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Alkylation of Resorcinol with Camphene in the Presence of Aluminum Phenolate and Aluminum Isopropoxide

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Abstract—Alkylation of resorcinol with camphene using aluminum phenolate and aluminum isopropoxide as catalysts was investigated. The conditions of the direct synthesis of *ortho*-alkylated resorcinol containing the isobornyl moiety were developed. The diastereomers of the symmetrically dialkylated resorcinol were examined by the high performance liquid chromatography and X-ray analysis.

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Sterically hindered dihydric phenols containing bulky alkyl substituents in the *ortho*-position to the hydroxy group are of great interest as intermediates in the synthesis of antioxidants and inhibitors for a wide range of applications. The alkylation of the dihydric phenols with olefins, including terpenes, using various acid catalysts (mineral acids, organic sulfonic acid) has been studied in detail previously [1–3]. Aluminum phenolate $(PhO)_3Al$ is known to be used in the catechol and resorcinol alkylation with cyclohexene and styrene [4, 5]. Due to a coherent orientation of the hydroxy groups of resorcinol, the reaction is completed much faster than in the case of catechol, and it is characterized by more complex isomeric composition of the reaction products. In the alkylation of styrene the isomeric composition of the reaction products is much less dependent on the experimental conditions, as it is largely determined by the steric hindrance, preventing the introduction of a bulk α-methylbenzyl moiety between the two OH-groups of resorcinol. The yield of dialkyl resorcinols was relatively high even when a large excess of resorcinol was used. Aluminum phenolate is known to be one of the most active *ortho*-orienting catalysts in the phenols alkylation [6, 7].

In the present work the alkylation of resorcinol **I** with camphene **II** in the presence of aluminum phenolate and aluminum isopropoxide $(i\text{-PrO})_3Al$ was studied. These organoaluminum compounds were used to obtain *in situ* mixed aluminum phenoxides acting as catalysts. In the alkylation of the dihydric phenols with $(PhO)_3Al$ and $(i\text{-PrO})_3Al$ an exchange occurs of the alkoxide or phenoxide groups of the catalyst and reagent [8, 9].

$$(RO)_3Al + HOC_6H_4OH \rightarrow (RO)_{3-n}Al(OC_6H_4OH)_n + ROH,$$
$$R = i\text{-Pr, Ph}; n = 1\text{–}3.$$

The alkylation of resorcinol **I** with camphene **II** was carried out with the catalytic amounts of $(PhO)_3Al$ and $(i\text{-PrO})_3Al$ at 120 and 160–170°C. The reaction conditions of the resorcinol alkylation with camphene are given in the Table.

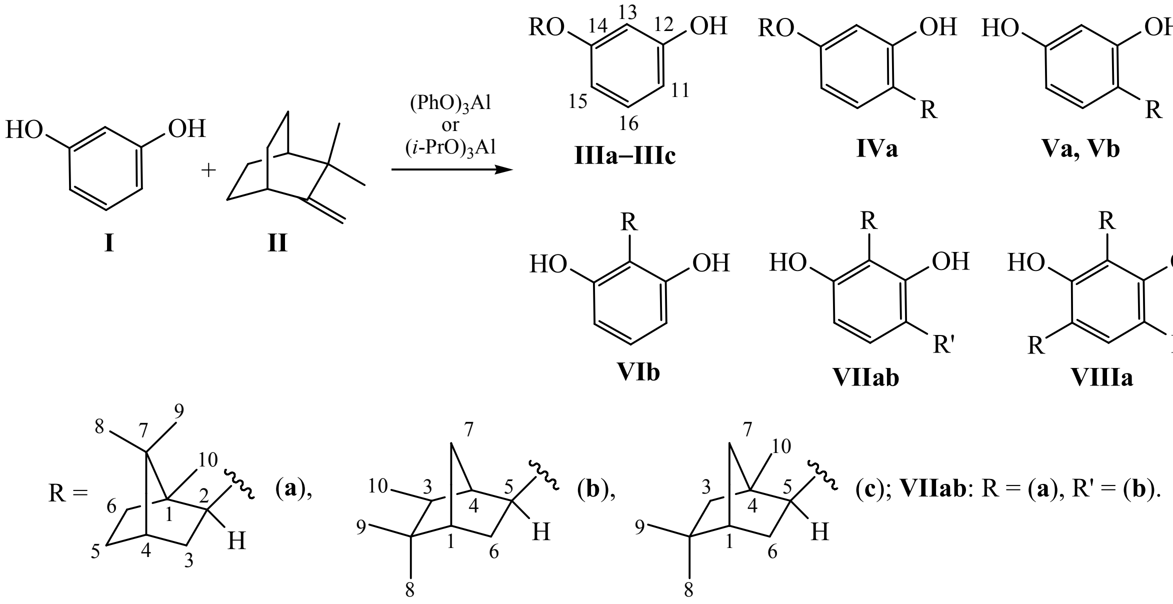
The alkylation of resorcinol **I** with camphene **II** at the molar ratio of 1:1 and 2:1 regardless of the catalyst gives rise to the *ortho*-alkylated resorcinol **Va** containing isobornyl substituent as the main product in the yield of 50–81%. When the equimolar amounts of resorcinol and camphene were used the raising of the reaction mixture temperature leads to a decrease in the process selectivity and an increase in the yield of the dialkylated resorcinols **VIIa, VIIb**, and **VIIIa**. The reaction with the use of excess resorcinol at 160–170°C in the presence of any of the studied catalysts results in the alkylation product **Va** and also phenols **Vb** and **VIb** containing isocamphyl moiety, besides the resins formation (up to 7%).

