Synthesis of new *o*-isobornylphenol derivatives

I. Yu. Chukicheva,[a]★ E. V. Buravlev,[a] L. V. Spirikhin,[b] A. V. Churakov,[c] and A. V. Kutchin[a]

[a]*Institute of Chemistry, Komi Science Center, Ural Branch of the Russian Academy of Sciences, 48 ul. Pervomaiskaya, 167982 Syktyvkar, Russian Federation. Fax: +7 (821 2) 21 8477. E-mail: chukicheva-iy@chemi.komisc.ru*
[b]*Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 69 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066. E-mail: chemorg@anrb.ru*
[c]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 954 1279. E-mail: churakov@igic.ras.ru*

The hydroxymethyl, pyridinium methyl, or dialkylaminomethyl groups were introduced into the aromatic ring of the *o*-isobornylphenol molecule.

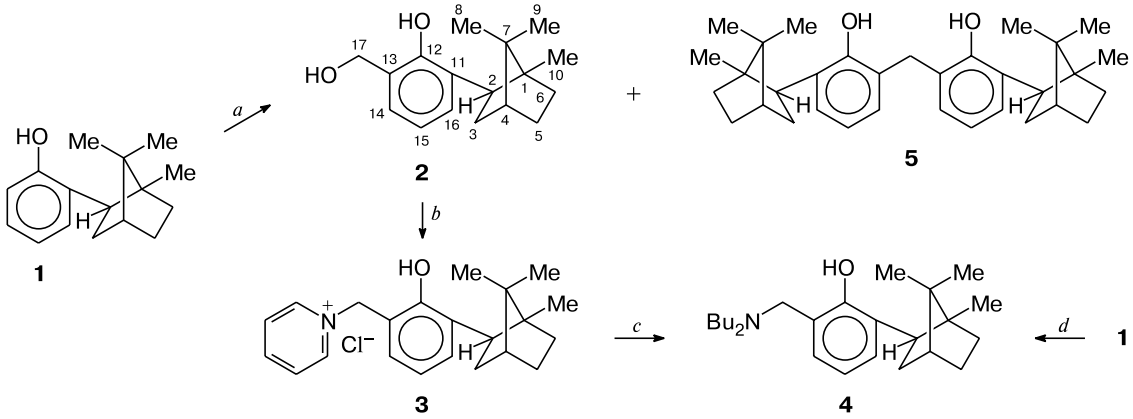
Key words: *o*-isobornylphenol, terpenoids, Mannich reaction, amines, phenols, formaldehyde, aminomethylation, hydroxymethylation.

Earlier,[1] we have reported the synthesis of *o*-isobornylphenol (**1**) containing a chiral substituent. Alkylation of phenol with optically active camphene afforded racemic terpenylphenol, which was formed as a result of Wagner—Meerwein—Claisen cascade rearrangements. Nevertheless, it is of interest to prepare optically active *o*-isobornylphenol. One of approaches to the solution of the problem of resolution of *o*-isobornylphenol (**1**) into optical isomers is based on additional functionalization of this compound. In the present study, we synthesized new derivatives of compound **1**, *viz.*, alcohol **2**, pyridinium salt **3**, and amine **4**, and examined side processes associated with the preparation of these compounds (Scheme 1).

Alcohol **2** was synthesized in 71% yield by refluxing *o*-isobornylphenol (**1**) and paraformaldehyde in toluene in the presence of boric acid.

The three-dimensional structure of compound **2** was established by X-ray diffraction analysis (Fig. 1). The bond lengths and bond angles are given in Table 1. The structure contains two crystallographically independent molecules characterized by very similar geometric parameters (bond lengths and bond angles) but different spatial orientations of the CH_2OH groups. The corresponding C(12)—C(13)—C(17)—O(12) and C(32)—C(33)—C(37)—O(22) torsion angles are −50.0(4) and −56.2(5)°, respectively. In both molecules, the phe-

Scheme 1



Reagents and conditions: *a*. CH_2O, H_3BO_3, toluene, 110 °C. *b*. $SOCl_2$, Py, 110 °C. *c*. Bu_2NH, MeOH, 65 °C. *d*. Bu_2NH, CH_2O, PhH, 80 °C.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1754—1757, October, 2006.

