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Compounds of the Menthane Series. Synthesis of Unsaturated Primary Alcohols with the *o*- and *p*-Menthane Skeletons

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Abstract—Precursors to terpene alcohols of the *o*- and *p*-menthane series (*o*-cimen-7-ol and *o*- and *p*-cimen-9-ols) were synthesized, and their reduction with lithium in ethylenediamine was studied. The reduction of *o*- and *p*-cimen-9-ols in the presence of isopropyl alcohol selectively afforded the corresponding 1,4-dihydro derivatives. Under analogous conditions, *o*-cimen-7-ol was converted into a mixture of unsaturated hydrocarbons. The reduction with lithium in ethylenediamine in the absence of isopropyl alcohol in all cases gave mixtures of menthene alcohols.

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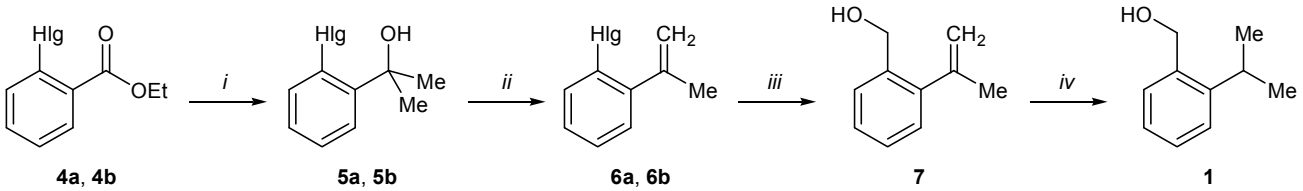
Oxygen-containing menthane compounds isolated from coniferous trees and plant essential oils include mainly tertiary terpene alcohols. Primary *p*-menthenols and *p*-menthadienols are rare components which were found in some valuable rose and lemon essential oils [1–3]. Perillic alcohol synthesized from β-pinene epoxide showed excellent antimicrobial and antitumor activities [4]. Primary alcohols derived from limonene are used as intermediate products in the synthesis of biologically active compounds [5–8]. Primary alcohols of the *o*-menthane series have not been reported in the literature.

In this work, partial reduction of the aromatic ring in isomeric cimenols was accomplished using a convenient and efficient system developed by us previously, namely Li–*i*-PrOH in the presence of a small amount of ethylenediamine [9, 10]. The substrates were (2-isopropylphenyl)methanol (*o*-cimen-7-ol, **1**) 2-(2-methylphenyl)propan-1-ol (*o*-cimen-9-ol, **2**), and 2-(4-methylphenyl)propan-1-ol (*p*-cimen-9-ol, **3**). Compound **1** was synthesized as shown in Scheme 1. The yield of tertiary alcohol **5a** from ethyl *o*-chlorobenzoate (**4a**) was higher (82%) than from bromine-containing analog **4b** (71%). Dehydration of alcohols **5a** and **5b** gave unsaturated compounds **6a** and **6b** which were alkylated with methylmagnesium iodide. The yield of primary alcohol **7** from bromo derivative **6b** was twice as high as that from chloro analog **6a**, which may be due to higher reactivity of bromoarenes in the Grignard reaction [11].

Steric structure of initial *o*- and *p*-tolylpropenes turned out to be essential in the synthesis of *ortho*- and *para*-cimen-9-ols. The hydroboration of 2-(2-methylphenyl)propene (**8**), followed by oxidation of intermediate organoborane, afforded 72% of a mixture of isomeric alcohols **2** and **9** at a ratio of 4 : 1 (Scheme 2). Analogous reaction of 2-(4-methylphenyl)propene (**13**) led to the formation of 90% of a mixture of primary and tertiary alcohols **3** and **14** at a ratio of 9 : 1 (Scheme 3).

