3250 cm^{-1}; ^{1}H NMR δ 1.0–2.3 (m, 16), 2.15 (s, 1, OH), 3.89 (t, 1, CHOH); mass spectrum *m/e* (rel intensity) 148 (38), 93 (24), 81 (54), 80 (100), 79 (46), 67 (50), 66 (29), 41 (36), 39 (24).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.66; H, 10.91.

Hydroboration–Hydrogen Peroxide Oxidation of *endo*-Tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (1). A suspension of 14.6 g (0.1 mol) of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (**1**) and 1.17 g (0.03 mol) of sodium borohydride in 50 ml of dry tetrahydrofuran kept at 25–30° was treated under nitrogen stream with 5.68 g (0.04 mol) of boron trifluoride etherate in 10 ml of tetrahydrofuran. After being stirred for 3 hr at ambient temperature, the reaction mixture was oxidized with hydrogen peroxide and worked up in the usual manner. The crude product (16 g, 96% yield) was found by Golay GC–MS to consist of 30% 4-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (**3**), 67% 3-*exo*-hydroxy-*endo*-tricyclo-[5.2.2.0^{2,6}]undec-8-ene (**4**), and 3% 8-hydroxy-*endo*-tricyclo[5.2.-2.0^{2,6}]undec-3-ene (**16**).[21] Jones oxidation of the above reaction product gave a mixture of ketones, from which *endo*-tricyclo[5.2.2.0^{2,6}]undec-3-en-8-one (**17**)[21] was separated on preparative VPC. The ketone **17** was reduced with lithium aluminum hydride to 8-*endo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-3-ene (**18**).[21] Hydrogenation of **18** over the palladium on charcoal catalyst gave 8-*endo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undecane (**19**), which was identical by comparison on Golay GC–MS with an authentic specimen prepared in the preceding paragraph.

Hydroboration–Sodium Dichromate Oxidation of Tricyclo[5.2.2.0^{2,6}]undec-3-ene (9). A sample (1.48 g, 0.01 mol) of tricyclo[5.2.2.0^{2,6}]undec-3-ene (**9**) and 0.19 g (0.005 mol) of sodium borohydride in 5 ml of tetrahydrofuran was allowed to react with 0.95 g (0.007 mol) of boron trifluoride etherate in 2 ml of tetrahydrofuran for 2 hr. The reaction mixture was oxidized with 2.4 g (0.008 mol) of sodium dichormate dihydrate in 1.8 ml of 95% sulfuric acid and 8 ml of water at 20–25° and worked up in the usual manner to give 1.5 g (92% yield) of crude product. Golay GC–MS showed the presence of two ketones in a ratio of 33:67. They were separable on preparative VPC. The less abundant component was, as determined by ^{13}C NMR spectroscopy, tricyclo[5.2.2.0^{2,6}]undecan-4-one (**21**): mp 81–82°; ir 1740 cm^{-1}; ^{1}H NMR δ 1.2–3.0 (m); ^{13}C NMR (multiplicity, rel intensity) 19.9 (t, 2), 26.5 (t, 2), 29.1 (d, 2), 36.2 (d, 2), 41.8 (t, 2), 220.6 ppm (s, 1); mass spectrum *m/e* (rel intensity) 164 (100, M$^+$), 93 (46), 81 (41), 80 (75), 79 (81), 67 (57), 41 (65), 39 (57).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.53; H, 9.65.

The more abundant component, tricyclo[5.2.2.0^{2,6}]undecan-3-one (**22**): ir 1730 cm^{-1}; ^{1}H NMR δ 1.0–3.1 (m); mass spectrum *m/e* (rel intensity) 164 (17, M$^+$), 83 (100), 80 (30), 79 (27), 67 (17).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.21; H, 10.02.

The spectra of **21** and **22** were in complete agreement with those of authentic specimens prepared by palladium-catalyzed hydrogenation of tricyclo[5.2.2.0^{2,6}]undec-8-en-4-one (**5**) and tricyclo[5.2.2.0^{2,6}]undec-8-en-3-one (**6**), respectively.

