

Synthesis of 2,11-Dehydrohomoadamantane (Tetracyclo[5.3.1.0^{2,4}.0^{3,9}]undecane) and 2,11-Dehydrohomoadamant-4-ene (Tetracyclo[5.3.1.0^{2,4}.0^{3,9}]undec-5-ene)^{1,2)}

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Bromination of tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene gave *endo*-2,*endo*-6- and *endo*-2,*exo*-6-dibromotetracyclo[5.3.1.0^{3,5}.0^{4,9}]undecanes along with *syn*-11,*endo*-2-dibromotricyclo[4.3.1.1^{3,8}]undec-4-ene (**10a**) in a ratio of 3:3:1. A thermal treatment of the mixture of these dibromides at 140–150 °C induced a skeletal rearrangement to afford **10a** and *syn*-11,*exo*-2-dibromotricyclo[4.3.1.1^{3,8}]undec-4-ene (**10b**) in 87% yield (**10a**:**10b**=2:5). The new “non-bridgehead” 2,11-dehydrohomoadamantane was obtained by the hydrogenation of **10a** and **10b** followed by Wurtz type reductive cyclization. The unsaturated analogue, 2,11-dehydrohomoadamant-4-ene was also synthesized from **10a** and **10b** by the similar cyclization reaction.

The chemistry of strained organic molecules has attracted a considerable attention of many chemists and is still actively being explored.³⁾ Strained cage compounds which usually contain a cyclopropane and/or cyclobutane ring in their frameworks have demonstrated a number of interesting and unusual chemical properties of carbon-carbon σ -bond.⁴⁾ Out of five possible “non-bridgehead” mono-dehydrohomoadamantanes, the strained cage compounds which incorporate a cyclopropane or cyclobutane ring in their cage structures (**1**–**5**), three (**2**, **3**, and **4**) of them have been synthesized and characterized so far.^{5–7)} As a consequence of our continuing interest in the strained cage compounds,^{5b,8)} we have investigated a synthetic pathway to 2,11-dehydrohomoadamantane (**1**), a new

entry to the “non-bridgehead” dehydrohomoadamantanes. We have recently prepared an interesting diene, tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene (**7**),^{8c)} which is a potential precursor to some substituted homoadamantane (tricyclo[4.3.1.1^{3,8}]undecane) derivatives. For example, the homoallylic carbocation (**8**) generated by electrophilic reaction of **7** may produce homoadamantane system *via* homoallyl-cyclopropyl-carbinyl-cyclobutyl rearrangement as is shown in Fig. 2.⁹⁾ We now wish to report here the synthesis of new “non-bridgehead” dehydrohomoadamantane, 2,11-dehydrohomoadamantane (**1**) as well as 2,11-dehydrohomoadamant-4-ene (**6**) *via* the above mentioned rearrangement.¹⁰⁾

Results and Discussion

When the diene (**7**) was treated with bromine in dichloromethane at 0 °C, three dibromides, *endo*-2,*endo*-6- and *endo*-2,*exo*-6-dibromotetracyclo[5.3.1.0^{3,5}.0^{4,9}]undecanes (**9a** and **9b**) and *syn*-11,*endo*-2-dibromotricyclo[4.3.1.1^{3,8}]undec-4-ene (**10a**), were obtained in 96% yield (**9a**:**9b**:**10a**=3:3:1 by PMR analysis). Although their complete separation was difficult because of their instabilities toward chromatographic treatment, low temperature recrystallizations made it possible to obtain **9a**, and **9b** in pure forms, respectively. The dibromides, **9a** and **9b**, showed no olefinic proton in their PMR spectra and a absorption band at 3010 cm⁻¹ indicative of a cyclopropane ring in their IR spectra. The presence of a plane of symmetry in **9a** was indicated by only one kind of carbinyl protons on the bromine substituted carbons at 4.48 ppm as a singlet shown in its PMR spectrum; this was also confirmed by CMR which demonstrated only seven kinds of carbons. On the other hand, the PMR spectrum of **9b** showed two kinds of carbinyl protons at 4.88 ppm as a triplet ($J=6$ Hz) and 4.83 ppm as a singlet. It has been already known that the *endo*-carbinyl proton on C₂ (or C₆) of tetracyclo[5.3.1.0^{3,5}.0^{4,9}]undecane deriva-

