Anomalous hydroalumination of methyl nopol ether with a $LiAlH_4$—$3AlBr_3$ system

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Hydroalumination of methyl nopol ether with a $LiAlH_4$—$3AlBr_3$ system is accompanied by a skeleton rearrangement and gives 6-dibromoalumo-7-methoxymethyl-2-menthene. Further hydroalumination affords a mixture of 2,6- and 2,5-bis(dibromoalumo)-7-(methoxymethyl)menthanes in 80:20 ratio. Hydrolysis and oxidation of these organoaluminum compounds were carried out.

Key words: nopol; 7-methoxymethyl-2-menthene; hydroalumination; oxidation; rearrangement; mechanism.

Complexes of aluminum halides with $LiAlH_4$ or Bu^i_2AlH are efficient hydrometallating reagents, and are much more active than dialkylaluminum hydrides.[1,2] The reaction of α-pinene with a $LiAlH_4$—$3AlBr_3$ system is known to give the product of hydroalumination of the trisubstituted double bond, (dibromoalumo)isopinocamphane.[2] We have found that hydroalumination of the methyl ether of (−)-nopol (**1**)* having a similar structure under analogous conditions (0.6 equiv. $LiAlH_4$—$3AlBr_3$, benzene, 20 °C, 1 h) is accompanied by skeletal rearrangement and affords 6-dibromoalumo-7-methoxymethyl-2-menthene (**3**) containing a disubstituted double bond, rather than the expected 3-bromoalumo-10-(methoxymethyl)isopinocamphane (**2**) (Scheme 1). Hydrolysis of organoaluminum compound **3** gives 7-methoxymethyl-2-menthene (**4**). It should be noted that the acid-catalyzed rearrangement of α-pinene yields products which contain the Δ^3 (rather than Δ^2) menthene moiety (terpinolene, limonene, and so on).[3,4]

The fact that *trans*-7-(methoxymethyl)menthane is formed in the hydrolysis of the product of further hydroalumination of compound **3** is evidence for the *trans*-configuration of unsaturated ether **4** (see below). The (1*R*,4*R*)-absolute configuration of compound **4** was established by its conversion into (1*S*,4*R*)-2-menthene (**5**) (Scheme 2).

Treatment of ether **4** with the $Ph_3P \cdot Br_2$ complex in chlorobenzene (125 °C, 4 h)[5] affords bromide **6**. The action of oxygen on the Grignard reagent obtained from compound **6** gives alcohol **7** which is oxidized with pyridinium chlorochromate (PCC) (CH_2Cl_2, 20 °C) to give aldehyde **8**. Treating compound **8** with a $NH_2OH \cdot HCl$—pyridine mixture followed by heating the oxime formed *in situ* with acetic anhydride (90 °C, 2 h)[6] yields nitrile **9**. Decyanation of nitrile **9** with a K—HMPA—Bu^tOH system in Et_2O at 20 °C (see Ref. 7) affords the target *trans*-2-menthene **5**, whose physicochemical constants are identical to those reported in the literature.[8] The specific rotation of compound **5** ($[\alpha]_D^{20}$ −38.0°, *c* 6.4, $CHCl_3$) corresponds to (1*S*,4*R*)-2-menthene of 35 % optical purity.[9] Since the optical purity of nopol used was[10] 91 % ($[\alpha]_D^{20}$ −36.6°, neat), partial racemization of the starting ether **1** is likely to occur in the course of hydroalumination.

Oxidation of compound **3** with oxygen gives 7-methoxymethyl-2-menthen-6-ol (**10**) in 74 % yield. Unlike the starting alkyldibromoalane, alcohol **10** is an equimolar mixture of diastereomers (according to ^1H and ^{13}C NMR spectroscopy). Reduction of this compound with a $NaBH_4$—$CoCl_2 \cdot 6H_2O$ system in ethanol[11] affords a mixture of diastereomeric 7-(methoxymethyl)menthan-2-ols (**11**) which were separated by column chromatography. Oxidation of secondary alcohols **10** and **11** with chromic acid (Et_2O, 20 °C) leads to *trans*-7-methoxymethyl-2-menthen-6-one (**12**) and its saturated analog (**13**) in 82 and 84 % yields, respectively.

