blue color was discharged by solid NH_4Cl, and the ammonia was allowed to evaporate at room temperature. The residue was diluted with water, acidified with 6 N HCl, and extracted with Et_2O. The ether extract was washed with water and dried (Na_2SO_4). Removal of the solvent afforded 140 mg of a gummy viscous liquid [IR ($CHCl_3$) 3480, 1730, 1600 cm^{-1}] which without further purification was dissolved in 10 mL of acetone and was subjected to Jones oxidation to yield 120 mg (75%) of **15e** as a light yellow viscous liquid. This was found to be a single component (VPC, NMR) of about 96% purity. Chromatographic purification over 5 g of silica gel with petroleum ether (bp 60–80 °C) as the eluent afforded the pure **15e**, which was found to be identical with the compound obtained from catalytic hydrogenation (NMR, IR, VPC).

Preparation of the Unsaturated Cyclobutanones 2c–e from the Diazo Ketones 1c–e. 7-Methoxy-2aα-methyl-2a,3,4,10-tetrahydrocyclobuta[*j*]fluoren-2(1*H*)-one (2c). A solution of 280 mg (1.0 mmol) of **1c** in 75 mL of $CHCl_3$ at 0 °C was treated with 0.5 mL (6.5 mmol) of TFA for 45 min to afford a gummy solid which was purified by chromatog. on 15 g of neutral alumina with ether–petroleum ether (bp 60–80 °C) (1:8) as the eluent to give 200 mg (78%) of pure **2c**. It was crystallized from petroleum ether bp (40–60 °C): mp 85–86 °C; IR (KBr) 2920, 2840, 1770, 1645, 1600, 1590, 1400, 1340, 1260, 1100, 975, 825 cm^{-1}; UV λ_{max} 260 nm (log ϵ 4.20); ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.67–2.01 (4 H, m, methylenes), 2.20–3.43 (4 H, m, Ar CH_2 and $COCH_2$), 3.80 (3 H, s, Ar OCH_3), 6.27 (1 H, br t, J = 6 Hz, C=CH), 6.66–7.30 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.22; H, 7.01.

9-Methoxy-2aα-methyl-2a,3,4,10-tetrahydrocyclobuta[*j*]-fluoren-2(1*H*)-one (2d). A solution of 280 mg (1 mmol) of the diazo ketone **1d** in 75 mL of chloroform at 0 °C was treated with 0.5 mL (6.5 mmol) of TFA for 45 min to afford a yellowish gummy solid. Chromatography on neutral alumina (5 g) with ether–petroleum ether (bp 60–80 °C) (1:6) gave 200 mg (78%) of pure **2d** which was recrystallized from ether–petroleum ether (bp 60–80 °C) mp 127–128 °C; IR (KBr) 2940, 2840, 1780, 1650, 1600, 1580, 1480, 1260, 1165, 1100, 1080, 785 cm^{-1}; UV λ_{max} 260 nm (log ϵ 4.23); ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.37–2.37 (4 H, m, methylenes), 2.93–3.13 (4 H, m, Ar CH_2 and $COCH_2$), 3.83 (3 H, s, Ar OCH_3), 6.27 (1 H, br t, J = 6 Hz, C=CH), 6.60–7.23 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.34; H, 7.34.

9-Methyl-2aα-methyl-2a,3,4,10-tetrahydrocyclobuta[*j*]-fluoren-2(1*H*)-one (2e). A solution of 200 mg (0.75 mmol) of **1e** in 50 mL of $CHCl_3$ at 0 °C was treated with 0.5 mL (6.5 mmol) of TFA for 45 min as above to furnish 170 mg (94%) of **2e** as a light yellow solid which was recrystallized from ether–petroleum ether (bp 40–60 °C) (1:4): mp 91–92 °C; IR (KBr), 2940, 2810, 1775, 1650, 1600, 1585, 1480, 1240, 1050, 950 cm^{-1}; UV λ_{max} 262 nm (log ϵ 4.21); ^1H NMR ($CDCl_3$) δ 1.33 (3 H, s, CH_3), 1.50–2.90 (4 H, m, methylenes), 2.30 (3 H, s, Ar CH_3), 2.91–3.15 (4 H, m, $COCH_2$ and Ar CH_2), 6.23 (1 H, br t, J = 5 Hz, C=CH), 6.95–7.38 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.60; H, 7.52.

