# SYNTHESIS OF SOME MONOTERPENOLS *via* CYCLOPROPYLCARBINYL REARRANGEMENT

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Received October 30th, 1985

Condensation of appropriately substituted aldehydes and Grignard reagents leads to cyclopropyl alcohols *V*—*VIII* chromatographically separated in all cases into individual diastereoisomers. Perchloric acid catalyzed cyclopropylcarbinyl rearrangement of *V*—*VIII* (as a mixture of diastereoisomers or individual isomers) gives unsaturated monoterpenols *IX*—*XII* with high regio- and stereospecificity.

In connection with our study on identification of isoprenoid components of bark beetle (genus *Ips*) pheromones we required authentic samples of hitherto unknown monoterpenols *IX*—*XII*. One of the feasible ways for their preparation may consist in the homoallylic rearrangement[1] of cyclopropyl alcohols *V*—*VIII* which, in turn, can be obtained by condensation of appropriate aldehydes and Grignard reagents. Here we report some results of the approach previously used for the synthesis of certain (ir)regular terpenols[2-4].

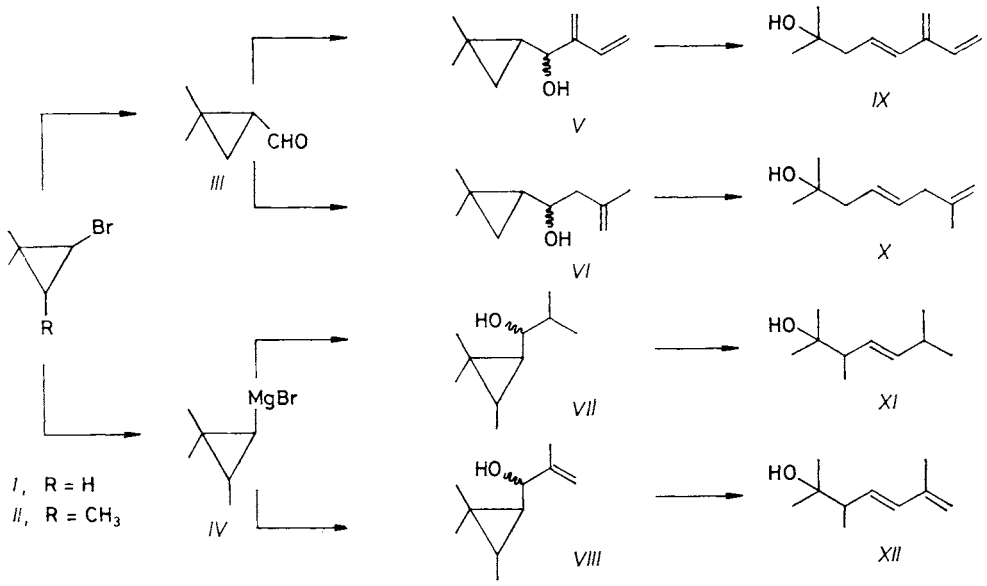
Bromides *I*, *II* were chosen as the starting material[5]. Lithiation of *I* followed by the reaction with N,N-dimethylformamide leads to the known[6] aldehyde *III* in a total yield of c. 35%. Its condensation with 1,3-butadien-2-yl- or 2-methylprop-2-enylmagnesium chlorides gives quantitatively the respective secondary alcohols *V*, *VI*.

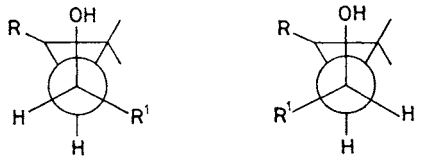
Unlike *I*, the bromide *II* was converted into its Li-derivative in a low yield but smoothly produced the Grignard reagent *IV*, *cf.*[3], which, in turn, quantitatively interacts with 2-methylpropanal and 2-methylprop-2-enal to give secondary alcohols *VII* and *VIII*, respectively. It is noteworthy that under the standard conditions of magnation of the initial c. 4 : 1 *E*/*Z*-mixture of the bromide *II* practically only *E*-component is consuming (GLC monitoring of the reaction). On that ground and taking into account our previous findings on stereochemistry of Grignard reagents derived from monocarbene adducts of isoprene and dimethylbutadiene[3] sterically more favourable *E*-geometry was assigned to the reagent *IV*; accordingly, *cf.*[7], the final products *VII*, *VIII* should also be regarded as having *E*-stereochemistry.

