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Unusual direction in the alkylation of 1-naphthol with camphene in the presence of aluminum phenoxide and isopropoxide

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Alkylation of 1-naphthol with camphene in the presence of aluminum phenoxide gives 2-isocamphyl-1-naphthol as a major product, while in the case of aluminum isopropoxide 2-isobornyl-1-naphthol is mainly formed and the content of 4-terpenyl-1-naphthols increases.

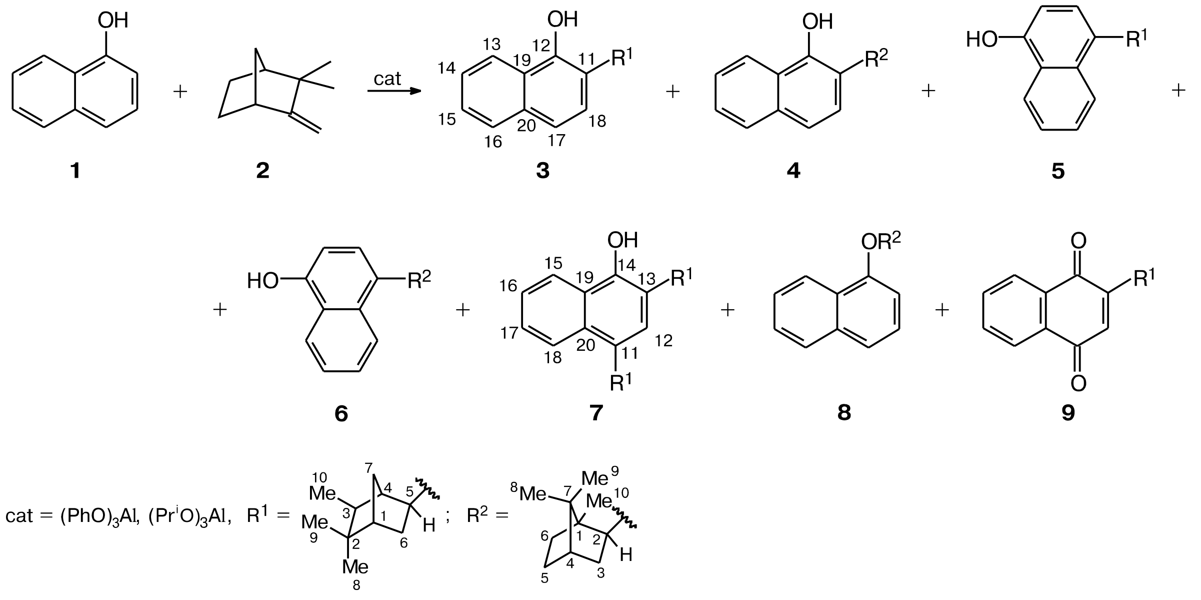
Key words: 1-naphthol, camphene, alkylation, aluminum alkoxides, terpenophenols.

Naphthols and their derivatives are widely used in chemical, pharmaceutical industry and perfumery. 1-Naphthol derivatives possess antiinflammatory activity and insecticide properties.[1] Alkylation products of 1-naphthol with α,β-unsaturated aldehydes display antibacterial, antiviral, mutagenic, antiproliferation, and antitumor activity.[2] It can be assumed that introduction of terpene substituents, which themselves possess physiological activity, in the naphthol molecule will give new biologically active compounds.

It is known that alkylation of naphthols takes place at *ortho-* or *para*-positions with respect to the hydroxy group. Alkylating agents can be olefins, alcohols, alkyl halides in the presence of different catalysts, for example, aluminum chloride, zirconium sulfate, boron trifluoride, solid acidic catalysts, such as acidic clays (Filtrol-24 and K-10), heteropolyacidic catalysts, and zeolites (ZSM-5).[3–5]

Earlier, systematic studies have been performed on alkylation of phenols with camphene with the use of aluminum phenoxides. Since the latter are *ortho*-directing

Scheme 1



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catalysts, the expected *o*-isobornylphenols were obtained in the reaction. Regio- and stereoselectivity are also due to the fact that the process proceeds intramolecularly in the organized coordination sphere of aluminum.[6—8]

In the present work, we study alkylation of 1-naphthol (**1**) with camphene (**2**) on catalysis with aluminum phenoxide and isopropoxide. The purpose of such studies consists in finding parameters providing directed synthesis of compounds with desired structures.