The different behavior of α-pinene and nopol derivative **1** with respect to the $LiAlH_4$—$3AlBr_3$ system is probably due to the fact that molecule **1** contains an ether oxygen atom. It is believed that $HAlX_2$ acts as the active electrophile[1,2] in the hydroalumination of alkenes with the $LiAlH_4$—$3AlX_3$ (X = Cl, Br) reagents. Coordination of $HAlBr_2$ by the ether fragment of compound **1** may give a complex capable of disproportionating to

* Nopol is 6,6-dimethyl-2-β-hydroxyethylbicyclo[3.1.1]hept-2-ene.

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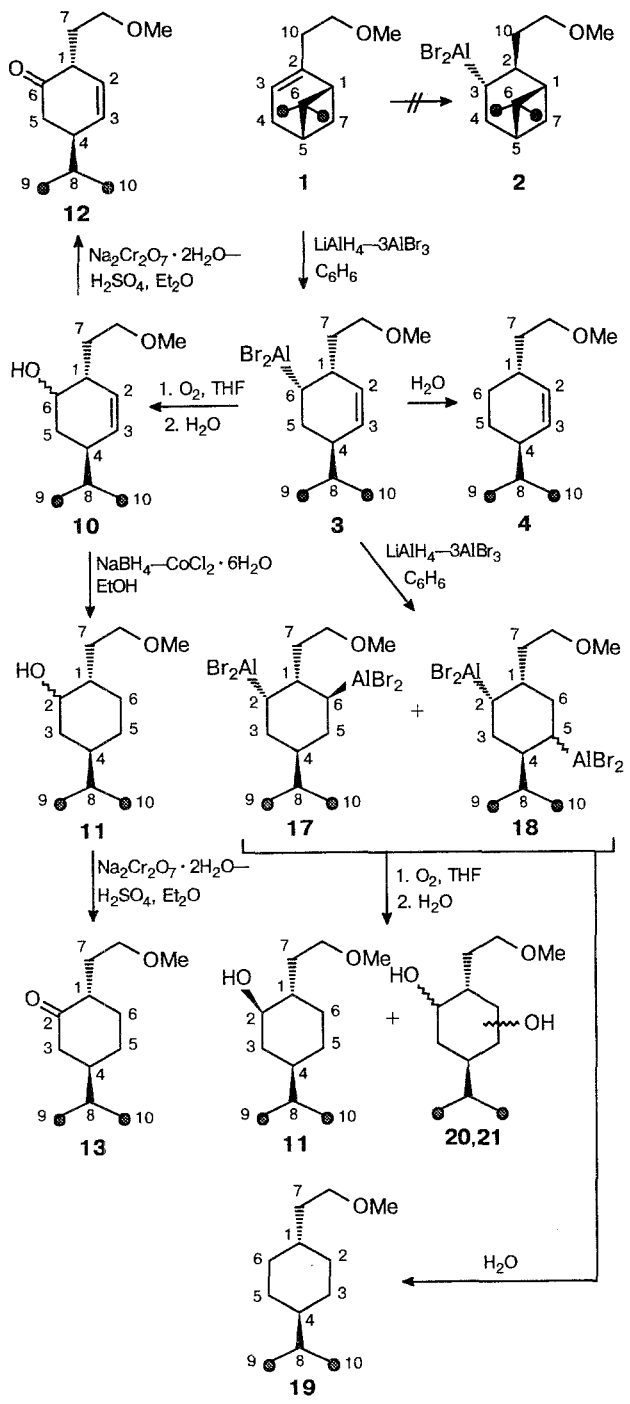
Scheme 1

