Total Synthesis of Racemic α-*trans*- and α-*cis*-Bergamotene and α-Pinene[1a]

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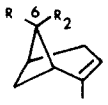
Abstract: The stereoselective total synthesis of racemic α-*trans*- (**1**) and of racemic α-*cis*-(**2**) bergamotene and the direct preparation of racemic α-pinene (**3**) from 4-methylbicyclo[3.2.1]oct-3-en-6-one (**14**) are described. The key steps involve formation of the cyclobutane ring by intramolecular ring closure of the bicyclic precursors **16d** and **18** and sodium amide initiated fragmentation of the β-trimethylsilyloxy ketone moiety of the resulting tricyclic derivatives **21b** and **22** to give the required 2-methylbicyclo[3.1.1]hept-2-ene skeletons **29** which contain stereocontrolled, differentiated functionality at the quaternary C-6 center. Functional group modification of **29** then completes the fully stereocontrolled, total synthesis of these natural substances.

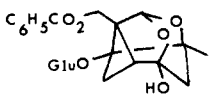
The mono- and sesquiterpenes comprising the pinane family of natural products are characterized structurally by the presence of a bicyclo[3.1.1]heptane nucleus. The widely distributed essential oil hydrocarbon α-*trans*-bergamotene[2] (**1**) and its cis isomer[3] (**2**) are representative of the known sesquiterpenes,[4] while the ubiquitous α-pinene (**3**) and the highly oxygenated paeoniflorin[5] (**4**) are illustrative of the structural



1 R_1=$CH_2CH_2CH{=}C(CH_3)_2$, R_2=CH_3

2 R_1=CH_3, R_2=$CH_2CH_2CH{=}CCCH_3)_2$

3 R_1=R_2=CH_3



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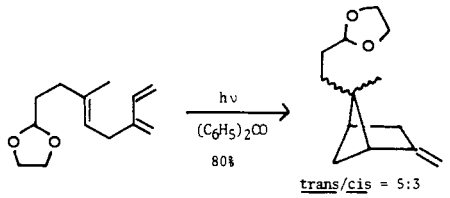
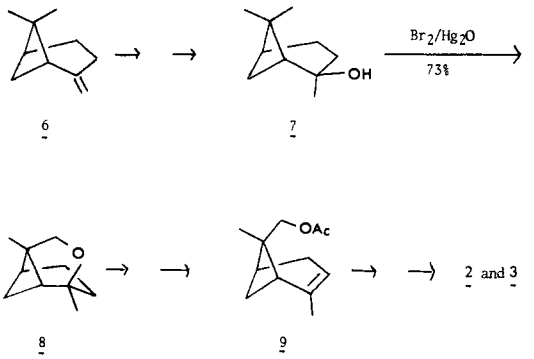
variety found in the monoterpene members of this family. Previous synthetic efforts have resulted in the preparation of the three α hydrocarbons **1**,[6] **2**,[7] and **3**,[8a,c] although the fundamental synthetic objectives presented by these substances, (1) the *direct* construction of the acid-labile 2-methylbicyclo[3.1.1]hept-2-ene skeleton and (2) the unambiguous stereocontrol of the quaternary C-6 carbon center, have only been partially achieved by these earlier endeavors.

Three basic routes have been used to prepare the symmetrically substituted 6,6-dimethylbicyclo[3.1.1]heptane nucleus: formation of the three-carbon bridge by ring closure of a cyclobutane substrate;[8a,b] preparation of the one-carbon bridge by intramolecular alkylation of a cyclohexanone derivative;[8c] and intramolecular photochemical [2 + 2] cycloaddition of an acyclic precursor.[8d] Of these, a photochemical [2 + 2] cycloaddition was employed as the key step in the synthesis of α-*trans*-bergamotene (**1**) to prepare a mixture of C-5 isomers **5** (5:3) in which the desired trans isomer predominated (eq 1).[6]



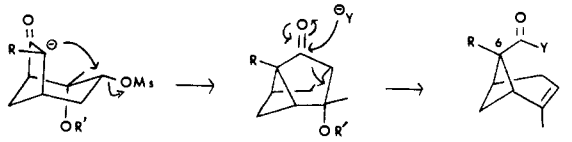
5 (1)

In the synthesis of α-*cis*-bergamotene (**2**) the required C-6 stereochemistry was established unambiguously by remote oxidative ring closure of alcohol **7** to give ether **8** which was transformed into acetate **9** and then **2**. The starting alcohol **7** was prepared in turn from naturally occurring β-pinene (**6**), thus avoiding the bicyclo[3.1.1]heptane nucleus synthesis altogether (eq 2).[7]



6 **7** **8** **9** (2)

We now report a general synthetic approach to the pinene class of natural products which involves the basic synthetic design outlined in eq 3. This scheme may be divided into four



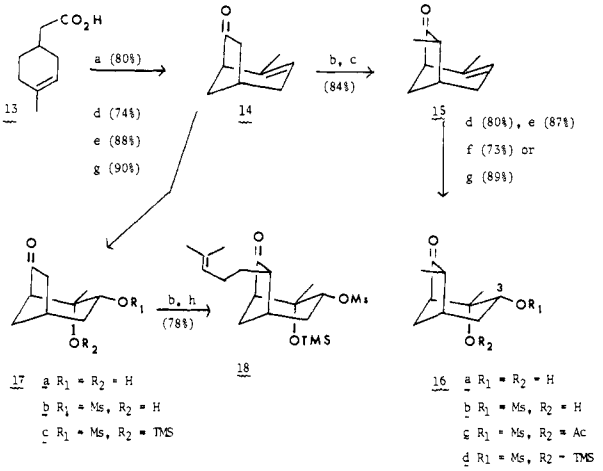
10 **11** **12** (3)

stages: (1) preparation of suitably substituted bicyclo[3.2.1]-octanones **10**; (2) formation of the required cyclobutane ring via intramolecular ring closure[9] of **10** (see arrows) to give tricyclo[3.2.1.$0^{3,6}$]octanones **11**; (3) fragmentation of the 1,3-dioxygen moiety of **11** as shown to generate directly the desired 2-methylbicyclo[3.1.1]hept-2-ene skeletons **12** with stereocontrolled, differentiated functionality at the quaternary C-6 center; and (4) appropriate functional group modification. The stereoselective total synthesis of each of the sesquiterpenes, α-*trans*- (**1**) and α-*cis*- (**2**) bergamotene, and the preparation of α-pinene (**3**) using this approach are described below.