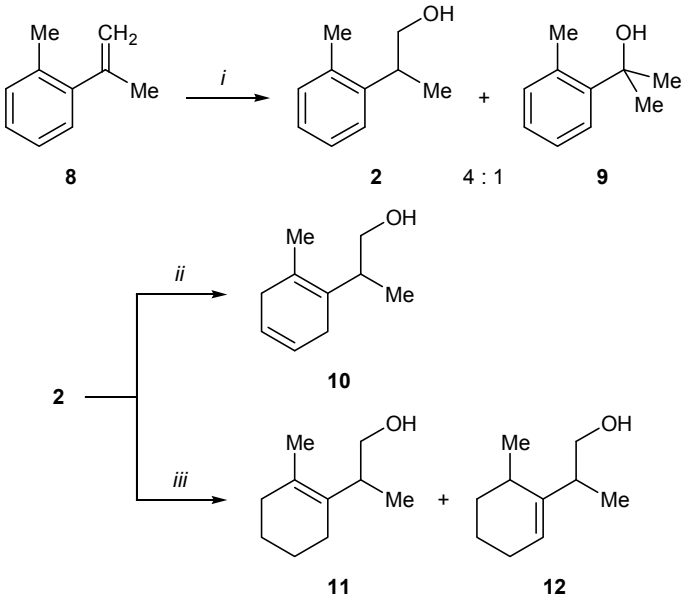
Scheme 1.



4a, **4b** **5a**, **5b** **6a**, **6b** **7** **1**

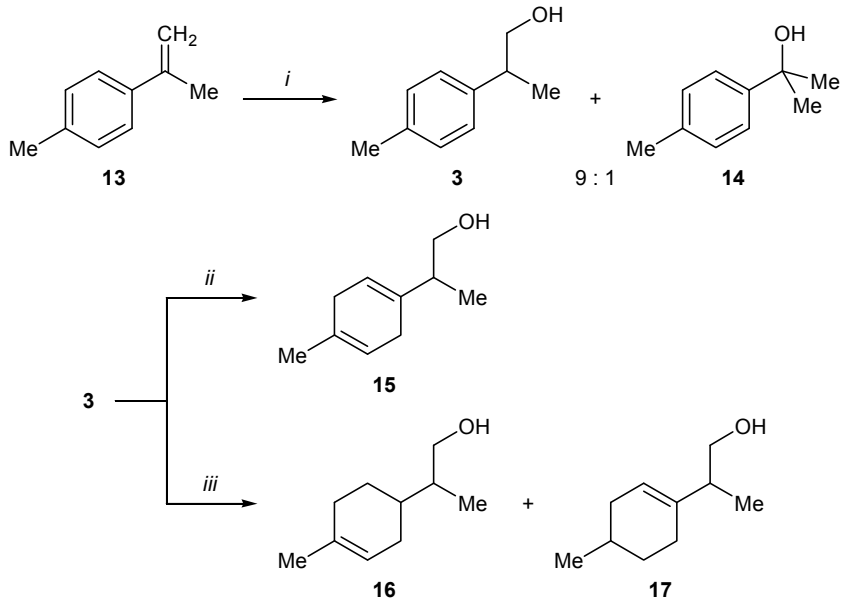
Hlg = Cl (**a**), Br (**b**); *i*: MeMgI, Et_2O; *ii*: phthalic anhydride; *iii*: MeMgI, CH_2O; *iv*: Na, PrOH.

Scheme 2.



i: $NaBH_4$, 1,4-dioxane, $BF_3 \cdot Et_2O$, NaOH, H_2O_2; *ii*: Li, ethylenediamine, *i*-PrOH; *iii*: Li, ethylenediamine.

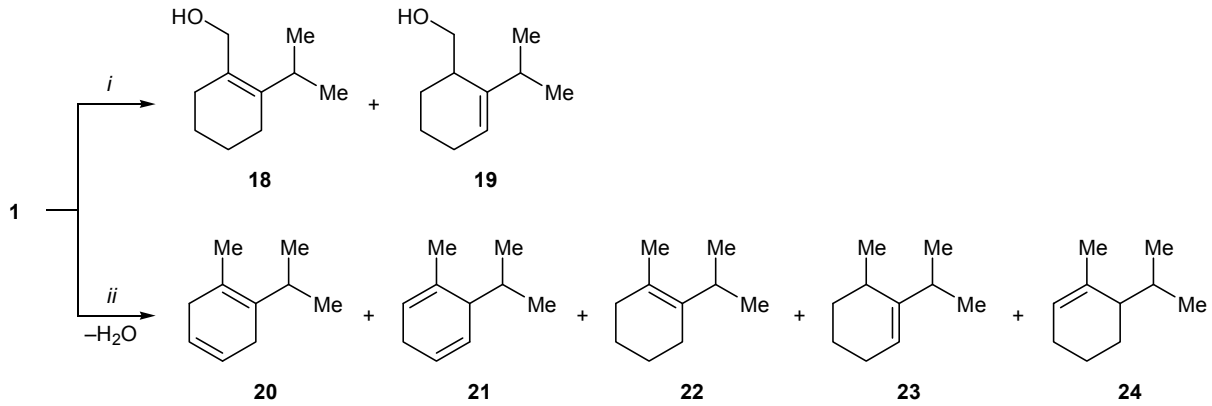
Scheme 3.



i: $NaBH_4$, 1,4-dioxane, $BF_3 \cdot Et_2O$, NaOH, H_2O_2; *ii*: Li, ethylenediamine, *i*-PrOH; *iii*: Li, ethylenediamine.