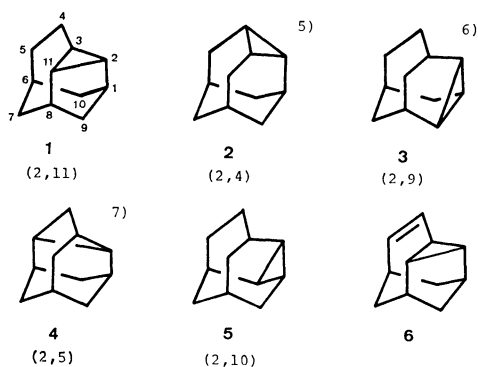


Fig. 1. “Non-bridgehead” dehydrohomoadamantanes.

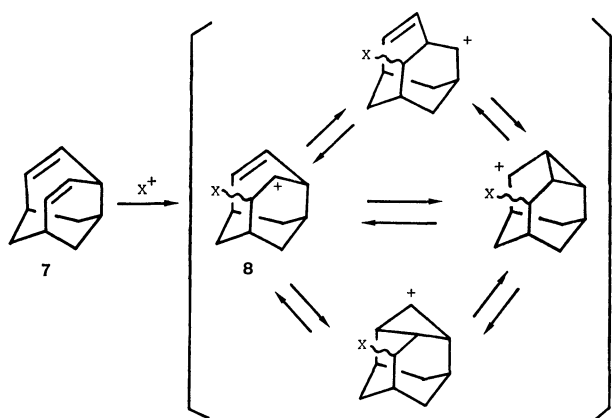
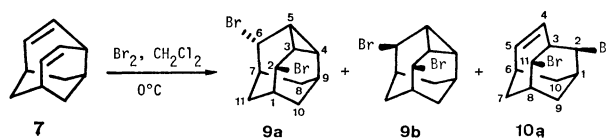
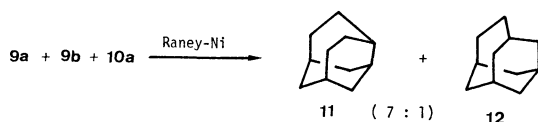


Fig. 2. Homoallyl-cyclopropylcarbinyl-cyclobutyl rearrangement.



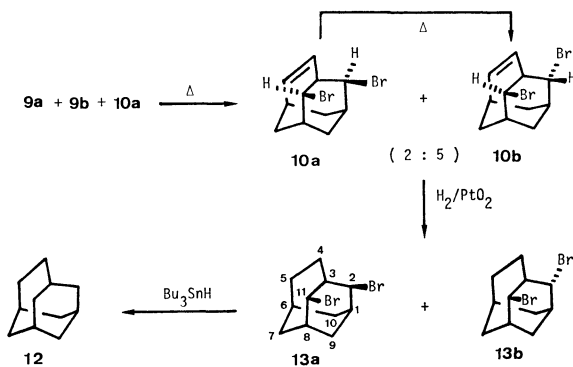
Scheme 1.

tives couples with the adjacent protons as a triplet with coupling constant of *ca.* 6 Hz but the *exo*-one does not in their PMR spectra.^{8a,11)} Accordingly, the structures of **9a** and **9b** were determined to be *endo*-2,*endo*-6- and *endo*-2,*exo*-6-dibromotetracyclo[5.3.1.0^{3,5}.0^{4,9}]undecanes, respectively. The above determination was further supported by the fact that reduction^{12,13)} of a mixture of the three dibromides by Raney-Ni gave tricyclo[5.3.1.0^{4,9}]undecane (**11**)⁸⁾ and homoadamantane (**12**) (**11**:**12**=7:1).