1066-5285/06/5510-1819

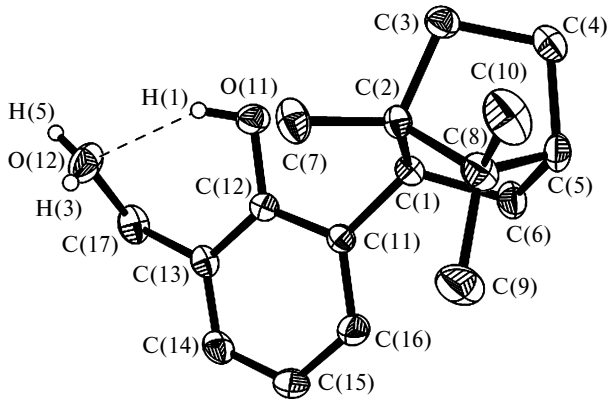


Fig. 1. Molecular structure of compound **2** (one crystallographically independent molecule is shown). The hydrogen atoms (except for those of the hydroxy groups) are omitted. The positions of the disordered H(3) and H(5) atoms are half occupied.

nol H(1) and H(2) atoms are involved in intramolecular hydrogen bonding with the oxygen atoms of the CH_2OH groups. In turn, the hydrogen atoms of these groups disordered over two positions are involved in intermolecular hydrogen bonds to form chains extended along the crystallographic axis *b*. One system of the half-occupied positions of the H(3), H(4), H(5), and H(6) atoms and hydrogen bonds involving these atoms are shown in Fig. 2. Another system is symmetrically dependent, and the same oxygen atoms are linked to each other by this system. The

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compound **2** (two independent molecules)

Molecule **2**A		Molecule **2**B	
Bond	*d*/Å	Bond	*d*/Å
O(11)—C(12)	1.361(3)	O(21)—C(32)	1.374(4)
O(12)—C(17)	1.431(4)	O(22)—C(37)	1.380(6)
C(1)—C(11)	1.521(4)	C(21)—C(31)	1.520(4)
C(13)—C(17)	1.489(4)	C(33)—C(37)	1.511(5)
Angle	ω/deg	Angle	ω/deg
C(12)—O(11)—H(1)	107(2)	C(32)—O(21)—H(2)	121(4)
C(17)—O(12)—H(3)	109.5	C(37)—O(22)—H(4)	109.5
C(17)—O(12)—H(5)	113.2	C(37)—O(22)—H(6)	117.8
O(12)—C(17)—C(13)	111.9(3)	O(22)—C(37)—C(33)	114.0(3)

geometric parameters of the hydrogen bonds are given in Table 2. The relative configuration of the C(1) and C(2) centers is 1*R**,2*S**.

In addition to alcohol **2**, unconsumed *o*-isobornylphenol (**1**) (9.5%) and an insignificant amount of the cross-linking product of two terpenylphenol molecules, *viz.*, compound **5** (6%) as a mixture of diastereomers **5′** and **5″** in a ratio of 2 : 1, were isolated by column chromatography. The diastereomers were identified by ^{1}H NMR spectroscopy. The protons of the CH_2 group in *meso* form **5′** are diastereotopic and give two signals, whereas these protons in racemate *dl*-**5″** are equivalent and give one signal.[2]