Large-scale preparation of the known[10] bicyclic keto olefin **14** was conveniently performed by treatment of 4-methyl-3-cyclohexene-1-acetic acid (**13**)[10] with trifluoroacetic anhydride in heptane to give **14** as the only isolated product (Scheme I). This direct intramolecular cyclization procedure provides an efficient, attractive alternative to the normal Friedel-Crafts route involving Lewis acid catalyzed cyclization of the corresponding acid chloride and subsequent elimination of the resulting keto chloride.[10,11]

Introduction of the methyl group destined to be a C-6 substituent in α-*cis*-bergamotene (**2**) and α-pinene (**3**) was accomplished by low-temperature alkylation of keto olefin **14**

Scheme I

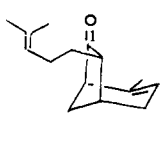


a, $(CF_3CO)_2O$, heptane, 0°, 30 min; b, $(iPr)_2NLi$, THF, -70°C; c, CH_3I, -70° to 25°C; d, OsO_4 (catalytic), NMO,[15] THF-H_2O, 25°C, 72 h; e, MsCl, Et_3N, CH_2Cl_2, -5°C; f, Ac_2O, Et_3N, 4-dimethylaminopyridine, CH_2Cl_2, rt, 25°C; g, Me_3SiCl, Et_3N, 4-dimethylaminopyridine, CH_2Cl_2, 25°C, 64% h, (15 eq), -78° to 25°C.

with methyl iodide to yield a single[12] monomethyl derivative **15**. Upon exposure to catalytic osmium tetroxide in the presence of reoxidizing agent keto olefin **15** gave the crystalline keto diol **16a**. Of the oxidizing agents examined (H_2O_2,[13] $NaClO_3$[14]) the recently described *N*-methylmorpholine *N*-oxide (NMO)[15] gave superior results. Alternatively, keto olefin **15** could be converted into diol **16a** using $KMnO_4$ in ethanol (58%).[16] The stereochemistry of **16a** is assigned on the premise that both the alkylation[12] and the cis hydroxylation involve attack from the less hindered, exo face of the bicyclo[3.2.1]-octenone nucleus. The presence of an *axial* C-3 hydrogen atom in diol **16a** and in mesylate alcohol **16b** (i.e., equatorial C-3 oxygen substituent) is confirmed by the NMR spectra of these derivatives which show an observed splitting for the C-3 hydrogen of $J = 17$ Hz, a result that is only consistent with the sum of a C_2–C_3 axial-axial and a C_2–C_3 equatorial-axial coupling constant.[17]

As shown in Scheme I, treatment of diol **16a** with methanesulfonyl chloride[18] furnished the secondary monomesylate **16b**, which upon treatment with either acetic anhydride or trimethylsilyl chloride in the *presence* of catalytic 4-dimethylaminopyridine[19] gave the bicyclic keto mesylates **16c** and **16d** in good yield. It is interesting to note that attempted functionalization of the tertiary hydroxyl group of **16b** with either of these reagents in the absence of 4-dimethylaminopyridine or with methanesulfonyl chloride failed.

Preparation of bicyclic keto mesylate **18** containing the isohexenyl substituent necessary for conversion into *α-trans*-bergamotene (**1**) via a sequence parallel to that described above presented a potential obstacle, namely, the need to effect a regioselective cis hydroxylation on a diene containing two trisubstituted double bonds (e.g., **19**). In practice, however, this



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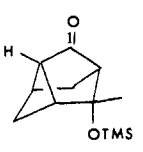

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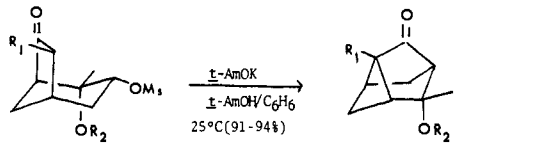
potential problem was avoided, as the sequence outlined in Scheme I provided desired bicyclic intermediate **18** efficiently. The key to this approach was the observation that at low temperature (−40 °C) keto mesylate **17c** undergoes preferential bimolecular alkylation to give the isohexenyl substituted bicyclic keto mesylate **18** in good yield. Under these conditions, only a trace of the intramolecular alkylation product, tricyclic ketone **20**, was observed. Conversion of olefin **14** into keto mesylate **17c** was unexceptional and proceeded smoothly as outlined in Scheme I.

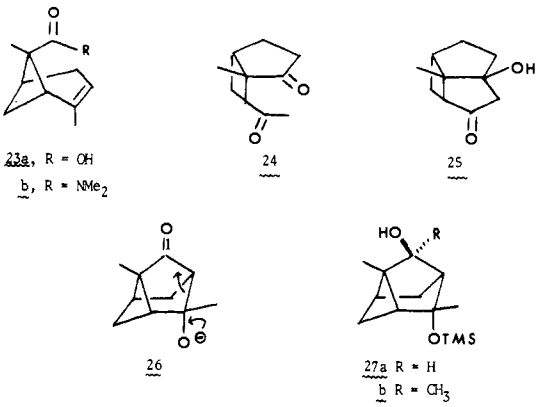
In both series intramolecular cyclization of the trimethylsilyl protected bicyclic keto mesylates **16d** and **18** was readily ac-



16 c R_1 = CH_3, R_2 = Ac
d R_1 = CH_3, R_2 = TMS
18 R_1 = $CH_2CH_2CH=C(CH_3)_2$

21 a R_1 = CH_3, R_2 = Ac
b R_1 = CH_3, R_2 = TMS
22 R_1 = $CH_2CH_2CH=C(CH_3)_2$

complished by treatment with potassium *tert*-amylate to yield the tricyclic ketones **21b** and **22** in excellent yield; analogous cyclization of acetate **16c** gave **21a** in 31% yield. Attempted fragmentation of the tricyclic methyl ketone **21** as depicted in eq 3 using oxygen anions failed to give any of the desired bicyclo[3.1.1]heptenyl acid **28a**. Treatment with either hydroxide or ethoxide furnished new products tentatively identified as **24** and **25** on the basis of spectral data (see Experimental Section for details). Apparently the desired fragmentation is not competitive with nucleophilic attack at the acetate moiety of **21a** or at the silicon atom in **21b** to give the β-alkoxy ketone **26** which undergoes retro-aldol condensation (see arrows) to yield **24** and its aldol product **25**. Alternatively, selective addition to the carbonyl group of the trimethylsilyl ketone **21b** could be achieved using lithium aluminum hydride or methyllithium to give the corresponding alcohols **27**. The adducts were single isomers and were assigned the structures shown on the basis of nucleophilic attack from the less hindered face of the carbonyl group of **21b**. All efforts to promote a fragmentation of the 1,3-dioxygen functionality of **27** under basic conditions, however, were uniformly unsuccessful.