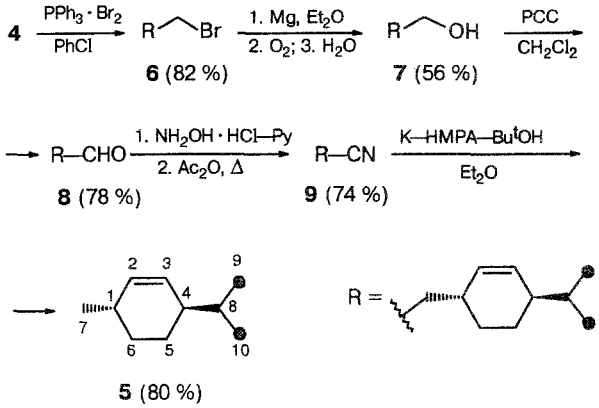


afford the $AlBr_2^+ \cdot 2ROMe$ cation, which is more electrophilic than the initial bromoalane.* The attack of $AlBr_2^+$ at the least sterically hindered side of the trisubstituted double bond yields carbocation **14**. The latter rearranges to form carbocation **15** as a result of two synchronous processes: a 1,3-hydride shift and opening of the cyclobutane ring.[13] Cation **15** gets a hydride ion from $H_2AlBr_2^+$ to give alkyldibromoalane **3** (Scheme 3).

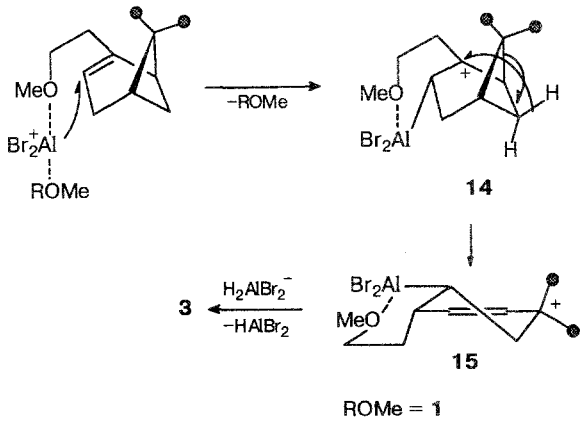
The partial racemization of compound **1** occurring in the course of the reaction probably results from the formation of minor amounts of the less stable carbocation **16**, which can be reversibly converted into its enantiomer through a 1,3-alkyl shift.[14]

Treatment of compound **1** with 1.2 equiv. of the $LiAlH_4—3AlBr_3$ system (20 °C, 4 h) affords a mixture of regioisomeric bis(dibromoalumo) derivatives **17** and **18** in ≈ 80:20 ratio (see Scheme 1). This is indicated by the analysis of the ^{13}C NMR spectra of the products of their deuterolysis. The predominant formation of com-

Scheme 2



Scheme 3



* A similar disproportionation has been described for solutions of the $AlBr_3 \cdot Et_2O$ complex in weakly polar solvents.[12]

pound **17** is probably due to coordination of $HAlBr_2$ by the O atom of the CH_3O group and to the shielding effect of the isopropyl fragment. The signals for C(2) and C(6), C(3) and C(5), and C(9) and C(10) in the ^{13}C NMR spectrum of the major regioisomer do not coincide, which attests to the absence of a symmetry plane and *trans*-orientation of the $AlBr_2$ substituents. The configuration of the minor isomer **18** was not specifically determined. It should be noted that minor amounts (5—10 %) of bis(dibromoalumo) derivatives also form in the preparation of mono(dibromoalumo) derivative **3** by the action of 0.6 equiv. of the $LiAlH_4$—$AlBr_3$ system on substrate **1**. Therefore, the corresponding saturated analogs are always detected among the products of transformations of compound **3**.