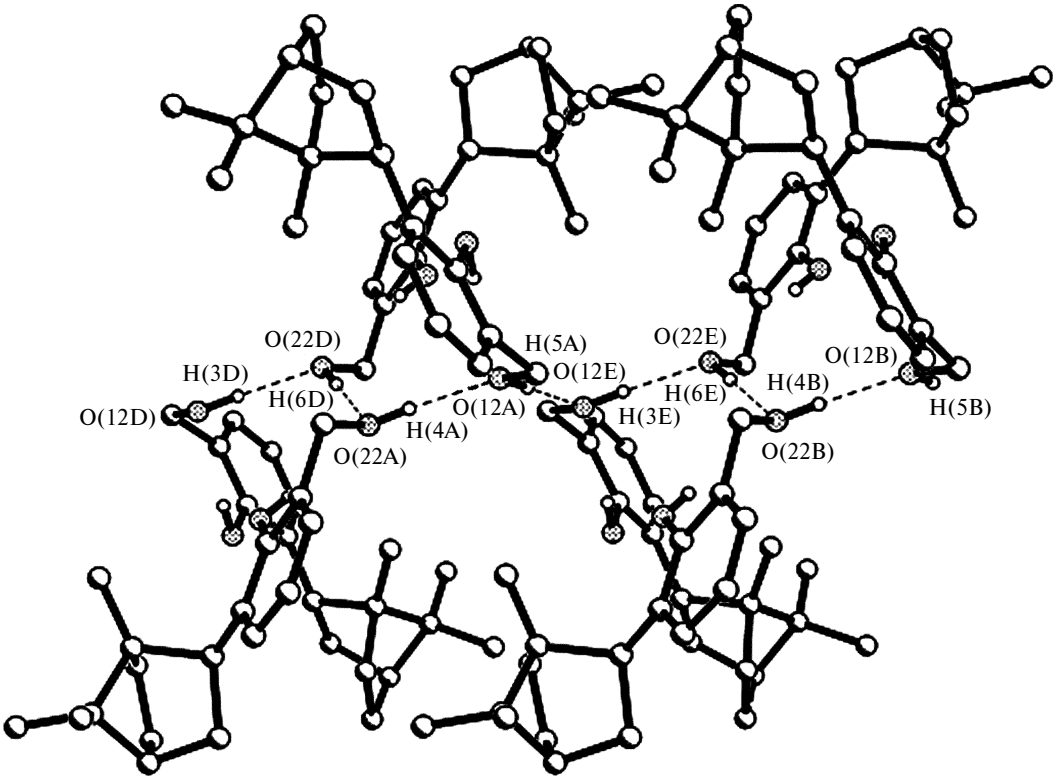
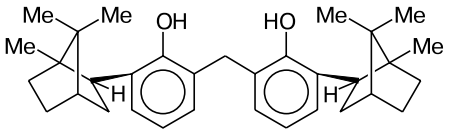


Fig. 2. Hydrogen-bonded chains of the molecules in the structure of **2** extended along the crystallographic axis *b*.

Table 2. Geometric characteristics (bond lengths (*d*) and bond angles (ω)) of the hydrogen bonds in the structure of **2** (D is a donor and A is an acceptor)

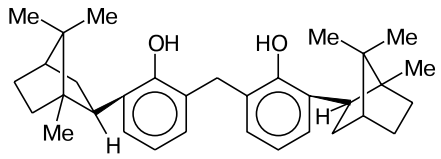
Bond D—H...A	*d*/Å			ω(D—H...A) /deg
	D—H	H...A	D...A	
O(11)—H(1)...O(12)	0.85(4)	2.00(4)	2.743(4)	146(3)
O(21)—H(2)...O(22)	0.76(5)	2.27(6)	2.805(5)	127(5)
O(12)—H(3)...O(22)	0.85	1.80	2.630(6)	163.2
O(22)—H(4)...O(12)	0.85	1.79	2.630(6)	168.3
O(12)—H(5)...O(12)#1	0.85	1.81	2.663(5)	179.1
O(22)—H(6)...O(22)#2	0.85	2.00	2.846(7)	178.4

Note. The symmetry codes: #1 — $-x$, $-y+3$, $-z$; #2 — $-x$, $-y+2$, $-z$.

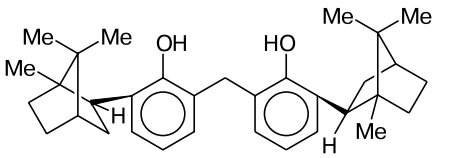


R,*S*

5′



S,*S*



R,*R*

5″

The reaction of alcohol **2** with thionyl chloride in pyridine produced pyridinium salt **3** in 98% yield. Heating of the latter with dibutylamine in methanol afforded tertiary amine **4** in 38% yield (see Scheme 1).

Amine **4** was also directly synthesized in 96% yield by the Mannich reaction[3] under reflux of *o*-isobornylphenol (**1**) in benzene in the presence of paraformaldehyde and dibutylamine.

The structures of the newly formed compounds **2—5** were confirmed by IR spectroscopy, NMR spectroscopy, and elemental analysis. In the transformations under study, the structure of the terpene fragment is retained.[4,5]

Experimental

The IR spectra were recorded on a MIR-8000 Fourier-transform spectrometer in KBr pellets (solids) and a thin layer (liquids). The ^{1}H and ^{13}C NMR spectra were measured on Bruker AMX-400 (400 MHz) and Bruker AM-300 (300 MHz) spectrometers in $CDCl_3$. The assignment of the signals was made using ^{13}C JMOD experiments. The melting points were measured on a Kofler hot-stage apparatus.