Results and Discussion

The reaction of equimolar amounts of 1-naphthol and camphene in the presence of aluminum phenoxide $(PhO)_3Al$ leads to the *ortho*-alkylated naphthol with isocamphylic structure of the terpene substituent (**3**) (the yield was 62%, Scheme 1, Table 1). This differs from the direction of alkylation of phenols, where the main product has an isobornylic fragment.[6,8]

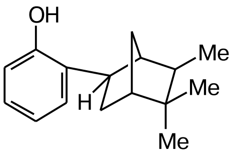
In addition, 19% of dialkylated naphthol with isocamphylic structure of the terpene substituents (**7**) was obtained.

The structures of these and described below naphthols were established by NMR spectroscopy. The signals for protons and carbon atoms of isocamphylic and isobornylic fragments correspond to the literature data.[6,8]

Alkylation of 1-naphthol with camphene when the ratio of the starting reactants is 2 : 1, respectively (see Scheme 1, Table 1), mainly leads to the same compound, however, isobornylic derivative **4** is formed as a side product. In addition, naphthols substituted at position 4 with isocamphylic (**5**) and isobornylic (**6**) substituents were isolated, as well as a poorly separable mixture of ethers of the type **8** with different terpene-type fragments.

The reaction of 1-naphthol with a two-fold excess of camphene leads to a complex mixture of C-alkylated products with terpene substituents of different structures (see Table 1). A disposition of naphthols to oxidation was confirmed by the side formation of naphthoquinone (**9**).

In addition to the alkylated 1-naphthols, alkylated phenols **10** and **11** were found among the reaction products.



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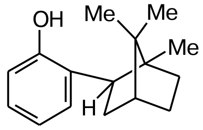

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Their appearance can be explained by the fact that alkylation of naphthol with $(PhO)_3Al$ is accompanied by the exchange of aroxyl groups of the catalyst and the reagent (Scheme 2). The liberated phenol reacts with camphene to form compounds **10** and **11**.

Scheme 2

$$(PhO)_3Al + \underset{\mathbf{1}}{C_{10}H_7OH} \longrightarrow (PhO)_{3-n}Al(C_{10}H_7O)_n + PhOH$$

Alkylation of naphthol at the *ortho*-position with respect to the hydroxy group confirms a suggestion that this reaction takes place in the coordination sphere of aluminum. Formation of alkylnaphthols with the terpene substituent of isobornylic and isocamphylic structure is explained by the fact that addition of naphthol to camphene is accompanied by the Wagner—Meerwein rearrangement and 6,2-hydride shift in the carbocation arising from camphene.[9—11] Naphthol, being a weak acid, can serve as a proton donor and activate the camphene molecule, thus promoting formation of carbocations.

The use of $(Pr^iO)_3Al$ as a catalyst at the equimolar ratio of 1-naphthol and camphene (see Scheme 1, Table 1) predominantly leads to *ortho*-alkylated naphthol with isobornylic structure of the terpene substituent (**4**). It is possible that naphthol as a stronger acid replaces the isopropyl group in aluminum isopropoxide to form aluminum naphthoxide, and the reaction proceeds significantly

Table 1. Results of alkylation of 1-naphthol with camphene

Naphthol : camphene	Conversion (%)	Content of reaction products (%)								
		3	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
					$(PhO)_3Al$ (10%)					
1 : 1	83	62	—	—	—	19	—	—	14	5
2 : 1	75	63	13	9.5		7	5	—	—	—
1 : 2	73	33	—	15.0	12	24	—	6	—	5
					$(Pr^iO)_3Al$ (10%)					
1 : 1	85	12	66	—	19	—	3	—	—	—
2 : 1	82	36	21	12	20	—	4	6	—	—
1 : 2	82	30	14	12	21	14	8	<1	—	—

* The reaction conditions: 160 °C, 6 h.

faster without secondary intramolecular rearrangements of the terpene substituent.