The reaction of resorcinol with the excess camphene at 160°C results in unsymmetricaly and symmetrically dialkylated resorcinols **VIIab** and

Reaction conditions and products of the alkylation of resorcinol with camphene

I:**II** ratio	Reaction conditions	Conversion, %	The reaction products ratio, %								
			III			**IVa**	**V**		**VIb**	**VIIab**	**VIIIa**[a]
			a	**b**	**c**		**a**	**b**			
Catalyst – $(PhO)_3Al$											
1:1	120°C, 8 h	99	9		–	–	58	–	–	8	25 (44/56)
	160–170°C, 8 h	90	8			–	30	5	–	19	37 (42/58)
1:2	120°C, 11 h	98	11	1	–	27	22	–	–	–	32 (43/57)
	160°C, 5 h	98	14			–	3	2	–	17	64 (39/61)
2:1	120°C, 8 h	98	2			–	74	–	2	–	18 (40/60)
	160–170°C, 11 h	98	–	–	56	28	8	–	–		
Catalyst – $(i\text{-}PrO)_3Al$											
1:1	120°C, 7 h	98	10		–	–	50	–	–	–	36 (38/62)
	160–170°C, 8 h	90	15			–	26	2	–	6	49 (34/66)
1:2	120°C, 10 h	98	10	4	–	30	17	–	–	–	38 (45/55)
	160°C, 5 h	100	7			–	5	3	–	36	49 (43/57)
2:1	120°C, 7 h	98	–	–	–	–	81	–	4	–	13 (45/55)
	160–170°C, 9 h	98	–	–	60	28	4	–	–		

[a] The ratio of *rac-*/*meso-*diastereomers is given in parentheses.



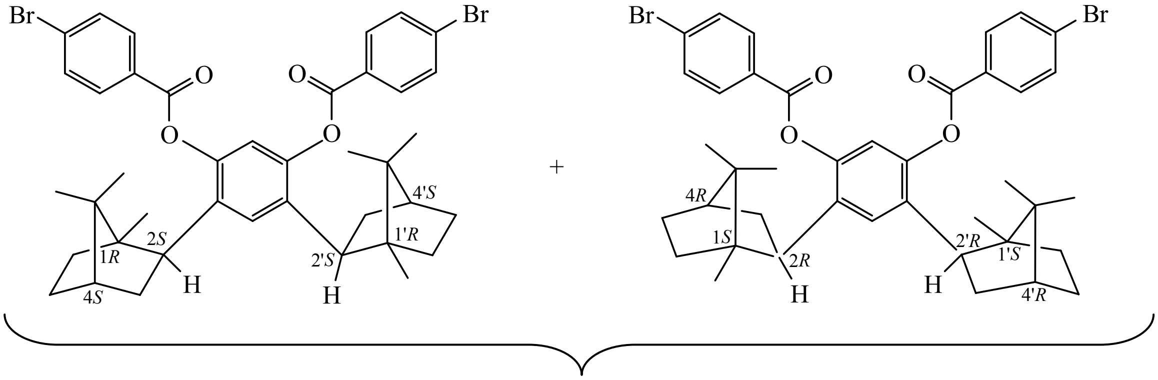
The carbon atoms are numbered to ease the interpretation of NMR spectra.

VIIIa, respectively. The alkylation at 120°C is nonselective process in this case. These regularities are preserved when using both catalysts.

Thus, the optimal condition for obtaining 4-isobornyl-1,3-dihydroxybenzene (74–81%) is the alkylation of the two-fold excess of resorcinol at 120° C in the presence of $(PhO)_3Al$ and $(i\text{-}PrO)_3Al$. The products composition of resorcinol alkylation with camphene is largely determined by the ratio of the initial components and does not depend on the structure of aluminum-containing compounds. The last statement confirms that the mixed aluminum phenoxide or aluminum phenoxyalkoxides [in the case of $(i\text{-}PrO)_3Al$] are generated *in situ*. The latter acts as the catalysts.

