Cyclohexyl(2-methylenecyclopropyl)carbinyl Carbocationic Rearrangements

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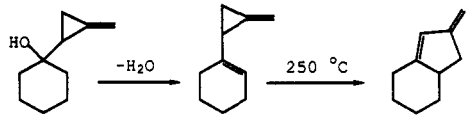
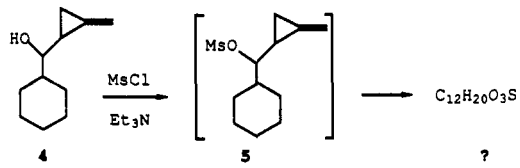
Synthetic chemistry based on methylene cyclopropane[1,2] has been developed over the past 15 years to afford convenient access to a variety of interesting and useful structures.[3] In exploratory studies contributing to this new chemistry,[4] methylenecyclopropane was lithiated[5] and combined with cyclohexanone to give the expected alcohol 1; dehydration of this alcohol with Burgess' reagent,[6] methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt, gave (2-methylenecyclopropyl)cyclohexene (2), which was converted over silylated glass beads[7] at 250 °C in 92% yield to 8-methylenebicyclo[4.3.0]non-6-ene (3).



1 2 3

A similar sequence starting with the diastereoisomers of cyclohexyl(2-methylenecyclopropyl)carbinol (4) was not realized, however, for attempts to achieve dehydration using several reagents and various reaction conditions gave rise instead to recovered starting materials, or complex mixture of products, or products of uncertain structures. Reaction of alcohol 4 with methanesulfonyl chloride and triethylamine in methylene chloride gave a white crystalline solid having a mass spectral molecular ion at m/z 244 corresponding to $C_{12}H_{20}O_3S$, the formula expected for the desired mesylate derivative 5; but the spectroscopic characteristics of the product made clear that it did not contain a methylenecyclopropane substructure.[4]



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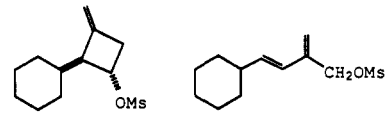
The IR spectrum showed bands appropriate for a methyl group at 1375 and 1450 cm^{-1} and a band at 890 cm^{-1} for a terminal methylene group. The ^1H NMR spectrum had two olefinic protons as a multiplet at δ 4.9 and a quartet at 4.7, a methyl group singlet at δ 2.9, and a broad multiplet from 2.0 to 0.9 ppm. In the ^{13}C NMR spectrum, olefinic carbons were found at δ 142.0 (s) and 107.6 (t). There were CH carbons at δ 73.2 and 58.2, three overlapping signals at δ 39.2, 38.8, and 38.4, and CH_2 carbons at δ 31.1, 29.7, 26.4, and 26.1 (two carbons). There were no carbons with chemical shifts less that δ 26.1, as one would have anticipated for structure 5; the cyclopropyl CH_2 group carbons in the two isomers of 4, for instance, have absorptions at δ 7.2 and 8.2. That some unexpected rearrangement had taken place was thus clear,[4] but other experimental priorities claimed attention, and the rearrangement was not elucidated.

An interest in the enzymic inactivation chemistry induced by (2-methylenecyclopropane)acetyl-CoA associated with the Jamacian vomiting sickness[8] prompted a renewed consideration of this rearrangement, and it has been readdressed. Two products formed when alcohol 4 is treated with methanesulfonyl chloride and triethylamine have been identified: the trans isomer of 2-cyclohexyl-3-methylenecyclobutyl mesylate (6) and 4(*E*)-cyclohexyl-2-methylenebut-3-en-1-yl mesylate (7).



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Results and Discussion

Reaction of the diastereoisomeric mixture of secondary alcohols 4 with methanesulfonyl chloride and triethylamine in anhydrous methylene chloride at 0 °C[9] afforded 90% of two mesylate ester products in a 5:1 ratio. They were not readily separated by preparative gas chromatography or thin-layer chromatography and were thus examined spectroscopically as the mixture.