Scheme 2.

When the mixture of the dibromides (**9a**, **9b**, and **10a**) was heated under the reduced pressure (140–150 °C/533 Pa), an intriguing skeletal rearrangement took place to give **10a** and *syn*-11,*exo*-2-dibromotricyclo[4.3.1.1^{3,8}]undec-4-ene (**10b**) in 87% yield (**10a**:**10b**=2:5 by PMR analysis). It was also observed that a prolonged heating converted **10a** into **10b**; this result implies that **10b** is more thermodynamically stable than **10a**. Catalytic hydrogenation of this mixture over PtO₂ gave the saturated dibromides, *syn*-11,*endo*-2- and *syn*-11,*exo*-2-dibromotricyclo[4.3.1.1^{3,8}]undecanes (**13a** and **13b**) in 26 and 53% yields, respectively. Since the saturated dibromides, **13a** and **13b**, were stable toward chromatographic treatment,

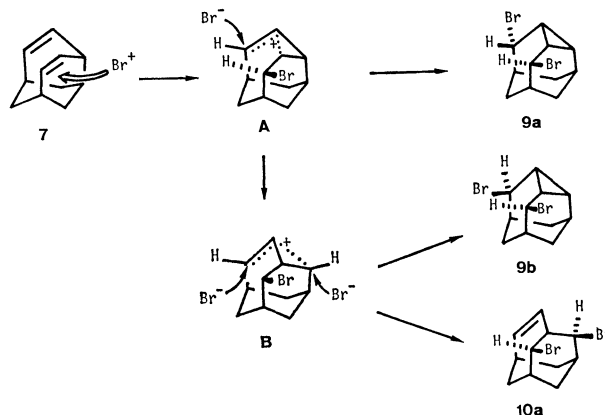


Scheme 3.

each of them was easily isolated by column chromatography on silica gel and could be completely characterized. Reduction of **13a** and **13b** with Bu₃SnH gave **12** in high yield, confirming the parent skeleton. The CMR and PMR spectra of **13a** showed only eight kinds of carbons and one kind of carbinyl protons on the bromine substituted carbons at 4.17 ppm as a singlet, respectively. Only *syn*-11,*endo*-2-dibromotricyclo[4.3.1.1^{3,8}]undecane can be responsible for the above spectra.¹⁴⁾ Consequently, **13b** was determined to be *syn*-11,*exo*-2-dibromotricyclo[4.3.1.1^{3,8}]undecane, because its PMR spectrum demonstrated two kinds of carbinyl protons at 5.10 ppm as a triplet (*J*=4.2 Hz) and 4.45 ppm as a singlet. Since the structures of **13a** and **13b** were established, those of the unsaturated dibromides, **10a** and **10b**, were deduced

to be *syn*-11,*endo*-2- and *syn*-11,*exo*-2-dibromotricyclo[4.3.1.1^{3,8}]undec-4-enes, respectively, on the basis of their CMR and PMR spectra. This deduction was confirmed by further chemical transformations (*vide infra*).

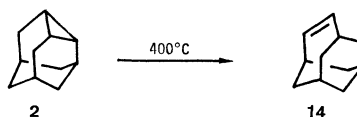
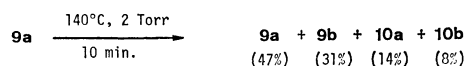
The following mechanistic pathway can well rationalize the formation of **9a**, **9b**, and **10a** in the bromination reaction of the diene **7**. The intervention of the homoallylic cations (A and B) may control the



Scheme 4.