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Registry No.—**1**, 54483-01-1; **3**, 56804-77-4; **4**, 56804-78-5; **5**, 56804-79-6; **6**, 56846-30-1; **7**, 56846-31-2; **8**, 56846-32-3; **9**, 56804-80-9; **10**, 56804-81-0; **11**, 56846-33-4; **13**, 56804-82-1; **14**, 56804-83-2; **15**, 56804-84-3; **19**, 56846-34-5; **20**, 56804-85-4; **21**, 56804-86-5; **22**, 56804-87-6; cyclohexa-1,3-diene, 592-57-4; cyclopentene, 142-29-0.

References and Notes

(1) K. Aigami, Y. Inamoto, N. Takaishi, K. Hattori, A. Takatsuki, and G. Tamura, *J. Med. Chem.*, **18**, 713 (1975).
(2) N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, K. Aigami, and E. Ōsawa, *J. Chem. Soc., Chem. Commun.*, 371 (1975).
(3) K. Aigami, Y. Inamoto, N. Takaishi, Y. Fujikura, and A. Akitsu, to be published.
(4) N. Takaishi, Y. Inamoto, and K. Aigami, *Chem. Lett.*, 1185 (1973).
(5) N. Takaishi, Y. Inamoto, K. Aigami, K. Tsuchihashi, and H. Ikeda, *Synth. Commun.*, **4**, 225 (1974).
(6) N. Takaishi, Y. Inamoto, and K. Aigami, *J. Org. Chem.*, **40**, 276 (1975).
(7) N. Cameli, G. Salvetti, and G. Sartori (Montecatini Co.), Italian Patent 730,703 (Dec 1, 1966); *Chem. Abstr.*, **69**, 51740y (1968).
(8) N. Takaishi, Y. Inamoto, K. Aigami, and E. Ōsawa, *J. Org. Chem.*, **40**, 1483 (1975).
(9) H. C. Brown and P. Geoghegen, Jr., *J. Am. Chem. Soc.*, **89**, 1522 (1967).
(10) H. C. Brown and P. J. Geoghegen, Jr., *J. Org. Chem.*, **35**, 1844 (1970).
(11) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, pp 49, 59, and 112.
(12) E. Pretsch, H. Immer, C. Pascual, K. Schaffner, and W. Simon, *Helv. Chim. Acta*, **50**, 105 (1967).
(13) C. Aso, T. Kunitake, and Y. Ishimoto, *J. Polym. Sci., Part A-1*, **6**, 1163 (1968).
(14) J. Meinwald, J. Crandall, and W. E. Hymans, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 866; R. C. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1957).
(15) H. C. Brown and W. J.Hammar, *J. Am. Chem. Soc.*, **89**, 1524 (1967).
(16) G. R. Wenzinger and J. A. Ors, *J. Org. Chem.*, **39**, 2060 (1974).
(17) P. E. Schueller and Y. E. Rhodes, *J. Org. Chem.*, **39**, 2063 (1974).
(18) The compound **12** formed in this reaction might be a mixture of the exo and endo epimers, although Golay VPC could not separate them.
(19) J. A. Osborn, F. H. Jardin, J. F. Young, and G. Willkinson, *J. Chem. Soc. A*, 1711 (1966).
(20) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).
(21) The compound showed only one peak on Golay VPC. However, in view of the result of Wilder et al.[22] on the oxymercuration of *endo*-dicyclopentadiene, the compound would probably be a mixture of 8 and 9 derivatives of tricyclo[5.2.2.0^{2,6}]undec-3-ene (**9**).
(22) P. Wilder, Jr., A. R. Portis, Jr., G. W. Wright, and J. M. Shepherd, *J. Org. Chem.*, **39**, 1636 (1974).
(23) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963).
(24) T. G. Traylor, *J. Am. Chem. Soc.*, **86**, 244 (1964).
(25) H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Am. Chem. Soc.*, **89**, 1525 (1967).
(26) It would be pointed out in this connection that 8,9-dihydro-*endo*-dicyclopentadiene (*endo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene) was quite unreactive toward mercuric acetate.[22]
(27) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. V. Jagt, *J. Am. Chem. Soc.*, **89**, 6381 (1967); H. C. Brown, I. Rothberg, and D. L. V. Jagt, *J. Org. Chem.*, **37**, 4098 (1972).
(28) T. G. Traylor, *Acc. Chem. Res.*, **2**, 152 (1969).
(29) The compounds **9** and **13** cannot be the models because they should react according to an exo cis addition mechanism as discussed above. Bicyclo[2.2.2]oct-2-ene cannot be a model either since it was shown[24] to react with a mixed mechanism in aqueous solvent.
(30) This is inferred from the regioselectivity in the oxymercuration of *cis*-4-methyl-2-pentene, which gave 91% 2- and 9% 3-hydroxy-4-methylpentane.[10]
(31) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959); H. B. Henbest and R. S. McElhinney, *Ibid.*, 1834 (1959).
(32) M. Malaiyandi and G. F. Wright, *Can. J. Chem.*, **41**, 1493 (1963).
(33) G. R. Krow and D. M. Fan, *J. Org. Chem.*, **39**, 2674 (1974).
(34) Actually, however, nonbonded repulsions in **23** do not seem to be so large as might be imagined. Indeed there is only one endo hydrogen (the endo-H-5). All the other hydrogens (H-3, H-4, H-8, and H-9) are perpendicular to the π bonds.
(35) Enthalpy changes on hydrogenation (ΔH_{hyd}) are −27.1, −28.3, and −33 kcal/mol for cyclohexene, bicyclo[2.2.2]oct-2-ene, and norbornene, respectively.[28]
(36) R. M. Coates and J. P. Chen, *Chem. Commun.*, 1481 (1970).
(37) N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, and K. Aigami, *J. Chem. Soc., Chem. Commun.*, 372 (1975).
(38) S. J. Cristol, W. K. Seifert, and S. B. Soloway, *J. Am. Chem. Soc.*, **82**, 2351 (1960).