The ^1H NMR spectrum of the minor mesylate ester shows four olefinic protons, a doublet at δ 6.02 (J = 16.3 Hz), a doublet of doublets at δ 5.75 (J = 6.9, 16.3 Hz), and two singlets at δ 5.24 and 5.21; there is a two-proton singlet at δ 4.85. There are four olefinic carbons in the ^{13}C spectrum, at 138.5, 125.7, 118.0, and 107.4 ppm. The close correspondences between these spectral indicators and the known NMR spectroscopic characteristics of 4(*E*)-

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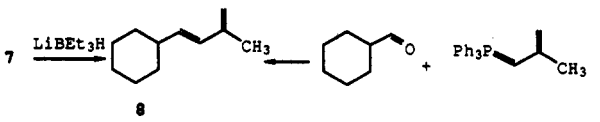
cyclohexyl-2-methylenebuta-1,3-diene[10,11] led to the minor product being tentatively assigned structure **7**.

Confirmation of this postulation was secured through a reduction[12] of the mesylate **7** with $LiBEt_3H$ to give the corresponding hydrocarbon **8**.[10,11] Capillary GC, MS, and NMR spectral comparisons between this reduction product and an authentic sample of **8** prepared from (2-methylpropenylidene)triphenylphosphorane[13] and cyclohexanecarboxaldehyde corroborated the assignment.



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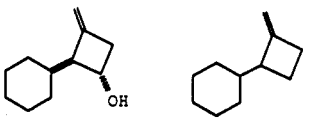
Conversion of the major rearrangement product to a hydrocarbon proved more difficult; $LiAlH_4$,[14] $LiAl(OMe)_3H$–CuI,[15] and $LiBEt_3H$[16] gave an alcohol (**9**) through O–S cleavage rather than displacement of the mesylate group. Under solvolytic conditions, however, aqueous diglyme containing 4 M $NaBH_4$,[17] a $C_{11}H_{18}$ product (**10**) was obtained.



9 **10**

The ^1H NMR spectra for mesylate **6**, alcohol **9**, and hydrocarbon **10** show similar multiplets in the olefinic region, and the patterns were recognized as quite similar to expectations based on precedent for methylenecyclobutane[18,19] and 2-methylenecyclobutanecarboxylic acid.[18] A reference sample of **10** was prepared through a short route based on the Wittig reaction of cyclohexanecarboxaldehyde with (cyclopropylidene)triphenylphosphorane[20] to give (cyclopropylidenemethyl)cyclohexane (**11**). Epoxidation of the double bond in **11** and rearrangement of the intermediate oxaspiropentane system[21] (**12**) gave 2-cyclohexylcyclobutanone (**13**), which in turn provided the hydrocarbon **10** through a Wittig reaction. Chromatographic and spectroscopic evidence showed it was identical to the $C_{11}H_{18}$ product derived from mesylate **6**.

The stereochemical assignments for mesylate **6** and alcohol **9** were obtained through recording ^1H NMR spectra as a function of an added lanthanide shift reagent, Eu(FOD)$_3$ (Figure 1). The ^1H NMR absorptions for the three

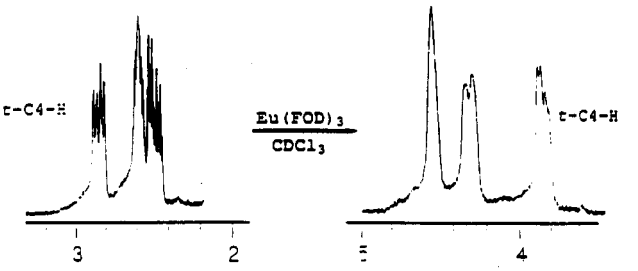
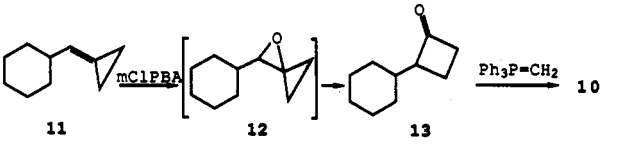


Figure 1. Lanthanide reagent Eu(FOD)$_3$ induced ^1H NMR spectroscopic chemical shifts for allylic hydrogens in alcohol **9**. A dozen spectra with progressive proportions of Eu(FOD)$_3$ showed C2-H and *c*-C4-H (cis to hydroxyl) signals shifting downfield about twice as fast as the *t*-C4-H resonance.