In all cases, cyclopropyl alcohols *V*—*VIII* are mixtures of diastereoisomers which are separable by means of flash-column chromatography. Among them the isomers *A* with the shorter GLC retention times on a polar column might be regarded as having

*threo*-like configuration (1*S**, 1′*S** for *V*, *VIII* and 1*S**, 1′*R** for *VI*, *VII*) as it was accepted previously for similar cyclopropyl alcohols[3,8–10]. It is noteworthy that within the pairs *erythro*-type components *B* (with configuration 1*S**, 1′*R** for *V*, *VIII* and 1*S**, 1′*S** for *VI*, *VII*) behave also as comparatively more polar ones under the conditions of adsorption chromatography on silica gel or alumina.

Both GLC data and results on preparative separation of diastereoisomers *A*, *B* revealed some stereoselectivity of the nucleophilic reactions discussed. Thus, the ratio $A/B \simeq 60:40$ found for alcohols *V*, *VI* is in accordance with that reported previously for the similar mixtures obtained from the same aldehyde *III* and aliphatic Grignard reagents[10]. The inverse ratio, $A/B \simeq 35:65$, was observed in the case of isomeric alcohols *VII*, *VIII* prepared from trimethylcyclopropylmagnesium bromide *IV*.




*V*, R = H; $R^1 = CH_2{=}CCH{=}CH_2$
*VI*, R = H; $R^1 = CH_2C(CH_3){=}CH_2$
*VII*, R = $CH_3$; $R^1 = CH(CH_3)_2$
*VIII*, R = $CH_3$; $R^1 = CH_3C{=}CH_2$

The structure of hitherto unknown cyclopropyl alcohols *V*–*VIII* was substantiated spectroscopically, the respective diastereoisomeric pairs being distinguishable owing to differences in $^1$H NMR spectra (100 MHz). The signals of gem-dimethyl group of isomers *A* are two single lines separated by c. 0·1 ppm whereas the similar signals of isomers *B* appear as unresolved six-proton singlets which, in addition, are shifted upfield by $\Delta\delta \approx 0{\cdot}08-0{\cdot}17$ ppm.

Like in previously discussed cases[2-4], under the action of catalytic amounts of $HClO_4$ cyclopropyl alcohols *V*–*VIII* undergo regiospecific cleavage of the three-membered ring to give under mild conditions up to 90% of homoallylic alcohols *IX*–*XII* whose structure was established on the basis of elemental and spectral analyses data. Hydrocarbons, whose structure was not elucidated, were formed as by-products in this reaction. According to GLC and $^1$H NMR data the isomerization observed is highly (≧98%) regioselective, the coupling constant values ($J$ = 15 to 16 Hz) for vicinal protons of the newly generated disubstituted C=C bond being indicative of its *trans*-geometry with c. 99% purity. This finding agrees with the data on preferential formation of *trans*-olefins in the course of acid catalyzed rearrangement of the secondary cyclopropyl alcohols[2-4,11]. The configuration of the latters may affect, in the general case, stereochemistry of the respective isomerization products[12,13]. Nevertheless, we have found the absence of such an effect within the series of substrates *V*–*VIII*: Both individual diastereoisomers and their mixtures gave *E*-olefins *IX*–*XII*. On the other hand, the reaction rate was noted to depend essentially on the structure of the starting alcohol. Thus, full conversion of *VII*, *VIII* proceeds in tetrahydrofuran at c. 25°C for less than 40 min whereas at least 2 h are required for the same transformation of *V*, *VI* the end product being contaminated in these cases with large ammounts of respective hydrocarbons. It seems likely that the existence of strong hydrogen bonding within the homoallylic fragment of the molecules *V*, *VI* (detected in their IR spectra at c. 3 575 $cm^{-1}$) does inhibit the isomerization. Carrying out the isomerization in the presence of c. 10 vol.% of acetone, which is apparently weakening hydrogen bonding, permits to decrease the reaction time to 1 h and to reduce simultaneously the formation of unwanted by-products.