If naphthol is in excess (see Table 1), *ortho*-alkylated products **3** and **4** predominate (57%). In addition, a considerable amount of *para*-alkylnaphthols **5** and **6** (32%) is formed. Alkylation of naphthol with an excess of camphene in the presence of $(Pr^iO)_3Al$ is unselective, like in the reaction involving $(PhO)_3Al$ (see Table 1). In addition, an excess of camphene in the reactions with $(PhO)_3Al$, as well as at any ratio of 1-naphthol and camphene in the alkylation in the presence of $(Pr^iO)_3Al$, isobornyl ether of 1-naphthol (**8**) is formed as a side product.

Recrystallization of 2-isocamphyl-1-naphthol (**3**) gave monocrystals as a mixture (the ratio 1 : 1, ^{1}H NMR and GLC data) with naphthoquinone **9**, which results from partial oxidation of naphthol **3**. The structure of cocrystal **3**•**9** (Fig. 1) was determined by X-ray diffraction study. In the elementary cell, molecules of naphthol and naphthoquinone are superimposed on each other, that leads to a disorder. In both cases, the π-conjugated fragments of the molecules (naphthol and the corresponding naphthoquinone) have planar structure and are in the *exo*-position to the bicyclic substituent. In the crystal structure, molecules form layers parallel to the plane *bc*, and their structure explain formation of the cocrystal. The layers consist of the chains along the crystallografic direction *b*, which are bound by the stacking-interaction in the perpendicular direction (along the axis *c*). In chains, molecules are bound by translation, therefore, it is logically to suppose that the molecules of naphthol and naphthoquinone alternate, which leads to the formation of the H-bound dimers (O—H...O: H...O 1.970 Å, O..O 2.769(6) Å, the bond angle O—H—O 156°) (Fig. 2). Molecules in columns bound by stacking-interaction apparently alternate as well. In this case, the two closest neighbors of each molecule of the column interact with it with different strength. The stronger interaction exist between molecules bound by the axis of symmetry $(-x, y, 0.5 - z)$. In this case, the electron-enriched naphthol is virtually completely superimposed with the electron-deficient quinone (the interplane angle is 13.1(2)°, the interplane distance is 3.278(4) Å, the shortest contact C(3)...C(3) is 3.063(2) Å). The weaker interaction exists between molecules bound by the center of symmetry $(-x, -y, -z)$ (the interplane angle is 0°, the interplane distance is 3.401(4) Å, the shortest contact C(3)...C(7) is 3.355(2) Å).

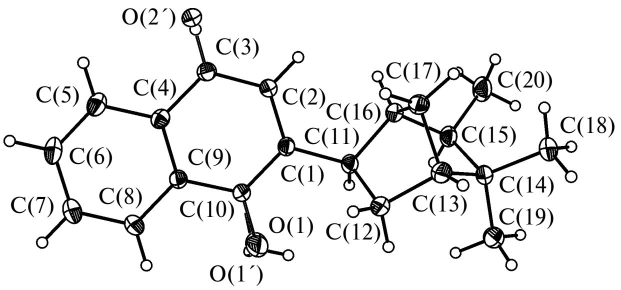

Fig. 1. General view of cocrystal **3**•**9** in representation of atoms by ellipsoids of thermal displacement with 50% probability. Superposition of molecules of naphthol **3** and naphthoquinone **9**.