The reduction of aromatic alcohols **2** and **3** to cyclohexadiene derivatives **10** and **15** was carried out at a substrate–lithium–isopropyl alcohol–ethylenediamine ratio of 1 : 6 : 12 : 0.5. The yields of 2-(2-methylcyclohexa-1,4-dien-1-yl)propan-1-ol (**10**) and 2-(4-methylcyclohexa-1,4-dien-1-yl)propan-1-ol (**15**) were 56 and 42%, respectively. When the ratio **2** (**3**)–Li–ethylenediamine was 1 : 8 : 20 (no isopropyl alcohol was added), *o*-cimen-9-ol **2** was converted into a mixture of 2-(2-methylcyclohex-1-en-1-yl)propan-1-ol (**11**) and 2-(6-methylcyclohex-1-en-1-yl)propan-1-ol (**12**) at a ratio of 4 : 3 with an overall yield of 92%, whereas *p*-cimen-9-ol **3** gave rise to 85% of a mixture of 2-(4-methylcyclohex-3-en-1-yl)propan-1-ol (**16**) and 2-(4-methylcyclohex-1-en-1-yl)propan-1-ol (**17**) at a ratio of 1 : 9. Under analogous conditions, alcohol **1** was reduced to a mixture of (2-isopropylcyclohex-1-en-1-yl)methanol (**18**) and (2-isopropylcyclohex-2-en-

Scheme 4.



i: Li, ethylenediamine; *ii*: Li, ethylenediamine, *i*-PrOH.

1-yl)methanol (**19**) at a ratio of 1:3.5 (overall yield 75%; Scheme 4).

The reduction of *o*-cimen-7-ol **1** with Li–*i*-PrOH–ethylenediamine was accompanied by elimination of the hydroxy group with formation of a mixture of unsaturated hydrocarbons **20**–**24**. This result was consistent with published data [12–14] on the Birch reduction of structurally related compounds, and the product composition was similar to that obtained in the reduction of *o*-cimene with the same system [9] (yield 90%, conversion 85%, **20**–**21**–**22**–**23**–**24** ratio 6:1:2:1:1).

Thus, the reducing system lithium–ethylenediamine can be used for the synthesis of primary unsaturated alcohols of the *o*- and *p*-menthane series from aromatic precursors. 1,4-Dihydro derivatives can be obtained by the reduction of *o*- and *p*-cimen-9-ols with lithium–isopropyl alcohol–ethylenediamine.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from thin films. The UV spectra of solutions in ethanol were measured on an SF-4D spectrophotometer. The ^{1}H NMR spectra were recorded on a Varian HA-100 spectrometer using carbon tetrachloride as solvent and tetramethylsilane (TMS) as internal standard. The ^{13}C NMR spectra were obtained on a Bruker WH-90 instrument at 22.63 MHz from solutions in $CDCl_3$ ($c \approx 30$ vol %) with TMS as internal standard (pulse duration 9 s, ~60°; pulse delay 12 s). Alcohols **1**, **2**, **7**, **10**–**12**, **18**, and **19** were analyzed on an LKhM-8MD chromatograph equipped with a thermal conductivity detector and a 3000×3-mm column packed with 5% of XE-60 on Chromaton N-AW-DMCS (0.20–0.25 mm); oven temperature 135°C, carrier gas nitrogen, flow rate 40 mL/min; relative retention time: 1.00 (**1**), 0.92 (**7**), 0.61 (**18**), 0.49 (**19**); oven temperature 160°C, relative retention time: 1.00 (**2**), 0.83 (**10**), 0.60 (**11**), 0.54 (**12**). Compounds **3** and **15**–**17** were analyzed on an LKhM-8MD model 3 chromatograph (flame ionization detector, 3000×3-mm column packed with 5% of XE-60 on Chromaton N-AW–DMCS (0.20–0.25 mm); oven temperature 150°C, carrier gas nitrogen, flow rate 50 mL/min; relative retention time: 1.00 (**3**), 0.91 (**15**), 0.61 (**16**), 0.51 (**17**).