23a, R = OH
b, R = NMe_2

24

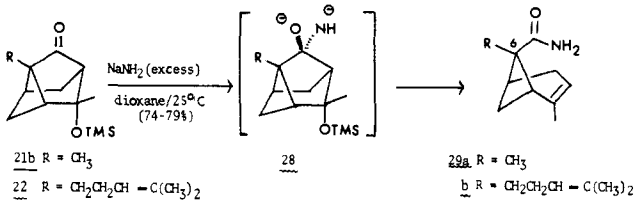
25

26

27a R = H
b R = CH_3

The desired ring fragmentation was achieved readily when a nitrogen nucleophile was substituted for the oxygen nucleophiles.[20] Treatment of tricyclic ketones **21b** and **22** with *excess* sodium amide in dioxane afforded the bicyclo[3.1.1]-heptenyl amides **29** as the only isolated products. In view of the observation that alcohols **27** resisted base-catalyzed fragmentation, the formation of amides **29** may involve the intermediacy of the dianion species **28**.[21]

With amides **29** possessing the required 2-methylbicyclo[3.1.1] hept-2-ene skeleton and differentiated functionality at C-6 center now in hand, the remaining functional group manipulations to give the natural α hydrocarbons appeared straightforward. In practice, however, all attempts to hydrolyze amide **29a** or the corresponding dimethylamide **23b**,



21b R = CH_3
22 R = $CH_2CH_2CH-C(CH_3)_2$

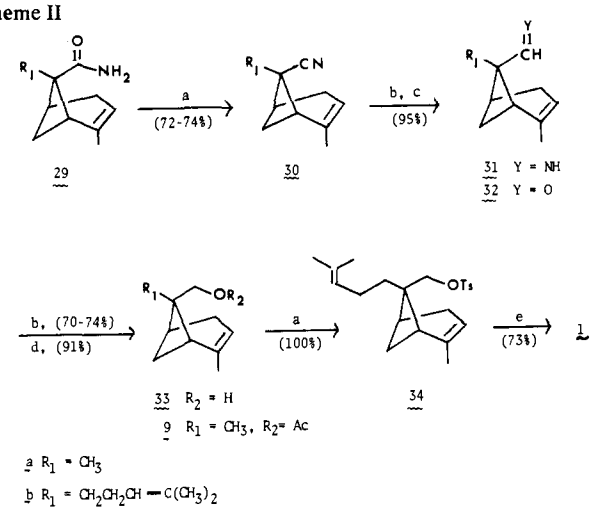
28

29a R = CH_3
b R = $CH_2CH_2CH-C(CH_3)_2$

prepared from **29a** by treatment with excess CH_3I and NaH, to acid **23a** failed. The primary amide **29a** was stable to aqueous NaOH,[22a] nitrosonium tetrafluoroborate,[22b] sodium peroxide[22c] in water, and NaH/carbon disulfide;[22d] tertiary amide **23b** was recovered after treatment with *t*-BuOK/H_2O in THF.[21d] This lack of reactivity can be attributed to the severe steric environment of the amide carbonyl carbon, i.e., a neopentyl center with one face completely shielded by the three-carbon bridge of the bicyclic skeleton, which precludes formation of the tetrahedral adduct necessary for hydrolysis.

Accordingly amides **29** were dehydrated with *p*-toluenesulfonyl chloride to give nitriles **30** which upon treatment with diisobutylaluminum hydride, followed by hydrolysis, were converted into aldehydes **32** (see Scheme II). The steric congestion associated with this neopentyl position was again reflected in the observation that hydrolysis of the initial imine reduction product **31b** to aldehyde **32b** required 70 h. Reduction of the C-6 methyl aldehyde **23a,** followed by acetylation, yielded racemic acetate **9** which was identical by IR, NMR, and VPC with a sample previously prepared[7] from chiral β-pinene.[23] Since the conversion of acetate **9** into α-*cis*-bergamotene (**2**) and into α-pinene (**3**) has been reported,[7] the stereoselective preparation of racemic **9** formally completes the total synthesis of these natural products. Although attempted Wolff-Kishner reduction of the isohexenyl aldehyde **32b** gave a number of unidentified products, **32b** was efficiently converted into racemic α-*trans*-bergamotene (**1**) as shown in Scheme II, thereby completing the first fully *stereocontrolled* total synthesis of this material.

Scheme II



a, TsCl, pyridine, 15°C, .. h; b, diisobutylaluminum hydride, C_6H_6, 25°C, 40 min; c, pyruvic acid, H_2O (buffer pH 4.5), 25°C, 60 h; d, Ac_2O, 4-dimethylaminopyridine, CH_2Cl_2, 25°C, 1 h; e, lithium triethylborohydride, THF, 25°C, 18h.

Experimental Section

General. All reactions were carried out in an inert nitrogen atmosphere and were routinely monitored by TlC or VPC using a Varian Aerograph 1200 instrument equipped with 5% SE-30 on Gas Chrom Q (100/120 mesh) 1/8 in. × 10 ft or 15% FFAP on Gas Chrom Q (100/120 mesh) 1/8 in. × 7 ft columns. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237B grading infrared spectrometer; NMR spectra were measured on a Perkin-Elmer R-12 spectrometer or a Varian HA-100 instrument and chemical shifts are reported in parts per million downfield (δ) from internal Me_4Si. High-resolution mass spectra were obtained using a CEC Model 21-100 mass spectrometer. The microanalytical determinations were done by Chemalytics, Inc., Tempe, Ariz.

4-Methylbicyclo[3.2.1]oct-3-en-6-one (14). Trifluoroacetic anhydride (63 g, 0.3 mol, distilled from P_2O_5) was added to a stirred suspension of 4-methyl-3-cyclohexene-1-acetic acid[10] (**13,** 29.9 g, 0.19 mol) in heptane (400 mL, distilled from P_2O_5). After standing at room temperature for 1 h, the mixture was heated at reflux for 3 h, and then a mixture of trifluoroacetic acid and heptane (ca. 250 mL) was removed by slow distillation (50–95 °C). After cooling, the residue was poured into ice and water and the organic phase was washed with saturated sodium bicarbonate. The organic phase was washed with brine, dried ($MgSO_4$), and distilled at atmospheric pressure through a 15-cm Vigreux column to remove excess heptane. The resulting residue was distilled to give 22.2 g (84%) of pure product **14,** bp 105–107 °C (30 mm). This material was identical with that prepared previously[10] as judged by IR, NMR, and VPC.

***exo*-4,7-Dimethylbicyclo[3.2.1]oct-3-en-6-one (15).** A solution of diisopropylamine (23.0 g, 0.23 mol, distilled from barium oxide) in THF (100 mL) was added to a chilled (ca. 5 °C) solution of *n*-butyllithium in hexane (0.21 mol, 150 mL). The mixture was stirred for 20 min and cooled to ca. −20 °C, and the bicyclic ketone **14** (27.2 g, 0.20 mol) in THF (100 mL) was added and the resulting mixture was stirred for 20 min at −20 °C. This mixture was cooled to ca. −70 °C and methyl iodide (42 g, 0.30 mol) in THF (50 mL) was added in a single portion. After the initial increase in temperature the reaction mixture was maintained at ca. −70 °C for 30 min, and then allowed to warm to room temperature with stirring (3 h). The mixture was quenched in 1.0 M sodium dihydrogen phosphate (100 mL) and extracted with ether. The organic phase was concentrated at reduced pressure, and the resulting residue was suspended in ether (200 mL), washed with cold 10% hydrochloric acid, saturated sodium bicarbonate, and brine, and dried ($MgSO_4$). This solution was filtered through a neutral Al_2O_3 column (50 g, activity III) using Et_2O and the eluent was evaporated at reduced pressure to give a residue which was distilled to yield 25.8 g (80%) of pure **15**: bp 113–114 °C (30 mm); IR (CCl_4) 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (d, 3, J = 7 Hz), 1.72 (m, 3) 1.4–3.0 (m, 7), and 5.37 ppm (m, 1).