Compounds **IVa**, **VIIab**, and **VIIIa** containing two terpene fragments in their molecules are the diastereomers mixtures due to the camphene rearrangements in the course of the alkylation. The presence of diastereomers is confirmed by the doubling of signals of the protons and carbon atoms from the certain groups in the ^1H and ^{13}C NMR spectra, respectively. In the case of the symmetrically dialkylated product **VIIIa**, which is a diastereomers mixture (*meso*-form and racemate), the individual diastereomers were isolated by the column chromatography and subsequent recrystallization. Their identification was performed by the analytical HPLC on a column with a Chiralcel OD-H chiral stationary phase. A chromatogram of *meso*-**VIIIa** contains one peak, while for compound *rac*-**VIIIa** gives rise to two peaks of the corresponding enantiomers in a ratio of ~1:1.

By the action 4-bromobenzoyl chloride, the diastereomer *rac*-**VIIIa** was transformed into the diacyl derivative *rac*-**IXa**, whose structure was studied by the X-ray diffraction.



rac-**IXa**

Compound **IXa** crystallizes in the centrosymmetric space group $P2_1/n$, and the symmetrically independent part of the unit cell contains one molecule (Fig. 1).

The relative configuration of the chiral centers of isobornyl moieties determined by the XRD analysis of the racemic compound **IXa** confirms also (1*R**,2*S**,4*S**,1'*R**,2'*S**,4'*S**)-stereochemistry of the starting dialkylated resorcinol *rac*-**VIIIa**.

The orientation of isobornyl substituents and ester groups in molecule **IXa** with respect to the central phenyl ring varies markedly. The atom C^{11} of terpene moiety is oriented in the same way as in the previously investigated *ortho*-isobornylphenol derivatives [10–12] [the torsion angle $C^{12}C^{11}C^2C^3$ is 20.0(4)°]. Its neighboring ester group is oriented almost perpendicularly to the phenyl ring plane [the torsion angle $C^{11}C^{16}O^3C^{34}$ is 111.4(3)°] as in the previously synthesized 2-isobornyl-4-methylphenol camphanate [12]. The $C^{12}C^{13}C^{17}C^{18}$ torsion angle defining the orientation of the second isobornyl group is 105.9(3)°. The ester group at the C^{14} atom is turned with respect to the phenyl ring to a much lesser degree [the torsion angle $C^{15}C^{14}O^1C^{27}$ is –57.9(3)°]. Analyzing the previously obtained results for the *ortho*-isobornylphenol derivatives, we can assume that the orientation of the isobornyl substituent at the C^{11} atom is the most preferred also for the isolated molecule. In this case, in terms of the steric factors, the second isobornyl fragment can have the same orientation. To find the structure-determining factors of molecule **IXa** in the crystal we carried out the conformational analysis of the model isobornylbenzene (Fig. 2) in the framework of the density functional theory by a GAUSSIAN program package [13].

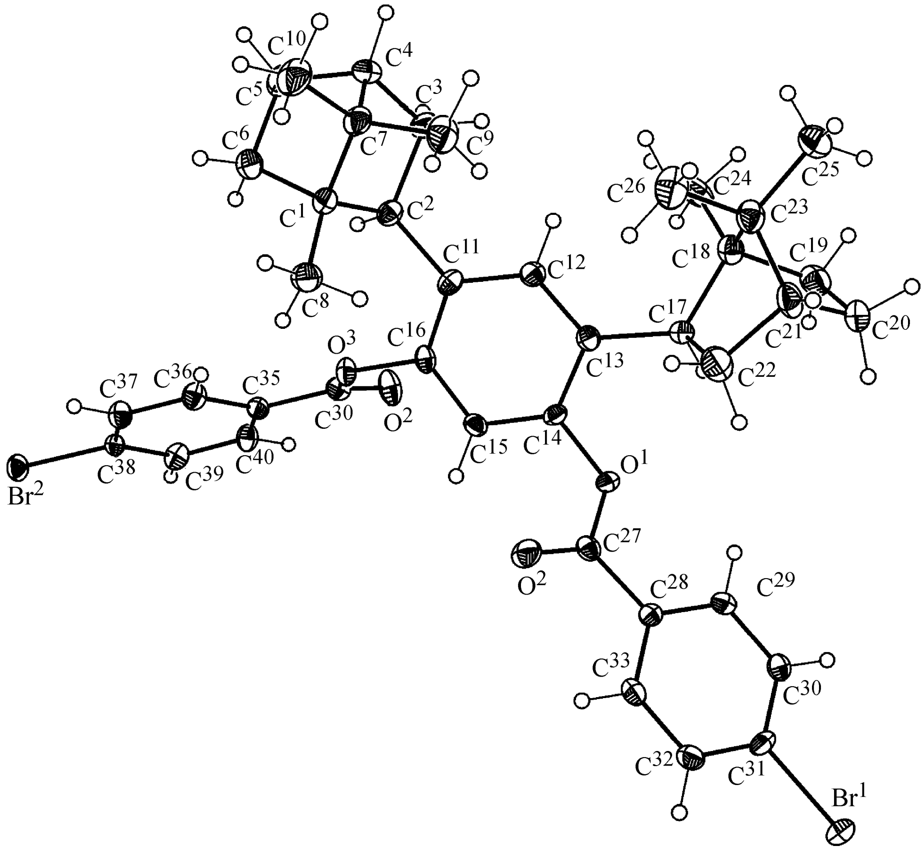


Fig. 1. General view of molecule **IXa** with atoms represented as thermal ellipsoids of 50% probability.