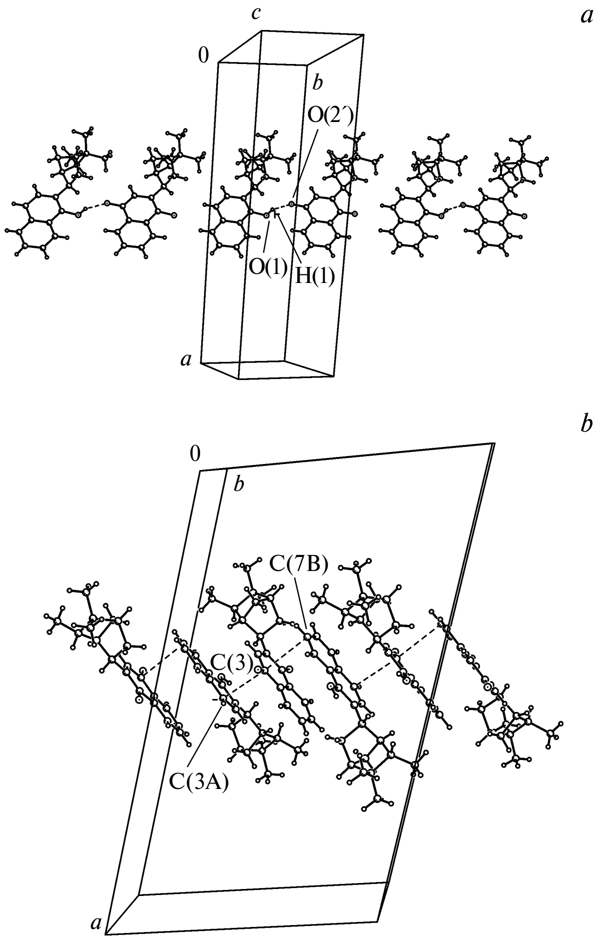

Fig. 2. Fragments of crystal packing of cocrystal **3**•**9**: the H-bound dimers (*a*) and stacking-columns (*b*).

To sum up, the cocrystal is stabilized by hydrogen bonds between the acidic proton of the hydroxy group and the keto group, the strong proton acceptor, as well as by very strong stacking-interaction between the electron-donating and electron-withdrawing rings.

In conclusion, the alkylation of 1-naphthol with camphene using $(PhO)_3Al$ and $(Pr^iO)_3Al$ as catalysts was studied for the first time. It was shown that composition of the alkylation products of 1-naphthol with camphene depends on the nature of the catalyst and on the ratio of the starting reactants. It was found that alkylation of 1-naphthol with camphene in the presence of $(PhO)_3Al$ predominantly gives the *ortho*-alkylated naphthol with the isocamphylic structure of the terpene fragment, whereas when $(Pr^iO)_3Al$ is used, the *ortho*-alkylated naphthol with isobornylic substituent is the predominant product. The result obtained allows one to chose direction of the reaction toward formation of the target products.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 300 spectrometer (^{1}H, 300.17 MHz; ^{13}C, 75.5 MHz) in $CDCl_3$ using signals of chloroform as a reference (δ_H 7.26, δ_C 76.90). Assignment of signals in ^{13}C NMR spectra was performed using the DEPT procedures. The ^{1}H and ^{13}C NMR spectroscopic data are given in Table 2.

Analysis of volatile reaction products was performed by GLC on a Shimadzu GC-2010AF chromatograph equipped with a HP-1 capillary column (60 m×0.25 mm×0.25 μm, the temperature regime was 100—240 °C, heating at 6 °C min^{-1}) and a flame-ionizing detector, helium was a carrier gas.

Reaction progress was monitored by TLC on Sorbfil plates, visualization of components was performed by treatment of plate with alcoholic solution of vanillin with subsequent heating to