Anal. ($C_{10}H_{14}O$) C, H.

The bicyclic ketone **15** (140 mg, 1.0 mmol) was dissolved in methanol (40 mL) containing potassium hydroxide (1.0 g, 18 mmol) and allowed to stand at room temperature for 3 days. The excess solvent was removed under reduced pressure, water (50 mL) was added, and the mixture was extracted with pentane. The pentane extracts were washed with brine, dried ($MgSO_4$), and evaporated to furnish 136 mg (96%) of a 1:1 mixture of bicyclic ketones **15** and its C-7 epimer: NMR ($CDCl_3$) δ 1.12 (d, 1.5, J = 7 Hz) and 1.15 ppm (d, 1.5, J = 7 Hz).

***exo-cis*-3,4-Dihydroxy-*exo*-4,7-dimethylbicyclo[3.2.1]octan-6-one (16a). A.** A solution of bicyclic ketone **15** (15.2 g, 0.10 mol), *N*-methylmorpholine *N*-oxide di- (?) hydrate[15] (NMO, 7.0 g, ca. 0.11 mol), and OsO_4 (40 mg, 0.16 mmol) in THF (100 mL) and water (20 mL) was stirred at room temperature for 31 h. Additional NMO (7.0 g, ca. 0.045 mol) was added and the mixture was stirred for 39 h. The reaction mixture was poured into a cold solution of 10% HCl (100 mL) and 15% $NaHSO_3$ (20 mL). The resulting solution was saturated with NaCl and extracted repeatedly with EtOAc. The combined organic phases were dried ($MgSO_4$) and filtered through Florsil (10 g), and, after evaporation at reduced pressure, the residue was crystallized from benzene–ethanol (4:1) to give 14.3 g (80%) of crystalline diol **16a**: mp 148–150 °C; IR (CH_2Cl_2) 3595, 1735 cm^{-1}; NMR ($CDCl_3$, CD_3OD (ca. 15% v/v), CF_3COOH (trace)) δ 1.10 (d, 3, J = 7 Hz), 1.27 (s, 3), 1.5–2.5 (m, 7), and 3.35 ppm (d of d, 1, $J_{AX} + J_{BX}$ = 17 Hz); mass spectrum *m/e* (rel intensity) 184 (molecular ion, 30), 139 (48), 97 (94), 43 (100).

Anal. ($C_{10}H_{16}O_3$) C, H.

B. Using the general procedure of Büchi,[14a] and employing $NaClO_3$, catalytic OsO_4 oxidation of bicyclic ketone **15** gave a 64% yield of crystalline **16a,** which was identical with that prepared above.

C. When 30% H_2O_2 was employed,[13] catalytic OsO_4 oxidation of **15** furnished a 55% yield of crystalline **16a**.

D. Using the procedure of Owen and Smith,[16] $KMnO_4$ oxidation of **15** afforded a 58% yield of crystalline **16a**.

4,7-Dimethyl-*exo*-4-hydroxy-*exo*-3-methanesulfonatobicyclo-[3.2.1]octan-6-one (16b). To a vigorously stirred solution of cis diol **16a** (12.0 g, 0.065 mol) in methylene chloride (400 mL) containing triethylamine (13.0 g, 0.13 mol, distilled from barium oxide) at −5 °C was added methanesulfonyl chloride (9.0 g, 0.078 mol) in CH_2Cl_2 (50 mL) in a dropwise manner such that the temperature did not exceed 10 °C.[18] After the addition was completed, the mixture was allowed to warm to room temperature with stirring for 1 h, and then it was quenched by shaking with ice water. The organic phase was successively washed with cold 10% hydrochloric acid (2 × 100 mL), saturated sodium bicarbonate (3 × 100 mL), and brine, then dried ($MgSO_4$) and filtered through neutral aluminum oxide (30 g, activity III) using methylene chloride (200 mL). After evaporation, the resulting crude residue was crystallized from benzene–methylene chloride (8:2) to give 15.0 g (87%) of **16b**: mp 120–122 °C; IR (CH_2Cl_2) 3570, 1740, 1175 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (d, 3, J = 7 Hz), 1.36 (s, 3), 1.5–2.6 (m, 8), 3.03 (s, 3), and 4.32 ppm (d of d, 1, $J_{AX} + J_{BX}$ = 17 Hz); mass spectrum *m/e* (rel intensity) 262 (molecular ion, 6), 139 (66), 43 (100).

Anal. ($C_{11}H_{18}O_5S$) C, H.

Treatment of **16b** with excess methanesulfonyl chloride under the conditions described above gave recovered **16b** as the only isolated product.

***exo*-4-Acetoxy-4,7-dimethyl-*exo*-3-methanesulfonatobicyclo[3.2.1]heptan-6-one (16c).** Acetic anhydride (9.0 g, 88 mmol) was added to a solution of bicyclic keto mesylate **16b** (7.1 g, 27 mmol), triethylamine (10.0 g, 0.10 mol), and 4-dimethylaminopyridine[19] (0.25 g) in methylene chloride (50 mL). The mixture was stirred at room temperature for 3 days. Diethyl ether (500 mL) was added and the mixture was washed successively with ice water, cold 10% hydrochloric acid (100 mL), saturated sodium bicarbonate (4 × 100 mL), and brine. The organic phase was dried ($MgSO_4$) and filtered through neutral aluminum oxide (50 g, activity III) using methylene chloride (700 mL). After concentration at reduced pressure, the solid residue was crystallized from benzene to give 6.0 g (73%) of **16c**: mp 130–132 °C; IR (KBr) 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.12 (d, 3, J = 7 Hz), 1.62 (s, 3), 1.6–2.6, 2.10 (m, s, 9), 3.07 (s, 3), 3.45 (m, 1), and 4.33 ppm (d of d, 1, $J_{AX} + J_{BX}$ = 17 Hz).

Anal. ($C_{13}H_{20}O_6S$) C, H.

