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Catalytic Alkylation of Pyrocatechol with Camphene

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Abstract—Regularities of the pyrocatechol alkylation with camphene in the presence of aluminum-containing homogeneous catalysts and heterogeneous acid catalysts were studied. The effect of the catalyst type on the reaction selectivity and the product composition was established. The most selective heterogeneous catalyst for the C-alkylation of pyrocatechol is montmorillonite KSF, which leads to a rearrangement of the terpene fragment to isocamphyl structure. Homogeneous organoalyuminum compounds are found to be nonselective catalysts for the alkylation of pyrocatechol at the benzene ring.

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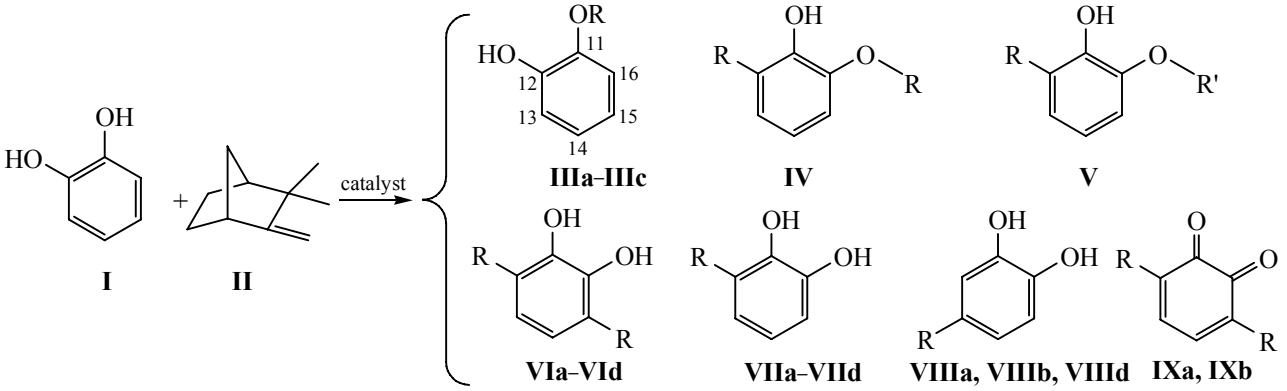
Alkylation of phenols, including dihydric, with terpenes (camphene, β-pinene) with the use of zeolites as catalysts to create an organized reaction medium has been described. However, the conversion of initial reagents and the selectivity of these processes were insignificant [1–3]. The regio- and stereoselectivity of the alkylation of phenols with camphene in the presence of aluminum alkoxides is ascribed to the proceeding of the intramolecular alkylation in the aluminum coordination sphere [4].

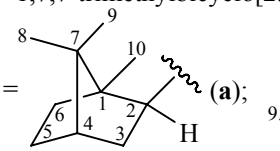
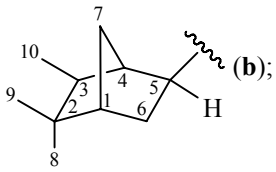
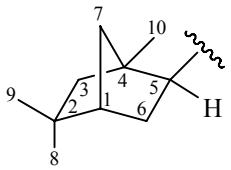
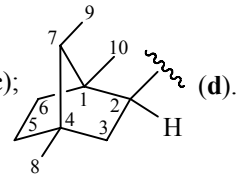
Previously, we studied the alkylation of dihydroxybenzenes with camphene in the presence of aluminum phenolate and aluminum isopropoxide [5, 6]. The aluminum phenoxide as one of the most active organo-aluminum catalysts was used as the catalyst for preparation *in situ* of mixed aluminum phenoxides. It was shown that the reaction of pyrocatechol with camphene at 160–170°C in the presence of aluminum phenoxide proceeded with the yield of up to 75.5% to afford the product of O-alkylation **IIIa**, the monoether with isobornyl structure of the terpene substituent.

It was found that C-alkylation of pyrocatechol occurred only at a sufficiently high temperature (200°C). Probably, in this case, the reaction conditions correspond to thermodynamic control of the reaction that results in the rearrangement of the ether of pyrocatechol to the product of the C-alkylation.