Table 2. The ^{1}H and ^{13}C NMR spectroscopic data for compounds **3—9**

Compound	NMR, δ (*J*/Hz)	
	^{1}H	^{13}C
3	0.95 (d, 3 H, Me(10), *J* = 2.7); 0.99 (s, 3 H, Me(8)); 1.16 (s, 3 H, Me(9)); 1.46—1.56 (m, 3 H, HC(3), HC(6), HC(7)); 1.86—1.93 (m, 2 H, HC(1), HC(7)); 2.18 (m, 1 H, HC(4)); 2.41—2.49 (m, 1 H, HC(6)); 3.01 (t, 1 H, HC(5), *J* = 7.5); 5.31 (s, 1 H, OH); 7.45—7.51 (m, 4 H, HC(13), HC(14), HC(15), HC(16)); 7.81 (d, 1 H, HC(18), *J* = 7.8); 8.18 (d, 1 H, HC(17), *J* = 7.8)	16.31 (C(10)); 24.77 (C(9)); 27.76 (C(8)); 33.03 (C(7)); 33.86 (C(6)); 39.81 (C(2)); 40.89 (C(4)); 49.48 (C(5)); 49.76 (C(3)); 51.00 (C(1)); 119.92 (C(17)); 121.17 (C(13)); 123.83 (C(18)); 124.27 (C(19)); 125.19 (C(15)); 125.44 (C(14)); 125.81 (C(11)); 127.50 (C(16)); 132.90 (C(20)); 148.16 (C(12))
4	0.86 (s, 3 H, Me(10)); 0.91 (s, 3 H, Me(8)); 1.00 (s, 3 H, Me(9)); 1.36—1.45 (m, 1 H, HC(5)); 1.48—1.56 (m, 1 H, HC(6)); 1.72—1.77 (m, 2 H, HC(3), HC(6)); 1.80—1.99 (m, 2 H, HC(4), HC(5)); 2.34—2.45 (m, 1 H, HC(3)); 3.22 (t, 1 H, H(2), *J* = 8.7); 5.27 (s, 1 H, OH); 7.45—7.56 (m, 4 H, HC(13), HC(14), HC(15), HC(16)); 7.80 (d, 1 H, HC(18), *J* = 7.8); 8.16 (d, 1 H, HC(17), *J* = 7.8)	12.56 (C(10)); 20.56 (C(9)); 21.37 (C(8)); 27.65 (C(5)); 34.11 (C(6)); 40.55 (C(3)); 45.65 (C(2)); 46.50 (C(4)); 48.06 (C(1)); 50.35 (C(7)); 119.49 (C(17)); 121.27 (C(13)); 122.17 (C(11)); 124.27 (C(19)); 125.21 (C(18)); 125.64 (C(14), C(15)); 127.46 (C(16)); 132.92 (C(20)); 149.80 (C(12))
5	0.92 (s, 3 H, Me(8)); 0.95 (d, 3 H, Me(10), *J* = 2.7); 1.03 (s, 3 H, Me(9)); 1.49—1.55 (m, 3 H, HC(3), HC(6), HC(7)); 1.79—1.92 (m, 3 H, HC(1), HC(7)); 1.97 (m, 1 H, HC(4)); 2.28—2.37 (m, 1 H, HC(6)); 2.92 (t, 1 H, HC(5), *J* = 7.5); 4.77 (s, 1 H, OH); 6.80 (d, 1 H, HC(12), *J* = 7.8); 7.38 (d, 1 H, HC(13), *J* = 7.8); 7.52—7.57 (m, 2 H, HC(16), HC(17)); 8.13 (d, 1 H, HC(18), *J* = 