Catalytic Hydrogenation of the Unsaturated Cyclobutanones 2c–e. 7-Methoxy-2aα-methyl-2a,3,4,5,5aα,10-hexahydrocyclobuta[*j*]fluoren-2(1*H*)-one (16c). A solution of 125 mg (0.5 mmol) of **2c** in 20 mL of ethanol was hydrogenated for 1 h in presence of 50 mg of 10% Pd/C to afford 120 mg (95%) of a mixture of two isomers in a ratio of 19:1 (VPC, ^1H NMR). Chromatographic purification and fractional crystallization from petroleum ether (bp 40–60 °C) furnished 100 mg (80%) of pure **16c**: mp 90–91 °C; IR (KBr) 2940, 2865, 1775, 1600, 1585, 1480, 1380, 1250, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (3 H, s, CH_3), 1.41–3.49 (11 H, complex m, methylenes and methine), 3.81 (3 H, s, Ar OCH_3), 6.51–7.22 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.60; H, 7.79.

9-Methoxy-2aα-methyl-2a,3,4,5,5aα,10-hexahydrocyclobuta[*j*]fluoren-2(1*H*)-one (16d). A solution of 125 mg (0.5 mmol) of the styrenoid cyclobutanone **2d** in 20 mL of ethanol was hydrogenated in presence of 50 mg of 10% Pd/C for 1 h to afford 120 mg (95%) of pure **16d** (VPC, ^1H NMR) which was recrystallized from petroleum ether (bp 60–80 °C) mp 126–127 °C; IR (KBr) 2920, 2840, 1780, 1600, 1590, 1480, 1385, 1265, 1110, 1080, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.40–3.47 (11 H, complex m, methylenes and methine) 3.83 (3 H, s, Ar OCH_3), 6.50–7.20 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.43; H, 7.93.

9-Methyl-2aα-methyl-2a,3,4,5,5aα,10-hexahydrocyclobuta[*j*]fluoren-2(1*H*)-one (16e). A solution of 110 mg (0.47 mmol) of **2e** in 20 mL of ethanol was hydrogenated for 1 h in presence of 60 mg of 10% Pd/C to furnish 100 mg (91%) of pure **16e** (VPC, ^1H NMR), which was recrystallized from petroleum ether (bp 60–80 °C): mp 123–124 °C; IR (KBr) 2940, 2860, 1780, 1600, 1490, 1380, 1250, 1120, 1060, 950, 840, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.35–3.25 (11 H, complex m, methylenes and methine), 2.30 (3 H, s, Ar CH_3), 6.88–7.39 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O$: C, 79.65; H, 7.86. Found: C, 79.53; H, 7.83.