For a reasonable time cost the used B972/6-31G* approximation allows obtaining the relative conformation energies at the semi-quantitative level [14], which is sufficient for the task solution. The torsion angle $C^1C^2C^3C^4$ was varied in the range from 0° to 180° in steps of 10°. The resulting dependence (Fig. 2) shows the presence of two minima, global and local. All the previously studied *ortho*-isobornylphenol derivatives have an orientation corresponding to this global minimum, which confirms the assumption that the molecular structure of the crystal is determined largely by the intramolecular interactions. The orientation of an isobornyl substituent at the C^{13} atom is situated near a local minimum. The energy loss is ~1.7 kcal mol^{-1}, which is probably compensated by the crystal packing effect. The crystal packing is built of the chains formed by the Br···Br bonds [$Br^1\cdots Br^2$, *d* 3.5744(4) Å, $\angle C^{31}Br^1\cdots Br^2$ 160.00(8)°, $\angle C^{38}Br^2\cdots Br^1$ 83.43(8)°], i. e., the Br^2 atom is an electron pair donor, and the C^{31}–Br^1 antibonding bond is an acceptor. The energy of such bond may equal 3–5 kcal mol^{-1}. It can lead to a less favorable orientation of the isobornyl substituent at the C^{13}atom. However, the structure is further stabilized by the numerous van der Waals interactions, each of which is considerably weaker (<0.5 kcal mol^{-1}), but the complex of such contacts can compete with the energy of the Br···Br bond and participate in the stabilization of the less favorable orientation of the terpene fragment.

Thus, the alkylation of resorcinol with camphene using $(PhO)_3Al$ and $(i\text{-}PrO)_3Al$ as the catalysts was used. The diastereomers of symmetrically dialkylated resorcinol were studied by the HPLC and X-ray diffraction analysis. The orientation of the terpene substituent in the *ortho*-isobornylphenol was examined by the quantum-chemical calculations using a model compound.

EXPERIMENTAL

The IR spectra were recorded on Shimadzu IR Prestige 21 FTIR spectrometer from KBr pellets. The ^1H and ^{13}C NMR spectra were registered on Bruker Avance II 300 spectrometer (300 and 75 MHz, respectively) in $CDCl_3$ at room temperature. The signals assignment was performed using the ^{13}C NMR spectra recorded in a JMOD mode and the two-dimensional NMR (HSQC, COSY, NOESY).

The control of the purity of the starting phenols and camphene and the analysis of the volatile reaction products were carried out by GLC on a Shimadzu GC-2010AF instrument with a flame-ionization detector (carrier-gas helium) on a capillary HP-1 column (Agilent, 60 m × 0.25 mm × 0.25 mm, ramp 100–240°C, the heating rate 6 deg min^{-1}). The melting points were determined on a Koeffler heating block.

The reaction progress was monitored by TLC on Sorbfil plates using petroleum ether–diethyl ether with an increase in the proportion of the latter as a solvent system. Components **I–VIII** were detected by treating with an alcoholic solution of vanillin followed by heating to 100–150°C. Ester **IXa** was detected by treatment with a solution of bromocresol purple followed by heating to 100–120°C. The reaction products were separated by the column chromatography using silica gel (Alfa Aesar, 70/230μ).

The natural camphene (racemate) containing only tricyclene impurity (according to GLC, 5%) was used. Resorcinol, phenol of chemical grade, triethylamine (Sigma-Aldrich), 4-bromobenzoyl chloride, and 4-dimethylaminopyridine (Alfa Aesar) were used without further purification. Toluene was dried with anhydrous CaCl$_2$ and distilled over metallic Na. (*i*-PrO)$_3$Al (Alfa Aesar) and (PhO)$_3$Al (synthesized *in situ*) were used as the catalyst.

The HPLC-investigation of diastereomers **VIIIa** was performed on an Agilent 1100 instrument using a Chiralcel OD-H column (Daicel, 250 × 4.6 mm, 10 μm) eluting with hexane–*i*-PrOH mixture (19:1 by volume) with the rate of 1.0 ml min^{-1}(UV detector, λ 224 nm, 20°C). Retention times for *rac*-**VIIIa** is 9.1 and 11.5 min, for *meso*-**VIIIa**, 12.6 min.

Alkylation of resorcinol with camphene in the presence of (PhO)$_3$Al, (*i*-PrO)$_3$Al *(general procedure).* To 0.08 g (0.85 mmol) of phenol heated to 160°C was added in small portions 0.008 g (0.3 mmol) of aluminum shavings. After the aluminum dissolution was complete, the reaction mixture was cooled to 40°C. To this mixture was added 0.71 g (7 mmol) of resorcinol **I** and the calculated amount of camphene **II**. When (*i*-PrO)$_3$Al was used, the reagents and catalyst were loaded simultaneously. The reaction temperature was maintained at 120°C or 160–170°C. The reaction completed with the substantial conversion of the initial reagents (GLC control). The reaction mixture was separated by the column chromatography. The reaction conditions and reaction products yields are presented in the Table.

