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Alkylation of Isobornylphenols with Styrene in the Presence of *p*-Toluenesulfonic Acid

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Abstract—The alkylation of racemic isobornylphenols with styrene in the presence of *p*-toluenesulfonic acid (5 mol %) afforded new hybrid compounds combining bulky terpene and phenylethyl fragments in a single molecule.

Keywords: 2-isobornyl-4-methylphenol, 2-isobornylphenol, 2-isobornyl-6-methylphenol, styrene, alkylation, diastereoisomers

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Sterically hindered phenols are widely used as antioxidants for stabilization of fuels, oils, polymeric materials, foodstuffs, etc., due to their ability to efficiently inhibit radical aging processes. Furthermore, these compounds are less toxic than unsubstituted phenols [1, 2]. The inhibitory activity of phenolic antioxidants depends on the position of substituents in the benzene ring and steric shielding of the hydroxy group [3]. Bulky substituents that effectively shield the OH group enhance the stability of phenoxy radicals and hence their inhibitory activity. Phenol derivatives with *tert*-butyl groups in the *ortho*-positions are the most widely known [2, 4]. Phenols containing phenylethyl fragments are used to stabilize polyolefins, latexes, and materials based on natural and synthetic rubber [1, 5, 6]. It is known [7] that phenols containing terpene fragment exceed their analogs with *tert*-butyl substituents in antioxidant activity. Therefore, the synthesis of phenols containing a bulky terpene and phenylethyl fragments in a single molecule attracts interest.

We previously synthesized hybrid antioxidants on the basis of phenol derivatives with terpene and *tert*-butyl substituents by alkylation of 2-*tert*-butyl-4-methylphenol with camphene and of 2-isobornylphenol with *tert*-butyl chloride in the presence of heterogeneous acid catalysts (montmorillonite KSF and FIBAN K-1) [7]. The kinetic characteristics and physicochemical properties of isobornylphenols with methyl and *tert*-butyl groups in the *ortho*-position indicated competing effects of the donor power and steric shielding of the alkyl substituent in the *ortho*-position with respect to the hydroxy group [9].

In the present work we studied the alkylation of racemic 2-isobornylphenol (**Ia**), 2-isobornyl-4-methylphenol (**Ib**), and 2-isobornyl-6-methylphenol (**Ic**) with styrene in the presence of *p*-toluenesulfonic acid monohydrate (5 mol %). The reactions were carried out according to the known procedure [10] on heating the reactants for 2–4 h at 100°C under solvent-free conditions, the reactant ratio being varied (see table).

The alkylation was characterized by complete conversion of the reactants. The reaction of phenol **Ia** with styrene gave a mixture of two alkylation products, 2-isobornyl-6-(1-phenylethyl)phenol (**IIa**) and 2-isobornyl-4-(1-phenylethyl)phenol (**IIIa**) (see table). At an equimolar reactant ratio or in the presence of excess **Ia**, the *ortho*-alkylation product (**IIa**) prevailed, whereas the use of excess styrene favored formation of a fairly complex mixture of products.

2-Isobornyl-4-methyl-6-(1-phenylethyl)phenol (**IIb**) was selectively formed in the alkylation of 2-isobornyl-4-methylphenol (**Ib**). As in the reaction with **Ia**, no bis-alkylation products were obtained in the presence of excess styrene. It is known that introduction of a second bulky substituent into phenol molecule

Alkylation of isobornylphenols with styrene

Phenol	Phenol-to-styrene ratio	Conversion, %	Yield, %			
			IIa	**IIb**	**IIIa**	**IIIc**
Ia	1 : 1	100	55	–	31	–
	2 : 1	100	72	–	28	–
	1 : 2	100	43	–	36[a]	–
Ib	1 : 1	92	–	76	–	–
	2 : 1	100	–	89	–	–
	1 : 2	100	–	83	–	–
Ic	1 : 1	96	–	–	–	85

[a] Intractable mixture of isomerization products of the terpene fragment of isobornylphenol and *para* isomer **IIIa**.

requires harsh conditions [2]. Obviously, our conditions were too mild to ensure bis-alkylation of isobornylphenols. Likewise, the alkylation of 2-isobornyl-6-methylphenol (**Ic**) afforded 2-isobornyl-4-(1-phenylethyl)-6-methylphenol (**IIIc**) as the only product (Scheme 1).