Hydrolysis of the mixture of **17** and **18** gives 7-(methoxymethyl)menthane (**19**). The *trans*-configuration of this compound has been determined by its conversion into *trans*-menthane[15] in 25 % overall yield similar to the conversion of unsaturated ether **4** into *trans*-2-menthene **5**. We did not manage to carry out the selective oxidation of only one of the Al—C bonds in the bis(dibromoalumo) derivatives. For example, bubbling oxygen through a THF solution of compounds **17** and **18** until they are 90 % converted and the subsequent hydrolysis afford a mixture of alcohol **11** and diols **20** and **21** in the 74:26 ratio. Compound **11** is a single diastereomer with *trans*-orientation of the methoxyethyl and hydroxyl groups and *cis*-orientation of the hydroxyl and isopropyl groups, which follows from a comparison of its ^{13}C NMR spectrum with the spectra of the pair of diastereomers obtained by hydrogenation of alcohol **10**.*

Thus, hydroalumination of **1** with the subsequent transformations of the resulting compounds is an efficient method for preparing compounds containing a Δ^2-menthene or menthane moiety.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer in $CDCl_3$ or C_6D_6 (for organoaluminum compounds). Optical rotation angles were measured on a Perkin Elmer 242-MC polarimeter. GLC analysis was carried out on a Chrom-5 chromatoghaph with a flame ionization detector in a He flow (40—50 mL min^{-1}), with a 1.2 m × 3 mm column packed with 5 % SE-30 on Inerton-super and a 3.7 m × 3 mm column packed with 5 % PEG-6000 on Inerton NAW; and on a Shimadzu chromatograph in a He flow (0.5 mL min^{-1}), with a 25 m × 0.2 mm quartz capillary column packed with PEG-20M. IR spectra were recorded on a UR-20 spectrometer in thin films. Mass spectra were obtained on an MX-1306 instrument with the energy of ionizing electrons equal to 15 eV and an ionization chamber temperature of 150 °C.

Methyl nopol ether (1) ($[\alpha]_D^{20}$ −35.9°, neat) was prepared by the reaction[16] of nopol ($[\alpha]_D^{20}$ −36.6°, neat) with NaH and MeI in THF.

All of the experiments with organoaluminum compounds were carried out under dry Ar additionally purified by bubbling through a 25 % solution of Bu^i_2AlH in dodecane. Diethyl ether, THF, and benzene were distilled just before use over $LiAlH_4$ or benzophenone ketyl. A filtered 6 *M* solution of $LiAlH_4$ in Et_2O and a 2.6 *M* solution of $AlBr_3$ in benzene decolorized by stirring with $LiAlH_4$ (0.2 g L^{-1}) at 40 °C were used.

Hydroalumination of methyl nopol ether (1) with the $LiAlH_4$—$3AlBr_3$ system. Benzene (5 mL) and a 6 *M* ethereal solution of $LiAlH_4$ (1 mL, 6 mmol) were placed into a flask equipped with a magnetic stirrer. Most of the solvent was evaporated under reduced pressure (10—15 Torr) and 30 mL of benzene and a 2.6 *M* solution of $AlBr_3$ in benzene (6.9 mL, 18 mmol) were added. The mixture was stirred for 1 h at 20 °C. To the reagent thus prepared, a solution of compound **1** (1.9 g, 10.6 mmol) in 20 mL of benzene was added dropwise, and the mixture was stirred for 1 h at 20 °C. After the excess of $LiAlH_4$ precipitated, the transparent solution of compound **3** was decanted and used in subsequent reactions. A mixture of bis(dibromoalumo) derivatives **17** and **18** (8:2) was prepared from compound **1** (10.6 mmol) and the $LiAlH_4$—$3AlBr_3$ system (12 mmol) according to a similar procedure (20 °C, 4 h).