In this research we continued the study on the alkylation of pyrocatechol **I** with camphene **II** in the presence of aluminum-containing homogeneous catalysts and heterogeneous acid catalysts aimed at the selective synthesis of the C-alkylated pyrocatechol. The alkylation conditions as well as the composition of the reaction products were determined by the structure of the initial phenols and olefins, as well as by the features of the used catalyst. The composition of the products of alkylation of phenols with camphene is complicated by the opportunity of skeletal rearrangements of the intermediate carbocation arising from camphene, the initial bicyclic monoterpene [7, 8].

We found that the use of aluminum pyrocatecholate at 120°C for the alkylation of pyrocatechol **I** with camphene **II** leads to the formation of the isobornyl catechol ether **IIIa** (78%) as the main product (see the table), like in the case of catalysis with aluminum phenoxide. Raising the temperature of the reaction mixture to 160°C leads to a decrease in the process selectivity: a mixture of the products of O- and C-alkylation is formed with different terpene substituents. Using $(acac)_2AlCl$ leads to the formation of almost equal amounts of products of O- and C-alkylation containing isobornyl and isocampenyl terpene substituents. The interaction of pyrocatechol **I** with camphene **II** catalyzed by the sulfonic acid cation exchanger FIBAN K-1 was carried out using different solvents (see the table). At boiling in methylene chloride (40°C) the alkylation proceeds with high selectivity and the formed product is the pyrocatechol monoester with isobornyl structure of terpene substituent **IIIa** in up to 99% yield.



IV, R = 2-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl); **V**, R = 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl, R' = 2,2,3-trimethylbicyclo[2.2.1]heptan-5-yl); **III, VI–IX**, R =  (**a**);  (**b**);  (**c**);  (**d**).

catalyst is one of the following substances: FIBAN K-1, FIBAN K-2, FIBAN K-3, aluminum pyrocatecholate, $(acac)_2AlCl$.

It was noted that raising the temperature of the reaction mixture by performing the reaction in hexane (70°C) or heptane (about 100°C) leads to a decrease in selectivity and the formation of a complex mixture of products of O- and C-alkylation with a different structure of terpene substituent. Dihydric phenols are easily oxidized, which may explain the appearance in these conditions of the oxidation products (18%), including dialkylated quinones **IXa** and **IXb** (see the table).

Use of FIBAN K-4 and FIBAN X-1 as catalysts in the same solvents does not lead to the pyrocatechol alkylation. This difference in efficiency between FIBANS K-1, X-1, and K-4 is due to the difference between their functional groups. FIBAN K-1 is a fibrous strong acidic cation exchanger (functional group is SO_3H). Its polymeric base is polypropylene fiber with the grafted copolymer of styrene and divinylbenzene. FIBAN K-4 is a weak acid cation exchanger (functional group is COOH). FIBAN X-1 is a fibrous chelating ion ex-changer containing functional groups $N(CH_2COO)_2$ and COOH.

An interesting feature of the alkylation of pyrocatechol **I** with camphene **II** in the presence of KSF clay (the clay from the group of layered silicates) is the predominant formation of products with isocamphyl terpene substituent. In addition, the main product of the alkylation of pyrocatechol **I** with camphene **II** is the *para*-alkylated pyrocatechol with isocamphyl terpene substituent (**VIIIb**, 38–57%) regardless of the temperature and the ratio of initial reagents (see the table). The interaction of pyrocatechol with an excess of camphene leads to the formation of a complex mixture of dialkylated phenols with the terpene substituents in *ortho*- and *para*-positions. In this case the products with isobornyl substituent also were not detected. Carrying out the reaction by refluxing in CH_2Cl_2 contributes to the selective formation of ether **IIIa** as in the case of FIBAN K-1.