4,7-Dimethyl-*exo*-3-methanesulfonato-*exo*-4-trimethylsiloxybicyclo[3.2.1]octan-6-one (16d). Trimethylsilyl chloride (6.2 g, 0.057 mol) was added to a methylene chloride solution (75 mL) of bicyclic keto mesylate **16b** (10.0 g, 0.938 mol), triethylamine (7.8 g, 0.076 mol, distilled from barium oxide), and a catalytic amount of 4-dimethylaminopyridine[19] (0.25 g). The mixture was stirred at room temperature for 40 h. The methylene chloride and excess trimethylsilyl chloride were removed under reduced pressure to yield a brown, viscous residue that was suspended in diethyl ether (500 mL) and filtered through silica gel (60 g). After evaporation the resulting residue was crystallized from hexane to yield 9.6 g (89%) of **16d**: mp 70–73 °C; IR (CCl_4) 1740, 1175, 1155, 1100, 1065, 1040, 1015 cm^{-1}; NMR ($CDCl_3$) δ 0.17 (s, 9), 1.10 (d, 3, J = 7 Hz), 1.42 (s, 3), 1.6–2.6 (m, 7), 3.02 (s, 3), and 4.27 ppm (d of d, 1, $J_{AX} + J_{BX}$ = 17 Hz); mass spectrum *m/e* (rel intensity) 319 (2), 254 (16), 211 (100), 153 (58), 73 (80).

Anal. ($C_{14}H_{26}O_5SSi$) C, H.

***exo-cis*-3,4-Dihydroxy-4-methylbicyclo[3.2.1]octan-6-one (17a).** A solution of osmium tetroxide (40 mg, 0.16 mmol) in *tert*-butyl alcohol (10 mL) and *N*-methylmorpholine *N*-oxide hydrate (19 g, ca. 0.12 mol)[15] was added to an acetone (70 mL) and water (70 mL) solution of the bicyclic ketone **14** (15 g, 0.11 mol) and stirred for 80 h at room temperature. A major portion of volatile solvents were removed at reduced pressure and the residue was acidified with cold 10% hydrochloric acid and then 15% sodium bisulfite (10 mL) was added. The aqueous mixture was saturated with sodium chloride and extracted repeatedly with ethyl acetate. The organic phases were combined, washed with brine, dried ($MgSO_4$), and filtered through Florisil (10 g). The crude residue was crystallized from ethyl acetate–ethanol (1:1) to give 13.7 g (74%) of **17a**: mp 146–147.5 °C; IR (CH_2Cl_2) 3580, 1740 cm^{-1}; NMR ($CDCl_3$, CD_3OD (ca. 25%), CF_3COOH (trace)) δ 1.28 (s, 3), 1.4–2.8 (m, 8), and 3.38 ppm (d of d, 1, $J_{AX} + J_{BX}$ = 17 Hz); mass spectrum *m/e* (rel intensity) 170 (molecular ion, 10), 152 (42), 125 (34), 83 (50), 71 (72), 43 (100).

Anal. ($C_9H_{14}O_3$) C, H.

***exo*-4-Hydroxy-*exo*-3-methanesulfonato-4-methylbicyclo-[3.2.1]octan-6-one (17b).** Bicyclic diol **17a** (12.8 g, 0.075 mol) was dissolved in methylene chloride (700 mL) containing triethylamine (12.6 g, 0.124 mol) and methanesulfonyl chloride (10 g, 0.087 mol) was added as described above for **16b**.[18] The crude mesylate, isolated as described above, was crystallized from methylene chloride to give 16.0 g (88%) of **17b**: mp 143–146 °C dec; IR (CH_2Cl_2) 3580, 1740, 1175 cm^{-1}; NMR ($CDCl_3$) δ 1.38 (s, 3), 1.5–3.0 (m, 9), 3.06 (s, 3), and 4.42 ppm (d of d, 1, $J_{AX} + J_{BX}$ = 17 Hz); mass spectrum *m/e* (rel intensity) 189 (8), 43 (100).

Anal. ($C_{10}H_{16}O_5S$) C, H.

***exo*-3-Methanesulfonato-4-methyl-*exo*-4-trimethylsiloxybicyclo[3.2.1]octan-6-one (17c).** A solution of bicyclic keto mesylate **17b** (12.5 g, 0.05 mol), triethylamine (10 g, 0.1 mol), trimethylsilyl chloride (9.2 g, 0.085 mol), and 4-dimethylaminopyridine[19] (1.0 g) in CH_2Cl_2 (250 mL) was stirred for 84 h at room temperature. After workup as described above for **16d** the crude product was crystallized from hexane to yield 14.5 g (90%) of **17c**; mp 85–86 °C; IR (CCl_4) 1745, 1180, 1165, 1150, 1100, 1075, 1040, 1020 cm^{-1}; NMR ($CDCl_3$) δ 0.18 (s, 9), 1.93 (s, 3), 1.7–2.9 (m, 8), 3.03 (s, 3), and 4.30 ppm (d of d, 1, $J_{AX} + J_{BX}$ = 17 Hz); mass spectrum *m/e* (rel intensity) 241 (20), 197 (74), 153 (74), 74 (100).

Anal. ($C_{13}H_{24}O_5SSi$) C, H.

3-*exo*-Methanesulfonato-7-(4-methylpent-3-en-1-yl)-4-methyl-*exo*-4-trimethylsiloxybicyclo[3.2.1]octan-6-one (18). A THF solution of lithium diisopropylamide (1.0 M, 7.2 mL, 7.2 mmol) was added to a stirred solution of trimethylsilyl mesylate **17c** (2.00 g, 6.2 mmol) in THF (50 mL) at −70 °C. After 15 min 5-iodo-2-methyl-2-pentene[24] (6.8 g, 32 mmol) was added in a single portion with vigorous stirring. After an initial increase in temperature the reaction was maintained at ca. −40 °C for 15 min and then allowed to warm to room temperature. After stirring for 3 h, the reaction was quenched by pouring into cold saturated ammonium chloride (100 mL) and then extracted with diethyl ether. The combined extracts were dried ($MgSO_4$) and the volatile material was removed under reduced pressure. The residue was chromatographed on silica gel (100 g) using pentane and then pentane–ether mixtures to give, in order of elution, 33 mg of a new material tentatively assigned structure **20** (IR 1765 cm^{-1}); the desired alkylation product **18**; and 821 mg of recovered starting material **17c**. After crystallization from hexane the second chromatography fraction gave 1.16 g (78%) of **18**: mp 74–75 °C; IR (CCl_4) 1740, 1180, 1155, 1040, 1005 cm^{-1}; NMR ($CDCl_3$) δ 0.18 (s, 9), 1.40 (s, 3), 1.68 (m, 6), 1.1–2.6 (m, 11), 3.00 (s, 3), 4.25 (d of d, 1, $J_{AX} + J_{BX}$ = 17 Hz), and 5.08 ppm (m, 1); mass spectrum *m/e* (rel intensity) 402 (molecular ion, 4), 2.79 (46), 153 (78), 143 (70), 82 (86), 73 (100).

Anal. ($C_{19}H_{34}O_5SSi$) C, H.