Thus, we regard the above sequence of transformations as a simple way to the monoterpenols *IX*–*XII* and their cyclopropane analogs *V*–*VIII*.

## EXPERIMENTAL

The boiling points are uncorrected. The infrared spectra were recorded in tetrachloromethane on a UR-20 spectrometer (VEB Carl Zeiss, Jena). The ultraviolet spectra were taken in ethanol on a Specord UV-VIS double beam recording spectrophotometer (VEB Carl Zeiss, Jena). The $^1$H NMR spectra were measured in tetrachloromethane on a Varian DA-60-IL or on a Tesla BS-497 (100 MHz) spectrometers with tetramethylsilane as internal standard. The chemical shifts are given in ppm ($\delta$-scale). The mass spectra were determined on a Varian MAT-CH-6 or on a LKB-2091 spectrometers at 70 eV. The GLC was carried out using a 2 m × 3 mm column with 15% Carbowax 20 M on Chromaton N-AW-HMDS.

2,2-*Dimethylcyclopropylcarboxaldehyde* (III): Slurry of Li-wire (1·6 g, 0·23 g-at) in hexane (65 ml) containing 7·15 g (48 mmol) of the bromide *I* was refluxed with stirring under argon for 2 h. A solution of the Li-derivative thus prepared (18 mmol) was decanted and treated with a solution of N,N-dimethylformamide (3 g, 41 mmol) in ether (5 ml) at −30°C for 0·5 h. The mixture was warmed to 25°C over 1 h and after 15 min was quenched with 5% HCl (10 ml) at 0°C. The organic phase was separated, the aqueous layer was neutralized and extracted with pentane. The combined solution was dried ($MgSO_4$) and concentrated under reduced pressure (17 kPa). The residue was distilled in the presence of hydroquinone (5 mg) to give *III* (1·6 g, 34%), b.p. 37–40°C (3·9 kPa), *cf.*[6]. $^1$H NMR spectrum: 0·96 (m, 2 H, $CH_2$), 1·20 and 1·24 (s, 6 H, $CH_3$), 1·68 (m, 1 H, $HC^1$), 9·40 (d, $J$ = 4 Hz, 1 H, CHO).

(1*S**,1′*S**)- and (1*S**,1′*R**)-1-(1′-*Hydroxy*-2′-*methylenobut*-3′-*enyl*)-2,2-*dimethylcyclopropanes* (V). To a cooled (−5°C), stirred under argon solution of the Grignard reagent, prepared according to[14] from 2-chloro-1,3-butadiene (4·65 g, 52·5 mmol) and Mg (1·36 g, 57 mg-at) in tetrahydrofuran (40 ml), a solution of *III* (1·5 g, 15 mmol) in tetrahydrofuran (5 ml) was added for 0·5 h. The mixture was warmed to 25°C, kept at this temperature for 40 min, then decomposed at 0°C with an excess of saturated aqueous $NH_4Cl$ solution. The usual work-up of the organic layer gave the product (2 g) which was chromatographed on silica gel (80 g). Gradient elution from hexane to hexane–ether (9 : 1 v/v) afforded, in the order of elution, 1·02 g (44%) of(1*S**,1′*S**)-*V* (isomer *A*) and 0·7 g (30%) of (1*S**,1′*R**)-*V* (isomer *B*).