7.8); 8.27 (d, 1 H, HC(15), *J* = 7.8)	16.22 (C(10)); 24.69 (C(9)); 27.64 (C(8)); 33.83 (C(7)); 35.34 (C(6)); 39.77 (C(2)); 40.52 (C(4)); 46.83 (C(5)); 49.70 (C(3)); 50.83 (C(1)); 107.79 (C(13)); 122.59 (C(15)); 124.42 (C(16)); 124.45 (C(12)); 125.41 (C(19)); 125.60 (C(17)); 126.06 (C(18)); 131.69 (C(11)); 135.06 (C(20)); 150.30 (C(12))
6	0.75 (s, 3 H, Me(10)); 0.99 (s, 3 H, Me(8)); 1.09 (s, 3 H, Me(9)); 1.52—1.59 (m, 2 H, HC(5), HC(6)); 1.78—1.84 (m, 2 H, HC(3), HC(6)); 2.00—2.04 (m, 2 H, HC(4), HC(5)); 2.39—2.47 (m, 1 H, HC(3)); 3.77 (t, 1 H, HC(5), *J* = 8.7); 4.85 (s, 1 H, OH); 6.87 (d, 1 H, HC(12), *J* = 7.8); 7.43 (d, 1 H, HC(13), *J* = 7.8); 7.55—7.59 (m, 2 H, HC(16), HC(17)); 8.19 (d, 1 H, HC(18), *J* = 7.8); 8.39 (d, 1 H, HC(15), *J* = 7.8)	13.96 (C(10)); 20.28 (C(9)); 21.32 (C(8)); 27.64 (C(5)); 33.83 (C(6)); 39.89 (C(3)); 45.56 (C(2)); 46.51 (C(4)); 49.03 (C(1)); 49.70 (C(7)); 108.43 (C(13)); 121.43 (C(15)); 124.50 (C(18)); 125.40 (C(19)); 125.54 (C(17)); 125.61 (C(12)); 126.38 (C(16)); 131.69 (C(11)); 135.06 (C(20)); 150.30 (C(14))
7	0.93 (d, 6 H, Me(10), Me(10´), *J* = 2.7); 0. 95 (s, 6 H, Me(8), Me(8´)); 1.11 (s, 6 H, Me(9), Me(9´)); 1.41—1.51 (m, 6 H, HC(3), HC(3´), HC(6), HC(6´), HC(7), HC(7´)); 1.75—1.88 (m, 4 H, HC(1), HC(1´), HC(7), HC(7´)); 2.11—2.19 (m, 2 H, HC(4), HC(4´)); 2.23—2.29 (m, 2 H, HC(6), HC(6´)); 3.01 (t, 2 H, HC(5), HC(5´)), *J* = 7.5); 5.34 (s, 1 H, OH); 6.75 (s, 1 H, HC(12)); 7.74—7.77 (m, 2 H, HC(15), HC(18)); 8.08—8.14 (m, 2 H, HC(16), HC(17))	16.23 (C(10), C(10´)); 24.76 (C(8), C(8´)); 27.54 (C(9), C(9´)); 32.18 (C(2), C(2´)); 33.34 (C(4), C(4´)); 40.90 (C(5), C(5´)); 48.65 (C(3), C(3´)); 49.74 (C(1), C(1´)); 50.34 (C(6), C(6´)); 120.95 (C(13)); 125.94 (C(15)); 126.60 (C(18)); 131.67 (C(16), C(17)); 132.02 (C(19)); 133.59 (C(12)); 131.06 (C(20)); 132.07 (C(11)); 155.57 (C(14))