***exo*-2-Acetoxy-2,6-dimethyltricyclo[3.2.1.$0^{3,6}$]octan-7-one (21a).** As outlined for **21b**, the acetoxy keto mesylate **16c** (1.30 g, 5.0 mmol) in benzene (15 mL) was allowed to react with a solution of potassium (0.21 g, 0.0054 g-atom) in 2-methyl-2-butanol (2.5 g, 28 mmol) for 2 h. The reaction mixture was quenched in cold 1 M sodium dihydrogen phosphate (50 mL) and extracted with ether. The ether extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The resulting residue was distilled to give a fraction, bp 85–100 °C (0.5 mm), which was purified further by preparative thin layer chromatography on silica gel using pentane–ether (9:1) to give 320 mg (31%) of pure **21a**: $R_f \sim 0.85$; IR (CCl_4) 1770, 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (s, 3), 1.40 (s, 3), 1.5–3.0, and 2.12 ppm (m, s, 10); mass spectrum *m/e* (rel intensity) 208 (molecular ion, 20), 166 (22), 148 (34), 120 (42), 105 (40), 96 (32), 43 (100).

Anal. ($C_{12}H_{16}O_3$) C, H.

2,6-Dimethyl-*exo*-2-trimethylsiloxytricyclo[3.2.1.$0^{3,6}$]octan-7-one (21b). Potassium (2 g, 0.051 g-atom, purified by Pearson's procedure[25]) was dissolved in 2-methyl-2-butanol (75 mL, distilled from sodium) and a solution of trimethylsilyl keto mesylate **16d** (3.65 g, 11.0 mmol) in benzene (75 mL) was added. The mixture was stirred for 18 h at room temperature, and then it was quenched by addition of cold 1 M sodium dihydrogen phosphate (70 mL). This mixture was extracted with ether, and the combined organic extracts were dried ($MgSO_4$) and concentrated at reduced pressure. The residue was distilled to yield 2.44 g (93%) of **21b**: bp 63–65 °C (0.5 mm); IR (CCl_4) 1765, 1260, 1250, 1165, 1045 cm^{-1}; NMR ($CDCl_3$) δ 0.16 (s, 9), 1.21 (s, 3), 1.23 (s, 3), and 1.7–2.3 ppm (m, 7); mass spectrum

m/e (rel intensity) 238 (molecular ion, 6), 181 (22), 168 (30), 143 (70), 96 (64), 73 (100).

Anal. ($C_{13}H_{22}O_2Si$) C, H.

2-Methyl-6-(4-methylpent-3-en-1-yl)-*exo*-2-trimethylsiloxytricyclo[3.2.1.0^{3,6}]octan-7-one (22). As outlined in **21b**, the trimethylsilyl keto mesylate **18** (2.78 g, 6.9 mmol) in benzene (75 mL) was allowed to react with a solution of potassium (7.0 g, 0.051 g-atom) in 2-methyl-2-butanol (75 mL) for 20 h at room temperature. Distillation of the crude residue gave 1.98 g (94%) of pure **22**: bp 115–120 °C (0.1 mm); IR (CCl_4) 1765, 1260, 1250, 1170, 1120, 1045 cm^{-1}; NMR ($CDCl_3$) δ 0.18 (s, 9), 1.20 (s, 3), 1.66 (d, 6, J = 7 Hz), 1.0–2.8 (m, 11), and 5.15 ppm (m, 1); mass spectrum *m/e* (rel intensity) 264 (4), 143 (98), 73 (100).

Anal. ($C_{18}H_{30}O_2Si$) C, H.

Attempted Fragmentation of 2,6-Dimethyl-*exo*-2-trimethylsiloxytricyclo[3.2.1.0^{3,6}]octan-7-one (21b). A. A solution of ketone **21b** (153 mg, 0.64 mmol) in ethanol (2 mL) was added to a solution of sodium (300 mg, 0.013 g-atom) in ethanol (20 mL). After stirring for 1.5 h, the reaction was quenched by addition of cold, saturated NH_4Cl (20 mL). After concentration at reduced pressure, water (50 mL) was added and the mixture was extracted with ether. The ether extracts were dried (Na_2SO_4) and evaporated at reduced pressure to give 82 mg of a residue which, when analyzed by VPC on 15% FFAP (100 to 200 °C at 10 °C/min) showed three components, retention times 8.2, 8.5, and 11.6 min, in the ratio of 7:1:1, respectively. GC/MS analysis (3% OV-101) revealed that all three components showed a molecular ion at *m/e* 166 (calcd for **24**, *m/e* 166); IR (CCl_4) 3500, 1745, and 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (s, ca. 3) and 2.08 ppm (s, ca. 3). These data are consistent with the tentative assignment of structure **24** to the 8.2-min retention time component, its C-7 epimer (**24**, acetyl group epimer) to the 8.5-min component, and the aldol structure **25** to the 11.6-min component (see B for verification of this last assignment).

B. A solution of **21b** (326 mg, 1.36 mmol) in THF (3 mL) was added to a stirred solution of potassium *tert*-butoxide (0.5 g, 4.5 mmol) and water (36 mg, 2 mmol) in THF (15 mL). After 3 h, cold saturated NH_4Cl (50 mL) was added, the mixture was extracted with ether, and the ether extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give 238 mg of a residue which, when analyzed by VPC on 15% FFAP (100 to 200 °C at 10 °C/min), showed the presence of starting ketone **21b** and the three products observed above, retention times 6.1, 8.2, 8.5, and 11.6 min in the relative ratio of 2:2:0.5:7, respectively. The 11.6-min retention time material was isolated by column chromatography on silica gel (13 g) using pentane–ether (7:3) to give 96 mg (42%) of product tentatively assigned structure **25**: IR (CCl_4) 3450 and 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.1–1.7 (m, 2), 1.23 (s, 3), 1.7–2.3 (m, 4), and 2.3–2.9 ppm (m, 5).

Anal. ($C_{10}H_{14}O_2$) Calcd mol wt, 166.0994; found, *m/e* 166.0996.

2,6-Dimethyl-7-hydroxy-*exo*-2-trimethylsiloxytricyclo-[3.2.1.0^{3,6}]octan-7-one (27a). A solution of $LiAlH_4$ (50 mg, 13 mmol) in ether (8 mL) was added to a stirred solution of tricyclic ketone **21b** (208 mg, 8.7 mmol) in ether (10 mL) at 0 °C. After 20 min ethyl acetate (1.0 g) was added followed by a cold saturated sodium potassium tartrate solution (50 mL). The mixture was extracted with ether and the combined extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give 205 mg (97%) of the crude alcohol **27a**: IR (CCl_4) 3600 cm^{-1}; NMR ($CDCl_3$) δ 0.14 (s, 9), 1.28 (s, 3), 1.57 (s, 3), 1.5–2.3 (m, 7), 2.38 (s, 1), and 3.76 ppm (m, 1).

Attempted Fragmentation of Alcohol 27a. A solution of alcohol **27a** (129 mg, 0.54 mmol) and sodium hydride (60 mg, 2.5 mmol) in dioxane (15 mL) was heated at reflux for 22 h. The cooled solution was quenched by sequential addition of ethanol and water. The resulting mixture was extracted with ether. The ether extracts were dried ($MgSO_4$) and evaporated to give a crude residue (ca. quantitative recovery) which contained only unchanged starting material as judged by NMR and VPC on 5% SE-30.