11 **12** **13**

allylic hydrogens in the 2-cyclohexyl-3-methylenecyclobutanol derived from the rearrangement and cleavage of the mesylate appear as a broad singlet for C2-H at δ 2.58 and as a geminal pair of C4 hydrogens at δ 2.83 and 2.45. With progressive increases in the concentration of Eu(FOD)$_3$, the allylic hydrogens of alcohol **9** all are shifted downfield, with the two initially at higher field experiencing the largest shifts. The relative chemical shift of the upfield geminal proton in the absence of shift reagent approaches, coincides with, and then appears shifted to lower field relative to the other C4-H as more and more shift reagent is added. This response to Eu(FOD)$_3$ accords with expectations for the trans isomer **9**; the cis isomer would have shown one of the C4 allylic protons shifting downfield faster than the other C4-H and C2-H.

The rearrangements observed upon treatment of alcohols **4** with methanesulfonyl chloride and triethylamine in CH_2Cl_2 may be formulated as proceeding through initial formation of mesylate isomers **5**, followed by heterolysis to give transient ion pairs and in turn the rearranged mesylates **6** and **7**. The former structure corresponds with the major product observed from the reaction of (2-methylenecyclopropyl)carbinylamine with aqueous nitrous acid, 3-methylenecyclobutanol.[22]

That trans stereochemistry is observed for the major product starting from either diastereomer of alcohol **4** and, presumably, mesylate **5** raises questions on the stereochemical, conformational, and energic characteristics of the carbocations that may be involved. Participation by the C1–C2 bond of the methylenecyclopropyl group with displacement would give a 2-cyclohexyl-3-methylenecyclobutyl carbocation (or a delocalized version of such a cation); reaction with the mesylate anion from the exo face, trans to the 2-cyclohexyl substituent, then could give the observed trans product. From one stereochemical version of the precursor mesylate, the initially formed ion could undergo a ring puckering conformational isomerization before reaction with the gegenion to give the same product (Scheme I).

This stereochemical preference has been observed for the diastereomeric (1-methyl-2-methylenecyclopropyl)-

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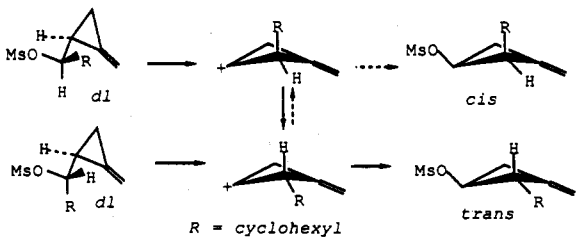
Scheme I



methylcarbinyl tosylates[23] and 3,5-dinitrobenzoates:[24] the 2,3-dimethyl-3-methylenecyclobutyl structures obtained through internal return or solvolysis in aqueous acetone favor the trans disposition of C2-methyl and C3-hydroxyl (or 3,5-dinitrobenzoyl) functions.

While earlier publications[22-24] on carbocationic rearrangements of (2-methylenecyclopropyl)carbinyl systems did not report products analogous to diene **7**, a structure probably derived through simple cleavage of the C1–C3 bond of the methylenecyclopropyl group to give initially a cross-conjugated allylic cation, more recent work has provided such examples: some alkyl(2-methylenecyclopropyl)carbinols react with formic acid to give both 2-alkyl-3-methylenecyclobutyl formates and 4(*E*)-alkyl-2-methylenebut-3-en-1-yl formates.[5e] Substituents on the (2-methylenecyclopropyl)carbinyl system or solvent or gegenion effects apparently control partitioning among the several reaction modes formally available and experimentally observed.

Experimental Section

Cyclohexyl(2-methylenecyclopropyl)carbinols 4. To a solution of methylenecyclopropane[1,2] (3 g, 55 mmol), pentane (30 mL), and TMEDA (11.17 mL, 74 mmol) at −78 °C under nitrogen was added slowly 74 mmol (43.5 mL of 1.7 M) of *tert*-butyllithium in pentane. The reaction mixture was kept at −78 °C for 1 h, brought to 0 °C for 30 min, and then cooled again to −78 °C and treated with cyclohexanecarboxaldehyde (6.36 g, 57 mmol). After 1 h at −78 °C, the reaction mixture was allowed to warm to rt; 15 mL of 5% aqueous HCl was added, and the organic phase was separated and washed with 15-mL portions of 5% HCl, water, and brine. Drying the solution over $MgSO_4$, filtration, concentration, and Kugelrohr distillation gave 3.59 g (39%) of alcohol **4** as a mixture of two diasterisomers in nearly equal proportions, according to capillary GC analyses. They were separated by preparative GC on a XF-1150 60/80 NAW Chromosorb W column for characterization: for the early eluting isomer, MS *m/z* (rel intensity) 166 (0.6, M^+), 95 (10), 83 (99), 67 (17), 55 (100), 41 (57), 39 (39); ^1H NMR δ 5.49 (m, 2 H), 2.97 (apparent t, *J* = 6.6 Hz, 2 H), 1.71 (m, 8 H), 1.16 (m, 6 H); ^{13}C NMR 133.3, 104.3, 78.6, 44.5, 29.0, 28.7, 26.6, 26.3, 26.2, 19.6, 8.2 ppm; for the second isomer, MS *m/z* 166 (0.03, M^+), 95 (9), 83 (88), 67 (14) 55 (100), 41 (39), 39 (24); ^1H NMR δ 5.41 (m, 2 H), AB pair at 2.85, 2.86 (AB dd, *J* = 6.4 Hz, 2 H), 1.70 (m, 8 H), 1.14 (m, 6 H); ^{13}C NMR 133.3, 104.4, 78.7, 44.1, 29.0, 28.9, 26.5, 26.3, 26.1, 20.8, 7.2 ppm.