Tertiary aromatic alcohols **9** and **14** synthesized previously [15, 16] were used in the GLC analysis of the hydroboration–oxidation products of **8** and **9**. Compounds **4a** and **4b** were commercial products. Alcohols **2**, **5a**, and **5b** were prepared as described in [17].

(2-Isopropylphenyl)methanol (1) was synthesized by reduction of 14.8 g (0.10 mol) of unsaturated alcohol **7** with 13.8 g (0.60 mol) of finely cut metallic sodium in 130 mL (1.80 mol) of propan-1-ol on stirring at 100°C, followed by conventional treatment. Yield 10.00 g (71%), purity 98% (GLC), bp 93–94°C (5 mm), d_4^{20} = 0.9305, n_D^{20} = 1.5202; MR_D = 46.59, calcd. 46.31. IR spectrum, ν, cm^{-1}: 3340, 1040 (OH), 3040, 1380, 1365 [$CH(CH_3)_2$]. ^{1}H NMR spectrum, δ, ppm: 1.18 d (6H, CH_3, J = 7 Hz), 2.80 m [1H, C**H**$(CH_3)_2$], 3.26 q (CH_2), 4.43 (1H, OH), 7.07 m (4H, H_{arom}). Found, %: C 79.80; H 9.11. $C_{10}H_{14}O$. Calculated, %: C 79.96; H 9.39.

2-(2-Methylphenyl)propan-1-ol (2). A solution of 30.2 mL (0.24 mol) of boron trifluoride–diethyl ether complex in 40 mL of anhydrous dioxane was added dropwise at 30–35°C to a mixture of 7.6 g (0.20 mol)

of $NaBH_4$, 300 mL of anhydrous dioxane, and 79.2 g (0.60 mol) of compound **8**. The mixture was stirred for 2 h at that temperature, excess $NaBH_4$ was decomposed by treatment with 60 mL of water, 64 mL of a 3 N solution of sodium hydroxide was added at 30–40°C, and 64 mL of 30% H_2O_2 was then added dropwise, maintaining the temperature not higher than 45°C. The mixture was stirred for 20 min, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×100 mL). The extracts were combined with the organic phase and dried over Na_2SO_4, the solvent was distilled off, and the residue, 65.00 g (74%), was subjected to vacuum distillation to isolate 44.00 g (50%) of **2**. Purity 99% (GLC), bp 105–106°C (6 mm), d_4^{20} = 1.0034, n_D^{20} = 1.5265; MR_D 45.99, calcd. 46.31; published data [18]: bp 135–136°C (24 mm). IR spectrum, ν, cm^{-1}: 3460, 1040 (OH), 3072, 3085, 1680, 1590, 1380 (CH_3). ^1H NMR spectrum, δ, ppm: 1.17 d (3H, C**H**$_3$CH, J = 6.8 Hz), 1.87 s (1H, OH), 2.31 s (3H, 2-CH_3), 3.21 m (1H, C**H**CH_3), 3.64 m (2H, CH_2), 7.21 m (4H, H_{arom}). Found, %: C 79.82; H 9.18. $C_{10}H_{14}O$. Calculated, %: C 79.96; H 9.39.

2-(2-Methylphenyl)propyl 2-nitrobenzoate. mp 55–56°C (from EtOH–petroleum ether, 3 : 1). Found, %: C 68.41; H 5.84; N 4.56. $C_{17}H_{17}NO_4$. Calculated, %: C 68.22; H 5.72; N 4.68.

2-(2-Methylphenyl)propyl 3,5-dinitrobenzoate. mp 115.5–116.5°C (from pentane). Found %: C 59.32; H 4.80; N 7.85. $C_{17}H_{16}N_2O_6$. Calculated, %: C 59.30; H 4.68; N 8.14.