Found for (1*S**,1′*S**)-*V*: b.p. 42°C (0·13 kPa), $n_D^{21}$ 1·4798. IR spectrum: 910, 960, 1 020, 1 035, 1 125, 1 140, 1 265, 1 380, 1 420, 1 455, 1 600, 1 635, 1 820, 3 070, 3 095, 3 580, 3 615 $cm^{-1}$. UV spectrum $\lambda_{max}$ 224 nm ($\varepsilon$ 15930). $^1$H NMR spectrum: 0·1–1·0 (m, 3 H, $HC^1$, $HC^3$); 1·12 and 1·22 (s, 6 H, $CH_3$); 3·80 (br. d, $J$ = 8 Hz, 1 H, CHO); 5·0–5·6 (m, 4 H, $H_2C$=C); 6·29 (dd, $J$ = 12 and 17 Hz, 1 H, HC=$CH_2$). Mass spectrum, *m/z* (%): 134 (30), 119 (57), 117 (14), 105 (32), 93 (16), 92 (34), 91 (85), 80 (15), 79 (100), 78 (26), 77 (44), 65 (16), 51 (12), 41 (37). For $C_{10}H_{16}O$ (152·2) calculated: 78·89% C, 10·59% H; found: 78·77% C, 10·59% H.

Found for (1*S**,1′*R**)-*V*: b.p. 49°C (0·13 kPa), $n_D^{22}$ 1·4781. IR spectrum: 910, 960, 1 000, 1 025, 1 125, 1 145, 1 230, 1 380, 1 425, 1 455, 1 595, 1 635, 1 820, 3 060, 3 095, 3 575, 3 610 $cm^{-1}$. UV spectrum: $\lambda_{max}$ 223 nm ($\varepsilon$ 16 300). $^1$H NMR spectrum: 0·3–1·0 (m, 3 H, $HC^1$, $HC^3$); 1·00 (br. s, 6 H, $CH_3$); 3·78 (br. d, $J$ = 8 Hz, 1 H, CHO); 5·0–5·6 (m, 4 H, $H_2C$=C); 6·25 (dd, $J$ = 12 and 17 Hz, 1 H, HC=$CH_2$). Mass spectrum, *m/z* (%): 134 (42), 119 (78), 117 (14), 105 (28), 93 (17), 92 (35), 91 (90), 80 (14), 79 (100), 78 (24), 77 (42), 65 (15), 59 (22), 55 (13), 53 (22), 51 (12), 43 (44), 41 (49). For $C_{10}H_{16}O$ (152·2) calculated: 78·89% C, 10·59% H; found: 78·88% C, 10·56% H.

(1*S**,1′*R**)- and (1*S**,1′*S**)-1-(1′-*Hydroxy*-3′-*methylbut*-3′-*enyl*)-2,2-*dimethylcyclopropanes* (VI). To a cooled (0°C), stirred under argon solution of the Grignard reagent prepared from 3-chloro-2-methylpropen-1 (2·7 g, 30 mmol) and Mg (1·44 g, 60 mg-at) in ether (40 ml), a solution of *III* (1·5 g, 15·3 mmol) in ether (3 ml) was added for 20 min. The mixture was worked-up as above, and the residue (2·5 g) was chromatographed under the same conditions to give (1*S**,1′*R**)-*VI* (isomer *A*) (1·06 g, 45%) and (1*S**,1′*S**)-*VI* (isomer *B*) (0·8 g, 34%).