Registry No. (±)-**1a**, 60059-29-2; (±)-**1b**, 60059-30-5; (±)-**1c**, 83681-18-9; (±)-**1d**, 83649-58-5; (±)-**1e**, 83664-24-8; (±)-**2c**, 83649-59-6; (±)-**2d**, 83649-60-9; (±)-**2e**, 83649-61-0; (±)-**3a**, 78284-39-6; (±)-**3b**, 83649-62-1; (±)-**3c**, 83649-63-2; (±)-**3d**, 83649-64-3; (±)-**3e**, 83649-65-4; (±)-**4a**, 83680-52-8; (±)-**4b**, 83680-53-9; (±)-**4c**, 83649-66-5; (±)-**4d**, 83649-67-6; (±)-**4e**, 83649-68-7; (±)-**5c**, 83649-69-8; (±)-**5c**·Na, 83649-70-1; (±)-**5c** chloride, 83649-71-2; (±)-**5d**, 83649-72-3; (±)-**5e**, 71685-84-2; (±)-**6**, 59323-55-6; (±)-**7**, 83649-73-4; (±)-**8**, 83649-74-5; (±)-**9** (isomer 1), 83649-75-6; (±)-**9** (isomer 2), 83649-76-7; (±)-**10** (isomer 1), 83649-77-8; (±)-**10** (isomer 2), 83649-78-9; (±)-**11**, 83649-79-0; (±)-**12**, 83649-80-3; (±)-**13**, 83649-81-4; (±)-**14a**, 83649-82-5; (±)-**14b**, 83649-83-6; (±)-**14c**, 83649-84-7; (±)-**14d**, 83649-85-8; (±)-**14e**, 83649-86-9; (±)-**15a**, 83680-54-0; (±)-**15b**, 83649-87-0; (±)-**15c**, 83649-88-1; (±)-**15d**, 83649-89-2; (±)-**15e**, 83649-90-5; (±)-**16c**, 83649-91-6; (±)-**16d**, 83649-92-7; (±)-**16e**, 83664-25-9; *p*-methoxybenzyl chloride, 824-94-2.

Magnesium-Induced Cyclizations of 2-(3-Iodopropyl)cycloalkanones. A Cyclopentane Annelation Method[1]

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A process for the stereoselective construction of a cyclopentane ring onto a preexisting cycloalkanone is developed. 2-(3-Iodopropyl)cycloalkanones, obtained by known methods from the parent cyclic ketones, were converted to bicyclo[*x*.3.0]alkan-1-ols in moderate to good yields by magnesium in THF. This cyclization shows a large preference for formation of the cis compounds. Attempts to extend this reaction to the formation of six- and seven-membered rings were largely unsuccessful.

The Barbier alternative[2] to the Grignard reaction involves the simultaneous interaction of an alkyl halide, an aldehyde or ketone, and magnesium metal in an ether solvent. This process has enjoyed some success with allylic

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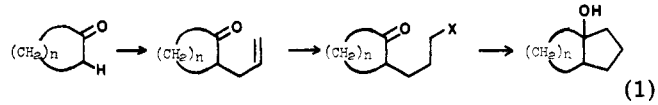
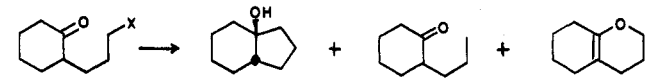
and benzylic halides for which coupling of the reactive halides is an important side reaction in the normal Grignard procedure. However, relatively little use of the Barbier method has been reported for less reactive halides owing to the difficulty experienced in initiating reaction and the competition with side reactions such as pinacol formation. Nonetheless, several studies on intramolecular versions of the Barbier reaction indicate some potential for the formation of cyclic alcohols.[3-5] This type of conversion constitutes the key step of the new cyclopentane annelation procedure illustrated in eq 1. The present study examines the synthetic potential of this process.



(1)

Cycloalkanones are readily transformed into their allyl derivatives by an ingenious adaptation of the Claisen rearrangement.[6-8] Subsequent photochemical addition of HBr gives the bromo ketones[8,9] that are readily converted to the corresponding iodides by NaI in acetone. Barbier cyclizations were performed by the method of Leroux,[3] which utilizes magnesium previously activated by treatment with $HgCl_2$ in THF solvent.

Reaction of iodide **1a** under the above conditions gave *cis*-hydrindanol (**2**) as the major product (77% of the volatile products; 61% isolated yield), along with lesser amounts of 2-propylcyclohexanone (**3**) and tetrahydrochroman (**4**). Interestingly, none of the isomeric *trans*-hydrindanol was observed by GC analysis, although as little as 1% would have been detected. Attempts to use the more readily available bromide **1b** were unsuccessful, a mixture of starting material and tetrahydrochroman (**4**) being generated. Likewise, reaction of iodide **1a** with lithium and *tert*-butyl alcohol in THF gave **4** as the major product.

