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Hexylthiylation of Allyl Ethers of Phenols

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Abstract—The reaction of allyl ethers of phenols with hexanethiol in the presence of azobis(isobutyronitrile) regioselectively affords 3-(hexylthio)propyl ethers of phenols, which hold promise as flotation agents.

Keywords: allyl ethers, phenols, azobis(isobutyronitrile), flotation agents

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Derivatives of ethers and esters containing sulfur and the phenol moiety exhibit properties of plant growth regulators, fungicides, and nematocides [1]; hybrid antioxidants [2]; and heat stabilizers for polymers [3]. One of the known methods for preparation of alkylthioethyl ethers of phenol is the reaction of alkanethiols with haloalkyl ethers of phenol [1].

In this study, we explore possibility of synthesis of previously unknown alkylthiopropyl ethers of phenols via addition of hexanethiol to allyl phenyl ethers according the procedure developed for allylphenols [4, 5]. Available allyl phenyl ethers are increasingly used in syntheses of various practically useful compounds [6–9].

EXPERIMENTAL

Infrared spectra were recorded on a Specord M-80 spectrometer. ^{13}C and ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer at operational frequencies of 75 and 300 MHz, respectively, using TMS as the internal standard and $CDCl_3$ as the solvent. GLC analysis was carried out on a Chrom-5 chromatograph with a 1 m × 5 mm column, using Inerton-supported Carbowax 20M (20%) as a stationary phase, a flame-ionization detector, and nitrogen as a carrier gas. Gas chromatography–mass spectrometry (GC–MS) investigation was accomplished on an Agilent instrument operation in the total ion current mode in the range of *m/z* 28–600 using electron ionization (70 eV), an HP-5MS 30 m × 5 mm chromatographic column with a stationary-phase film thickness of 0.25 μm, helium as a carrier gas, an injector temperature of 250°C, and an ion source temperature of 230°C.

Allyl ethers of phenol (1), 2-*tert*-butyl- (2), 4-*tert*-butyl- (3), and 2,4-di-*tert*-butylphenols (4) were synthesized from the corresponding phenols using 3-chloropropene-1 according to the published procedure [10].

3-(Hexylthio)propyl ethers of phenols (5–8) were prepared via thiylation of allyl phenyl ethers using hexanethiol in the presence of azobis(isobutyronitrile) (AIBN) in an argon atmosphere at 75–80°C for 30 h according to the procedure described in [5].

3-(Hexylthio)propyl ether of phenol (5). Yield 95%, n_D^{20} 1.5255, d_4^{20} 0.989. IR, ν, cm^{-1}: 1244 (Ar–O–C), 1496 (Ar). ^{1}H NMR, δ, ppm: 0.89 (t, 3H, $C^{11}H_3$, $^3J = 6.5$ Hz), 1.30 (m, 6H, $C^{8-10}H_2$), 1.59 (m, 2H, C^7H_2), 2.20 (m, 2H, C^3H_2), 2.62 (m, 4H, $C^{4,6}H_2$), 4.07 (t, 2H, C^2H_2, $^3J = 6.1$ Hz), 6.8–7.3 (m, 5H, Ar). ^{13}C NMR, δ, ppm: 14.12 (C^{11}); 22.63 (C^{10}); 28.64, 29.43, 29.67, 31.50, 32.29 ($C^{3,4,6-8}$); 66.20 (C^2); 114.53, 120.85, 129.48 (CHAr); 158.92 (CAr). Mass spectrum, *m/z* (I_{rel}, %): 252 (31) $[M]^+$, 159 (100), 94 (15), 75 (14), 43 (9). Found (%): C 71.04, H 9.15, S 12.35. Calculated for $C_{15}H_{24}SO$ (%): C 71.43, H 9.52, S 12.70.