The alkylation products were mixtures of diastereoisomers at a ratio of ~1 : 1. By column chromatography we succeeded in isolating pure diastereoisomers of **IIa** and **IIb**, but we failed to separate stereoisomers of **IIIa** and **IIIc**. The structure of the isolated compounds was confirmed by NMR spectroscopy.

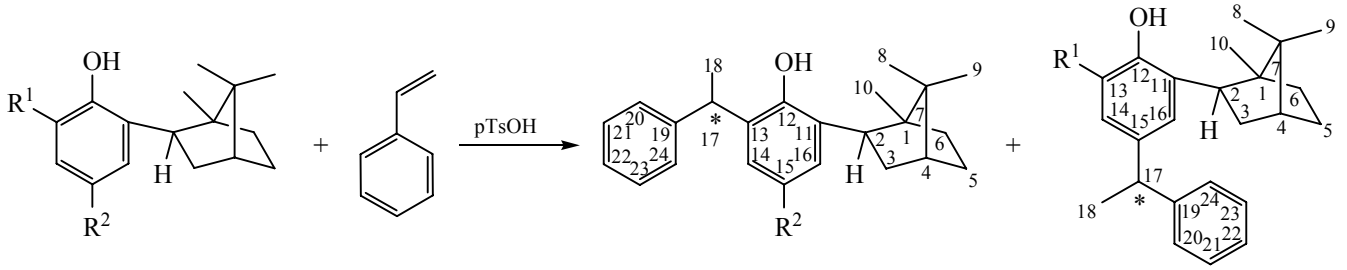
EXPERIMENTAL

Ther ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 300 spectrometer at 300.17 and 75.48 MHz, respectively, using $CDCl_3$ as solvent. The progress of reactions was monitored by TLC on Sorbfil plates using cyclohexane–diethyl ether (50 : 1) as eluent. The products were isolated and purified by column chromatography on silica gel (70/230 mesh; from Alfa Aesar).

General procedure for the alkylation of isobornylphenols with styrene. A mixture of required amounts of 2-isobornylphenol, styrene, and *p*-toluenesulfonic acid (5 mol %) was stirred for 2–4 h at 100°C. When the reaction was complete, the mixture was cooled and dissolved in diethyl ether. The solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure, and the residue was subjected to chromatographic separation. The yields are given in table.

2-(1-Phenylethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]-heptan-2-yl)phenol (IIa). IR spectrum (KBr), ν, cm^{-1}: 3531.66, 3603.03 (OH); 1597.06 (C=C); 702.09, 752.24 (=CH); 1371.39, 1381.03, 1444.68 (CH_3, CH_2). First diastereoisomer: ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.79 s (3H, $C^{10}H_3$), 0.88 s (3H, C^9H_3), 0.95 s (3H, C^8H_3), 1.31–1.49 m (2H, H^5, H^6), 1.51–1.64 m (2H, H^3, H^6), 1.69 d (3H, $C^{18}H_3$, *J* = 7.2), 1.80–1.95 m (2H, H^4, H^5), 2.24–2.31 m (1H, H^3), 3.11 t (1H, H^2, *J* = 8.4), 4.34–4.39 m (1H, H^{17}), 4.66 s (1H, OH), 6.97–7.02 m (1H, $1H^5$), 7.09 s (1H, $1H^6$), 7.20 d (1H, H^{14}, *J* = 7.5), 7.24–7.38 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.24 (C^{10}), 20.26 (C^9), 21.31 (C^8), 21.48 (C^{18}), 27.57

Scheme 1.



Ia–Ic **IIa, IIb** **IIIa, IIIc**

$R^1 = R^2 = H$ (**a**); $R^1 = H$, $R^2 = CH_3$ (**b**); $R^1 = CH_3$, $R^2 = H$ (**c**).