From the product mixture a 3,5-dinitrobenzoate derivative was prepared and recrystallized from aqueous ethanol to constant mp, 83–84 °C. Anal. Calcd for $C_{18}H_{20}O_6N_2$: C, 59.99; H, 5.59; N, 7.77. Found: C, 60.12; H, 5.78; N, 7.73.

Reaction of Carbinols 4 with Methanesulfonyl Chloride. To 294 mg (1.8 mmol) of **4** and 274 mg (2.7 mmol) of triethylamine in 10 mL of CH_2Cl_2 at 0 °C was added 227 mg (2.0 mmol) of MsCl over 10 min. After another 15 min at 0 °C, the reaction mixture was washed with ice water, cold 5% HCl, aqueous $NaHCO_3$, and brine. The organic phase was filtered through a silica gel column and eluted with CH_2Cl_2. Concentration under reduced pressure gave 389 mg (90%) of crude product as a light yellow oil: according to capillary GC/MS analyses, there were two mesylate esters present in a 5:1 ratio. A minor component (3% of product mixture) very similar in chromatographic characteristics to the major product was detected. Attempts to separate the two main products by preparative GC and TLC were not successful, and the mixture was examined spectroscopically. For the major product, ***trans*-2-cyclohexyl-3-methylenecyclobutyl mesylate (6)**: MS *m/z* (rel intensity) 244 (M^+, Varian MAT CH-5 determination), 162 (10), 148 (22), 133 (32), 119 (33) 105 (62), 91 (50), 79 (88), 67 (51), 55 (100), 41 (92), 39 (52); ^1H NMR, olefinic hydrogens δ 4.95 (m, 1 H), 4.77 (apparent q, *J* = 6.7 Hz, 1 H); ^{13}C NMR 141.8, 107.4, 73.1, 58.0, 39.1, 38.7, 38.3, 31.0, 29.5, 26.3, 26.02, 25.99 ppm. For the minor product, **4(*E*)-cyclohexyl-2-methylenebut-3-en-1-yl mesylate (7)**: MS *m/z* 244 (3, M^+), 148 (41), 133 (36), 119 (30), 105 (94), 91 (90), 79 (100), 67 (76), 55 (36), 41 (76), 39 (42); ^1H NMR δ 6.02 (d, *J* = 16.3, 1 H), 5.75 (dd, *J* = 6.9, 16.3 Hz, 1 H), 5.24 (s, 1 H), 5.21 (s, 1 H), 4.85 (s, 2 H, CH_2OMs); ^{13}C NMR 138.5, 125.7, 118.0, 107.4, 69.8, 61.4, 38.7, 38.6, 38.4, 26.2 ppm.