3-(Hexylthio)propyl ether of 2-*tert*-butylphenol (6). Yield 85%, n_D^{20} 1.4998, d_4^{20} 0.939. IR, ν, cm^{-1}: 1230 (Ar–O–C), 1489 (Ar). ^{1}H NMR, δ, ppm: 0.90 (t, 3H, CH_3, $^3J = 6.6$ Hz), 1.30 (m, 6H, $C^{8-10}H_2$), 1.41 (s, 9H, $C^{1'}(CH_3)_3$), 1.59 (m, 2H, C^7H_2), 2.10 (m, 2H, C^3H_2), 2.62 (m, 4H, $C^{4,6}H_2$), 4.09 (t, 2H, C^2H_2, $^3J = 6.0$ Hz), 6.8–7.3 (m, 4H, Ar). ^{13}C NMR, δ, ppm: 14.08 (C^{11}); 22.59 (C^{10}); 28.60, 29.07, 29.67, 29.73, 31.49, 32.24 ($C^{3,4,6-9}$); 29.91 ($C(\underline{C}H_3)_3$); 34.82 ($\underline{C}(CH_3)_3$); 66.16 (C^2); 111.81, 120.26, 126.59, 127.01 (CHAr); 137.83, 157.60 (CAr). Mass spectrum, *m/z* (I_{rel}, %): 308 (20) $[M]^+$, 159 (100), 135 (11), 75 (15), 43 (10). Found

(%): C 73.65, H 10.02, S 10.05. Calculated for $C_{19}H_{32}SO$ (%): C 74.03, H 10.39, S 10.39.

3-(Hexylthio)propyl ether of 4-*tert*-butylphenol (7). Yield 85%, n_D^{20} 1.5201, d_4^{20} 0.975. IR, ν, cm^{-1}: 1246 (Ar–O–C), 1512 (Ar). ^{1}H NMR, δ, ppm: 0.91 (t, 3H, CH_3, ^3J = 6.7 Hz), 1.35 (m, 6H, $C^{8-10}H_2$), 1.41 (c, 9H, $C^{1'}(CH_3)_3$), 1.62 (m, 2H, C^7H_2), 2.10 (m, 2H, C^3H_2), 2.62 (m, 4H, $C^{4,6}H_2$), 4.07 (t, 2H, C^2H_2, ^3J = 6.1 Hz), 6.8–7.3 (m, 4H, Ar). ^{13}C NMR, δ, ppm: 13.96 (C^{11}); 22.47 (C^{10}); 28.52, 28.52, 29.37, 29.54, 31.43, 32.15 ($C^{3,4,6-9}H_2$); 31.36 ($C(\underline{C}H_3)_3$); 33.92 ($\underline{C}(CH_3)_3$); 66.13 (C^2); 113.86, 126.08 (CHAr); 143.19, 156.55 (CAr). Mass spectrum, *m/z* (I_{rel}, %): 308 (16) $[M]^+$, 159 (100), 135 (5), 75 (17), 43 (11). Found (%): C 73.70, H 9.98, S 10.01. Calculated for $C_{19}H_{32}SO$ (%): C 74.03, H 10.39, S 10.39.

3-(Hexylthio)propyl ether of 2,4-di-*tert*-butylphenol (8). Yield 65%, n_D^{20} 1.4790, d_4^{20} 0.902. IR, ν, cm^{-1}: 1234 (Ar–O–C), 1498 (Ar). ^{1}H NMR, δ, ppm: 0.91 (t, 3H, CH_3, ^3J =6.7 Hz), 1.3 and 1.4 (s and s, 18H, $2C^{1'}(CH_3)_3$), 1.35 (m, 6H, $C^{8-10}H_2$), 1.60 (m, 2H, C^7H_2), 2.10 (m, 2H, C^3H_2), 2.64 (m, 4H, $C^{4,6}H_2$), 4.09 (t, 2H, C^2H_2, ^3J = 6.0 Hz), 6.8–7.4 (m, 3H, Ar). ^{13}C NMR, δ, ppm: 14.01 (C^{11}); 22.52 (C^{10}); 28.55, 29.07, 29.62, 29.76, 31.41, 32.19 ($C^{3,4,6-9}H_2$); 29.92, 31.56 ($2C(\underline{C}H_3)_3$); 34.20, 35.00 ($2\underline{C}(CH_3)_3$); 66.10 (C^2); 111.06, 111.78, 123.82 (CHAr); 136.95, 142.36, 155.27 (CAr). Mass spectrum, *m/z* (I_{rel}, %): 364 (20) $[M]^+$, 159 (100), 75 (10), 57 (14), 43 (8). Found (%): C 75.41, H 10.55, S 8.30. Calculated for $C_{23}H_{40}SO$ (%): C 75.82, H 10.99, S 8.79.