2-(4-Methylphenyl)propan-1-ol (3) was synthesized as described above for *ortho* isomer **2** by adding a solution of 12 mL (0.11 mol) of boron trifluoride–diethyl ether complex in 30 mL of anhydrous dioxane to a mixture of 3.00 g (0.08 mol) of $NaBH_4$, 100 mL of anhydrous dioxane, and 32.00 g (0.24 mol) of *p*-tolylpropene **13**. Decomposition of intermediate organoborane with 25 mL of 3 N NaON and 25 mL of 30% H_2O_2 gave 30.00 g (90%) of a mixture of compounds **3** and **14**, which was subjected to vacuum distillation to isolate 20.00 g (60%) of **3** with a purity of 99% (GLC), bp 97–98°C (5 mm), d_4^{20} = 0.9848, n_D^{20} = 1.5265; MR_D = 46.41, calcd. 46.31. IR spectrum, ν, cm^{-1}: 3390, 1045 (OH), 3095, 3060, 1660, 825 (1,4-C_6H_4), 1375 (CH_3). ^1H NMR spectrum, δ, ppm: 1.10 d (3H, C**H**$_3$CH, J = 7.04 Hz), 2.14 s (1H, OH), 2.17 s (3H, 4-CH_3), 2.67 m (1H, CH), 3.41 m (2H, CH_2), 6.43 m (4H, H_{arom}). Found, %: C 79.66; H 9.03. $C_{10}H_{14}O$. Calculated, %: C 79.96; H 9.39.

2-(2-Chlorophenyl)propan-2-ol (5a). A 38% solution of ammonium chloride, 58 mL, was added at –5°C to the product obtained by reaction of 26.50 g (0.14 mol) of ester **4a** in 35 mL of anhydrous diethyl ether with methylmagnesium iodide [prepared from 9.1 g (0.37 mol) of magnesium and 53.3 g (0.37 mol) of freshly distilled methyl iodide in 85 mL of anhydrous diethyl ether]. The ether layer was separated by decanting, and the pasty precipitate was extracted with diethyl ether (3×35 mL). The extracts were combined, dried over Na_2SO_4, and evaporated. Yield 19.40 g (82%), purity 95% (GLC), bp 99–100°C (5 mm), d_4^{20} = 1.1576, n_D^{20} = 1.5420; MR_D 46.43, calcd. 46.55; published data [19]: mp 23.7°C, bp 79.2°C (2.2 mm), n_D^{20} = 1.5416. IR spectrum, ν, cm^{-1}: 3460, 1175 (OH), 1370, 1385 [$C(CH_3)_2$], 690 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.64 s (6H, CH_3), 2.46 s (1H, OH), 6.9–7.7 m (4H, H_{arom}). Found, %: C 63.00; H 6.42; Cl 20.71. $C_9H_{11}ClO$. Calculated, %: C 63.35; H 6.50; Cl 20.78.

2-(2-Chlorophenyl)propan-2-yl benzoate. mp 113–114°C (from EtOH). Found, %: C 69.35; H 5.20; Cl 12.81. $C_{16}H_{15}ClO_2$. Calculated, %: C 69.95; H 5.50; Cl 12.90.

2-(2-Chlorophenyl)propan-2-yl 2-nitrobenzoate. mp 55–56°C (from EtOH–petroleum ether, 3 : 1). Found, %: C 60.22; H 4.30; Cl 10.95; N 4.20. $C_{16}H_{14}NClO_4$. Calculated, %: C 60.10; H 4.41; Cl 11.09. N 4.38.

2-(2-Chlorophenyl)propan-2-yl 3,5-dinitrobenzoate. mp 88–89°C (from pentane). Found, %: C 52.30; H 3.61; Cl 9.60; N 7.52. $C_{16}H_{13}N_2ClO_6$. Calculated, %: C 52.69; H 3.59; Cl 9.72; N 7.69.

2-(2-Bromophenyl)propan-2-ol (5b) was synthesized in a similar way from 100.00 g of ester **4b**. Yield 65.00 g (71%), purity 99% (GLC), bp 91–92°C (1.5 mm), d_4^{20} = 1.4212, n_D^{20} = 1.5665; MR_D 49.41, calcd. 49.55; published data [19]: bp 112°C (5.2 mm), n_D^{20} = 1.5634. IR spectrum, ν, cm^{-1}: 3470, 1180 (OH), 1390, 1370 [$C(CH_3)_2$], 690 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.69 s (6H, CH_3), 2.57 s (1H, OH), 7.06–7.65 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 146.4 (C^1), 120.1 (C^2), 134.7 (C^3), 127.1 (C^4, C^5), 127.9 (C^6), 73.0 (CHO), 29.5 (CH_3). Found, %: C 50.01; H 5.20; Br 36.85. $C_9H_{11}BrO$. Calculated, %: C 50.26; H 5.16; Br 37.15.