Thus, the studied heterogeneous catalysts promote selective formation of desired products. Using KSF and FIBAN K-1 in a low-temperature regime contributes to the O-alkylation and the formation of ethers with isobornyl structure of the terpene fragment. The most selective heterogeneous catalyst for the C-alkylated pyrocatechol is montmorillonite KSF, which leads to the terpene fragment rearrangement into isocamphyl structure. Homogeneous organoaluminum compounds are nonselective catalysts for the alkylation of the

Conditions of alkylation of pyrocatechol with camphene and the products obtained

Ratio **I**:**II**: (mol)	Reaction conditions	Conversion, %	Ratio of reaction products, %																		
			III			**IVa**	**Va**	**VI**				**VII**				**VIII**				**IX**
			a	**b**	**c**			**b**	**a**	**c**	**d**	**b**	**a**	**c**	**d**	**b**	**a**	**c**	**d**	
FIBAN K-1																				
1:1	100°C, C_7H_{16}, 2 h	85	1	–	–	–	–	3	3			20	12		–	26	7	–	–	8
	70°C, C_6H_{14}, 4 h	99	24	8	3	7	5	8	6		–	8	5			8	7		–	2
	40°C, CH_2Cl_2, 2 h	90	99	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
KSF																				
1:1	40°C, CH_2Cl_2, 3 h	99	87	13	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	100°C, C_7H_{16}, 2 h	98	–	4	–	4	17	–	–	–	–	16	8			51	–	–	–	–
	100°C, 3 h	91	–	–	–	–	–	11	9	4	8	7	3	–	–	57	–	–	–	–
	160°C, 2 h	98	1			–	–	9	14			12	3	3	15	40	–	–		3
1:2	100°C, 4 h	98	8	7	–	10	1	21	–	–	–	6	4		–	38	5		–	
	160°C, 3 h	98	–	–	–	–	–	31				12				50	–	7		–
Aluminum pyrocatecholate																				
1:1	120°C, 10 h	50	78	6	1	–	–	–	–	–	–	–	5	–	–	–	10	–		–
	160°C, 3 h	80	37	14	4	3	–	–	5			4	11	–	–	5	16	–	–	–
$(acac)_2AlCl$																				
1:1	160°C, 4 h	90	38	13	–	–	–	–	–	–	–	2	22	–	–	3	13	–	–	–

pyrocatechol ring. The alkylation products are mainly the compounds with isobornyl terpene substituent.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II 300 instrument (operating frequency 300 MHz and 75 MHz respectively), solvent deuterochloroform. As the internal reference the signals of chloroform (δ_H 7.26 ppm, δ_C 76.90 ppm) were used. The purity of starting materials was checked and the analysis of reaction products was carried out by GLC on a Shimadzu GC-2010AF chromatograph using a capillary column HP-1 (60 m×0.25 mm×0.25 μ, temperature 100–240°C, heating rate 6°C per minute). Flame ionization detector, carrier gas helium. Melting point was determined on a Koeffler heating block.

The reaction progress was monitored by TLC on Sorbfil plates using the solvent system petroleum ether–diethyl ether with increasing fraction of the latter. For the detection of substances the plate was treated with a solution of $KMnO_4$ (25 g of $KMnO_4$, 300 ml of H_2O, 0.5 ml of conc. H_2SO_4), as well as with a solution of vanillin (1 g of vanillin, 5 ml of conc. H_2SO_4, 100 ml of 95% ethanol) followed by heating to 100–150°C.

For column chromatography Silica gel 60 (70–230 μm) was used. In the syntheses the following catalysts were used: montmorillonite KSF from Acros Organics, cation exchangers FIBAN K-1, K-4, and X-1 provided by the Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus.

Alkylation of pyrocatechol with camphene in the presence of aluminum-containing catalysts. In a two-neck 100 ml flask equipped with a thermometer and reflux condenser was heated a mixture of 0.80 g (7 mmol) of pyrocatechol, 1 g (7 mmol) of camphene, and 10 wt % of aluminum pyrocatecholate or $(acac)_2AlCl$ with respect to the initial pyrocatechol. During the reaction the temperature was maintained at 120°C and 160°C to complete conversion of camphene (control by GLC and TLC). After the reaction completion the reaction mixture was cooled, diluted with diethyl ether, 50% hydrochloric acid was poured to it to decompose the catalyst, then the mixture was washed with saturated $NaHCO_3$ and water until neutral

reaction. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The pyrocatechol alkylation products were isolated using column chromatography.