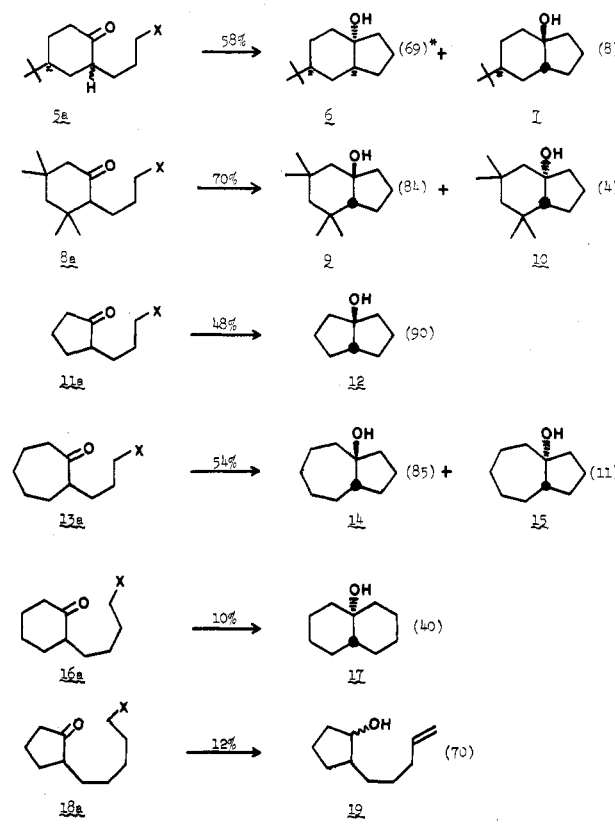


1 **2** (77) **3** (7) **4** (13)

a X = I; b X = Br

Similar transformations of ketones **5a**, **8a**, **11a**, and **13a** were also performed as illustrated in Scheme I. The indicated yields are those obtained after purification by column chromatography to remove unidentified minor byproducts. The figures in parentheses show the percentage of the total volatile product as ascertained by GC analysis. Acceptable isolated yields of pure bicyclic alcohols were obtained in all of the cyclopentane annelations examined.

Scheme I



* Percentage of the volatile products

Most of the alcohol products were identified by comparison with authentic samples available from a related study.[8] Authentic samples of **9** and **10** were obtained by the $LiAlH_4$ reduction of bicyclic epoxides **20** and **21**, respectively.[8] The assignment of structure **7** to the minor alcohol obtained from **5a** is based on its nonidentity with the C-1 epimer of the major alcohol **6**.[8] While the C-1 epimer of **7** cannot be rigorously excluded as the minor alcohol, it is not very likely that this highly strained product (which would have to be generated via cyclization of an unfavorable conformation) is formed to the exclusion of the more stable alcohol **7**.

20 **21**

The high stereoselectivity observed for cis ring closure in the formation of **2** appears to be general. The 4-*tert*-butylcyclohexanone **5a** gives two bicyclo[4.3.0]nonanols, both of which have a cis ring fusion. These isomeric alcohols are undoubtedly formed from the two C-2 epimers of **5a** that are expected to be present in roughly the same ratios as the product alcohols. (For example, the equilibrium cis to trans ratio for 2-allyl-4-*tert*-butylcyclohexanone is 85:15.)[7] Thus, it appears that cyclization is faster than base-promoted epimerization under the reaction conditions utilized. Although cis cyclization is also highly favored with the tetramethylcyclohexanone **8a**, it is noteworthy that a small amount of the trans-fused hydrindanol **10** is observed with this heavily substituted substrate. It is not surprising that annelation of cyclo-

(1) Support from Indiana University in the form of a Grant-in-Aid of Research is gratefully acknowledged.