2-(2-Bromophenyl)propan-2-yl benzoate. mp 115–116°C (from EtOH). Found, %: C 59.95; H 4.65; Br 25.12. $C_{16}H_{15}BrO_2$. Calculated, %: C 60.20; H 4.75; Br 25.03.

2-(2-Bromophenyl)propan-2-yl 4-nitrobenzoate. mp 67–68°C (from EtOH–petroleum ether, 3 : 1). Found, %: C 52.45; H 4.00; Br 21.72; N 3.71. $C_{16}H_{14}BrNO_4$. Calculated, %: C 52.77; H 3.87; Br 21.94; N 3.85.

2-(2-Bromophenyl)propan-2-yl 3,5-dinitrobenzoate. mp 84–85°C (from pentane). Found, %: C 47.60; H 3.05; Br 19.20; N 28.21. $C_{16}H_{13}BrN_2O_6$. Calculated, %: C 46.98; H 3.19; Br 19.53; N 28.01.

2-(2-Chlorophenyl)propene (6a). A mixture of 15.90 g (0.10 mol) of alcohol **5a** and 15 g (0.12 mol) of phthalic anhydride was heated for 24 h at 125–130°C. Vacuum distillation of the resulting oily material (12.80 g) gave 11.30 g (79%) of **6a**. Purity 98% (GLC), bp 57–58°C (5 mm), d_4^{20} = 1.0598, n_D^{20} = 1.5330; MR_D 44.69, calcd. 44.56; published data [20]: bp 72–73°C (14 mm), n_D^{25} = 1.5324. IR spectrum, ν, cm^{-1}: 3085, 1642, 910 (C=CH_2), 1370 (CH_3), 730 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.06 s (3H, CH_3), 4.90 m and 5.12 m (2H, =CH_2), 7.92–7.30 m (4H, H_{arom}). Found, %: C 70.68; H 6.02; Cl 23.13. C_9H_9Cl. Calculated, %: C 70.83; H 5.94; Cl 23.23.

2-(2-Bromophenyl)propene (6b) was synthesized in a similar way by dehydration of 65.00 g (0.33 mol) of compound **5b** with 49.50 g (0.36 mol) of phthalic anhydride. The oily crude product, 49.50 g, was distilled under reduced pressure. Yield 46.50 g (77%), purity 98% (GLC), bp 64–65°C (1 mm), d_4^{20} = 1.5365, n_D^{20} = 1.5595; MR_D 47.50, calcd. 47.46; published data [21]: bp 55–65°C (0.9 mm), n_D^{27} = 1.553. IR spectrum, ν, cm^{-1}: 3090, 1648, 910 (C=CH_2), 740 (C–Br). ^{1}H NMR spectrum, δ, ppm: 2.07 m (3H, CH_3), 4.95 m and 5.23 m (2H, =CH_2), 7.03–7.37 m (3H, H_{arom}), 7.58 d (1H, 3-H, J = 7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 145.5 (C^1), 128.1 (C^2), 129.5 (C^3, C^4), 126.9 (C^5), 132.8 (C^6), 121.7 (C^7), 116.0 (C^8), 23.5 (CH_3). Found, %: C 54.51; H 4.40; Br 40.35. C_9H_9Br. Calculated, %: C 54.85; H 4.60; Br 40.55.

(2-Isopropenylphenyl)methanol (7). Formaldehyde generated by depolymerization of 30.00 g (1.00 mol) of paraformaldehyde (preliminarily dried over P_2O_5) at 170–180°C was passed in a stream of nitrogen through a solution of Grignard reagent prepared from 17.00 g (0.09 mol) of compound **6b** in 150 mL of anhydrous diethyl ether and 2.80 g (0.12 mol) of magnesium, maintaining the temperature at 40°C. The mixture was treated with 80 g of finely crushed ice, the yellow precipitate was dissolved in 80 mL of a 2 N solution of sodium sulfate, and the solution was steam-distilled. The distillate was extracted with diethyl ether (3×50 mL), and the combined extracts were dried over Na_2SO_4 and evaporated. Yield 8.00 g (66%), purity 98% (GLC), bp 103–104°C (5 mm), d_4^{20} = 1.0193, n_D^{20} = 1.5470; MR_D 46.11, calcd. 45.84. IR spectrum, ν, cm^{-1}: 3360, 1050 (OH), 3080, 1658, 910 (C=CH_2), 3040, 730 (1,2-C_6H_4). ^{1}H NMR spectrum, δ, ppm: 2.04 (3H, CH_3), 2.14 s (1H, OH), 4.63 s (2H, C**H**$_2$OH), 4.91 q and 5.23 q (2H, =CH_2, J = 1.4 Hz), 7.11–7.59 m (4H, H_{arom}). Found, %: C 80.79; H 7.94. $C_{10}H_{12}O$. Calculated, %: C 81.04; H 8.16.