Found for (1*S**,1′*R**)-*VI*: b.p. 70°C (0·9 kPa), $n_D^{22}$ 1·4522. IR spectrum: 875, 895, 955, 1 010, 1 030, 1 070, 1 140, 1 270, 1 380, 1 420, 1 455, 1 655, 1 800, 3 060, 3 080, 3 570, 3 620 $cm^{-1}$. $^1$H NMR spectrum: 0–0·8 (3 H, $HC^1$, $HC^3$); 1·08 and 1·16 (s, 6 H, $CH_3C^2$); 1·74 (br. s, 3 H, $CH_3C$=C); 2·22 (m, 2 H, $CH_2C$=C); 3·18 (m, 1 H, CHO); 4·78 and 4·81 (br. s, 2 H, $H_2C$=C). Mass spectrum, *m/z* (%): 139 (6), 136 (25), 121 (26), 108 (12), 107 (27), 105 (11), 99 (68), 94 (16), 93 (79), 91 (28), 81 (100), 80 (29), 79 (58), 77 (26), 69 (16), 68 (15), 67 (23), 59 (20), 57 (19), 55 (40), 53 (29), 43 (64), 41 (66). For $C_{10}H_{18}O$ (154·2) calculated: 77·86% C, 11·76% H; found: 77·67% C, 11·82% H.

Found for (1*S**,1′*S**)-*VI*: b.p. 76°C (0·9 kPa), $n_D^{23}$ 1·4519. IR spectrum: 875, 895, 950, 975,

1 010, 1 030, 1 065, 1 125, 1 265, 1 380, 1 415, 1 455, 1 650, 1 800, 3 060, 3 075, 3 575, 3 615 $cm^{-1}$. $^1H$ NMR spectrum: 0·1—0·7 (m, 3 H, $HC^1$, $HC^3$); 1·02 (br. s, 6 H, $CH_3C^2$); 1·73 (br. s, 3 H, $CH_3C{=}C$); 2·19 (br. d, $J$ = 6 Hz, 2 H, $CH_2C{=}C$); 3·21 (m, 1 H, CHO); 4·70 and 4·74 (br. s, 2 H, $H_2C{=}C$). Mass spectrum, *m/z* (%): 139 (1), 136 (31), 121 (36), 108 (12), 107 (33), 105 (15), 99 (27), 95 (15), 94 (21), 93 (100), 91 (32), 81 (97), 80 (42), 79 (69), 77 (34), 68 (17), 67 (24), 59 (20), 55 (33), 53 (30), 43 (55), 41 (59). For $C_{10}H_{18}O$ (154·2) calculated: 77·86% C, 11·76% H; found: 77·63% C, 11·87% H.

(1*S**,1′*R**)- and (1*S**,1′*S**)-(*E*)-1-(1′-*Hydroxy*-2′-*methylpropyl*)-2,2,3-*trimethylcyclopropanes* (VII). To a cooled (0°C), stirred under argon solution of the Grignard reagent *IV* (12 mmol), prepared from *II* (4·89 g, 30 mmol) and Mg (0·96 g, 40 mg-at) in ether (35 ml), a solution of isobutyraldehyde (0·86 g, 12 mmol) in ether (3 ml) was added for 15 min. Further usual work-up gave the product (2 g) which was chromatographed on neutral alumina (60 g, Brockmann act. II). Gradient elution from hexane to hexane–ether (4 : 1 v/v) yielded 0·45 g (24%) of (1*S**,1′*R**)-*VII* (isomer *A*) and 0·86 g (46%) of (1*S**,1′*S**)-*VII* (isomer *B*).

Found for (1*S**,1′*R**)-*VII*: b.p. 48°C (0·3 kPa), $n_D^{23}$ 1·4439. IR spectrum: 1 020, 1 120, 1 175, 1 250, 1 380, 1 465, 3 625 $cm^{-1}$. $^1H$ NMR spectrum: 0·1—0·8 (m, 2 H, $HC^1$, $HC^3$); 0·90 and 0·93 (d, $J$ = 7 Hz, 6 H, $CH_3CHCH_3$); 1·03 (d, $J$ = 6 Hz, 3 H, $CH_3C^3$); 1·04 and 1·12 (s, 6 H, $CH_3C^2$); 1·64 (m, 1 H, $CH_3CHCH_3$); 2·80 (dd, $J$ = 6·5 and 9 Hz, 1 H, CHO). Mass spectrum, *m/z* (%): 138 (44), 123 (77), 109 (13), 96 (15), 95 (100), 93 (11), 83 (13), 82 (57), 81 (59), 79 (13), 77 (11), 70 (15), 69 (58), 67 (58), 59 (26), 55 (51), 53 (16), 43 (55), 41 (57). For $C_{10}H_{20}O$ (156·3) calculated: 76·86% C, 12·90% H; found: 76·64% C, 12·87% H.