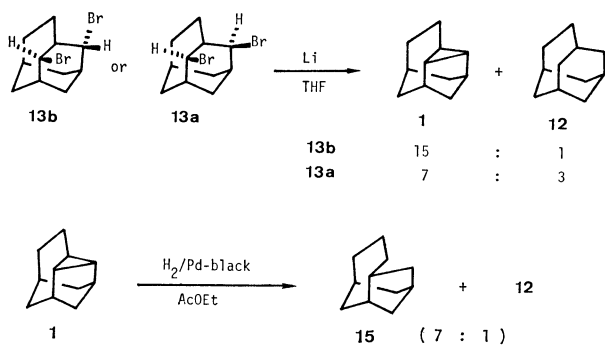
stereochemistry of the bromine addition. The analogous homoallylic cations were quoted in the bromination reactions of bicyclo[2.2.1]heptadiene¹⁵⁾ and bicyclo[2.2.2]octadiene.¹³⁾

Since the thermal rearrangement of **9a** and **9b** seems interesting, the pure **9a** was heated under the same conditions as above in order to obtain further insight about the stereochemical outcome of the bromine substituents. Unfortunately, it was observed by PMR that **9a** was easily isomerized to **9b** under the reaction conditions. For example, after 10 min, the mixture consisted of **9a**, **9b**, **10a**, and **10b** in a ratio of 47:31:14:8. Although the stereochemical course of this rearrangement could not be established, this process was much easier than the thermal isomerization of 2,4-dehydrohomoadamantane itself (**2**) to homoadamant-4-ene (tricyclo[4.3.1.1^{3,8}]undec-4-ene) (**14**) at 400 °C.¹⁶⁾



Scheme 5.

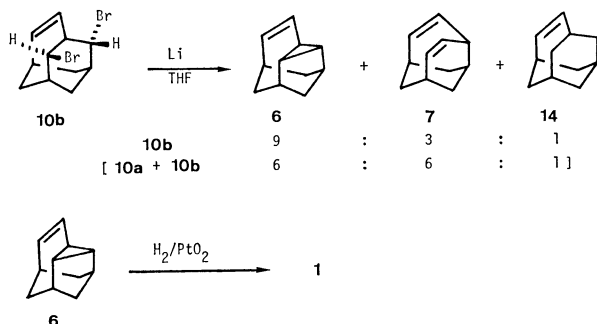
Now that 2,11-dibromotricyclo[4.3.1.1^{3,8}]undecanes (**13a** and **13b**) have become in our hands, the next step is reductive cyclization to 2,11-dehydrohomoadamantane (**1**). When **13b** was treated with lithium in dry THF at room temperature for 3.5 h, **1** was obtained in 94% yield along with a slight amount of homoadamantane (**12**) (**1**:**12**=15:1 by GLC analysis).



Scheme 6.

The similar treatment of **13a** with lithium gave the same products in 81% yield (**1**:**12**=7:3). The structure of **1** was confirmed by elemental analysis and spectroscopic data including its CMR spectrum which showed eight kinds of carbons due to its symmetry. Furthermore, hydrogenation of **1** over Pd-black gave 4-homoprotoadamantane (tricyclo[5.3.1.0^{3,9}]undecane) (**15**)¹⁷ and **12** in 78% yield (**15**:**12**=7:1 by GLC analysis). This is a marked contrast with the fact that **2** is hydrogenated to give only **12**.^{5a)}

Whereas **13b** gave predominantly the cyclized product, the similar reaction of the unsaturated dibromide **10b** with lithium afforded a mixture of 2,11-dehydrohomoadamant-4-ene (**6**), the diene **7**, and **14** in 80% yield (**6**:**7**:**14**=9:3:1 by GLC analysis). The same treatment of a mixture of **10a** and **10b** gave **6**, **7**, and **14** in a ratio of 6:6:1 in 89% yield. The structure of **6** was particularly reflected in its CMR spectrum (eight kinds of carbons due to its symmetry) and further ascertained by the hydrogenation to **1**.



Scheme 7.