(C^5), 34.06 (C^3), 39.63 (C^{17}), 39.86 (C^6), 45.64 (C^2, C^4), 48.11 (C^7), 49.81 (C^1), 119.71 (C^{15}), 125.03 (C^{16}), 126.30 (C^{14}), 126.66 (C^{22}), 127.53 (C^{21}, C^{23}), 128.88 (C^{20}, C^{24}), 130.08 (C^{11}), 130.94 (C^{13}), 145.29 (C^{19}), 152.79 (C^{12}). Second diastereoisomer: ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.71 s (3H, $C^{10}H_3$), 0.93 s (3H, C^9H_3), 1.00 s (3H, C^8H_3), 1.35–1.57 m (2H, H^5, H^6), 1.67–1.71 m (2H, H^3, H^6), 1.74 d (3H, $C^{18}H_3$, *J* = 7.2), 1.79–2.03 m (2H, H^4, H^5), 2.28–2.37 m (1H, H^3), 3.20 t (1H, H^2, *J* = 9.0), 4.35–4.42 m (1H, H^{17}), 4.74 s (1H, OH), 7.04 t (1H, $1H^5$, *J* = 7.8), 7.22 d (2H, H^{14}, $1H^6$, *J* = 7.5), 7.32–7.41 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.19 (C^{10}), 20.41 (C^9), 21.15 (C^8), 21.55 (C^{18}), 27.64 (C^5), 34.09 (C^3), 39.68 (C^{17}), 39.90 (C^6), 45.60 (C^2), 45.67 (C^4), 48.15 (C^7), 49.82 (C^1), 119.83 (C^{15}), 125.30 (C^{16}), 126.34 (C^{14}), 126.74 (C^{22}), 127.54 (C^{21}, C^{23}), 128.88 (C^{20}, C^{24}), 130.30 (C^{11}), 131.07 (C^{13}), 145.19 (C^{19}), 152.71 (C^{12}).

4-(1-Phenylethyl)-6-(1,7,7-trimethylbicyclo-[2.2.1]-heptan-2-yl)phenol (IIIa). IR spectrum (KBr), ν, cm^{-1}: 3535.52 (OH), 1604.77 (C=C), 819.75 (=CH), 1371.39, 1454.33, 1498.69 (CH_3, CH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.84 s and 0.90 s (3H, $C^{10}H_3$), 0.86 s (3H, C^9H_3), 0.92 s and 0.98 s (3H, C^8H_3), 1.37–1.54 m (4H, H^3, H^5, H^6), 1.68 d (3H, $C^{18}H_3$, *J* = 7.2), 1.85–2.00 m (2H, H^4, H^5), 2.15–2.25 m (1H, H^3), 3.16 t (1H, H^2, *J* = 9.0), 4.13–4.17 m (1H, H^{17}), 4.62 s (1H, OH), 6.70 s (1H, $1H^6$), 6.73 s (1H, H^{14}), 6.93–6.96 m (1H, $1H^3$), 7.21–7.36 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.40 and 12.52 (C^{10}), 20.16 and 20.21 (C^9), 21.50 (C^{18}), 21.96 and 22.28 (C^8), 27.59 (C^5), 33.96 and 34.14 (C^3), 40.02 and 40.15 (C^6), 44.20 and 44.33 (C^{17}), 45.60 and 45.64 (C^2, C^4), 48.03 (C^7), 49.75 (C^1), 114.79 and 115.06 (C^{15}), 125.29 and 125.47 (C^{16}), 125.86 (C^{14}), 126.55 (C^{22}), 127.91 (C^{21}, C^{23}), 128.30 (C^{20}, C^{24}), 129.38 (C^{11}), 137.80 and 137.97 (C^{13}), 147.06 (C^{19}), 152.81 (C^{12}).