Found for (1*S**,1′*S**)-*VII*: b.p. 48°C (0·3 kPa), $n_D^{21}$ 1·4448. IR spectrum: 975, 1 020, 1 120, 1 175, 1 250, 1 380, 1 460, 3 625 $cm^{-1}$. $^1H$ NMR spectrum: 0·1—0·5 (m, 2 H, $HC^1$, $HC^3$); 0·84 and 0·88 (d, $J$ = 7 Hz, 6 H, $CH_3CHCH_3$); 0·95 (br. d, 6 H, $CH_3C^2$); 1·02 (d, $J$ = 6 Hz, 3 H, $CH_3C^3$), 1·60 (m; 1 H, $CH_3CHCH_3$); 2·79 (dd, $J$ = 6·5 and 9 Hz, 1 H, CHO). Mass spectrum, *m/z* (%): 138 (54), 124 (14), 123 (100), 109 (14), 96 (14), 95 (95), 93 (12), 83 (11), 82 (53), 81 (69), 79 (16), 77 (11), 70 (13), 69 (58), 67 (58), 59 (25), 55 (44), 53 (17), 43 (30), 41 (51). For $C_{10}H_{20}O$ (156·3) calculated: 76·86% C, 12·90% H; found: 76·60% C, 12·93% H.

(1*S**,1′*S**)- and (1*S**,1′*R**)-(*E*)-1-(1′-*Hydroxy*-2′-*methylprop*-2′-*enyl*)-2,2,3-*trimethylcyclopropanes* (VIII). Following the same procedure described for *VII*, (1*S**,1′*S**)-*VIII* (isomer *A*) (0·46 g, 25%) and (1*S**,1′*R**)-*VIII* (isomer *B*) (0·94 g, 51%) were obtained starting from *IV* (12 mmol) and 2-methylprop-2-enal (0·84 g, 12 mmol).

Found for (1*S**,1′*S**)-*VIII*: b.p. 52°C (0·3 kPa), $n_D^{20}$ 1·4587. IR spectrum: 900, 970, 1 020, 1 045, 1 380, 1 455, 1 650, 1 805, 3 080, 3 610 $cm^{-1}$. $^1H$ NMR spectrum: 0·2—0·4 (m, 2 H, $HC^1$, $HC^3$); 1·00 (d, $J$ = 6 Hz, 3 H, $CH_3C^3$); 1·04 and 1·14 (s, 6 H, $CH_3C^2$); 1·74 (br. s, 3 H, $CH_3C{=}C$); 3·46 (br. d, $J$ = 8·5 Hz, 1 H, CHO); 4·68 and 4·86 (br. s, 2 H, $H_2C{=}C$). Mass spectrum, *m/z* (%): 139 (1·5), 136 (2), 121 (8), 96 (45), 91 (19), 84 (31), 83 (100), 81 (14), 79 (15), 77 (13), 71 (25), 69 (20), 67 (15), 59 (43), 55 (96), 44 (46), 43 (51), 41 (77). For $C_{10}H_{18}O$ (154·2) calculated: 77·86% C, 11·76% H; found: 77·61% C, 11·63% H.