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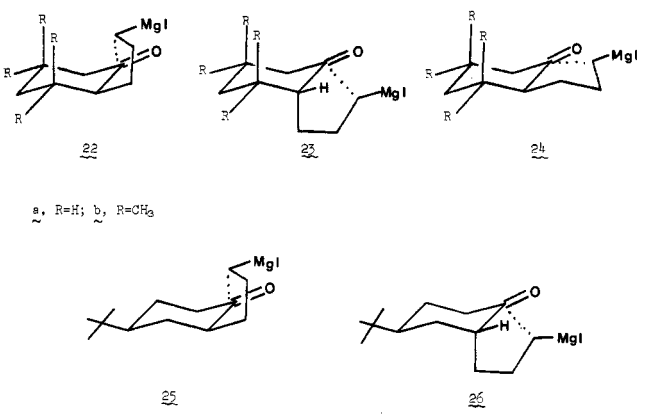
pentanone **11a** gives exclusively the substantially more stable *cis*-bicyclo[3.3.0]octane system. However, of potentially greater synthetic interest is the ca. 8:1 preference for cis cyclization of **13a** to form the important bicyclo[5.3.0]decane skeleton. Synthetic approaches[10] to the construction of this carbocyclic system have often experienced difficulties in the stereoselective generation of the cis and trans forms that are very similar in stability.[11]

The cis annelation of the five-membered ring onto a preformed cyclohexanone can, in principle, arise from either of the two transition-state conformations indicated by structures **22a** and **23a**. (For the purpose of illustration the species undergoing cyclization is depicted as the Grignard reagent; similar arguments apply for other likely intermediates.) Thus, cis-fused products can be generated either by axial attack at the carbonyl carbon by an equatorial side-chain moiety (**22a**) or by equatorial approach to the ketone by an axially oriented side chain (**23a**). One or both of these processes must be more favorable than alternative **24a** (equatorial attack of an equatorial side chain), which would have given the unobserved trans-fused product. The results with the *tert*-butyl analogue suggest that both modes of cis cyclization are feasible, since cis products are formed exclusively when the side chain is forced into either the equatorial (**25**) or axial (**26**) positions by the conformation-anchoring *tert*-butyl substituent. The absence of trans cyclization from either **1a** or **5a** is attributed to the angle strain introduced into the propyl side chain in bringing the reactive center within reasonable proximity to the carbonyl carbon along a route more or less perpendicular to the plane of the carbonyl function. This type of approach appears to be strain free in either **22a** or **23a**.

The small quantity of trans alcohol **10** obtained from the tetramethylcyclohexanone **8a** indicates that some trans cyclization (conformation **24b**) can be observed when cis cyclization via **22b** is seriously impeded by 1,3-diaxial interactions between the methyls and the attacking side chain. Conformation **23b** presumably accounts for much, if not all, of the cis cyclization from **8a**. The methyl substituents in this reactant should enhance the equilibrium percentage of the conformation with the 2-substituent oriented axially[12] and this should be reflected in the relative rate of cyclization by way of **23b**. This analysis further suggests that the parent compound **1a** undergoes appreciable reaction via **22a**, otherwise a similar or larger trans/cis ratio would be expected for the parent compound relative to the tetramethyl derivative. Finally, the more flexible cycloheptanone ring allows trans cyclization to become a significant competing process in the reaction with **13a**.

Attempts to extend this annelation process to larger rings were less successful. 2-(4-Bromobutyl)cyclohexanone (**16a**) does give hydroxydecalin (**17**), but only in 10% isolated yield. A large percentage of the volatile product consisted of the reduction product, 2-butylcyclohexanol. It is noteworthy, however, that only the trans alcohol **17** was observed from **16a**. The more flexible four-carbon side chain apparently attacks the carbonyl group exclusively from an equatorial direction, just the opposite of the situation with the shorter side chain in the cyclopentane



22 23 24

a, R=H; b, R=CH_3

25 26

annelations discussed above.