(1*R*,4*R*,6*S*)-6-Dibromoalumo-7-methoxymethyl-2-menthene (3). ^1H NMR, δ: 1.03 and 1.07 (both d, ^3J = 6.9 Hz, 6 H, CH_3); 1.40—2.60 (m, 8 H, CH, CH_2); 3.51 (s, 3 H, CH_3O); 3.60—4.00 (m, 2 H, CH_2O); 5.56 and 5.92 (both d, ^3J = 10.3 Hz, 2 H, CH=CH). ^{13}C NMR, δ: 19.60 and 19.85 (both q, C(9), C(10)); 25.55 (d, C(6)); 26.02 (t, C(5)); 32.01 (d, C(8)); 32.98 (t, C(7)); 34.62 (d, C(1)); 40.54 (d, C(4)); 64.12 (q, C(12)); 80.51 (t, C(11)); 129.52 (d, C(3)); 134.02 (d, C(2)).

(1*R*,2*S*,4*R*,6*S*)-2,6-Bis(dibromoalumo)-7-(methoxymethyl)menthane (17). ^{13}C NMR, δ: 20.32 and 20.81 (both q, C(9), C(10)); 31.55 and 32.88 (both t, C(3), C(5)); 31.80 and 32.37 (both d, C(2), C(6)); 33.57 (d, C(8)); 37.89 (t, C(7)); 43.52 (d, C(1)); 46.06 (d, C(4)); 65.50 (t, C(11)); 84.47 (q, C(12)).

Hydrolysis of compounds 3 and 17, 18. A solution of compound **3** or a mixture of **17** and **18** (10.6 mmol) in benzene was stirred under reduced pressure (50 → 1 Torr) at 20 °C until the solvent was wholly removed. The residue was dissolved in 50 mL of Et_2O with cooling to −78 °C and at −10 °C 30 mL of water was added dropwise to the resulting solution. The mixture was stirred for 0.5 h, the organic layer was separated, and the aqueous layer was extracted with Et_2O (3×20 mL). The combined ethereal extract was washed with water (30 mL), dried with $MgSO_4$, and concentrated. Fractional distillation afforded 1.6 g (84 %) of compound **4** or 1.3 g (68 %) of compound **19**.

(1*R*,4*R*)-7-Methoxymethyl-2-menthene (4). b.p. 72 °C (1 Torr), $[\alpha]_D^{20}$ −35.2° (*c* 14.2, $CHCl_3$). ^1H NMR, δ: 0.87 and 0.88 (both d, ^3J = 6.8 Hz, 6 H, CH_3); 1.12—2.20 (m, 9 H, CH_2, CH); 3.33 (s, 3 H, CH_3O); 3.44 (t, ^3J = 6.8 Hz, 2 H, CH_2O); 5.56 (s, 2 H, CH=CH). ^{13}C NMR, δ: 19.26 and 19.58 (both q, C(9), C(10)); 25.66 (t, C(5)); 29.90 (t, C(6)); 32.31 (d, C(8)); 33.22 (d, C(1)); 36.49 (t, C(7)); 42.23 (d, C(4)); 58.42 (q, C(12)); 70.70 (t, C(11)); 130.50 (d, C(3)); 132.12 (d, C(2)). MS (*m/z*): 182 $[M]^+$.

* The signals for C(1)—C(4), C(6), and C(7) in the spectrum of the 1,2-*cis*-isomer are at a higher field and the signal for C(5) is at a lower field than those in the spectrum of the 1,2-*trans*-isomer.[15]

***trans*-7-(Methoxymethyl)menthane (19),** b.p. 72 °C (1 Torr). ^{13}C NMR, δ: 19.72 (q, C(9), C(10)); 29.58 (t, C(3), C(5)); 32.83 (d, C(8)); 33.48 (t, C(2), C(6)); 34.73 (d, C(1)); 37.07 (t, C(7)); 44.05 (d, C(4)); 58.35 (q, C(12)); 70.82 (t, C(11)). MS (*m/z*): 184 $[M]^+$.