The course of the reactions was monitored by TLC on Sorbfil plates using hexane—Et_2O, 4 : 1, and $CHCl_3$—MeOH—NH_3 (conc.), 100 : 10 : 1, solvent systems. To detect the compounds, the plates were treated with a $KMnO_4$ solution (15 g of $KMnO_4$, 300 mL of H_2O, and 0.5 mL of concentrated H_2SO_4). The spots of amines were visualized using a 0.5% ninhydrin solution in ethanol with the addition of glacial AcOH (3%, v/v) followed by heating of the plates to 100—120 °C.

Benzene and toluene were dried over $CaCl_2$ and distilled over sodium metal. Petroleum ether (the fraction with b.p. 65—70 °C) was used. Freshly distilled thionyl chloride, pyridine, dibutylamine, methanol, chloroform, and hexane were used. Paraformaldehyde and boric acid were of reagent grade quality.

2-(Hydroxymethyl)-6-*exo*-(1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl)phenol (2). According to a known procedure developed for the synthesis of benzyl alcohols,[6] a mixture of *o*-isobornylphenol (**1**) (2 g, 8.7 mmol), boric acid (0.83 g, 0.13 mmol), and paraformaldehyde (0.4 g, 0.13 mmol) in toluene (30 mL) was refluxed in a flask equipped with a Dean—Stark trap for 60 h to provide azeotropic removal of water. Paraformaldehyde was added portionwise (0.1 g, 0.03 mmol per portion) at 4 h intervals. After completion of the reaction, excess toluene was removed under reduced pressure. Water (30 mL) was added to the residue, and the mixture was kept for 12 h to accomplish hydrolysis of the intermediate salicylylic borate. Then the mixture was extracted with diethyl ether (3×20 mL), the combined extracts were washed with water (30 mL), the solvent was removed under reduced pressure, and the residue was chromatographed on a column (Silicagel L 100/200μ, a gradient of Et_2O in light petroleum as the eluent). Alcohol **2** was obtained in a yield of 1.55 g (71%); the starting phenol **1**, in a yield of 0.19 g (9.5%); and product **5**, in a yield of 0.06 g (6%).

Compound 2, m.p. 80—84 °C. Found (%): C, 78.72; H, 9.37. $C_{17}H_{24}O_2$. Calculated (%): C, 78.42; H, 9.29. IR (KBr), ν/cm^{-1}: 3438 (OH of phenol), 3596 (OH of alcohol), 1183 (C—O), 2951, 2876, 1456 (Me, CH_2), 3029, 758 (=C—H), 1595 (C=C). ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 0.81 (s, 3 H, C(10)H_3); 0.87 (s, 3 H, C(9)H_3); 0.93 (s, 3 H, C(8)H_3); 1.36—1.43 (m, 1 H, H(5)); 1.50—1.70 (m, 3 H, H(3) + 2 H(6)); 1.86—1.88 (m, 2 H, H(5), H(4)); 2.15—2.24 (m, 1 H, H(3)); 2.44 (m, 1 H, C(17)—OH); 3.30 (t, 1 H, H(2), J = 8.9 Hz); 4.75 (dd, 1 H, H(17), J = 12.7 Hz, J = 3.7 Hz); 4.89 (dd, 1 H, H(17), J = 12.7 Hz, J = 4.6 Hz); 6.81—6.88 (m, 2 H, H(14), H(16)); 7.31 (dd, 1 H, H(15), J = 7.1 Hz, J = 1.6 Hz); 7.51 (s, 1 H, C(12)—OH). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 12.30 (C(10)); 20.33 (C(9)); 21.40 (C(8)); 27.47 (C(5)); 33.99 (C(3)); 39.71 (C(6)); 44.82 (C(2)); 45.60 (C(4)); 47.91 (C(7)); 49.79 (C(1)); 64.98 (C(17)); 118.94 (C(16)); 123.74 (C(13)); 125.07 (C(14)); 128.15 (C(15)); 131.25 (C(11)); 155.37 (C(12)).