The 4-Homoadamantyl Cation. II.[1] Mechanistic Studies on Lewis Acid Catalyzed Conversion of Homoadamantene to 2-Methyladamantane by Carbon-13 Labeling Techniques. Convenient Synthesis of 4-Homoadamantanone-*5*-^{13}C and Homoadamantene-*4*-^{13}C

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The Lewis acid catalyzed conversion of homoadamantene-*4*-^{13}C in CS_2 yielded 20% of 2-methyladamantane with the majority of the label equally distributed between the α position and the methyl group, indicating that only the olefinic carbons were involved in this rearrangement. The mechanism probably involves protonation of the olefinic bond by $AlX_3 \cdot H_2O$ to form the classical 4-homoadamantyl cation. This cation appears to rearrange rapidly to an unsymmetrically bridged 2-adamantylcarbinyl cation which yields 2-methyladamantane by hydride abstraction. The degenerate homoadamantyl rearrangement is retarded in such a low polar solvent as CS_2 presumably by intimate ion pairing. 4-Homoadamantanone-*5*-^{13}C was prepared in 46% overall yield by addition of $(CH_3)_3Si^{13}CN$ to adamantanone followed by $LiAlH_4$ reduction of the α-trimethylsilyloxy nitrile and Demjanow–Tiffeneau ring enlargement of the resulting α-aminomethyl alcohol [$(CH_3)_3Si^{13}CN$ was obtained in 88% yield from $(CH_3)_3SiCl$ and $Ag^{13}CN$]. This synthetic procedure appears to be a convenient general method for the preparation of ^{13}C-labeled ketones and their derivatives.

Lewis acid catalyzed rearrangements of polycyclic hydrocarbons are extremely useful methods for the preparation of adamantane and other diamonoid molecules.[4,5] The catalyst reacts with a promoter present in the reaction mixture to form carbonium ions which initiate intermolecular hydride transfers involving the hydrocarbon.[4a,f] The resulting carbonium ions then undergo a series of hydride transfers and 1,2-alkyl shifts leading to the thermodynamically most stable products, diamonoid hydrocarbons.[4a,f]

Although these processes have been known[4] for some time to involve carbonium ion intermediates, the first studies of these intermediates appeared in the literature only recently. Whitlock and Siefken constructed a rearrangement graph for tricyclodecane isomers showing the interrelationships among the isomers.[6] There are at least 2897 pathways between tetrahydrodicyclopentadiene and adamantane but no studies have yet succeeded in isolation and identification of intermediates during this isomerization.[4f] Most of the studies up to 1970 have only provided suggestive mechanistic information.[4,5a,6,7] Schleyer and co-workers[8] recently proposed a plausible pathway for the rearrangement of tetrahydrodicyclopentadiene to adamantane