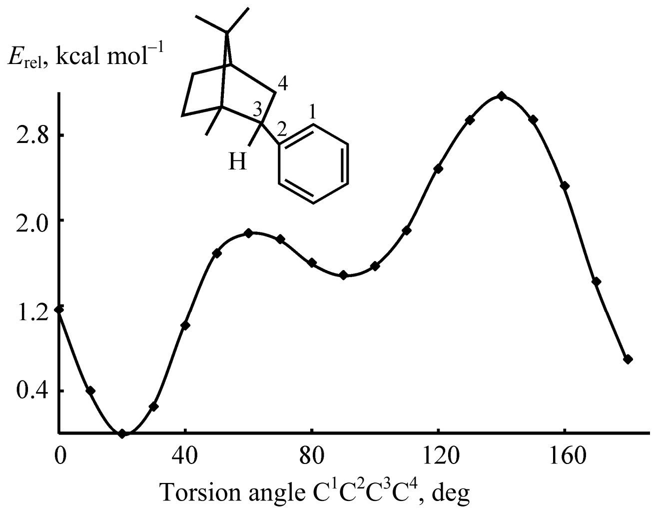


Fig. 2. Dependence of the relative conformational energy on the torsion angle C^{1}C^{2}C^{3}C^4 for the model isobornylbenzene compound.

The spectral characteristics of compounds **IIIa**, **Va**, **Vb,** and **VIb** correspond to the published data [1].

***exo*-3-(2,2,3-Trimethylbicyclo[2.2.1]hept-5-yloxy)-phenol (IIIb).** Viscous brown oil.^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.99 s (3H, C^{10}H$_3$), 0.98 s (3H, C^{9}H$_3$), 0.97 s (3H, C^{8}H$_3$),1.50–1.56 m (3H, H^3, H^6, H^7); 1.80–1.93 m (1H, H^1), 1.97–1.99 m (1H, H^4), 2.28–2.32 m (1H, H^3), 3.37–3.38 m (1H, H^5), 5.51 s (1H, OH), 6.35 s (1H, H^{12}), 6.36–6.52 m (2H, H^{14}, H^{16}), 7.11–7.20 m (1H, H^{15}). ^{13}C NMR spectrum, δ$_C$, ppm: 16.43 (C^{10}), 27.85 (C^9), 24.99 (C^8), 33.63 (C^7), 39.49 (C^4), 40.09 (C^1), 48.65 (C^3), 49.33 (C^5), 50.6 (C^6), 79.80 (C^5), 102.92 (C^{12}), 107.19 (C^{14}), 108.12 (C^{16}), 128.68 (C^{15}), 156.63 (C^{11}), 159.42 (C^{13}).

***exo*-3-(1,5,5-Trimethylbicyclo[2.2.1]hept-2-yloxy)-phenol (IIIc)** was characterized in a mixture with the esters **IIIa** and **IIIb**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.93 s (3H, C^{10}H$_3$), 0.91 s (3H, C^{9}H$_3$), 0.89 s (3H, C^{8}H$_3$), 3.95 d. d (1H, H^2, *J* 3.9, 3.3), 4.99 s (1H, OH), 6.35 s (1H, H^{12}), 6.36–6.52 m (2H, H^{14}, H^{16}), 7.14 t (1H, H^{15}). ^{13}C NMR spectrum, δ$_C$, ppm: 15.13 (C^{10}), 24.99 (C^9), 27.34 (C^8), 29.68 (C^4), 29.68 (C^7), 33.86 (C^6), 35.19 (C^3), 49.33 (C^1), 86.22 (C^5), 102.92 (C^{12}), 107.19 (C^{14}), 108.12 (C^{16}), 128.68 (C^{15}), 156.63 (C^{11}), 159.42 (C^{13}).