Alkylation of pyrocatechol with camphene in the presence of acid catalysts. In the case of sulfonic acid cation exchangers, FIBAN K-1, K-4, and X-1, catalyst was taken in amount 10 wt % with respect to the initial pyrocatechol; montmorillonite KSF was taken in a weight ratio 1:1 to the pyrocatechol. The mixture of pyrocatechol, camphene, and the catalyst taken in the calculated amounts was heated at a desired temperature in a two-neck flask equipped with a thermometer and a reflux condenser. The reaction was carried out either in an organic solvent, or in melt. The reaction conditions are shown in the table.

Upon the reaction completion the mixture was dissolved in diethyl ether, filtered from the catalyst, and the reaction products was separated by column chromatography. The structure of these compounds was evaluated using the spectral methods (NMR).

Spectral and chromatographic characteristics of compounds **IIIa–IIIc, VIIa**, **VIIb**, and **VIIIa** are identical to those described earlier [5].

2-(1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl)-6-(1,7,7-trimethylbicyclophenol[2.2.1]heptan-2-yloxy) phenol (IV). Colorless powder, mp 136°C. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.83 s (3H, $CH_3^{10'}$), 0.88 s (3H, $CH_3^{9'}$), 0.94 s (3H, $CH_3^{8'}$), 0.95 s (3H, CH_3^{10}), 1.03 s (3H, CH_3^{9}), 1.07 s (3H, CH_3^{8}, 1.03–1.14 m (4H, H^6, H^5, $H^{6'}$, $H^{5'}$), 1.31–1.45 m (4H, H^4, $H^{6'}$, H^6, $H^{4'}$) , 1.64–1.67 m (4H, H^3, H^5, $H^{3'}$, $H^{5'}$) , 1.85–1.91 m (2H, H^3, $H^{3'}$), 3.32 t (1H, H^2, *J* 6 Hz), 4.10–4.19 m (1H, H^2), 5.86 s (1H, OH), 6.70 d (1H, H^{16}, *J* 9 Hz), 6.79 t (1H, H^{15}, *J* 9 Hz), 6.96 d (1H, H^{14}, *J* 9 Hz). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 12.31 (C^{10}, $C^{10'}$), 20.36 (C^8, $C^{8'}$), 21.43 (C^9, $C^{9'}$), 27.55 (C^5, $C^{5'}$), 34.24 (C^6, $C^{6'}$), 39.80 (C^3, $C^{3'}$), 45.29 (C^4), 47.00 ($C^{2'}$, $C^{4'}$), 47.82 ($C^{1'}$), 49.32 (C^7), 48.08 (C^1), 50.00 ($C^{7'}$), 85.71 (C^2), 109.54 (C^{16}), 118.26 (C^{14}), 120.15 (C^{15}), 129.73 (C^{13}), 145.32 (C^{11}), 147.11 (C^{12}).

2-(2,2,3-Trimethylbicyclo[2.2.1]heptan-2-yl)-6-(1,7,7-trimethylbicyclophenol[2.2.1]heptan-2-yloxy) phenol (V). Colorless oil. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.87 d (3H, $CCH_3^{10'}$, *J* 6 Hz), 1.06 d (6H, $CH_3^{8'}$, $CH_3^{9'}$, *J* 6 Hz), 1.09 s (6H, CH_3^{8}, CH_3^{9}), 1.16 s (3H, CH^{10}), 1.18–1.22 m (3H, H^6, H^5, $H^{7'}$), 1.46–1.49 m (7H, H^6, $H^{6'}$, H^5, $H^{1'}$, $H^{7'}$, $H^{3'}$, H^4), 1.67–1.69 m (1H, H^3), 1.70–1.94 m (3H, H^3, $H^{6'}$, $H^{4'}$), 3.11 t (1H, $H^{5'}$, *J* 6 Hz), 4.10–4.21 m (1H, H^2), 5.81 s (1H, OH), 6.73 d (1H, H^{16}, *J* 9 Hz), 6.82 d (1H, H^{15}, *J* 9 Hz), 7.00 d (1H, H^{14}, *J* 9 Hz). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 12.03 (C^{10}), 16.01 ($C^{10'}$), 20.38 (C^8), 20.79 (C^9), 24.49 ($C^{8'}$), 27.73 ($C^{9'}$), 30.36 (C^5), 32.04 ($C^{7'}$), 32.68 ($C^{4'}$), 33.67 ($C^{6'}$), 34.27 (C^6), 39.57 (C^3), 39.83 ($C^{5'}$), 40.66 (C^4), 45.88 (C^1), 47.21 ($C^{2'}$, $C^{3'}$), 49.65 (C^7), 49.81 ($C^{1'}$), 85.78 (C^2), 109.33 (C^{16}), 118.17 (C^{14}), 118.81 (C^{15}), 133.56 (C^{13}), 143.72 (C^{11}), 144.46 (C^{12}).