(*to be continued*)

Table 2 (*continued*)

Compound	NMR, δ (*J*/Hz)	
	^{1}H	^{13}C
8	0.92 (s, 3 H, Me(10)); 1.18 (s, 3 H, Me(8)); 1.25 (s, 3 H, Me(9)); 1.68—1.75 (m, 2 H, HC(5), HC(6)); 1.87—1.88 (m, 1 H, HC(6)); 1.81—1.88 (m, 2 H, HC(3), HC(5)); 1.99—2.01 (m, 2 H, HC(4), HC(5)); 2.48—2.59 (m, 1 H, HC(3)); 4.43 (q, 1 H, HC(2), *J* = 3.7, *J* = 3.3); 6.78—6.81 (d, 1 H, HC(12), *J* = 7.8); 7.51—7.53 (m, 2 H, HC(13), HC(14)), 7.81—7.84 (m, 2 H, HC(16), HC(17)); 8.26—8.30 (m, 2 H, HC(15), HC(18))	12.12 (C(10)); 19.77 (C(9)); 20.43 (C(8)); 27.48 (C(5)); 34.30 (C(6)); 39.67 (C(3)); 45.44 (C(4)); 47.12 (C(1)); 49.51 (C(7)); 84.48 (C(2)); 105.14 (C(12)); 119.43 (C(14)); 119.61 (C(18)); 122.38 (C(17)); 125.01 (C(13)); 125.93 (C(16)); 126.24 (C(15)); 127.43 (C(19)); 134.72 (C(20)); 153.37 (C(11))
9	0.83 (d, 3 H, Me(10), *J* = 2.7); 0.93 (s, 3 H, Me(8)); 1.09 (s, 3 H, Me(9)); 1.41—1.56 (m, 3 H, HC(3), HC(6), HC(7)); 1.72—1.79 (m, 2 H, HC(1), HC(7)); 2.20 (m, 1 H, HC(4)); 2.25—2.30 (m, 1 H, HC(6)); 2.91 (t, 1 H, HC(5), *J* = 7.5); 7.30 (s, 1 H, HC(18)); 7.44 (d, 1 H, HC(16), *J* = 7.8); 7.60—7.65 (m, 2 H, HC(14), HC(15)); 7.74 (d, 1 H, HC(13), *J* = 7.8)	16.29 (C(10)); 24.80 (C(9)); 27.55 (C(8)); 32.70 (C(7)); 33.64 (C(6)); 39.74 (C(2)); 40.30 (C(4)); 48.64 (C(5)); 49.87 (C(3)); 50.91 (C(1)); 119.49 (C(18)); 121.27 (C(13)); 122.17 (C(11)); 131.90 (C(19)); 132.76 (C(16)); 141.20 (C(15)); 141.83 (C(14)); 205.30 (C(12), C(17))

100—150 °C. Separation of reaction products was carried out by column chromatography on silica gel (Silica gel 70/230 μm, eluent: light petroleum—Et$_2$O with increasing content of the latter). Natural camphene (racemate) was used in the work, which according to the GLC data contains no other compounds, except tricyclene (5%). Compounds (Pr^{i}O)$_3$Al (Alfa Aesar) and (PhO)$_3$Al (synthesized *in situ*) were used as catalysts.

Alkylation of 1-naphthol with camphene in the presence of (PhO)$_3$Al and (Pr^{i}O)$_3$Al (general procedure). Phenol (0.19 g, 2 mmol) was heated to 160 °C in a three-neck flask equipped with a reflux condenser and thermometer, followed by addition in small portions of aluminum foil (0.017 g, 0.6 mmol). After aluminum was completely dissolved in phenol (~30 min), the solution was cooled to 40 °C, followed by addition of 1-naphthol (2.0 g, 14 mmol) and the corresponding amount of camphene (1, 2, or 0.5 equiv.). The reaction was carried out under argon, keeping temperature of the melt 160—170 °C for 6 h. After the reaction reached completion, the mixture was dissolved in CHCl$_3$, passed through a short layer of Al$_2$O$_3$ with addition of activated coal, excess solvent was evaporated at reduced pressure. The reaction mixture was separated by column chromatography. The yields of the reaction products are given in Table 1. Compounds **3**—**9** were isolated in the individual state, their spectral characteristics are given in Table 2. For the analysis of the NMR spectra to be convenient, the numeration of carbon atoms is given in Scheme 1.

When aluminum isopropoxide (0.14 g, 0.7 mmol) was used, the reactants and catalyst were added simultaneously; the reaction and separation of alkylation products were carried out as described above.

2-(2,2,3-Trimethylbicyclo[2.2.1]hept-*exo*-5-yl)-1-naphthol (3). Colorless powder, m.p. 88—90 °C, R_f 0.54 (eluent: light petroleum—Et$_2$O (3 : 1)). Found (%): C, 85.65; H, 8.61. C$_{20}$H$_{24}$O. Calculated (%): C, 85.67; H, 8.63.

2-(1,7,7-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-1-naphthol (4). Viscous yellow oil, R_f 0.67 (eluent: light petroleum—Et$_2$O (3 : 1)). Found (%): C, 85.69; H, 8.65. C$_{20}$H$_{24}$O. Calculated (%): C, 85.67; H, 8.63.