The experiment designed to generate a seven-membered ring was even more disappointing. In this instance cyclopentanone **18a** gave a low yield of volatile product that consisted mainly of cyclopentanol **19**. While the mechanism for the production of this alcohol is uncertain at best, it should be noted that the conversion is the intramolecular equivalent of the reduction of ketones by Grignard reagents, a commonly observed side reaction in the addition of Grignard reagents to ketones.[13]

The Barbier reaction is generally formulated in terms of formation of an organometallic intermediate, followed by addition of this species to the carbonyl compound in the usual manner.[2] However, there is little mechanistic evidence to bolster this point of view, and in one instance of an analogous reaction using lithium instead of magnesium, evidence against such a process has been reported.[14] Consequently, the discussion of the cyclization process in terms of intermediate organomagnesium species is reasonable speculation at best. Other mechanistic descriptions can be formulated, the most obvious of which involve free-radical intermediates of the type that have recently been implicated in the formation of Grignard reagents.[15] Further study of appropriate systems will be necessary before more definitive mechanisms can be provided for the cyclizations encountered in this study.

Experimental Section

General Procedures. Melting points were determined on a Thomas-Hoover Unimelt apparatus. Infrared spectra (IR) were recorded with a Perkin-Elmer Model 467 infrared grating spectrometer on liquid films or CCl_4 solutions between NaCl plates. Proton nuclear magnetic resonance (NMR) spectra were obtained with Varian T-60 and HR-220 spectrometers and are reported for $CDCl_3$ solutions at 60 MHz unless otherwise indicated. ^{13}C NMR spectra were recorded with a Varian XL-100-12 instrument; chemical shifts are reported in parts per million relative to internal tetramethylsilane for CCl_4 solutions. Gas chromatography (GC) was performed on Varian Aerograph 600D and Varian Aerograph A-700 instruments with columns of 10% Carbowax on Chromosorb P. Elemental analyses were determined by Midwest Microlabs Inc.

All reactions were performed under an atmosphere of dry nitrogen. Tetrahydrofuran was dried over lithium aluminum hydride and distilled immediately before use. Anhydrous magnesium sulfate was employed for all drying operations. A small amount of potassium carbonate was added in all drying operations and in distillations to prevent acid-catalyzed reactions. Solutions were concentrated by rotary evaporation. All compounds were vacuum transferred or sublimed after column chromatography.

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Reaction of Bromide 1b with Magnesium. A suspension of 0.60 g (25 mmol) of magnesium and 0.05 g of $HgCl_2$ in 50 mL of THF was heated to 50 °C. Bromide **1b** (3.00 g, 13.7 mmol) in 30 mL of THF was added dropwise over a 30-min period and the resulting mixture was refluxed overnight. After hydrolysis the resulting mixture was decanted from the excess magnesium and extracted with ether. The ether extracts were washed with water and dried. After evaporation of solvent, the residue was distilled to afford 1.21 g (40%) of bromide **1b** and 0.91 g (48%) of tetrahydrochromane **4**:[16] bp 92–94 °C (26 torr); IR 5.91 μM; NMR δ 0.9–2.3 (m, 12), 3.95 (t, 2).

Reaction of Iodide 1a with Lithium and *tert*-Butyl Alcohol. Iodide **1a** was prepared from 2.02 g (9.22 mmol) of bromide **1b** and NaI in acetone as described in the following experiment. A solution of crude iodide **1a** and 1.37 g (18.5 mmol) of *tert*-butyl alcohol in 50 mL of THF was stirred and 3.3 g (480 mmol) of lithium wire, in small pieces, was added to the reaction mixture.[17] The mixture was rapidly heated to 50 °C, when an exothermic reaction ensued, causing the reaction mixture to reflux. The reaction mixture was maintained at reflux for 4 h and cooled. After workup in the manner of the preceding experiment, the product was distilled to give 0.75 g (59%) of **4**.

Reaction of Iodide 1a with Magnesium. A solution of 3.00 g (13.7 mmol) of bromide **1b** and 4.2 g (28 mmol) of NaI in 50 mL of acetone was stirred for 2 h. After concentration, the reaction mixture was partitioned between ether and water. The ether extract was washed with 10% $NaHSO_3$ solution and water and dried. Evaporation of solvent gave crude iodide **1a**, which was used without further purification.