Bis{2-hydroxy-3-*exo*-(1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)phenyl}methane (5), a 2 : 1 mixture of diastereomers, m.p. 160—163 °C. Found (%): C, 84.02; H, 9.68. $C_{33}H_{44}O_2$. Calculated (%): C, 83.85; H, 9.38. IR (KBr), ν/cm^{-1}: 3571, 3384 (OH), 1211, 1001 (C—O), 2953, 2876, 1456 (Me, CH_2), 3021, 747 (=C—H), 1593 (C=C).

Major diastereomer *meso*-**5′**. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 0.76 (s, 6 H, C(10)H_3, C(10′)H_3); 0.85 (s, 6 H, C(9)H_3, C(9′)H_3); 0.88 (s, 6 H, C(8)H_3, C(8′)H_3); 1.29—1.49 and 1.57—1.72 (both m, 4 H each), 1.86—1.92 (br.s, 4 H), 2.15—2.27 (m, 2 H) (H(3), H(3′), H(4), H(4′), H(5), H(5′), H(6), H(6′)); 3.06 (t, 2 H, H(2), H(2′), J = 8.7 Hz); 3.91 and 4.04 (both d, 1 H each, H(17), J = 14.6 Hz); 6.09 (s, 2 H, 2 OH); 6.84—6.89 (m, 2 H, H(15), H(15′)); 7.10—7.27 (m, 4 H, H(14), H(14′), H(16), H(16′)). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 12.32 (C(10), C(10′)); 20.11 (C(9), C(9′)); 21.29 (C(8), C(8′)); 27.49 (C(5), C(5′)); 31.52 (C(17)); 34.04 (C(3), C(3′)); 40.01 (C(6), C(6′)); 45.42 (C(2), C(2′)); 45.89 (C(4), C(4′)); 48.08 (C(7), C(7′)); 49.62 (C(1), C(1′)); 120.26 (C(16), C(16′)); 126.19 (C(13), C(13′)); 126.40 (C(14), C(14′)); 127.97 (C(15), C(15′)); 129.55 (C(11), C(11′)); 151.97 (C(12), C(12′)).

Minor diastereomer *dl*-**5″**. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 0.79 (s, 6 H, C(10)H_3, C(10′)H_3); 0.85 (s, 6 H, C(9)H_3, C(9′)H_3); 0.88 (s, 6 H, C(8)H_3, C(8′)H_3); 1.29—1.49 and 1.57—1.72 (both m, 4 H each), 1.86—1.92 (br.s, 4 H), 2.15—2.27 (m, 2 H) (H(3), H(3′), H(4), H(4′), H(5), H(5′), H(6), H(6′)); 3.06 (t, 2 H, H(2), H(2′), J = 8.7 Hz); 3.97 (s, 2 H, H(17)); 5.89 (s, 2 H, 2 OH); 6.84—6.89 (m, 2 H, H(15), H(15′)); 7.10—7.27 (m, 4 H, H(14), H(14′), H(16), H(16′)). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 12.48 (C(10), C(10′)); 20.33 (C(9), C(9′)); 21.35 (C(8), C(8′)); 27.49 (C(5), C(5′)); 31.83 (C(17)); 34.33 (C(3), C(3′)); 40.21 (C(6), C(6′)); 45.46 (C(2), C(2′)); 45.94 (C(4), C(4′)); 48.08 (C(7), C(7′)); 49.67 (C(1), C(1′)); 120.16 (C(16), C(16′)); 125.79 (C(13), C(13′)); 126.55 (C(14), C(14′)); 127.80 (C(15), C(15′)); 129.97 (C(11), C(11′)); 152.21 (C(12), C(12′)).