Found for (1*S**,1′*R**)-*VIII*: b.p. 58°C (0·3 kPa), $n_D^{21}$ 1·4575. IR spectrum: 900, 980, 1 020, 1 050, 1 380, 1 460, 1 650, 1 805, 3080, 3 610 $cm^{-1}$. $^1H$ NMR spectrum: 0·2—0·7 (m, 2 H, $HC^1$, $HC^3$); 1·01 (br. s, 6 H, $CH_3C^2$); 1·08 (d, $J$ = 6 Hz, 3 H, $CH_3C^3$); 1·74 (br. s, 3 H, $CH_3C{=}C$); 3·51 (br. d, $J$ = 8·5 Hz, 1 H, CHO); 4·71 and 4·85 (br. s, 2 H, $H_2C{=}C$). Mass spectrum, *m/z* (%): 139 (3), 136 (4), 121 (11), 96 (37), 84 (20), 83 (62), 81 (21), 71 (20), 69 (24), 67 (20), 59 (20), 55 (100), 43 (48), 41 (100). For $C_{10}H_{18}O$ (154·2) calculated: 77·86% C, 11·76% H; found: 77·65% C, 11·56% H.

2-*Methyl*-6-*methyleneocta*-4(*E*),7-*diene*-2-*ol* (IX). A solution of the above mixture of alcohols *V* (1·44 g, (1*S**,1′*S**)/(1*S**,1′*R**) ≈ 3 : 2) in tetrahydrofuran–acetone (10 : 1 v/v, 55 ml) containing

0·5 ml of 30% $HClO_4$ was kept at c. 25°C for c. 1 h until no starting compound(s) *V* could be detected by TLC and GLC in the reaction mixture. The latter was diluted with ether (40 ml), washed with 15% $NaHCO_3$, dried ($MgSO_4$), and evaporated *in vacuo* to give 1·28 g (89%) of *IX* readily polymerizable on distillation, chromatography and storage under an inert atmosphere.

Found for the freshly distilled sample of *IX*: b.p. 63°C (0·13 kPa), $n_D^{22}$ 1·4969. IR spectrum: 850, 895, 910, 975, 990, 1 125, 1 140, 1 220, 1 270, 1 370, 1 430, 1 460, 1 590, 1 640, 1 685, 1 780, 1 955, 3 090, 3 585, 3 615 $cm^{-1}$. UV spectrum: $\lambda_{max}$ 215 ($\varepsilon$ 10 400), 238 nm ($\varepsilon$ 9 000). $^1H$ NMR spectrum: 1·17 (s, 6 H, $CH_3C^2$); 2·21 (br. d, $J$ = 6·5 Hz, 2 H, $HC^3$); 4·9–5·5 (m, 4 H, $H_2C{=}C$); 5·83 (dt, $J$ = 16 and 6·5 Hz, 1 H, $HC^4$); 6·12 (br. d, $J$ = 16 Hz, 1 H, $HC^5$); 6·37 (br. dd, $J$ = 10 and 17·5 Hz, 1 H, $HC^7$). Mass spectrum, *m/z* (%): 137 (2), 134 (1), 119 (3), 94 (26), 91 (11), 79 (47), 77 (11), 59 (100), 55 (12), 53 (11), 43 (54), 41 (25). For $C_{10}H_{16}O$ (152·2) calculated: 78·89% C, 10·59% H; found: 78·48% C, 10·46% H.

2,7-*Dimethylocta*-4(*E*),7-*diene*-2-*ol* (X). Similarly, starting from the mixture of alcohols *VI* (1·4 g, (1*S**,1′*R**)/(1*S**,1′*S**) ≈ 3 : 2) the crude reaction product (1·3 g) gave, after chromatography on silica gel (20 g) using hexane–ether mixture (5 : 1 v/v) as eluent, and further distillation, 1·05 g (75%) of *X*, b.p. 83°C (1 kPa), $n_D^{23}$ 1·4583. IR spectrum: 895, 980, 1 125, 1 140, 1 375, 1 450, 1 650, 3 580, 3 615 $cm^{-1}$. $^1H$ NMR spectrum: 1·12 (s, 6 H, $CH_3C^2$); 1 69 (br. s, 3 H, $CH_3C^7$); 2·10 (br. d, $J$ = 6 Hz, 2 H, $HC^3$); 2·68 (br. d, $J$ = 5 Hz, 2 H, $HC^6$); 4·68 (br. s, 2 H, $HC^8$); 5·45 (m, 2 H, $HC^4$, $HC^5$). Mass spectrum, *m/z* (%): 139 (2), 136 (6), 121 (7), 96 (42), 93 (21), 81 (55), 79 (20), 77 (12), 59 (100), 55 (10), 43 (30), 41 (17). For $C_{10}H_{18}O$ (154·2) calculated: 77·86% C, 11·76% H; found: 77·63% C, 11·60% H.