4-Methyl-2-(1-phenylethyl)-6-(1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-yl)phenol (IIb). IR spectrum (KBr), ν, cm^{-1}: 3533.59, 3604.96 (OH), 1600.92 (C=C), 862.18 (=CH), 1371.39, 1381.03, 1458.18 (CH_3, CH_2). First diastereoisomer: ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.85 s (3H, $C^{10}H_3$), 0.95 s (3H, C^9H_3), 1.02 s (3H, C^8H_3), 1.43–1.56 m (2H, H^5, H^6), 1.60–1.69 m (2H, H^3, H^6), 1.76 d (3H, $C^{18}H_3$, *J* = 7.2), 1.94–2.00 m (2H, H^4, H^5), 2.29–2.38 m (1H, H^3), 2.44 s (3H, CH_3–C^{15}), 3.15 t (1H, H^2, *J* = 8.7), 4.40–4.42 m (1H, H^{17}), 4.54 s (1H, OH), 7.07 s (1H, $1H^6$), 7.15 s (1H, H^{14}), 7.33–7.40 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.24 (C^{10}), 20.29 (C^9), 21.33 (C^8), 21.51 (C^{18}), 21.75 (CH_3–C^{15}), 27.59 (C^5), 33.99 (C^3), 39.64 (C^{17}), 39.82 (C^6), 45.60 (C^2), 45.63 (C^4), 48.11 (C^7), 49.79 (C^1), 125.58 (C^{16}), 126.60 (C^{14}), 126.91 (C^{22}), 127.52 (C^{21}, C^{23}), 128.45 (C^{11}), 128.85 (C^{20}, C^{24}), 129.88 (C^{13}), 130.75 (C^{15}), 145.37 (C^{19}), 150.54 (C^{12}). Second diastereoisomer: ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.64 s (3H, $C^{10}H_3$), 0.86 s (3H, C^9H_3), 0.93 s (3H, C^8H_3), 1.36–1.40 m (2H, H^5, H^6), 1.58–1.65 m (2H, H^3, H^6), 1.69 d (3H, $C^{18}H_3$, *J* = 7.2), 1.81–1.95 m (2H, H^4, H^5), 2.22–2.30 m (1H, H^3), 2.36 s (3H, CH_3–C^{15}), 3.09 t (1H, H^2, *J* = 8.7), 4.26–4.33 m (1H, H^{17}), 4.49 s (1H, OH), 6.96 s (1H, $1H^6$), 7.07 s (1H, H^{14}), 7.26–7.35 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.08 (C^{10}), 20.35 (C^9), 20.96 (C^8), 21.28 (C^{18}), 21.49 (CH_3–C^{15}), 27.57 (C^5), 33.94 (C^3), 39.58 (C^{17}), 39.84 (C^6), 45.50 (C^2), 45.63 (C^4), 48.05 (C^7), 49.72 (C^1), 125.78 (C^{16}), 126.56 (C^{14}), 126.85 (C^{22}), 127.44 (C^{21}, C^{23}), 128.53 (C^{11}), 128.74 (C^{20}, C^{24}), 130.03 (C^{13}), 130.89 (C^{15}), 145.22 (C^{19}), 150.38 (C^{12}).

2-Methyl-4-(1-phenylethyl)-6-(1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-yl)phenol (IIIc). IR spectrum (KBr), ν, cm^{-1}: 3579.88, 3606.89 (OH), 1600.92 (C=C), 773.46 (=CH), 1371.39, 1450.47, 1475.54 (CH_3, CH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.80 s and 0.81 s (3H, $C^{10}H_3$), 0.85 s (3H, C^9H_3), 0.88 s (3H, C^8H_3), 1.43– 1.48 m (2H, H^5, H^6), 1.66 d (3H, $C^{18}H_3$, *J* = 7.2), 1.67–1.69 m (2H, H^3, H^6), 1.82–1.96 m (2H, H^4, H^5), 2.13–2.20 m (1H, H^3), 2.26 s (3H, CH_3–C^{13}), 3.10 t (1H, H^2, *J* = 9.8), 4.08–4.12 m (1H, H^{17}), 4.58 s (1H, OH), 6.85 s (1H, $1H^6$), 7.06 s (1H, H^{14}), 7.21–7.34 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.59 (C^{10}), 16.33 (C^{18}), 20.20 and 20.23 (CH_3–C^{13}), 21.45 (C^9), 21.96 (C^8), 27.59 (C^5), 34.49 (C^3), 40.32 (C^6), 44.23 and 44.34 (C^{17}), 45.61 (C^2), 45.95 (C^4), 48.02 (C^7), 49.62 (C^1), 122.33 (C^{13}), 125.78 (C^{16}), 127.03 (C^{14}), 127.24 (C^{22}), 127.54 (C^{21}, C^{23}), 128.26 (C^{20}, C^{24}), 128.70 (C^{11}), 137.09 and 137.22 (C^{15}), 146.90 and 147.10 (C^{19}), 150.10 (C^{12}).

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