3,6-Di-(1,7,7-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl)benzo-1,2-diol (VIa). Yellow oil. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.84 s (6H, CH_3^{10}, $CH_3^{10'}$), 0.90 s (6H, CH_3^{9}, $CH_3^{9'}$), 1.26 s (3H, CH_3^{8}, $CH_3^{8'}$), 3.04 t (2H, H^2, $H^{2'}$, *J* 6 Гц), 4.65 s (2OH), 1.39–1.48 m (6H, H^4, $H^{4'}$, H^5, $H^{5'}$, H^6, $H^{6'}$), 1.55–1.68 m (3H, H^3, $H^{3'}$, H^5, $H^{5'}$, H^6, $H^{6'}$), 1.84-1.85 m (1H, H^3), 6.71-6.95 m (2H, H^{15}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 12.43 (C^{10}, $C^{10'}$), 20.61 (C^9, $C^{9'}$), 21.45 (C^8, $C^{8'}$), 27.59 (C^5, $C^{5'}$), 34.38 (C^6, $C^{6'}$), 40.11 (C^3, $C^{3'}$), 45.53 (C^2, $C^{2'}$), 46.13 (C^4, $C^{4'}$), 48.84 (C^1, $C^{1'}$), 49.93 (C^7, $C^{7'}$), 125 (C^{15}, C^{16}), 142.4 (C^{11}, C^{14}), 145.18 (C^{12}, C^{13}).

3,6-Di-(2,2,3-Trimethylbicyclo[2.2.1]hept-*exo*-2-yl)benzo-1,2-diol (VIb). Yellow oil. заменить на: ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.92 d (6H, CH_3^{10}, $CH_3^{10'}$, *J* 6 Hz), 0.94 s (6H, CH_3^{9}, $CH_3^{9'}$), 1.08 s (3H, CH_3^{8}, $CH_3^{8'}$), 2.91 t (2H, H^5, $H^{5'}$, *J* 6 Hz), 5.24, 5.18 s (1H each, 2OH), 1.35-1.49 m (4H, H^6, $H^{6'}$, H^7, $H^{7'}$), 1.63–1.88 m (6H, H^7, $H^{7'}$, H^1, $H^{1'}$, H^4, $H^{4'}$), 2.17–2.34 m (2H, H^3, $H^{3'}$), 6.71–6.95 m (2H, H^{15}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 16.2 (C^{10}, $C^{10'}$), 27.6 (C^9, $C^{9'}$), 24.8 (C^8, $C^{8'}$), 33.5 (C^7, $C^{7'}$), 40.7 (C^6, $C^{6'}$), 32.6 (C^5, $C^{5'}$), 50.9 (C^4, $C^{4'}$), 39.6 (C^3, $C^{3'}$), 48.8 (C^2, $C^{2'}$), 49.7 (C^1, $C^{1'}$), 116.61 (C^{15}, C^{16}), 130.80 (C^{11}, C^{14}), 141.45 (C^{12}, C^{13}).