A mixture of 0.6 g (24 mmol) of magnesium and 0.1 g of $HgCl_2$ in 50 mL of THF was heated to 45 °C. The heat source was removed and a solution of iodide **1a** in 30 mL of THF was added over a period of ca. 30 min. During addition the temperature of the reaction mixture was maintained at 45–50 °C, initially by regulating the rate of addition of the iodide and later by external heating. After refluxing overnight, the reaction mixture was hydrolyzed with water and the resulting mixture decanted from the excess magnesium. The reaction mixture was extracted with ether, and the ether extracts were washed with water and dried. GC analysis of this solution showed 13% of tetrahydrochroman (**4**), 7% of propylcyclohexanone (**3**), 77% of hydrindanol (**2**), and 3% of an unidentified compound. No *trans*-bicyclo[4.3.0]nonan-1-ol could be observed even though 1% would have been detected. Evaporation of solvent, followed by column chromatography of the residue on silica gel with 20% ether–hexane afforded 0.11 g (6%) of **3**, 0.11 g (6%) of **4**, and 1.17 g (61%) of **2**:[18,19] mp 49–50 °C; IR (CCl_4) 2.78, 6.85, 6.96, 10.5, 10.9, 11.6, 11.8 μM; ^{13}C NMR δ 20.2, 23.4, 24.1 (2), 29.0, 35.1, 35.5, 46.2, 80.0.

Reaction of Iodide 5a with Magnesium. In the same fashion, 2.18 g (7.92 mmol) of bromide **5b** was converted into iodide **5a**, which was subsequently reacted with 0.39 g (16 mmol) of magnesium and 0.1 g of $HgCl_2$ in THF. After workup, GC analysis showed a mixture of **6** and **7** in a ratio of 69:8 along with four unidentified products comprising 23% of the product mixture. The crude product was recrystallized from pentane to give 0.90 g (58%) of the mixture of 4-*tert*-butylbicyclo[4.3.0]nonan-1-ols **6** and **7**. ^{13}C NMR analysis of the mixture showed resonances for the major isomer **6** at 80.7, 47.7, and 47.2 ppm and for the minor isomer **7** at 41.2 and 40.5 ppm.

Reaction of Iodide 8a with Magnesium. In the same manner, 4.00 g (14.5 mmol) of bromide **8b** was converted into iodide **8a**. Subsequent reaction of **8a** with 0.70 g (29 mmol) of magnesium and 0.1 g of $HgCl_2$ in 100 mL of THF followed by aqueous workup gave a mixture of 84% of **9**, 4% of **10**, and 12% of three unidentified materials as indicated by GC analysis. Column chromatography on silica gel with 20% ether–hexane afforded 1.99 g (70%) of the mixture of 3,3,5,5-tetramethylbicyclo[4.3.0]nonan-1-ols **9** and **10**.

Reaction of Iodide 11a with Magnesium. Iodide **11a** was prepared from 1.85 g (9.2 mmol) of bromide **11b** by the usual procedure. After reaction with 0.73 g (30 mmol) of magnesium, GC analysis showed a mixture of 90% of *cis*-bicyclo[3.3.0]octan-1-ol (**12**) and 10% of three unidentified materials. Column chromatography on silica gel with 10% ether–hexane gave an oil that was vacuum transferred to yield 0.55 g (48%) of **12**.

Reaction of Iodide 13a with Magnesium. Bromide **13b** (3.22 g, 14.8 mmol) was converted into iodide **13a** followed by reaction with 0.72 g (30 mmol) of magnesium and 0.1 g of $HgCl_2$ as described above. The crude product was analyzed by GC and shown to contain a mixture of 85% of *cis*-bicyclo[5.3.0]decan-1-ol (**14**), 11% of *trans*-bicyclo[5.3.0]decan-1-ol (**15**), and 4% of two unidentified products. Column chromatography on silica gel with 10% ether–hexane gave 1.05 g (46%) of **14** and 0.19 g (8%) of **15**.