Finally, it should be mentioned that the new "non-bridgehead" dehydrohomoadamantane **1** may be a possible precursor hitherto unknown 2,4-disubstituted 4-homoprotoadamantanes, considering that the C₂-C₃ bond of **1** is easily cleaved upon hydrogenation as is described above.¹⁸⁾ In addition, **6** is an interesting cage molecule because it incorporates a vinylcyclopropane moiety which has long been known as a reactive grouping.¹⁹⁾

Experimental

All the temperatures were uncorrected. Melting points were measured in sealed capillaries. The IR spectra were recorded on a Shimadzu IR-27 spectrometer. The mass

spectra were taken by using a Hitachi RMS-4 mass spectrometer. The exact mass spectrum was obtained on a Hitachi RMU-8GN mass spectrometer. The PMR and CMR spectra were obtained on Varian EM-390 or EM-360 and CFT-20 spectrometers, tetramethylsilane being chosen as the internal standard. Microanalyses were performed in Kyoto University Elemental Analysis Center.

The Reaction of Tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene (7) with Bromine. To a solution of **7** (400 mg; 2.70 mmol) in dichloromethane (20 ml) was added dropwise bromine (480 mg; 3.00 mmol) at 0 °C. Then, the reaction mixture was washed with 10% Na₂S₂O₃ aq and brine, and dried (Na₂SO₄). After filtration, the solvent was evaporated to give a colorless oil, which contained *endo*-2,*endo*-6-dibromotetracyclo[5.3.1.0^{3,5}.0^{4,9}]undecane (**9a**), *endo*-2,*exo*-6-dibromotetracyclo[5.3.1.0^{3,5}.0^{4,9}]undecane (**9b**), and *syn*-11,*endo*-2-dibromotetracyclo[4.3.1.1^{3,8}]undec-4-ene (**10a**) in a ratio of 3:3:1 (PMR analysis) (808 mg; 96%). When this oil was stored in a refrigerator, colorless crystals appeared. After a small amount of pentane was added, the crystals were collected by filtration and washed with cold pentane to give pure **9a** (197 mg). The filtrate was condensed under reduced pressure and amorphous solids appeared. The solids were collected by filtration, recrystallized from a small amount of pentane at low temperature, and then kept in a refrigerator for a few days to afford pure **9b** (40 mg). **9a**: mp 79–83 °C (dec). MS *m/e* (rel intensity): 308, 306, 304 (M⁺, 5, 9, 5), 227 (96), 225 (100), 145 (59). IR (KBr): 3010 (weak), 2925, 1170, 940, 775, 690 cm⁻¹. PMR δ (CDCl₃): 4.48 (2H, s), 2.50–0.90 (12H, br. complex m). CMR δ (CDCl₃): 55.3 (2CH), 36.1 (2CH), 35.1 (CH₂), 27.2 (2CH₂), 23.0 (2CH), 20.9 (CH), 15.3 (CH). Found: C, 43.07; H, 4.90%. Calcd for C₁₁H₁₄Br₂: C, 43.16; H, 4.61%. **9b**: mp 57–61 °C (dec). MS *m/e* (rel intensity): 308, 306, 304 (M⁺, 6, 12, 6), 227 (96), 225 (100), 145 (63). IR (KBr): 3010 (weak), 2925, 905, 735, 710 cm⁻¹. PMR δ (CCl₄): 4.88 (1H, t, *J*=6.0 Hz), 4.83 (1H, s), 2.40–1.00 (12H, br. complex m). CMR δ (CDCl₃): 61.0 (CH), 53.7 (CH), 36.0 (CH), 35.6 (CH₂), 35.0 (CH), 30.7 (CH₂), 27.3 (CH₂), 24.6 (CH), 22.9 (CH), 21.7 (CH), 20.6 (CH). Found: C, 43.08; H, 4.77%. Calcd for C₁₁H₁₄Br₂: C, 43.16; H, 4.61%. The dibromide (**10a**) could not be isolated in a pure form because of its unstability toward thermal and chromatographic treatments. Its spectral data were deduced from the mixture and described below.