2,3,6-*Trimethylhept*-4(*E*)-ene-2-ol (XI). A solution of the mixture of alcohols *VII* (0·35 g, (1*S**,1′*R**)/(1*S**,1′*S**) ≈ 2 : 3) in tetrahydrofuran (25 ml) containing 0·2 ml of 30% $HClO_4$ was kept at 25°C for 40 min. Further usual work-up and chromatography of the crude product (0·32 g) under the conditions indicated for *X*, followed by distillation gave 0·29 g (83%) of *XI*, b.p. 49°C (0·3 kPa), $n_D^{23}$ 1·4425. IR spectrum: 945, 980, 1 040, 1 120, 1 180, 1 340, 1 370, 1 385, 1 465, 1 555, 1 660, 3 580, 3 620 $cm^{-1}$. $^1H$ NMR spectrum: 0·91 (d, $J$ = 7 Hz, 3 H, $CH_3C^3$); 0·93 (d, $J$ = 7 Hz, 6 H, $CH_3C^6$); 1·02 (s, 6 H, $CH_3C^2$); 1·9–2·3 (m, 2 H, $HC^3$, $HC^6$); 5·29 (m, 2 H, $HC^4$, $HC^5$). Mass spectrum, *m/z* (%): 141 (1), 138 (7), 123 (18), 98 (20), 95 (15), 81 (14), 69 (34), 67 (11), 59 (100), 56 (20), 55 (18), 43 (18), 41 (19). For $C_{10}H_{20}O$ (156·3) calculated: 76·86% C, 12·90% H; found: 76·85% C, 12·89% H.

2,3,6-*Trimethylhepta*-4(*E*),6-*diene*-2-*ol* (XII). Following the same procedure described for *XI*, the mixture of alcohols *VIII* (0·4 g, (1*S**,1′*S**)/(1*S**,1′*R**) ≈ 2 : 3) was converted into *XII* (0·27 g, 67·5%) (the reaction was completed in 15 min), b.p. 54°C (0·27 kPa), $n_D^{22}$ 1·4839. IR spectrum: 890, 950, 975, 1 115, 1 175, 1 370, 1 440, 1 460, 1 550, 1 610, 3 085, 3 580, 3 620 $cm^{-1}$. UV spectrum: $\lambda_{max}$ 230 nm ($\varepsilon$ 22 400). $^1H$ NMR spectrum: 1·05 (d, $J$ = 7 Hz, 3 H, $CH_3C^3$); 1·14 (s, 6 H, $CH_3C^2$); 1·83 (br. s, 3 H, $CH_3C^6$); 2·19 (m, 1 H, $HC^3$); 4·88 (br. s, 2 H, $HC^7$); 5·56 (dd, $J$ = 8 and 16 Hz, 1 H, $HC^4$); 6·14 (br. d, $J$ = 16 Hz, 1 H, $HC^5$). Mass spectrum, *m/z* (%): 139 (13), 136 (2), 121 (7), 97 (10), 96 (100), 81 (44), 59 (65), 43 (18). For $C_{10}H_{18}O$ (154·2) calculated: 77·86% C, 11·76% H; found: 77·64% C, 11·74% H.

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