3,6-Di-(2,2,4-Trimethylbicyclo[2.2.1]hept-*exo*-5-yl)benzo-1,2-diol (VIc). Yellow oil. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.03 s (6H, CH_3^{9}, $CH_3^{9'}$), 1.06 s (6H, CH_3^{8}, $CH_3^{8'}$), 1.26 s (6H, CCH_3^{10}, $CCH_3^{10'}$), 1.25–1.43 m (4H, H^3, $H^{3'}$, H^7, $H^{7'}$), 1.50–1.71 m (4H, H^6, $H^{6'}$, H^1, $H^{1'}$), 1.75–1.85 m (6H, H^1, $H^{1'}$, H^3, $H^{3'}$, H^7, $H^{7'}$), 2.15–2.4 m (2H, H^6, $H^{6'}$), 2,7 t (2H, H^5, $H^{5'}$), 5.00 s (2OH), 6.65 s (2H, H^{15}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 17.00 (C^{10}, $C^{10'}$), 26.78 (C^9, $C^{9'}$), 28.98 (C^8, $C^{8'}$), 33.00 (C^6, $C^{6'}$), 33.49 (C^7, $C^{7'}$), 39.64 (C^2, $C^{2'}$), 40.76 (C^5, $C^{5'}$), 45.29 (C^3, $C^{3'}$), 39.64 (C^2, $C^{2'}$), 49.77 (C^1, $C^{1'}$), 51.04 (C^4, $C^{4'}$), 143.00 (C^{12}, C^{13}), 132 (C^{11}, C^{14}), 110.99 (C^{15}, C^{16}).

3,6-Di-(1,4,7-*anti*-trimethylbicyclo[2.2.1]hept-*exo*-2-yl)benzo-1,2-diol (VId). Yellow oil. ^{1}H NMR

spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.6 s (6H, CH_3^9, $CH_3^{9'}$), 0.80 s (6H, CH_3^8, $CH_3^{8'}$), 1.05 s (6H, CCH_3^{10}, $CCH_3^{10'}$), 1.35–1.75 m (8H, $2H^5$, $2H^{5'}$, $2H^6$, $2H^{6'}$), 1.8–1.95 m (2H, $2H^3$, $2H^{3'}$), 2.00 m (2H, H^7, $H^{7'}$), 2.15–2.48 m (2H, H^2, $H^{2'}$), 5.13, 5.29 s (1H each, 2OH), 6.7–6.85 m (2H, H^{14}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 8.36 (C^8, $C^{8'}$), 17.16 (C^9, $C^{9'}$), 19.02 (C^{10}, $C^{10'}$), 34.45 (C^5, $C^{5'}$), 37.73 (C^6, $C^{6'}$), 45.12 (C^4, $C^{4'}$), 46.55 (C^3, $C^{3'}$), 49.04 (C^7, $C^{7'}$), 50.00 (C^1, $C^{1'}$), 51.06 (C^2, $C^{2'}$), 139.43(C^{11}, C^{14}), 140.63 (C^{12}, C^{13}), 112.59 (C^{15}, C^{16}).

3-(*exo*-2,2,4-Trimethylbicyclo[2.2.1]hept-5-yl)-benzo-1,2-diol (VIIc). Yellow oil. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0,84 s (3H, CH_3^9), 0.9 s (3H, CH_3^8), 1.13 s (3H, CCH_3^{10}), 1.35–1.50 m (2H, H^3, H^7), 1.61–1.75 m (3H, H^1, H^3, H^7), 1.79–1.98 (1H, H^6), 2.15–2.38 m (1H, H^6), 2.7 t (1H, H^5), 5.2 s (2OH), 6.6–6.7 m (3H, H^{13}, H^{14}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 11.09 (C^{10}), 14.09 (C^9), 24.34 (C^8), 30.30 (C^6), 34.11 (C^7), 39.21 (C^2), 40.93 (C^5), 45.68 (C^3), 39.60 (C^2), 48.87 (C^1), 51.00 (C^4), 143.21 (C^{13}), 142.8 (C^{12}), 130.00 (C^{11}), 118.23 (C^{14}), 116.51 (C^{15}), 111.05 C^{16}).

3-(*exo*-1,4,7-Trimethylbicyclo[2.2.1]hept-2-yl)-benzo-1,2-diol (VIId). Yellow oil. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0,73 s (3H, CH_3^9), 0.74 d (3H, CH_3^8, *J* 6Hz), 1.06 s (3H, CCH_3^{10}), 1.35–1.50 m (2H, H^3, H^7), 1.61–1.75 m (3H, H^1, H^3, H^7), 1.79–1.98 m (1H, H^6), 2.15–2.38 m (1H, H^6), 2.7 t (1H, H^5), 5.2 s (2OH), 6.6–6.7 m (3H, H^{13}, H^{14}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 8.30 (C^{10}), 17.16 (C^9), 19.02 (C^8), 30.296 (C^6), 34.114 (C^7), 39.215 (C^2), 40.93 (C^5), 45.68 (C^3), 39.60 (C^2), 48.87 (C^1), 51.00 (C^4), 142.58 (C^{13}), 141.31 (C^{12}), 129.96 (C^{11}), 118.74 (C^{14}), 116.65 (C^{15}), 111.23 C^{16}).