Reduction of 9a, 9b, and 10a with Raney-Ni. A solution of the dibromides, **9a**, **9b**, and **10a** (139 mg; 0.45 mmol), triethylamine (91 mg; 0.90 mmol), and excess Raney-Ni-W₂ (ca. 0.5 g) in cyclohexane was vigorously stirred under hydrogen for 24 h. The reaction mixture was filtered and washed with 5% HCl aq and brine and dried (Na₂SO₄). After being passed through a silica-gel column, the solvent was evaporated to give two hydrocarbons [46 mg; 68%, **11**:**12**=7:1 (GLC analysis, PEG 20 M, 90 °C)]. Each of the products was isolated by preparative GLC and shown to be completely identical with the authentic sample in GLC retention time and PMR.

Reduction of the Dibromides, 9a, 9b, and 10a. (1) A mixture of the dibromides (243 mg; 0.79 mmol) and Bu₃SnH (433 mg; 1.49 mmol) in ether (30 ml) was refluxed for 30 h under nitrogen. After the solvent was evaporated, the residue was chromatographed on silica gel. Elution by hexane gave **7** (87 mg; 71%). (2) To a suspension of LiAlH₄ (75 mg; 1.97 mmol) in ether (10 ml) was added dropwise a solution of the dibromides (93 mg; 0.30 mmol) in ether (10 ml) and the mixture was stirred at room temperature for 24 h. After a small amount of saturated Na₂SO₄

aq was added to the mixture, the ether layer was separated by decantation and washed with brine, and dried (Na_2SO_4). Filtration followed by evaporation of the solvent gave **7** as a sole product (38 mg; 86%). (3) To a mixture of the dibromides (141 mg; 0.48 mmol), magnesium (35 mg; 1.46 mmol) in dry THF (5 ml) was added a few drops of methyl iodide. The reaction mixture was refluxed overnight under nitrogen, poured onto water, and extracted with ether. The extract was shown to contain only **7** by GLC analysis.

Thermal Rearrangement of 9a, 9b, and 10a to 10a and 10b. Distillation of a mixture of **9a**, **9b**, and **10a** (1041 mg; 3.40 mmol) at 140–150 °C (533 Pa) by means of Kugelrohr gave **10a** and **10b** (903 mg; 87%) in a ratio of 2:5 (PMR analysis). When the mixture (450 mg) was heated at 150 °C for 3 h under atmospheric pressure and then distilled (140–150 °C/267 Pa), only **10b** was obtained (385 mg; 85%). *syn*-11, *exo*-2-Dibromotricyclo[4.3.1.1^{3,8}]undec-4-ene (**10b**): mp 123–1255 °C. MS *m/e* (rel intensity): 308, 306, 304 (M^+ , 9, 16, 9), 227 (98), 225 (100), 145 (76). IR (KBr): 3025 (weak), 2925, 950, 730, 710, 670 cm^{-1} . PMR δ (CCl_4): 6.20 (1H, t, $J=9.0$ Hz), 5.70 (1H, t, $J=9.0$ Hz), 4.90 (1H, t, $J=4.5$ Hz), 4.67 (1H, s), 3.03 (1H, t, $J=7.5$ Hz), 2.90–1.40 (9H, br. complex m). CMR δ (CDCl_3): 140.5 (CH), 130.2 (CH), 58.6 (CH), 53.0 (CH), 49.6 (CH), 37.9 (CH), 37.5 (CH), 35.5 (CH_2), 32.4 (CH_2), 30.3 (CH), 27.3 (CH_2). Found: C, 43.43; H, 4.90%. Calcd for $\text{C}_{11}\text{H}_{14}\text{Br}_2$: C, 43.16; H, 4.61%. The following spectroscopic data for **10a** were deduced from those of the mixture of **10a** and **10b**. *syn*-11, *endo*-2-Dibromotricyclo[4.3.1.1^{3,8}]undec-4-ene (**10a**): PMR δ (CCl_4): 6.05 (2H, m), 4.55 (2H, s), 3.30–1.10 (10H, br. complex m). CMR δ (CDCl_3): 140.5 (CH), 132.1 (CH), 53.1 (2CH), 47.6 (CH), 38.1 (2 CH_2), 35.5 (2CH), 30.3 (CH), 24.7 (CH_2).