***exo,exo*-2-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl)-5-(1,7,7-trimethylbicyclo[2.2.1]hept-2-yloxy)-**

phenol (IVa). Brown oil.^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.82 s (3H, $C^{10}H_3$), 0.87 s (3H, C^9H_3), 0.89 s (3H, $C^{10'}H_3$), 0.90 s (3H, C^8H_3), 1.01 s/1.02 s (3H, $C^{9'}H_3$, two diastereomers), 1.08 s/1.10 s (3H, $C^{8'}H_3$, two diastereomers), 1.23–1.28 m (4H, H^6, $H^{6'}$, H^5, $H^{5'}$), 1.62–1.66 m (5H, H^6, $H^{6'}$, H^5, $H^{5'}$, $H^{4'}$), 1.79–1.87 m (4H, H^3, $H^{3'}$), 2.20–2.26 m (1H, H^4), 3.00–3.07 m (1H, H^2), 4.00–4.07 m (1H, $H^{2'}$), 4.79 s (1H, OH), 6.35 s/6.36 s (1H, H^{13}, two diastereomers), 6.43 d/6.45 d (1H, H^{15}, *J* 2.3/1.9, two diastereomers), 7.16 d (1H, H^{16}, *J* 9.0).^{13}C NMR spectrum, δ$_C$, ppm: 11.79 ($C^{10'}$), 12.40 (C^{10}), 20.15 ($C^{9'}$), 20.24 (C^9), 20.35 ($C^{8'}$), 21.46 (C^8), 27.40 ($C^{5'}$), 27.54 (C^5), 34.09 ($C^{3'}$), 34.24 (C^3), 39.64 ($C^{6'}$), 39.93 (C^6), 45.10/45.14 (C^2, two diastereomers), 45.33 ($C^{4'}$), 45.58 (C^4), 46.99 (C^1), 47.94 ($C^{1'}$); 49.17 ($C^{7'}$); 49.54 (C^7), 84.42/84.50 ($C^{2'}$, two diastereomers), 102.55/102.90 (C^{13}, two diastereomers), 106.54/107.08 (C^{15}, two diastereomers), 120.98 (C^{11}), 128.49/128.53 (C^{16}), 155.48 (C^{12}), 156.88 (C^{14}).

***exo,exo*-2-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl)-6-(2,2,3-trimethylbicyclo[2.2.1]hept-5-yl)benzene-1,3-diol (VIIab).** Viscous brown oil. IR spectrum (thin layer), ν, cm^{-1}: 3624 and 3436 (O–H, phenol), 1286 [δ(OH), phenol], 1646 and 1614 (C=C, benzene ring), 1392 and 1376 (δ *gem*-dimethyl), 1084 and 1376 (1,2,3-substitution), 950 (1,2,4-substittion). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.78 s (3H, $C^{10'}H_3$), 0.84 s (3H, $C^{9'}H_3$), 0.87 s (3H, $C^{8'}H_3$), 0.92 br. d (3H, $C^{10}H_3$), 0.94 br.s (3H, C^8H_3), 1.08 s (3H, C^9H_3), 1.18–1.42 m (3H, $H^{5'}$, $H^{6'}$, H^3), 1.51–1.64 m (3H, $H^{6'}$, H^6, $H^{3'}$), 1.68–1.94 m (5H, $H^{5'}$, H^7, $H^{4'}$, H^1), 2.10–2.20 m (2H, H^6, $H^{3'}$), 2.26–2.38 m (1H, H^4), 2.91 br. t (1H, $H^{2'}$), 3.02–3.08 m (1H, H^5), 4.85 br.s (1H, OH), 5.01 and 5.03 two br.s (1H, OH, two diastereomers), 6.27 d/6.29 d (1H, H^{15}, *J* 8.5/8.5, two diastereomers), 6.94 d (1H, H^{16}, *J* 8.5).^{13}C NMR spectrum, δ$_C$, ppm: 12.33 ($C^{10'}$), 16.45 (C^{10}), 20.15 ($C^{9'}$), 21.43 ($C^{8'}$), 24.98 (C^8), 27.82 ($C^{5'}$), 27.87 (C^8), 33.94 (C^6), 34.21/3.27 ($C^{3'}$, two diastereomers), 35.39 (C^7), 39.61(C^2), 40.03 ($C^{6'}$), 41.02/41.09 (C^5, two diastereomers), 45.46 ($C^{2'}$), 45.78 ($C^{4'}$), 48.03 ($C^{7'}$, $C^{1'}$), 49.28/49.34 (C^1, two diastereomers), 50.41/50.43 (C^3, two diastereomers), 50.56/ 50.62 (C^4, two diastereomers), 107.54/107.59 (C^{16}, two diastereomers), 125.17 (C^{16}), 118.21 (C^{11}), 121.49 (C^{13}), 151.98, 153.69 (C^{12}, C^{14}).

***exo*-4,6-Di-(1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)benzene-1,3-diol (VIIIa),** diastereomers mixture. Individual diastereomers were separated by the recrystallization from hexane.

***rac*-VIIIa**. Light-brown powder, mp 207–209°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.80 s (6H, $C^{10}H_3$, $C^{10'}H_3$), 0.87 s (6H, C^9H_3, $C^{9'}H_3$), 0.91 s (6H, C^8H_3, $C^{8'}H_3$), 1.33–1.46 m (4H, H^6, $H^{6'}$), 1.61–1.68 m (4H, H^5, $H^{5'}$), 1.87–1.91 m (4H, H^3, $H^{3'}$), 2.14–2.21 m (4H, H^4, $H^{4'}$), 3.02 t (2H, H^2, $H^{2'}$, *J* 8.7), 4.58 s (2H, 2OH), 6.31 s (1H, H^{13}), 7.23 s (1H, H^{16}).^{13}C NMR spectrum, δ$_C$, ppm: 12.46 (C^{10}, $C^{10'}$), 20.25 (C^9, $C^{9'}$), 21.50 (C^8, $C^{8'}$), 27.56 (C^5, $C^{5'}$), 34.26 (C^3, $C^{3'}$), 40.07 (C^6, $C^{6'}$), 45.47 (C^2, $C^{2'}$), 45.58 (C^4, $C^{4'}$), 47.90 (C^1, $C^{1'}$), 49.54 (C^7, $C^{7'}$), 102.49 (C^{13}), 120.39 (C^{11}, C^{15}), 127.96 (C^{16}), 152.89 (C^{12}, C^{14}).