Reduction of compounds 1–3 (*general procedures*). *a*. A mixture of 75.00 g (0.50 mol) of compound **2** or **3**, 360 g (6.00 mol) of isopropyl alcohol, and 15.00 g (0.25 mol) of anhydrous ethylenediamine was heated under stirring to 85–95°C, the heating bath was removed, and 20.70 g (3.00 mol) of finely cut lithium was added over a period of 30 min on cooling with tap water. After complete dissolution of lithium, the mixture was stirred for 20 min, cooled to room temperature, and diluted with 0.5 L of water. The organic phase was separated, washed with water (3×200 mL), and dried over Na_2SO_4. The yield of the reduction products was 75–92%, the conversion being 54% (**2**) and 68% (**3**). Fractionation in a column with 60 theoretical plates gave primary cyclohexadiene alcohols which did not absorb above λ 225 nm in the UV spectrum.

2-(2-Methylcyclohexa-1,4-dien-1-yl)propan-1-ol (10). Yield 56%, purity 90% (GLC), bp 83–84°C (1 mm), d_4^{20} = 0.9665, n_D^{20} = 1.4992; MR_D 46.28, calcd. 46.77. IR spectrum, ν, cm^{-1}: 3360, 1035 (OH), 3065, 3035, 1695, 980, 670 (C=C, C=CH), 1380 (CH_3). ^{1}H NMR spectrum, δ, ppm: 1.35 d (3H, $C^{10}H_3$, J = 6.9 Hz), 1.62 s (3H, C^7H_3), 5.70–5.40 m (2H, CH=CH), 3.65–3.40 m (3H, CH_2O, CH), 2.60 s (1H, OH), 2.40–1.80 m (4H, CH_2). Found, %: C 78.49; H 10.90. $C_{10}H_{16}O$. Calculated, %: C 78.90; H 10.56.

2-(4-Methylcyclohexa-1,4-dien-1-yl)propan-1-ol (15). Yield 42%, purity 92% (GLC), bp 79–80°C (1 mm), d_4^{20} = 0.9686, n_D^{20} = 1.4986; MR_D 46.12, calcd. 46.77. IR spectrum, ν, cm^{-1}: 3380, 1045 (OH), 3025, 1660, 825 (C=CH), 1380 (CH_3). ^{1}H NMR spectrum, δ, ppm: 0.87–1.05 m (3H, $C^{10}H_3$), 1.57 m (3H, C^7H_3), 2.47 m (5H, CH_2, OH), 3.26–3.88 m (3H, CH, CH_2O), 5.33 m (2H, C=CH). Found, %: C 79.10; H 10.40. $C_{10}H_{16}O$. Calculated, %: C 78.90; H 10.56.

b. A mixture of 7.00 g (0.50 mol) of alcohol **1**–**3** and 600.00 g (10.00 mol) of anhydrous ethylenediamine was heated to 90–100°C, and 27.40 g (4.00 mol) of finely cut lithium was added. As the metal dis-

solved, the mixture turned bright blue. It was heated for 48 h at 90°C until the blue color disappeared completely, cooled, and treated with 0.5 L of water. The organic phase was separated, the aqueous phase was extracted with diethyl ether (3×100 mL), the extracts were combined with the organic phase and dried over Na_2SO_4, and the solvent was distilled off. Yield 70–75%, conversion 75% (**1**), 66% (**2**), 80% (**3**). Fractionation in a column with 60 theoretical plates gave primary menthene alcohols.

2-(2-Methylcyclohex-1-en-1-yl)propan-1-ol (11). Purity 98% (GLC), bp 78–79°C (3 mm), d_4^{20} = 0.9463, n_D^{20} = 1.4910; MR_D 47.21, calcd. 47.24. IR spectrum, ν, cm^{-1}: 3370, 1040 (OH), 1665 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.91 d (3H, C^{10}H$_3$, J = 6.8 Hz), 1.50–2.15 m (9H, OH, CH$_2$), 1.65 s (3H, C^{7}H$_3$), 2.96 m (1H, CH), 3.44 m and 3.51 m (2H, CH$_2$O). Found, %: C 78.08; H 11.55. $C_{10}H_{18}O$. Calculated, %: C 77.87; H 11.76.