Reaction of Iodide 16a with Magnesium. In the same manner, bromide **16b**[20] (2.07 g, 8.88 mmol) was converted into iodide **16a**, which was treated with 0.44 g (18.0 mmol) of magnesium and 0.05 g of $HgCl_2$. The crude product contained a mixture of 28% of 2-butylcyclohexanone, 40% of *trans*-bicyclo[4.4.0]decan-1-ol (**17**), and 33% of three unidentified products. Column chromatography on silica gel with 10% ether–hexane gave 0.13 g (10%) of **17** and 0.21 g (15%) of 2-butylcyclohexanone.[21] The cis isomer of **17** was shown not to be present by comparison with an authentic sample.

Reaction of Iodide 18a with Magnesium. In the same manner as the preceding experiment, iodide **18a** was prepared from 3.50 g (15.0 mmol) of bromide **18b**.[20] Iodide **18a** was reacted with 0.73 g (30 mmol) of magnesium and 0.1 g of $HgCl_2$ and worked up as usual. GC analysis showed a mixture of at least six products with one product comprising ca. 70% of the mixture. The major product was isolated by column chromatography on silica gel with 10% ether–hexane. Vacuum transfer afforded 0.28 g (12%) of **19**: IR (CCl_4) 2.77, 3.23, 6.10, 10.9 μM; NMR δ 1.0–2.2 (m, 13), 3.79 (q, 1), 4.8–5.2 (m, 2), 5.6–6.3 (m, 1).[22]

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.66; H, 11.59.

3,3,5,5-Tetramethyl-*cis*-bicyclo[4.3.0]nonan-1-ol (9). A solution of 0.54 g (2.78 mmol) of **20** and 0.15 g (4.0 mmol) of $LiAlH_4$ in 25 mL of THF was refluxed for 48 h and worked up as usual. Column chromatography on silica gel with 20% ether–hexane gave 0.26 g (47%) of **9**: IR 2.79, 2.93, 7.25, 7.35, 8.23, 9.71, 9.81, 10.0 μM: NMR (220 MHz) δ 0.77 (s, 3), 0.85 (s, 3), 1.14 (s, 6), 1.1–1.8 (m, 12).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.68; H, 12.29.

3,3,5,5-Tetramethyl-*trans*-bicyclo[4.3.0]nonan-1-ol (10). A mixture of 0.61 g (3.13 mmol) of epoxide **21** and 0.15 g (4.0 mmol) of $LiAlH_4$ in 25 mL of THF was heated at reflux for 48 h. Following the usual workup, column chromatography on silica gel with 10% ether–hexane afforded 0.24 g (39%) of **10**: IR 2.78, 2.87, 8.19, 9.65, 11.7 μM; NMR (220 MHz) δ 0.82 (s, 3), 0.85 (s, 3), 1.06 (s, 3), 1.17 (s, 3), 1.2–1.8 (m, 12).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.84; H, 12.23.

Registry No. **1a**, 83587-93-3; **1b**, 10468-37-8; **2**, 13366-92-2; **3**, 94-65-5; **4**, 7106-07-2; **5a**, 83587-94-4; **5b**, 83587-25-1; **6**, 83587-33-1; **7**, 83587-95-5; **8a**, 83587-96-6; **8b**, 83587-28-4; **9**, 83587-97-7; **10**, 83587-98-8; **11a**, 83587-99-9; **11b**, 10468-38-9; **12**, 52318-93-1; **13a**, 83588-00-5; **13b**, 62547-86-8; **14**, 27935-18-8; **15**, 27935-17-7; **16a**, 76402-75-0; **16b**, 51953-08-3; **17**, 1654-87-1; **18a**, 83588-01-6; **18b**, 51566-66-6; *trans*-**19**, 83588-02-7; **20**, 77516-44-0; **21**, 77550-63-1.

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