***meso*-VIIIa.** Light-brown powder, mp190–193°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.82 s (6H, $C^{10}H_3$, $C^{10'}H_3$), 0.87 s (6H, C^9H_3, $C^{9'}H_3$), 0.88 s (6H, C^8H_3, $C^{8'}H_3$), 1.37–1.47 m (4H, H^6, $H^{6'}$), 1.62–1.66 m (4H, H^5, $H^{5'}$), 1.86–1.89 m (4H, H^3, $H^{3'}$), 2.17–2.23 m (4H, H^4, $H^{4'}$), 3.04 t (2H, H^2, $H^{2'}$, *J* 8.7), 4.63 s (2H, 2OH), 6.31 s (1H, H^{13}), 7.19 s (1H, H^{16}).^{13}C NMR spectrum, δ$_C$, ppm: 12.45 (C^{10}, $C^{10'}$), 20.40 (C^9, $C^{9'}$), 21.33 (C^8, $C^{8'}$), 27.49 (C^5, $C^{5'}$), 34.17(C^3, $C^{3'}$), 40.06 (C^6, $C^{6'}$), 45.43 (C^2, $C^{2'}$), 45.56 (C^4, $C^{4'}$), 47.76 (C^1, $C^{1'}$), 49.46 (C^7, $C^{7'}$), 102.60 (C^{13}), 120.65 (C^{11}, C^{15}), 127.41 (C^{16}), 153.01 (C^{12}, C^{14}).

***rac*-IXa.** To a solution of 0.038 g (0.1 mmol) of ***rac*-VIIIa** in 3 ml of toluene were added 0.065 g (0.3 mmol) of 4-bromobenzoyl chloride, 0.04 ml (0.3 mmol) of Et_3N, and 0.0012 g (0.01 mmol) of 4-dimethylaminopyridine. The mixture was heated with stirring under argon for 0.5 h. Then the reaction mixture was concentrated and chromatographed (eluent – benzene).

4,6-Bis{(1*R,2*S**,4*S**)-1,7,7-Trimethylbicyclo-[2.2.1]hept-2-yl}-1,3-phenylene bis(4-bromobenzoate) [*rac*-IXa].** Yield 0.069 g (93%), colorless powder, mp 206–209°C. IR spectrum, ν, cm^{-1}: 1742 (C=O, ester), 1256 (C–O), 1171, 1094, 1072 (C–O–O), 1011 (C–Br). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.85 s, 0.86 s, 0.92 s (18H, C^8H_3, $C^{8'}H_3$, C^9H_3, $C^{9'}H_3$, $C^{10}H_3$, $C^{10'}H_3$), 1.10–1.28 m (4H, H^5, $H^{5'}$, H^6, $H^{6'}$), 1.50–1.67 m (4H, H^3, $H^{3'}$, H^6, $H^{6'}$), 1.73–1.86 m (4H, H^4, $H^{4'}$, H^5, $H^{5'}$), 2.10–2.19 m (2H, H^3, $H^{3'}$), 3.01 t (2H, H^2, $H^{2'}$, *J* 8.8), 7.06 s and 7.57 s (2H, H^{13}, H^{16}), 7.68 d (4H, H^{19}, $H^{19'}$ $H^{19''}$, $H^{19'''}$, *J* 8.6), 8.07 d (4H, H^{20}, $H^{20'}$ $H^{20''}$, $H^{20'''}$, *J* 8.6). ^{13}C NMR spectrum, δ$_C$, ppm: 13.14 (C10, C10'), 20.55 and 21.42 (C^8, $C^{8'}$, C^9, $C^{9'}$), 27.32 (C^5, $C^{5'}$), 34.53 (C^3, $C^{3'}$), 40.26 (C^6, $C^{6'}$), 45.47 (C^4, $C^{4'}$), 46.24 (C^2, $C^{2'}$), 47.98 (C^7, $C^{7'}$), 50.04 (C^1, $C^{1'}$), 116.30, 128.32 (C^{13}, C^{16}), 128.35, 128.98, and 132.17 (C^{11}, C^{15}, C^{18}, $C^{18'}$, C^{21}, $C^{21'}$), 131.56 and 132.09 (C^{19}, $C^{19'}$, C^{20}, $C^{20'}$,

C^{22}, $C^{22'}$, C^{23}, $C^{23'}$), 147.59 (C^{12}, C^{14}), 164.04 (C^{17}, $C^{17'}$). Found, %: C 64.02; H 6.13. $C_{40}H_{44}Br_2O_4$. Calculated, %: C 64.18; H 5.92.