***N*-{2-Hydroxy-3-*exo*-(1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)benzyl}pyridinium chloride (3).** Alcohol **2** (1 g, 3.8 mmol) was dissolved in pyridine (0.34 mL, 4.9 mmol). Then thionyl chloride (0.36 mL, 4.2 mmol) was added dropwise with stirring at −10 °C, after which a precipitate formed. The reaction mixture was heated to 105 °C for 6 h until liberation of sulfur dioxide ceased (at 50 °C, dissolution of the precipitate started; at 70 °C, gas evolution started). The reaction mixture was cooled to ~20 °C, water was added, and the mixture was extracted with chloroform. The combined organic fractions were dried with anhydrous Na_2SO_4. All excess solvent was removed under reduced pressure, and compound **3** was obtained in a yield of 1.3 g (98%), m.p. 99—105 °C. Found (%): C, 73.78; H, 7.98. $C_{22}H_{28}ClNO$. Calculated (%): C, 73.83; H, 7.89. IR (KBr), ν/cm^{-1}: 3438 (OH), 1213, 1022 (C—O), 2953, 2878, 1460 (Me, CH_2), 3058, 758 (=C—H), 1634, 1582 (C=C). ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 0.56 (s, 3 H, C(10)H_3); 0.77 (s, 3 H, C(9)H_3); 0.79 (s, 3 H, C(8)H_3); 1.18—1.28 (m, 1 H), 1.37—1.58 (m, 3 H), 1.77 (br.s, 1 H), 2.02—2.10 (m, 1 H) (H(3), H(4), H(5), H(6)); 3.12—3.37 (m, 1 H, H(2)); 6.10 (d, 1 H, H(17), J = 13.7 Hz); 6.27 (d, 1 H, H(17), J = 14.1 Hz); 6.87 (t, 1 H, H(15), J = 7.6 Hz); 7.26—7.34 (m, 2 H, H(14), H(16)); 7.82 and 9.12 (both br.s, 4 H, H(18), H(19), H(21), H(22)); 8.27 (t, 1 H, H(20), J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 12.35 (C(10)); 20.30 (C(9)); 21.32 (C(8)); 27.36 (C(5)); 33.92 (C(3)); 39.36 (C(6)); 45.03 (C(2)); 45.55 (C(4)); 48.03 (C(7)); 49.88 (C(1)); 61.88 (C(17)); 120.67 (C(16)); 120.99 (C(13)); 127.58 (C(19), C(21)); 128.76 (C(14)); 130.41 (C(15)); 134.77 (C(11)); 144.59 (C(18), C(22)); 144.70 (C(20)); 155.16 (C(12)).

2-(Dibutylamino)methyl-6-{*exo*-(1,7,7-trimethylbicyclo-[2.2.1]hept-2-yl)}phenol (4). ***A.*** Pyridinium salt **3** (0.2 g, 0.56 mmol) was dissolved in methanol (2 mL). Then dibutylamine (0.09 mL, 0.56 mmol) and triethylamine (0.08 mL, 0.56 mmol) were added. The reaction mixture was refluxed for 6 h, and all excess solvent was removed under reduced pressure. The remainder was subjected to column chromatography (Silicagel L 100/200μ, a gradient of diethyl ether in light petroleum as the eluent). Amine **4** was obtained in a yield of 0.08 g (38.6%). Found (%): C, 80.98; H, 11.23. $C_{25}H_{41}NO$. Calculated (%): C, 80.80; H, 11.12. IR (thin layer), ν/cm^{-1}: 2955, 2932, 2874, 1453, 1375 (Me, CH_2), 1244, 1078 (C—N), 1213 (C—O), 1595, 1582 (C=C), 750 (=C—H). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 0.80 (s, 3 H, C(10)H_3); 0.85 (s, 3 H, C(9)H_3); 0.91 (t, 6 H, C(21)H_3, C(25)H_3, J = 7.4 Hz); 0.92 (s, 3 H, C(8)H_3); 1.25—1.39 (m, 5 H), 1.48—1.65 (m, 7 H), 1.83—1.90 (m, 2 H), 2.14—2.21 (m, 1 H) (H(3), H(4), H(5), H(6), H(19), H(20), H(23), H(24)); 2.40—2.60 (m, 4 H, H(18), H(22)); 3.33 (t, 1 H, H(2), J = 9.0 Hz); 3.62 and 3.84 (both d, 1 H each, H(17), J = 14.0 Hz); 6.73 (t, 1 H, H(15), J = 7.8 Hz); 6.79 and 7.22 (both d, 1 H each, H(14), H(16), J = 6.0 Hz, J = 7.8 Hz); 11.49 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 12.10 (C(10)); 13.99 (C(21), C(25)); 20.34 (C(9)); 20.64 (C(20), C(24)); 21.49 (C(8)); 27.55 (C(5)); 28.45 (C(19), C(23)); 33.87 (C(3)); 39.64 (C(6)); 44.65 (C(2)); 45.78 (C(4)); 47.85 (C(7)); 49.79 (C(1)); 52.98 (C(18), C(22)); 58.28 (C(17)); 117.65 (C(16)); 121.43 (C(13)); 125.69 (C(14)); 126.91 (C(15)); 130.51 (C(11)); 157.32 (C(12)).