syn-11, *endo*-2- and *syn*-11, *exo*-2-Dibromotricyclo[4.3.1.1^{3,8}]undecanes (**13a** and **13b**). A mixture of **10a** and **10b** (915 mg; 2.99 mmol) and PtO_2 (40 mg) in methanol (50 ml) was vigorously stirred under hydrogen. After one equivalent of hydrogen had been absorbed, the catalyst was removed by filtration and the solvent was evaporated to give a crude mixture (886 mg), which was chromatographed on silica gel. Elution by hexane afforded **13b** (599 mg; 53%) and, subsequently, **13a** (240 mg; 26%). **13a**: mp 158–159 °C. MS *m/e* (rel intensity): 229, 227 (M^+-Br , 20, 20), 147 (100), 119 (42), 105 (33), 91 (51). IR (KBr): 2925, 1455, 1215, 1180, 940, 700 cm^{-1} . PMR δ (CCl_4): 4.17 (2H, s), 3.20–1.06 (14H, br. complex m). CMR δ (CDCl_3): 56.9 (2CH), 48.5 (CH), 36.8 (2 CH_2), 35.6 (2CH), 31.9 (CH_2), 30.8 (CH_2), 29.6 (CH), 24.2 (CH_2). Found: C, 42.90; H, 5.18%. Calcd for $\text{C}_{11}\text{H}_{16}\text{Br}_2$: C, 42.88; H, 5.23%. **13b**: mp 162–163 °C. MS *m/e* (rel intensity): 229, 227 (M^+-Br , 29, 30), 147 (100), 119 (29), 91 (44). IR (KBr): 2925, 1455, 665 cm^{-1} . PMR δ (CCl_4): 5.10 (1H, t, $J=4.2$ Hz), 4.45 (1H, s), 2.93–1.15 (14H, br. complex m). CMR δ (CDCl_3): 62.9 (CH), 59.2 (CH), 49.4 (CH), 36.4 (CH), 35.7 (CH_2), 35.0 (CH), 33.8 (CH_2), 32.4 (CH_2), 32.2 (CH_2), 29.9 (CH), 27.8 (CH_2). Found: C, 42.95; H, 5.26%. Calcd for $\text{C}_{11}\text{H}_{16}\text{Br}_2$: C, 42.88; H, 5.23%.

Reduction of 13a or 13b with Bu_3SnH . A solution of **13b** (140 mg; 0.45 mmol) and Bu_3SnH (610 mg, 2.10 mmol) in benzene (10 ml) was refluxed under nitrogen for 3 h. The reaction mixture was washed with brine and dried (Na_2SO_4). After filtration, the solvent was evaporated to give a crude mixture, which was shown to contain only one hydrocarbon product by GLC analysis (PEG 20 M, 100 °C). The product was collected by preparative GLC and shown to be identical with authentic homoadamantane (tricyclo[4.3.1.1^{3,8}]undecane) (**12**) in GLC retention time and PMR,

The similar treatment of **13a** (68 mg; 0.22 mmol) with Bu_3SnH (175 mg; 0.60 mmol) to above also gave **12** as a sole product.