2-(Hexylthio)propyl ether of phenol (9). Mass spectrum, *m/z* (I_{rel}, %): 252 (0.5) $[M]^+$, 159 (100), 89 (25), 75 (15), 43 (16).

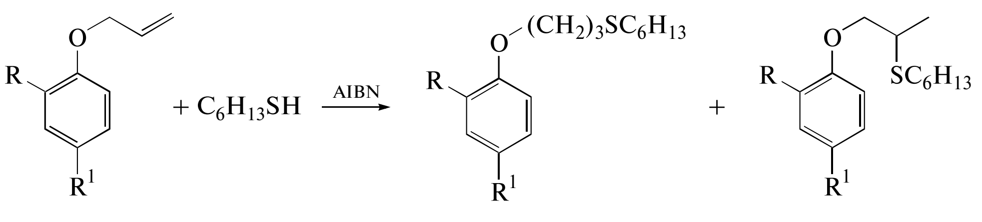
2-(Hexylthio)propyl ether of 2-*tert*-butylphenol (10). Mass spectrum, *m/z* (I_{rel}, %): 308 (0.1) $[M]^+$, 159 (100), 89 (18), 75 (8), 43 (9).

2-(Hexylthio)propyl ether of 4-*tert*-butylphenol (11). Mass spectrum, *m/z* (I_{rel}, %): 308 (0.6) $[M]^+$, 159 (100), 89 (19), 75 (7), 43 (9).

2-(Hexylthio)propyl ether of 2,4-di-*tert*-butylphenol (12). Mass spectrum, *m/z* (I_{rel}, %): 364 (0.4) $[M]^+$, 159 (100), 89 (13), 75 (5), 43 (8).

RESULTS AND DISCUSSION

The reaction of allyl ethers of phenol (**1**), 2-*tert*-butyl- (**2**), 4-*tert*-butyl- (**3**), and 2,4-di-*tert*-butylphenols (**4**) with equimolar amount of hexanethiol in the presence of AIBN in argon atmosphere at 75–80°C for 30 h results in the formation of the corresponding 3-(hexylthio)propyl ethers of phenols **5**–**8**:



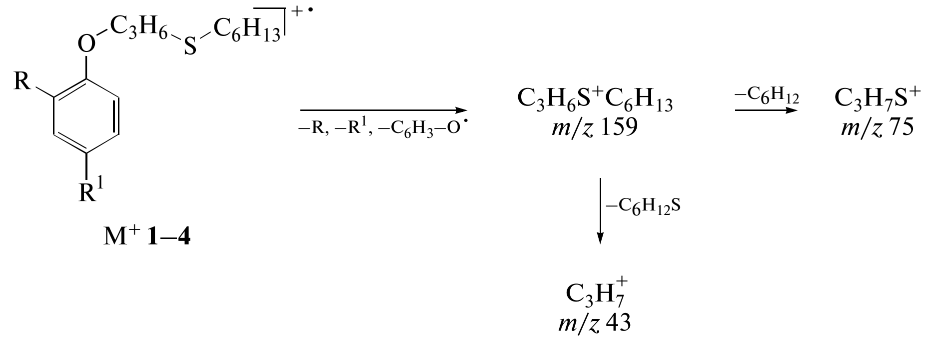
1–4 **5–8** **9–12**

R = R_1 = H (**1**, **5**, **9**); R = *t*-Bu, R_1 = H (**2**, **6**, **10**); R = H, R_1 = *t*-Bu (**3**, **7**, **11**); R = R_1 = *t*-Bu (**4**, **8**, **12**).