2-(6-Methylcyclohex-1-en-1-yl)propan-1-ol (12). Purity 98% (GLC), bp 73–74°C (5 mm), d_4^{20} = 0.9448, n_D^{20} = 1.4880; MR_D 47.03, calcd. 47.24. IR spectrum, ν, cm^{-1}: 3370, 1035 (OH), 3060, 1675, 815 (C=CH). ^{1}H NMR spectrum, δ, ppm: 0.99 d (3H, C^{7}H$_3$, J = 7.0 Hz), 1.03 d (3H, C^{10}H$_3$, J = 6.8 Hz), 1.45–2.45 m (7H, OH, CH$_2$), 2.90 m (1H, CH), 3.45 m and 3.53 m (2H, CH$_2$O), 5.51 m (1H, C=CH). Found, %: C 77.59; H 11.90. $C_{10}H_{18}O$. Calculated, %: C 77.87; H 11.76.

2-(4-Methylcyclohex-3-en-1-yl)propan-1-ol (16). Purity 95% (GLC), bp 99–100°C (1 mm), d_4^{20} = 0.9442, n_D^{20} = 1.4845; MR_D 46.90, calcd. 47.24. IR spectrum, ν, cm^{-1}: 3055, 1035 (OH), 3060, 1675, 815 (C=CH). ^{1}H NMR spectrum, δ, ppm: 0.79–2.64 m (8H, CH$_2$, CH), 0.86 d (3H, CHC**H**$_3$, J = 6.75 Hz), 1.65 s (3H, CH$_3$C=), 2.79 s (1H, CH), 3.38 m (2H, CH$_2$O), 5.30 m (1H, C=CH). Found, %: C 78.01; H 11.92. $C_{10}H_{18}O$. Calculated, %: C 77.87; H 11.76.

2-(4-Methylcyclohex-1-en-1-yl)propan-1-ol (17). Purity 95% (GLC), bp 68–70°C (7 mm), d_4^{20} = 0.9346, n_D^{20} = 1.4820; MR_D 47.04, calcd. 47.24; published data [22]: bp 105–109°C (10 mm). IR spectrum, ν, cm^{-1}: 3390, 1040 (OH), 3060, 1665, 820 (C=CH), 1375 (CH$_3$). ^{1}H NMR spectrum, δ, ppm: 0.81–0.98 m (6H, CH$_3$), 1.09–2.21 m (8H, CH, CH$_2$), 2.68 m (1H, OH), 3.29 m (2H, CH$_2$O), 5.33 m (1H, C=CH). Found, %: C 77.58; H 11.45. $C_{10}H_{18}O$. Calculated, %: C 77.87; H 11.76.

(2-Isopropylcyclohex-1-en-1-yl)methanol (18). Purity 96% (GLC), bp 90–91°C (5 mm), d_4^{20} = 0.9517, n_D^{20} = 1.4930; MR_D 47.10, calcd. 47.24. IR spectrum, ν, cm^{-1}: 3370, 1040 (OH), 1665 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.91 d (3H, C^{10}H$_3$, J = 6.8 Hz), 1.50–2.15 m (9H, OH, CH$_2$), 1.65 s (3H, C^{7}H$_3$), 2.96 m (1H, CH), 3.44 m and 3.51 m (2H, CH$_2$O). Found, %: C 77.43; H 11.58. $C_{10}H_{18}O$. Calculated, %: C 77.87; H 11.76.

(2-Isopropylcyclohex-2-en-1-yl)methanol (19). Purity 92% (GLC), bp 85–87°C (5 mm), d_4^{20} = 0.9529, n_D^{20} = 1.4900; MR_D 46.80, calcd. 47.24. IR spectrum, ν, cm^{-1}: 3370, 1040 (OH), 1665 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.91 d (3H, C^{10}H$_3$, J = 6.8 Hz), 1.50–2.15 m (9H, OH, CH$_2$), 1.65 s (3H, C^{7}H$_3$), 2.96 m (1H, CH), 3.44 m and 3.51 m (2H, CH$_2$O). Found, %: C 78.34; H 11.38. $C_{10}H_{18}O$. Calculated, %: C 77.87; H 11.76.

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