2,11-Dehydrohomoadamantane (1). A mixture of **13b** (596 mg; 1.94 mmol) and small pieces of lithium (458 mg; 65.00 mmol) in dry THF was stirred at room temperature under nitrogen for 3.5 h and poured onto ice-water. Organic materials were extracted with ether and washed with brine (three times), and dried (Na_2SO_4). After filtration, the solvent was evaporated to give **1** along with a slight amount of **12** (268 mg; 94%, **1**:**12**=15:1 by GLC analysis; PEG 20 M, 100 °C). The analytical sample was obtained by preparative GLC. Similarly, the reaction of **13a** (197 mg; 0.58 mmol) with lithium also afforded **1** and **12** in a ratio of 7:3 (70 mg; 81%). **1**: mp 124–127 °C. MS *m/e* (rel intensity): 148 (M^+ , 27), 79 (100). IR (CCl_4): 3030, 2930, 1450 cm^{-1} . PMR δ (CCl_4): 3.00–1.05 (16H, br. complex m). CMR δ (CDCl_3): 54.0 (CH_2), 36.7 (2 CH_2), 36.2 (CH_2), 34.7 (CH), 34.6 (2CH), 28.5 (CH), 28.4 (2CH), 23.6 (CH_2). Found: C, 88.89; H, 10.95%. Calcd for $\text{C}_{11}\text{H}_{16}$: C, 89.12; H, 10.88%.

Hydrogenation of 1. A suspension of **1** (45 mg; 0.30 mmol) and Pd-black (25 mg) in ethyl acetate (4 ml) was vigorously stirred under hydrogen until **1** disappeared. After removal of the catalyst by filtration, the solvent was evaporated to give a mixture of 4-homoprotadamantane (**15**) and **12** (36 mg; 78%) in a ratio of 7:1 (GLC analysis; PEG 20 M, 100 °C). Pure **15** was obtained by preparative GLC and shown to be identical with the authentic sample.¹⁷⁾

2,11-Dehydrohomoadamant-4-ene (6). A mixture of **10b** (602 mg; 1.97 mmol) and small pieces of lithium (543 mg; 77.6 mmol) in dry THF (30 ml) was stirred for 20 h at room temperature under argon and poured onto ice-water. After filtration, organic materials were extracted with dichloromethane and washed with brine, and dried (Na_2SO_4). After filtration, the solvent was evaporated to give a mixture of three hydrocarbons, **6**, **7**, and **14** (230 mg; 80%), in a ratio of 9:3:1 (GLC analysis; PEG 20 M, 100 °C). Pure **6** (144 mg, 50%) was secured by preparative GLC. **6**: mp 109–110 °C. MS *m/e* (rel intensity): 146 (M^+ , 52), 80 (100). IR (KBr): 3020, 2925, 2875, 1670, 1465, 1445, 1350, 1050, 960, 790, 750, 705 cm^{-1} . PMR δ (CCl_4): 5.97 (1H, d, $J=10.5$ and 8.0 Hz), 5.67 (1H, d, $J=10.5$ Hz), 2.90–1.20 (12H, br. complex m). CMR δ (CDCl_3): 139.6 (CH), 126.3 (CH), 54.4 (CH_2), 37.9 (2CH), 33.7 (CH), 30.8 (2 CH_2), 29.7 (CH), 25.6 (2CH). Found: *m/e* 146.1098. Calcd for $\text{C}_{11}\text{H}_{14}$: M, 146.1095.

Hydrogenation of 6 to 1. A suspension of **6** (20 mg; 0.13 mmol) and PtO_2 (2 mg) in methanol (2 ml) was vigorously stirred under hydrogen. After one equivalent of hydrogen was absorbed, the mixture was filtered and the solvent was evaporated to give almost pure **1** (13 mg; 64%).

We thank Dr. Ryusei Konaka of Shionogi Pharmaceutical Co. Ltd., for obtaining the exact mass spectrum of **6**.

References

- 1) Part of this work has been presented in the 36th annual meeting of Chemical Society of Japan held in Osaka, 3S16, (1977).
- 2) Provided that there is no ambiguity, we use trivial nomenclature for simplicity.
- 3) A. Greenberg and J. F. Liebman, "Strained Organic Molecules," Academic Press, New York (1978).
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