X-Ray analysis of compound *rac*-IXa. The single crystals of ***rac*-IXa** were obtained by slow evaporation of a solution of this compound from a hexane–ethyl acetate–Et_2O solvent system. Colorless plate-like crystals, $C_{40}H_{44}Br_2O_4$ (M 748.57), at 100 K are monoclinic; a 12.1240(9), b 16.9609(13), c 17.0689(13) Å; β 96.122(2), V 3489.9(5) $Å^3$, space group $P2_1/n$, Z 4, d_{calc} 1.425 g cm^{-3}. The experimental set of 38256 reflections was obtained on a Bruker SMART APEX2 CCD diffractometer (MoK_α-radiation, θ 28°) using a single-crystal sample of 0.25×0.12×0.03 mm. Processing of the source array of the measured intensities was carried out by a SAINT and SADABS programs included into APEX2 software package [15] with a correction for extinction. The structure was solved by the direct method and refined by a full-matrix anisotropic approximation for the nonhydrogen atoms with respect to F^2_{hkl}.The hydrogen atoms were placed into the geometrically calculated positions and refined using the *rider* model [$U_{iso}(H) = nU_{eq}(C,O)$, where n = 1.5 for the methyl carbon atoms, n =1.2 for the remaining carbon atoms]. 8410 independent reflections were used for refinement (R_{int} 0.0703). The refinement convergence for all the independent reflections $wR_2$was 0.0867 [R_1 0.0396 for 6200 reflections with $I > 2\sigma(I)$]. All calculations were performed on an IBM PC using a SHELXTL software package [16]. The atomic coordinates and temperature factors are deposited into the Cambridge structural data base (CCDC 827024).

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REFERENCES

1. Fomenko, V.V., Korchagina, D.V., Salakhutdinov, N.F., Ione, K.T., and Barkhash, V.A., *Zh. Obshch. Khim.*, 2000, vol. 36, no. 12, p. 1819.
2. Kuzakov, E.V. and Shmidt, E.N., *Khim. Prirod. Soed.,* 1998, no. 5, p. 653.
3. Stern, M.H., Regan, T.H., Maier, D.P., Robeson, C.D., and Thweatt, J.G., *J. Org. Chem.*, 1973, vol. 38, p. 1264.
4. Kozlikovskii, Ya.B., Koshchii, V.A., and Butov, S.A., *Zh. Org. Khim.*, 1986, vol. 22, no. 3, p. 606.
5. Kozlikovskii, Ya.B., Koshchii, V.A., Butov, S.A., and Ovsiyuk, T.F., *Zh. Org. Khim.*, 1988, vol. 24, no. 4, p. 827.
6. Kheifits, L.A. and Aul’chenko, I.S., *Khimiya i tekhnologiya dushistykh veshchestv i efirnykh masel* (Chemistry and Technology of Fragrances and Essential Oils), Moscow: Pishchevaya Promyshlennost’, 1968, no. 8, p. 142.
7. Chukicheva, I.Yu. and Kuchin, A.V., *Ross. Khim. Zh.,* 2004, vol. 48, no. 3, p. 21.
8. Inoyatov, F.Kh., Abubakirov, R.Sh., Mikaya, A.I., Khrapova, I.M., Perchenko, V.N., Plate, N.A., *Izv. Akad. Nauk, Ser. Khim.,* 1993, no. 5, p. 992.
9. Gun’ko, V.M. and Roev, L.M., *Theor. Eksp. Khim.*, 1982, no. 1, p. 85.
10. Buravlev, E.V., Chukicheva, I.Yu., Suponitskii, K.Yu., and Kuchin, A.V., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 7, p. 1177.
11. Chukicheva, I.Yu., Shumova, O.A., Suponitskii, K.Yu., and Kuchin, A.V., *Izv. Akad. Nauk, Ser. Khim.,* 2011, no. 3, p. 496.
12. Buravlev, E.V., Chukicheva, I.Y., Suponitsky, K.Y., Vikharev, Yu.B., Grishko V.V., and Kutchin, A.V., *Lett. Org. Chem.*, 2011, vol. 8, no. 5, p. 301.
13. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, Jr., J.A., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *GAUSSIAN 03, Revision E.01*, Wallingford, CT, USA, Gaussian, Inc., 2004.
14. Suponitsky, K.Y., Tafur, S., and Masunov, A.E., *J. Chem. Phys*., 2008, vol. 129, no. 4, p. 044109.
15. *APEX2 and SAINT Software Package*, Madison, Wisconsin, USA, Bruker AXS Inc., 2005.
16. Sheldrick, G.M., *Acta Cryst. (A)*, 2008, vol. 64, p. 112.