7-Hydroxy-2,6,7-trimethyl-*exo*-2-trimethylsiloxytricyclo-[3.2.1.0^{3,6}]octan-7-one (27b). A solution of methyllithium (1.9 M, 1.2 mL, 2.3 mmol) in ether was added to a stirred solution of tricyclic ketone **21b** (300 mg, 1.26 mmol) in tetrahydrofuran (10 mL) at −30 °C. The mixture was allowed to warm to room temperature over a period of 20 min, and then cold, saturated ammonium chloride (50 mL) was added and the resulting mixture was extracted with ether. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure, leaving 331 mg (103%) of crude **27b**: IR (CCl_4) 3600 cm^{-1}; NMR ($CDCl_3$) δ 0.14 (s, 9), 1.13 (s, 3), 1.17 (s, 3), 1.67 (s, 3), and 1.4–2.4 ppm (m, 8).

Attempted Fragmentation of Alcohol 27b. A solution of alcohol **27b** (93 mg, 0.36 mmol) and sodium hydride (50 mg, 2.1 mmol) in dioxane (15 mL) was heated at reflux for 25 h. A residue was recovered, as described for **27a**, which contained unchanged starting material and, tentatively, the diol derived from **27b** by loss of the trimethylsilyl group, as judged by NMR, IR, and VPC on 5% SE-30.

***endo*-6-Carbamoyl-2,6-dimethylbicyclo[3.1.1]hept-2-ene (29a).** A solution of tricyclic ketone **21b** (1.80 g, 7.5 mmol) in dioxane (10 mL) was added at room temperature to a stirred suspension of sodium amide, freshly prepared from sodium (3.1 g, 0.13 g-atom) in dry dioxane (50 mL) containing some NH_3 (ca. 10 mL). After stirring for 40 h, EtOH was added cautiously, and the mixture was poured into ice water and extracted with ether. The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to furnish a residue that was purified by sublimation (100 °C, 0.5 mm) to give 920 mg (74%) of pure **29a**: mp 155–157 °C; IR (CH_2Cl_2) 3400, 3505, 1680, 1590 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (d, 1, J = 7 Hz), 1.52 (s, 3), 1.73 (m, 3), 2.0–2.8 (m, 5), and 5.0–5.8 ppm (m, 3); mass spectrum *m/e* (rel intensity) 165 (molecular ion, 94), 121 (100), 73 (94).

Anal. ($C_{10}H_{15}NO$) C, H, N.

***endo*-6-(*N,N*-Dimethylcarbamoyl)-2,6-dimethylbicyclo[3.1.1]-hept-2-ene (23b).** A stirred suspension of sodium hydride (200 mg, 8.3 mmol), bicyclic amide **29a** (160 mg, 0.98 mmol), and methyl iodide (1.5 g, 10 mmol) in THF (15 mL) was heated at reflux for 16 h. After concentration at reduced pressure, the residue was suspended in a mixture of ether (50 mL), ethanol (2 mL), and cold, saturated ammonium chloride (50 mL), which was extracted with additional ether. The combined ether extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give 193 mg (103%) of crude liquid **23b**: IR (CCl_4) 1634 cm^{-1}; NMR ($CDCl_3$) δ 1.22 (d, 1, J = 10 Hz), 1.48 (s, 3), 1.83 (m, 3), 2.1–2.8 (m, 5), 2.85 (s, 3), 2.91 (s, 3), and 4.90–5.35 ppm (m, 1).

Anal. ($C_{12}H_{19}NO$) Calcd mol wt, 193.1467; found, *m/e* 193.1460.

Attempted Hydrolysis of Amide 23b. To a stirred suspension of potassium *tert*-butoxide (0.50 g, 4.4 mmol) in THF (10 mL), a mixture of water (40 mg, 2.2 mmol) and amide **23b** (100 mg, 0.51 mmol) in THF (5 mL) was added. The mixture was heated at reflux for 4 days. After quenching in water the basic solution was extracted with ether, and after drying over $MgSO_4$ evaporation of the ether phase yielded 85 mg of residue which contained starting amide **23b** as well as other unidentified products as judged by VPC analysis on 5% SE-30. The basic aqueous layer was acidified with 10% hydrochloric acid and extracted with diethyl ether. The extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure, to yield only a negligible amount of acid residue (ca. 1 mg).

6-*endo*-Carbamoyl-2-methyl-6-(4-methylpent-3-en-1-yl)bicyclo-[3.1.1]hept-2-ene (29b). Using the procedure described for **29a**, tricyclic ketone **22** (400 mg, 1.3 mmol) yielded a residue that was purified by chromatography on silica gel (20 g) using ether, and then crystallized from hexane to give 241 mg (79%) of **29b**: mp 103–104 °C; IR (CH_2Cl_2) 3395, 1680, 1590 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (d, 1, J = 8 Hz), 1.5–2.0 (m, 9), 1.8–3.0 (m, 9), and 4.9–6.0 ppm (m, 4); mass spectrum *m/e* (rel intensity) 164 (100), 119 (52), 41 (56).

Anal. ($C_{15}H_{23}NO$) C, H, N.

***endo*-6-Cyano-2,6-dimethylbicyclo[3.1.1]hept-2-ene (30a).** *p*-Toluenesulfonyl chloride (0.33 g, 1.7 mmol) in pyridine (3 mL, distilled from barium oxide) was added to a solution of bicyclic amide **29a** (25 mg, 1.5 mmol) in pyridine (3 mL) and allowed to stand for 13 h at room temperature. The mixture was poured into ether (50 mL), filtered through Celite, washed with saturated sodium bicarbonate, dried (K_2CO_3), and concentrated at reduced pressure. The resulting residue was purified by chromatography on silica gel (10 g) with pentane–ether (4:1) to give 160 mg (72%) of liquid nitrile **30a**: IR (CCl_4) 2235 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (d, 1, J = 7 Hz), 1.64 (s, 3), 1.79 (m, 3), 2.1–3.0 (m, 5), and 5.40 ppm (m, 1); mass spectrum *m/e* (rel intensity) 147 (molecular ion, 30), 146 (78), 132 (100).

Anal. ($C_{10}H_{13}N$) Calcd mol wt, 147.1045; found, *m/e* 147.1048.

***endo*-6-Cyano-2-methyl-6-(4-methylpent-3-en-1-yl)bicyclo-[3.1.1]hept-2-ene (30b).** Using the procedure described for **30a**, bicyclic amide **29b** (210 mg, 0.9 mmol) furnished 153 mg (79%) of liquid **30b**: IR (CCl_4) 2230 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (d, 1, J = 8 Hz), 1.6–2.0 (m, 9), 1.85–2.9 (m, 9), and 4.9–5.6 ppm (m, 2).