The addition of hexanethiol to the double bond of allyl ethers of phenols proceeds regioselectively, since the yields of phenols **5**–**8** make 65–95% and the yields of 2-(hexylthio)propyl ethers of phenols **9**–**12** do not exceed 4–6% in all cases. The relative reactivity of allyl phenyl ethers in the hexylthiylation reaction decreases in the order of compounds **1** > **2** = **3** > **4**. Compared to 2-allyl-4-*tert*-butyl- and 2-allyl-6-*tert*-butylphenols, for which the yield of thiylation products is 90 or 50%, respectively [5], the reactivities of *ortho*- and *para*-substituted allyl ethers of phenols **2** and **3** do not differ.

The composition and structure of compounds **5**–**8** were confirmed by elemental analysis, IR, ^{1}H and ^{13}C NMR, and GC–MS data. Compared to allyl ethers of phenols **1**–**4**, there are no absorption bands of double bond at 1640 and 912–920 cm^{-1} in the IR spectra of thiylation products **5**–**8**. The ^{1}H and ^{13}C NMR spectra of **1**–**4** do not contain the signals of olefin protons and carbon atoms, but they show the chemical shifts of methyl [δ 0.89 (**5**), 0.90 ppm (**6**–**8**)], methylene (1.30–4.10 ppm) protons and nine carbon atoms (δ 13.19–66.20 ppm) of (hexylthio)propoxy groups.

The mass spectra of 3-(hexylthio)propyl ethers of phenols **5**–**8** show the peaks of molecular ions M^+ at *m/z* 252, 30% (**5**); *m/z* 308, 24 and 29% (**6**, **7**); and *m/z* 364, 27% (**8**) and the peaks of the diagnostic fragments $C_3H_6SC_6H_{13}$, $(C_3H_7S)^+$, and $(C_3H_7)^+$ at *m/z* 159, 75, and 43, respectively, which result, as it was expected [11], from the rupture of the C–O and C–S bonds:



R = R^1 = H (**5**); R = *t*-Bu, R^1 = H (**6**); R = H, R^1 = *t*-Bu (**7**); R = R_1 = *t*-Bu (**8**).

Compounds **9**–**12** were not isolated in the individual form. The fact of their formation was confirmed by GC–MS data. In contrast to 3-(hexylthio)propyl, the molecular ions of 2-(hexylthio)propyl ethers of phenols **9**–**12** exhibit low stability toward electron impact (abundance of the M^+ + peak is 0.1–0.6%). As in the case of 3-(hexylthio)propyl ethers, the primary route of degradation of the molecular ion of 2-(hexylthio)propyl ethers of phenols is associated with the detachment of the phenoxy, *tert*-butyl, or di-*tert*-butylphenoxy group and the formation of the $[C_3H_6SC_6H_{13}]^+$ ion having the maximal abundance.

Resulting 3-(hexylthio)propyl ether of phenol **9** was tested in froth flotation of Kuzbas coal [12]. It was shown that the use of **9** (without separation from reaction mixture) as a frothing–collecting agent compared to tractor fuel kerosene in a mixture with still residue of butyl alcohol production can increase coal extraction by 3.1% and reduce the reagent consumption by a factor of 1.5.

Thus, the addition of hexanethiol to allyl ethers of phenol in the presence of AIBN proceeds regioselectively with the predominant formation of anti-Markovnikov products. The resulting 3-(2-hexylthio)propyl ethers of phenols can find practical application as flotation agents, plant growth regulators, fungicides, nematocides, and intermediate products in organic synthesis.

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