B. Isobornylphenol **1** (0.4 g, 1.7 mmol) and paraformaldehyde (0.06 g, 2.0 mmol) were mixed in dry benzene (20 mL) at ~20 °C, dibutylamine (0.86 mL, 2.0 mmol) was added, and the mixture was refluxed for 15 h.[3] After completion of the reaction, all excess solvent was removed under reduced pressure. The remainder was separated on a column with Silicagel Alfa Aesar 70/230μ using a gradient of diethyl ether in light petroleum as the eluent. Amine **4** was obtained in a yield of 0.62 g (96%).

X-ray diffraction study of compound 2. X-ray diffraction data were collected on an automated Enraf-Nonius CAD4 diffractometer at ~20 °C with the use of Mo-Kα radiation (λ = 0.71073 Å, graphite monochromator). Crystals of **2** ($C_{17}H_{24}O_2$, M = 260.36) are monoclinic, space group $P2_1/c$, a = 16.378(9) Å, b = 7.622(7) Å, c = 25.153(7) Å, β = 109.28(4)°, V = 2964(3) Å^3, Z = 8, d_{calc} = 1.167 g cm^{-3}, μ(Mo-Kα) = 0.074 mm^{-1}, F(000) = 1136. The intensities of 7062 reflections (of which 5191 reflections were independent, R_{int} = 0.0611) were measured using the ω scanning technique in the range 2.48° < θ < 24.97° (−19 ≤ h ≤ 18, −1 ≤ k ≤ 9, −3 ≤ l ≤ 29). The X-ray data were corrected for Lorentz and polarization factors.[7] Absorption was ignored. The structure was solved by direct methods (SHELX-86).[8] All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method against F^2 (SHELXL-97).[9] All hydrogen atoms (except for the phenol H(1) and H(2)) atoms were placed in calculated positions; the H(1) and H(2) atoms were located in a difference electron density map. The disordered hydrogen atoms of the $CH_2O\underline{H}$ groups were refined with half occupancies, because two of these atoms (H(5) and H(6)) are too close to the inversion centers and are involved in hydrogen bonds between the equivalent molecules. The H(1) and H(2) atoms were refined isotropically. All other hydrogen atoms were refined using a riding model. The final R factors were as follows: R_1 = 0.0599, wR_2 = 0.1716 for 2491 reflections with $I > 2\sigma(I)$, 358 parameters were refined; GOF 1.035, the residual electron density (max/min) was −0.440/−0.388 e Å^{-3}.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-33005).

References

1. I. Yu. Chukicheva, A. V. Kutchin, L. V. Spirikhin, O. Ya. Borbulevich, A. V. Churakov, and A. I. Belokon´, *Khim. Komp. Model., Butlerovsk. Soobshch.* [*Chem. Comp. Simul., Butlerov Commun.*], 2003, **4**, 14 (in Russian).
2. V. M. Potapov, *Stereokhimiya* [*Stereochemistry*], Khimiya, Moscow, 1988, 124 (in Russian).
3. K.-W. Chi, Y. S. Ahn, K. T. Shim, T. H. Park, and J. S. Ahn, *Bull. Korean Chem. Soc.*, 1999, **20**, 973.
4. I. Yu. Chukicheva, A. V. Kutchin, L. V. Spirikhin, and E. U. Ipatova, *Khim. Komp. Model., Butlerovsk. Soobshch.* [*Chem. Comp. Simul., Butlerov Commun.*], 2003, **4**, 9 (in Russian).
5. L. A. Kheifits, G. I. Moldovanskaya, and L. M. Shulov, *Zh. Org. Khim.*, 1965, **1**, 1057 [*J. Org. Chem. USSR*, 1965, **1** (Engl. Transl.)].
6. M. L. Belyanin, V. D. Filimonov, and E. A. Krasnov, *Zh. Prikl. Khim.,* 2001, **74**, 100 [*Russ. J. Appl. Chem.*, 2001, **74** (Engl. Transl.)].
7. K. Harms, *XCAD4. Program for the Lp-Correction of Nonius CAD4 Data*, Marburg (Germany), 1997.
8. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
9. G. M. Sheldrick, *SHELXL-97. Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.

Received December 22, 2005;
in revised form August 15, 2006