4(*E*)-Cyclohexyl-2-methylenebuta-1,3-diene (8). (1) From Mesylate 7. A mixture of mesylates **6** and **7** (100 mg, 0.41 mmol) in 10 mL of THF under nitrogen at 0 °C was treated with 0.82 mL of 1 M $LiBEt_3H$ in THF. The reaction mixture was allowed to warm to rt and, after 3 h, it was diluted with water and with 5 mL of 1:1 3 N NaOH:30% H_2O_2. The organic layer was separated and the aqueous layer was extracted with pentane (2 × 10 mL). The combined organic material was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated. Preparative GC on a 20% ββ-OTPN on 60/80 Chromosorb P column gave a pure sample of the hydrocarbon product for characterization: MS *m/z* (rel intensity) 150 (48, M^+), 135 (62), 121 (20), 107 (49), 93 (53), 81 (53), 79 (98), 67 (100), 41 (63), 39 (53); ^1H NMR δ 6.11 (d, *J* = 15.9 Hz, 1 H), 5.60 (dd, *J* = 7.0, 15.9 Hz, 1 H), 4.87 (s, 2 H), 2.01 (br m, 1 H), 1.83 (s, 3 H), 1.71 (br m, 4 H), 1.2 (br m, 6 H); ^{13}C NMR 142.4, 136.8, 130.2, 114.2, 40.8, 33.0, 26.2, 26.1, 18.7 ppm (compare literature values in ref 11).

(2) From Cyclohexanecarboxaldehyde. (2-Methylallyl)-triphenylphosphonium chloride was prepared from 20 g (76 mmol) of triphenylphosphine and 7 g (77 mmol) of methallyl chloride in 45 mL of THF and 5 mL of diglyme.[13] When 28.1 mL of 1.7 M phenyllithium (48 mmol of PhLi) in cyclohexane–ether was added with stirring, a deep red solution was obtained; 5.72 g (51 mmol) of cyclohexanecarboxaldehyde was added dropwise at rt and the reaction mixture was concentrated by slow distillation over 5 h to about 30 mL, then left at rt overnight. It was washed with water (3 × 50 mL); the organic phase was washed with brine, dried over K_2CO_3, filtered, and concentrated by distillation. Kugelrohr distillation gave 3.0 g (42%) of hydrocarbon product, which was purified by preparative GC on a 20% ββ-ODPN on 60/80 Chromosorb P column. The MS, ^1H NMR, and ^{13}C NMR spectra are essentially identical to those of the product obtained from mesylate **7**.

2-Cyclohexyl-1-methylenecyclobutane (10) from Mesylate 6. To a solution of 3.03 g (80 mmol) of $NaBH_4$ and 0.8 g (20 mmol) of NaOH in 20 mL of 65% aqueous diglyme (7 mL of water, 13 mL of bis(2-methoxyethyl) ether) at 50 °C was added 50 mg (0.2 mmol) of a mixture of mesylates **6** and **7**. The reaction mixture was maintained at 50 °C for 1 week and then was cooled, diluted with water, and extracted with pentane. The pentane solution was dried over K_2CO_3 and $CaSO_4$, filtered, and concentrated, and the major hydrocarbon product was collected by preparative GC on a 10% XF-1150 on 60/80 NAW Chromosorb W column: MS *m/z* (rel intensity) 150 (0.01, M^+), 135 (25), 122 (79), 107 (45), 93 (58), 79 (100), 67 (83), 55 (69), 41 (89), 39 (76); ^1H NMR δ 4.73 (m, 2 H), 2.67 (m, 1 H), 2.52 (m, 2 H), 1.95 (m, 1 H), 1.84 (m, 1 H), 1.68 (m, 5 H), 1.36 (m, 1 H), 1.21 (m, 3 H), 0.91 (m, 2 H); ^{13}C NMR 153.9, 104.4, 50.4, 41.4, 31.1, 29.8, 29.1, 26.7, 26.3, 26.2, 20.8 ppm.

(Cyclopropylidenemethyl)cyclohexane (11). A solution of (cyclopropylidene)triphenylphosphorane was prepared from 28.5 g (61 mmol) of (3-bromopropyl)triphenylphosphonium bromide and 5.05 g of 60% NaH in mineral oil (126 mmol of NaH) in 150 mL of dimethoxyethane and was cooled to rt; cyclohexanecarboxyladehyde was added (7.28 g, 65 mmol) and

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the reaction mixture was warmed to 70 °C for 5 h. The mixture was filtered and the collected salts were washed with hexane. The combined organic material was washed with 3% HCl and brine, dried over K_2CO_3, and eluted through a silica gel column with hexane. Concentration and Kugelrohr distillation gave 2.04 g (25%) of product; further purification was accomplished through preparative GC using a 20% Carbowax 20M on 60/80 Chromosorb W column. 11: MS *m/z* (rel intensity) 136 (0.6, M^+), 121 (40), 107 (20), 95 (12), 93 (56), 81 (100), 79 (93), 67 (44); ^1H NMR δ 5.69 (m, 1 H), 2.16 (m, 1 H), 1.71 (m, 5 H), 1.14 (m, 9 H); ^{13}C NMR 124.0, 118.8, 40.7, 33.0, 26.3, 26.2, 2.5, 1.2 ppm.