Oxidation and hydrolysis of compounds 3 and 17, 18. Oxidation of dibromoalumo derivatives was carried out by bubbling dry air (20 °C, 2 h) through a solution of compound **3** or a mixture of compounds **17** and **18** in THF. Then the reaction mixture was hydrolized by 40 mL of water (−10 °C), saturated with NaCl, and worked-up as described above. Column chromatography (L 40/100 silica gel, hexane—EtOAc, 2:1) afforded 1.5 g (74 %) of alcohol **10** or 0.91 g (43 %) of alcohol **11** and 0.34 g (15 %) of a mixture of diols **20** and **21**. Reduction of alcohol **10** with a $NaBH_4$—$CoCl_2 \cdot 6H_2O$ system in ethanol[11] followed by chromatography gave (2*R*)-**11** and (2*S*)-**11**.

(1*R*,4*R*,6*R*)- and (1*R*,4*R*,6*S*)-7-methoxymethyl-2-menthen-6-ols (10). ^1H NMR, δ: 0.83 and 0.86 (both d, ^3J = 6.8 Hz, 6 H, CH_3); 1.10—2.30 (m, 7 H, CH_2, CH); 3.32 (3.43) (s, 3 H, CH_3O); 3.36—3.58 (m, 3 H, CH_2O, CHO); 3.80 (4.03) (br.c, 1 H, OH); 5.32 (5.36) and 5.49 (5.63) (both d.d, $^3J_1$ = 9.8 Hz, $^3J_2$ = 1.9 Hz, 2 H, CH=CH). ^{13}C NMR, δ: 18.98 (19.39) and 19.51 (19.29) (both q, C(9), C(10)); 31.35 (31.87) (t, C(7)); 31.72 (31.64) (d, C(8)); 34.17 (34.93) (d, C(5)); 36.59 (38.80) (d, C(4)); 42.38 (44.34) (C(1)); 58.52 (58.67) (q, C(12)); 66.94 (72.78) (d, C(6)); 71.03 (72.00) (t, C(11)); 128.40 and 130.34 (130.18 and 130.62) (both d, C(2), C(3)).

(1*S*,2*S*,4*R*)-7-(Methoxymethyl)menthan-2-ol (11), $[\alpha]_D^{20}$ +6.6° (*c* 4.52, $CHCl_3$). ^1H NMR, δ: 0.87 and 0.88 (both d, ^3J = 6.6 Hz, 6 H, CH_3); 1.18—1.95 (m, 11 H, CH_2, CH); 3.36 (s, 3 H, CH_3O); 3.38—3.56 (m, 3 H, CH_2O, CHO); 4.0 (br.s, 1 H, OH). ^{13}C NMR, δ: 19.50 and 19.79 (both q, C(9), C(10)); 26.46 (t, C(7)); 29.12 (t, C(6)); 32.50 (d, C(8)); 32.80 (t, C(5)); 36.66 (t, C(3)); 36.77 (d, C(1)); 39.48 (d, C(4)); 58.59 (q, C(12)); 68.76 (d, C(2)); 70.70 (t, C(11)).

(1*S*,2*R*,4*R*)-7-(Methoxymethyl)menthan-2-ol (11), $[\alpha]_D^{20}$ −5.8° (*c* 6.91, $CHCl_3$). ^1H NMR, δ: 0.87 (d, ^3J = 6.8 Hz, 6 H, CH_3); 0.92—2.05 (m, 11 H, CH_2, CH); 3.20 (d.t, $^3J_1$ = 10.0 Hz, $^3J_2$ = 4.0 Hz, 1 H, CHO); 3.37 (s, 3 H, CH_3O); 3.38—3.58 (m, 2 H, CH_2O); 3.80 (br.s, 1 H, OH). ^{13}C NMR, δ: 19.68 and 19.77 (both q, C(9), C(10)); 29.01 and 31.90 (both t, C(5), C(6)); 32.45 (d, C(8)); 34.41 (t, C(7)); 38.51 (t, C(3)); 42.71 (d, (C(4)); 44.37 (d, C(1)); 58.42 (q, C(12)); 71.79 (t, C(11)); 74.73 (d, C(2)).

Oxidation of alcohols **10** and **11** with chromic acid yielded ketones **12** and **13**.