4-(2,2,3-Trimethylbicyclo[2.2.1]hept-*exo*-5-yl)-1-naphthol (5). Viscous brown oil, R_f 0.39 (eluent: light petroleum—Et$_2$O (3 : 1)). Found (%): C, 85.66; H, 8.64. C$_{20}$H$_{24}$O. Calculated (%): C, 85.67; H, 8.63.

4-(1,7,7-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl)-1-naphthol (6). Viscous brown oil, R_f 0.40 (eluent: light petroleum—Et$_2$O (3 : 1)). Found (%): C, 85.66; H, 8.65. C$_{20}$H$_{24}$O. Calculated (%): C, 85.67; H, 8.63.

2,4-Bis(2,2,3-trimethylbicyclo[2.2.1]hept-*exo*-5-yl)-1-naphthol (7). Viscous pale yellow oil, R_f 0.68 (eluent: light petroleum). Found (%): C, 86.46; H, 9.69. C$_{30}$H$_{40}$O. Calculated (%): C, 86.48; H, 9.68.

1,7,7-Trimethylbicyclo-2-*exo*-(1-naphthoxy)bicyclo[2.2.1]-heptane (8). Colorless oily liquid; R_f 0.75 (eluent: light petroleum). Found (%): C, 85.65; H, 8.65. C$_{20}$H$_{24}$O. Calculated (%): C, 85.67; H, 8.63.

2-(2,2,3-Trimethylbicyclo[2.2.1]hept-*exo*-5-yl)-1,4-dihydronaphthalene-1,4-dione (9). Viscous red oil, R_f 0.30 (eluent: light petroleum—Et$_2$O (3 : 1)). Found (%): C, 81.62; H, 7.51. C$_{20}$H$_{22}$O$_2$. Calculated (%): C, 81.60; H, 7.53.

Physicochemical parameters of the isolated alkylated phenols **10** and **11** agree with the literature data.[6—8]

X-ray diffraction analysis of products 3 and 9. Monocrystals of cocrystallization product **3**·**9** were obtained by slow concentration of the solution in the hexane—Et$_2$O solvent mixture at ~20 °C. Crystals **3**·**9** (C$_{20}$H$_{24}$O·C$_{20}$H$_{22}$O$_2$) at 100 K are monoclinic, a = 26.8405(12) Å, b = 7.6292(3) Å, c = 15.5959(7) Å, V = 3038.5(2) Å^3, β = 107.93(10)°, Z = 4, the space group is $C2/c$, μ = 0.077 mm^{-1}, d_{calc} = 1.256 g cm^{-3}, the crystal size is 0.36×0.28×0.21 mm. Intensities of 18805 reflections were measured on a SMART APEX2 CCD difractometer (λ(Mo-Kα) = = 0.71073 Å, graphite monochromator, ω-scanning with the step 0.5°, 2θ < 60°). Processing of the starting massif of measured intensities was performed using the APEX2 program package.[12] The structure was solved by the direct method and refined by the full-matrix least squares method in anisotropic approximation for nonhydrogen atoms at F^2_{hkl}. Hydrogen atom were placed into geometrically calculated positions, excluding the hydroxyl hydrogen, whose position was localized from the differential synthesis of electron density, and then the distance O—H was normalized by the value 0.85 Å. Hydrogen atoms were refined using the riding model ($U_{\rm iso}$(H) = $nU_{\rm eq}$(C,O), where n = 1.5 for the carbon atoms of the methyl groups and the oxygen atom, n = 1.2 for the rest of C atoms). 4448 independent reflections ($R_{\rm int}$ = 0.0292) were used for the refining. Convergence of the refining on all the independent reflections wR_2 = 0.1215 (R_1 = = 0.0459 for 3593 reflections with $I > 2\sigma(I)$). All the calculations were performed using the SHELXTL program package.[13]

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