Anal. ($C_{15}H_{21}N$) C, H, N.

***endo*-6-Hydroxymethyl-2,6-dimethylbicyclo[3.1.1]hept-2-ene (33a).** A solution of diisobutylaluminum hydride (Dibal) in benzene (25%, 3 mL, ca. 5 mmol) was added to bicyclic nitrile **30a** (161 mg, 1.1 mmol) in benzene (15 mL). The reaction mixture was maintained initially at ca. 7 °C and then allowed to warm to room temperature for 2 h. This mixture was then cautiously poured into a layer of ether (50 mL) over cold 10% potassium hydroxide (50 mL) containing potassium sodium tartrate (10 g). This mixture was stirred for 1 h and then extracted with ether. The combined ether extracts were washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure. The residue contained imine **31a** and aldehyde **32a** in a ratio of ca. 6:4 as judged by NMR. This mixture was dissolved in THF (10 mL) and 0.5 M pyruvic acid in water (10 mL, adjusted to pH 4.5 by addition of 10% KOH) was added. After stirring for 16 h at room temperature, the solution was made basic with 10% KOH, saturated with NaCl, and extracted with ether. The combined ether extracts were evaporated under reduced pressure to furnish 148 mg (90%) of crude aldehyde **32a:** IR 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.15–1.3 (m, 1), 1.28 (s, 3), 1.75–1.95 (m, 3), 2.0–2.7 (m, 7), 5.1–5.35 (m, 1), and 9.35 ppm (s, 1).

Aldehyde **32a** (148 mg, 0.98 mmol) in benzene (5 mL) was added to Dibal in benzene (25%, 2 mL, 3 mmol) and the mixture was stirred for 15 min at room temperature. After workup as described above, the crude product was purified by chromatography on silica gel (10 g) using pentane–ether (1:1 v/v) to give 110 mg (74%) of liquid alcohol **33a:** IR (CH_2Cl_2) 3630, 3020, 1435, 1025 cm^{-1}; NMR ($CDCl_3$) 1.27, 1.24 (s, d, 2, J = 8 Hz), 1.35 (s, 3), 1.72 (m, 3), 1.9–2.7 (m, 5), an AB quartet with doublets centered at 3.59 and 3.37, 5.27 ppm (m, 1).

Anal. ($C_{10}H_{16}O$) Calcd mol wt, 152.1201; found, *m/e* 152.1196.

***endo*-6-Hydroxymethyl-2-methyl-6(4-methylpenten-3-en-1-yl)-bicyclo[3.1.1]hept-2-ene (33b).** As described for **33a,** reduction of **30b** (250 mg, 1.2 mmol) with Dibal (5 mmol) furnished a 3:7 mixture of imine **31b** and aldehyde **32b** in ca. quantitative yield. A portion of this mixture (75 mg) was treated with pyruvic acid as described above to yield 70 mg of a 2:8 mixture of **31b** and **32b.** Reduction of this mixture with Dibal (3.3 mmol) as described above, followed by purification by chromatography on silica gel (10 g) with pentane–ether (7:3) gave 10 mg of imine **31b** and 46 mg (70%) of liquid alcohol **33b:** IR (CCl_4) 3020, 1445, 1020 cm^{-1}; NMR ($CDCl_3$) 0.9–1.4 (m, 1), 1.20 (d, 1, J = 8 Hz) 1.4–1.8 (m, 9), 1.7–2.2 (m, 9), an AB quartet with doublets centered at 3.46 and 3.66 (2, J = 10 Hz), and 5.0–5.4 ppm (m, 2).

Anal. ($C_{10}H_{16}O$) Calcd mol wt, 220.1827; found, *m/e* 220.1826.

***endo*-6-Acetoxymethyl-2,6-dimethylbicyclo[3.1.1]hept-2-ene (9).** Bicyclic alcohol **33a** (73 mg, 0.48 mmol) was allowed to react with acetic anhydride (63 mg, 0.62 mmol) and 4-dimethylaminopyridine[19] (88 mg, 0.72 mmol) in methylene chloride (12 mL) for 1.5 h at room temperature. The mixture was quenched by addition of saturated sodium bicarbonate, and then extracted with methylene chloride; the organic extracts were combined, dried ($MgSO_4$), and evaporated under reduced pressure. The crude acetate was purified by column chromatography on silica gel (5 g) with pentane–ether (7:3 v/v) to give 85 mg (91%) of pure acetate **9**, which was identical by IR, NMR, and VPC with an authentic sample prepared previously:[23] IR (CCl_4) 3025, 1740, 1470, 1445, 1440, 1385, 1375, 1360, 1250, 1240, 1230, 1030 cm^{-1}; NMR ($CDCl_3$) δ 1.24 (d, 1, J = 7 Hz), 1.33 (s, 3), 1.70 (m, 3), 2.04 (s, 3), 1.9–2.6 (m, 5), an AB quartet with doublets centered at 3.85 and 4.05 (2, J = 10 Hz), and 5.28 ppm (m, 1).

Anal. ($C_{12}H_{18}O_2$) Calcd mol wt, 194.1307; found, *m/e* 194.1304.

Racemic α-*trans*-Bergamotene (1). Bicyclic alcohol **33b** (46 mg, 0.21 mmol) in pyridine (0.5 mL) was added to *p*-toluenesulfonyl chloride (46 mg, 0.25 mmol) in pyridine (0.5 mL) under N_2 atmosphere and was allowed to stand for 46 h at 0 °C. The pyridine was evaporated at reduced pressure and the residue was suspended in CCl_4 (10 mL) and filtered. The crude tosylate **34** showed NMR ($CDCl_3$) δ 1.1–1.5 (m, 2), 1.5–2.0 (m, 12), 2.0–2.6 (m, 5), 2.45 (s, 3), 3.98 (s, 3), 4.9–5.4 (m, 2), and 7.2–8.1 ppm (m, 4). Crude tosylate **34** and lithium triethylborohydride (42 mg, 4.0 mmol) in THF (4 mL) were stirred at room temperature for 18 h. Cold 10% KOH (10 mL) was added and the mixture was extracted with pentane. The organic extracts were washed with brine, dried (Na_2SO_4), filtered through silica gel (2 g), and then concentrated to give 31 mg (73%) of **1** which was purified by preparative VPC on 5% SE-30; the IR spectrum of this synthetic material was identical with that published[2c] for the natural material; NMR ($CDCl_3$) δ 0.84 (s, 3), 1.20 (d, 1, J = 8 Hz), 1.5–1.8 (m, 9), 1.7–2.5 (m, 9), and 5.4–5.0 ppm (m, 2); mass spectrum *m/e* (rel intensity) 204 (molecular ion, 24), 119 (100), 93 (78), 41 (42).

Anal. ($C_{15}H_{24}$) Calcd mol wt, 204.1878; found, *m/e* 204.1880.

References and Notes

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