(1*R*,4*R*)-7-Methoxymethyl-2-menthen-6-on (12), $[\alpha]_D^{20}$ −31.3° (*c* 6.45, $CHCl_3$). ^1H NMR, δ: 0.94 (d, ^3J = 6.8 Hz, 6 H, CH_3); 1.65—1.76 (m, 1 H, C(8)H); 1.76—2.10 (m, 2 H, C(7)H_2); 2.35—2.55 (m, 3 H, C(5)H_2, C(4)H); 3.00 (m, 1 H, C(1)H); 3.30 (s, 3 H, CH_3O); 3.44 (t, 2 H, CH_2O, ^3J = 6.4 Hz); 5.71 and 5.88 (both d.d, $^3J_1$ = 9.9 Hz, $^3J_2$ = 1.8 Hz, 2 H, CH=CH). ^{13}C NMR, δ: 18.93 and 19.18 (both q, C(9), C(10)); 30.70 (t, C(7)); 32.27 (d, C(8)); 41.48 (t, C(5)); 44.17 and 45.18 (both d, C(1), C(4)); 58.31 (q, C(12)); 69.93 (t, C(11)); 128.91 (d, C(2)); 130.44 (d, C(3)); 211.80 (s, C(6)). IR (ν/cm^{-1}): 1720, 720. MS (*m/z*): 196 $[M]^+$.

(1*S*,4*R*)-7-(Methoxymethyl)menthan-2-on (13), $[\alpha]_D^{20}$ +4.1° (*c* 9.75, $CHCl_3$). ^1H NMR, δ: 0.88 and 0.89 (both d, ^3J = 5.8 Hz, 6 H, CH_3); 1.20—1.65 (m, 5 H, C(5)H_2, C(6)H_2, C(8)H); 2.85 (m, 1 H, C(4)H); 2.00—2.50 (m, 5 H, C(3)H_2, C(7)H_2, C(1)H); 3.30 (s, 3 H, CH_3O); 3.40 (m, 2 H, CH_2O). ^{13}C NMR, δ: 19.14 and 19.43 (both q, C(9), C(10)); 28.66 and 28.91 (both t, C(5), C(6)); 32.57 (d, C(8)); 33.03 (t, C(7)); 45.52 (t, C(3)); 46.57 (d, C(1), C(4)); 58.59 (q, C(12)); 70.27 (t, C(11)); 212.60 (s, C(2)). MS (*m/z*): 198 $[M]^+$.

(1*R*,4*R*)-7-Bromomethyl-2-menthene (6). A solution of ether **4** (7.8 g, 42.1 mmol) in 20 mL of chlorobenzene was added dropwise to a solution of complex $Ph_3P \cdot Br_2$ heated to 125 °C, which was prepared *in situ* from Ph_3P (13.2 g, 50.5 mmol) and Br_2 (4.0 g, 50.5 mmol) in 70 mL of chlorobenzene (25 °C). The reaction mixture was stirred for 4 h at 125 °C and cooled to 20 °C. The precipitate of Ph_3PO was separated by centrifuging and washed with 50 mL of pentane, and the combined solution was concentrated at 100—150 Torr. Distillation of the residue gave 7.9 g (82 %) of compound **6**, b.p. 85 °C (1 Torr), $[\alpha]_D^{20}$ −29.2° (*c* 17.1, $CHCl_3$). ^1H NMR, δ: 0.87 and 0.89 (both d, ^3J = 6.8 Hz, 6 H, CH_3); 0.95—2.35 (m, 9 H, CH_2, CH); 3.40 (m, 2 H, CH_2Br); 5.52 and 5.62 (both d.d, $^3J_1$ = 10.0 Hz, $^3J_2$ = 1.9 Hz, 2 H, CH=CH). ^{13}C NMR, δ: 19.30 and 19.62 (both q, C(9), C(10)); 25.24 (t, C(5)); 28.95 (t, C(6)); 31.60 (t, C(7)); 32.18 (d, C(8)); 34.73 (d, C(1)); 39.57 (t, C(11)); 42.09 (C(4)); 130.68 (d, C(3)); 131.58 (C(2)). MS (*m/z*): 230 and 232 $[M]^+$.