2-Cyclohexylcyclobutanone (13). Olefin 11 (1.28 g, 9.4 mmol) in 65 mL of CH_2Cl_2 was treated with 2.43 g (14 mmol) of *m*-chloroperbenzoic acid. Analysis by TLC after 45 min indicated that the reaction had gone to completion. The reaction mixture was washed with aqueous $NaHCO_3$, aqueous $NaHSO_3$, and brine, dried over K_2CO_3, filtered, and concentrated. Preparative GC using a 10% FFAP on Chromosorb W column gave the pure ketone: MS *m/z* (rel intensity) 152 (0.01, M^+), 134 (17), 124 (18), 95 (15), 81 (100) 80 (94); ^1H NMR δ 3.11 (m, 1 H), 2.90 (m, 2 H), 2.06 (m, 1 H), 1.93 (m, 1 H), 1.67 (m, 6 H), 1.12 (m, 5 H); ^{13}C NMR 212.3, 66.4, 44.3, 38.6, 31.0, 30.3, 26.3, 26.0, 14.4 ppm.

2-Cyclohexyl-1-methylenecyclobutane (10). A solution of methylenetriphenylphosphorane in 25 mL of freshly distilled THF was prepared using 715 mg (2 mmol) of methyltriphenylphosphonium bromide and 0.87 mL of a 2.3 M solution (2 mmol) of *n*-butyllithium in hexanes. Ketone 13 (150 mg, 1.0 mmol) was added, and the reaction mixture was heated at reflux overnight. It was cooled and combined with 100 mL of water, and the aqueous phase was extracted with pentane (4 × 25 mL). The combined organic material was washed with water and brine, dried ($MgSO_4$), filtered, and concentrated by distillation to leave 140 mg of crude product. Preparative GC on a 20% $\beta\beta\beta$-OTPN on 60/80 Chromosorb P column afforded pure material: MS *m/z* (rel intensity) 150 (1.4, M^+), 135 (28), 122 (91), 107 (47), 93 (64), 79 (100), 67 (84), 55 (62), 41 (81); ^1H NMR δ 4.73 (m, 2 H), 2.66 (m, 1 H), 2.53 (m, 2 H), 1.96 (m, 1 H), 1.84 (m, 1 H), 1.65 (m, 5 H), 1.38 (m, 1 H), 1.21 (m, 3 H), 0.92 (m, 2 H); ^{13}C NMR 153.9, 104.4, 50.4, 41.4, 31.1, 29.9, 29.1, 26.7, 26.3, 26.2, 20.8 ppm.

***trans*-2-Cyclohexyl-3-methylenecyclobutanol (9).** A mixture of mesylate products (85 mg, 0.35 mmol) derived from a preparative GC purified sample of the early eluting isomer of carbinol 4 in 20 mL of ether was reduced with 30 mg (0.8 mmol) of $LiAlH_4$ under nitrogen. A normal workup gave just one alcohol product (capillary GC/MS)) which was isolated by preparative GC on a 20% Carbowax 60/80 NAW Chromosorb P column: MS *m/z* (rel intensity) 166 (0.8, M^+), 151 (5), 133 (13), 122 (20), 107 (17), 95 (24), 81 (63), 67 (53), 55 (100), 41 (83), 39 (62); ^1H NMR δ 4.87 (m, 2H), 4.04 (apparent q, J = 6.8 Hz, 1 H), 2.83 (m, 1 H), 2.58 (m, 1 H), 2.47 (m, 1 H), 1.60 (m, 6 H), 1.14 (m, 5 H); ^{13}C NMR 144.3, 105.6, 66.9, 61.0, 40.5, 39.6, 31.6, 29.9, 26.5, 26.19, 26.15 ppm.

When a mixture of both diastereoisomers of carbinol 4 was allowed to react with methanesulfonyl chloride, and the product mixture of mesylate 6 and 7 was reduced with $LiAlH_4$, only a single alcohol product (9) was obtained in significant yield, according to capillary GC/MS and NMR criteria.

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Supplementary Material Available: ^1H NMR for compounds 6, 7, 8–11, and 13 and capillary GC traces of compounds 8–11 and 13 (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.