4-(*exo*-2,2,3-Trimethylbicyclo[2.2.1]hept-5-yl)-benzo-1,2-diol (VIIIb). Yellow oil. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.90 d (3H, CCH_3^{10}, *J* 6 Hz), 1.05 s (6H, CH_3^9, CH_3^8), 1.32–1.39 m (2H, H^6, H^7), 1.69–1.90 m (3H, H^7, H^1, H^4), 2.16–2.24 m (2H, H^3, $H^{6'}$), 2.7 t (1H, H^5), 5.65 s (2OH), 6.68–6.93 m (3H, H^{12}, H^{15}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 16.28 (C^{10}), 24.84 (C^8), 27.56 (C^9), 32.00 (C^5), 33.42 (C^7), 39.46 (C^3), 40.54 (C^6), 49.03 (C^1), 49.73 (C^4), 49.50 (C^2), 114.38 (C^{15}), 115.25 (C^{16}), 119.41 (C^{12}), 140.98 (C^{11}), 141.28 (C^{13}), 143.27 (C^{14}).

3,6-Di-(*exo*-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl)-benzo-1,2-quinone (IXa). Yellow oil. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.80–1.10 m (18H, CCH_3^{10}, $CCH_3^{10'}$, CH_3^9, $CH_3^{9'}$, CH_3^8, $CH_3^{8'}$), 1.16–1.37 m (6H, $2H^6$, $2H^{6'}$, H^7, $H^{7'}$), 1.40–1.95 m (4H, H^7, $H^{7'}$, H^1, $H^{1'}$), 2.99 t (2H, H^2, $H^{2'}$, *J* 6 Hz), 6.78–6.85 m (2H, H^{15}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 16.19 (C^{10}, $C^{10'}$), 25.00 (C^9, $C^{9'}$), 27.31 (C^8, $C^{8'}$), 29.70 (C^5, $C^{5'}$), 33.38 (C^6, $C^{6'}$), 39.32 (C^3, $C^{3'}$), 44.89 (C^4, $C^{4'}$), 45.39 (C^2, $C^{2'}$), 48.39 (C^7, $C^{7'}$), 50.7 (C^1, $C^{1'}$), 134.14 (C^{15}, C^{16}),145.02 (C^{11}, C^{14}), 180.01 (C^{12}, C^{13}).

3,6-Di-(*exo*-2,2,3-Trimethylbicyclo[2.2.1]hept-2-yl)-benzo-1,2-quinone (IXb). Yellow oil. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.84–0.98 m (6H, CCH_3^{10}, $CCH_3^{10'}$), 1.11 s (12H, CH_3^8, $CH_3^{8'}$, CH_3^9, $CH_3^{9'}$), 1.15–1.35 m (6H, $2H^6$, $2H^{6'}$, H^7, $H^{7'}$), 1.40–1.95 m (4H, H^7, $H^{7'}$, H^1, $H^{1'}$), 2.05–2.20 m (4H, H^4, $H^{4'}$, H^3, $H^{3'}$), 2.70 m (2H, H^5, $H^{5'}$), 6.65–6.75 m (2H, H^{15}, H^{16}). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ, ppm: 14.00 (C^{10}, $C^{10'}$), 24.75 (C^8, $C^{8'}$), 27.5 (C^9, $C^{9'}$), 32.89 (C^5, $C^{5'}$), 33.65 (C^7, $C^{7'}$), 40.67 (C^6, $C^{6'}$), 41.20 (C^3, $C^{3'}$), 50.70 (C^4, $C^{4'}$), 49.55 (C^1, $C^{1'}$), 49,63 (C^2, $C^{2'}$), 124.60 (C^{15}, C^{16}), 145.00 (C^{14}, C^{11}), 182.00 (C^{12}, C^{13}).

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