The subsequent steps of the conversion of ether **4** into *trans*-2-menthene **5** were carried out as described previously.[6—8] The following compounds were prepared.

(1*R*,4*R*)-7-Formyl-2-menthene (8), $[\alpha]_D^{20}$ −30.4° (*c* 13.8, $CHCl_3$). ^1H NMR, δ: 0.87 and 0.88 (both d, ^3J = 6.8 Hz, 6 H, CH_3); 0.90—2.20 (m, 6 H, C(5)H_2, C(6)H_2, C(4)H, C(8)H); 2.40 (m, 2 H, C(7)H_2); 2.65 (m, 1 H, C(1)H); 5.51 and 5.63 (both d.d, $^3J_1$ = 10.0 Hz, $^3J_2$ = 2.0 Hz, 2 H, CH=CH); 9.80 (t, ^3J = 2.6 Hz, 1 H, CH=O). ^{13}C NMR, δ: 19.22 and 19.56 (both q, C(9), C(10)); 25.17 (t, C(5)); 29.93 (t, C(6)); 31.04 (d, C(1)); 32.00 (d, C(8)); 41.76 (d, C(4)); 50.33 (t, C(7)); 130.19 (d, C(3)); 132.10 (d, C(2)); 202.60 (d, C(11)). MS (*m/z*): 166 $[M]^+$.

(1*R*,4*R*)-7-Cyano-2-menthene (9), $[\alpha]_D^{20}$ −30.2° (*c* 8.95, $CHCl_3$). ^1H NMR, δ: 0.87 and 0.88 (both d, ^3J = 6.8 Hz, 6 H, CH_3); 0.95—2.20 (m, 6 H, C(5)H_2, C(6)H_2, C(4)H, C(8)H); 2.30 (d, ^3J = 6.9 Hz, 2 H, C(7)H_2); 2.45 (m, 1 H, C(1)H); 5.55 and 5.74 (both d, ^3J = 10.1 Hz, 2 H, CH=CH). ^{13}C NMR, δ: 19.16 and 19.50 (both q, C(9), C(10)); 24.07 (t, C(7)); 24.73 (t, C(5)); 29.16 (t, C(6)); 31.93 (d, C(8)); 33.17 (d, C(1)); 41.60 (d, C(4)); 118.75 (s, C(11)); 128.14 (d, C(3)); 133.77 (d, C(2)). MS (*m/z*): 163 $[M]^+$.

(1*R*,4*R*)-2-menthene (5)[8,9], $[\alpha]_D^{20}$ −38.0° (*c* 6.4, $CHCl_3$). ^1H NMR, δ: 0.87 and 0.89 (both d, ^3J = 6.8 Hz, 6 H, CH_3); 0.96 (d, ^3J = 7.4 Hz, 3 H, CH_3); 1.00—2.20 (m, 7 H, CH_2, CH); 5.54 (s, 2 H, CH=CH). ^{13}C NMR, δ: 19.33 and 19.65 (both q, C(9), C(10)); 22.08 (q, C(7)); 25.71 (t, C(5)); 31.03 (d, C(1)); 31.93 (t, C(6)); 32.27 (d, C(8)); 42.01 (d, C(4)); 130.01 (d, C(3)); 134.09 (d, C(2)).

The conversion of *trans*-7-(methoxymethyl)menthane (**19**) into *trans*-menthane was accomplished according to a similar scheme.[17] ^{13}C NMR, δ: 19.73 (q, C(9), C(10)); 22.83 (q, C(7)); 29.90 (t, C(3), C(5)); 32.94 (d, C(1), C(8)); 35.71 (t, C(2), C(6)); 43.94 (d, C(4)).

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