

Synthesis of Cyclohexylphenols

M. V. Postnova, S. G. Koshel', N. V. Lebedeva,
E. A. Kuznetsova, and G. N. Koshel'

Yaroslavl State Technical University, Moskovskii pr. 88, Yaroslavl, 150023 Russia
e-mail: koshel@polytech.yaroslavl.su

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Abstract—Catalytic alkylation of phenols with cyclohexanol gives *o*- and *p*-cyclohexylphenols as the major products. The effect of temperature, catalyst nature, and reactant concentration on the reaction outcome was studied.

Cyclohexylation of aromatic hydrocarbons and their functional derivatives underlies an efficient procedure [1, 2] which was developed by us for the preparation of functionalized biphenyls and terphenyls as initial compounds and intermediate products in the synthesis of liquid-crystalline thermotropic polymers, biologically active substances, photographic materials, etc. [3]. On the other hand, an analogous reaction with phenols was studied insufficiently. Therefore, in the present work we determined optimal conditions for the reaction of phenol (**I**) with cyclohexanol (**II**) (Table 1). The major reaction products are *o*-cyclohexylphenol (**III**) and *p*-cyclohexylphenol (**IV**). Also, relatively small amounts of cyclohexyl phenyl ether (**V**) and dicyclohexylphenols **VI** were formed as by-products (Scheme 1).

As follows from the data in Table 1, the most favorable conditions include the use of orthophosphoric acid, reactant ratio H_3PO_4 :**II**:**I** 4.20:1.0:1.5, temperature 130°C, and reaction time 2.5–3 h. In this case the conversion of phenol **I** and alcohol **II** is almost quantitative, and the yield of compounds **III** and **IV** is 34 and 26%, respectively (calculated on the reacted cyclohexanol; overall yield 77%).

Under the same conditions we performed alkylation with cyclohexanol of *p*-cresol, resorcinol, hydroquinone, and pyrocatechol. The yields of the corre-

sponding cyclohexyl-substituted derivatives were 68–70% (calculated on the initial cyclohexanol). The products were identified by IR and ^1H NMR spectroscopy and GLC data. Their properties are given in Table 2.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrophotometer from samples prepared as thin films. The ^1H NMR spectra were obtained on a Tesla BS-467 instrument from solutions in acetone- d_6 using HMDS as internal reference. GLC analysis was performed on a Khrom-4 chromatograph equipped with a flame-ionization detector; steel column, 2.5 m; stationary phase 10% of SKTFT-50Kh on Chromaton N-AW-DMCS; carrier gas nitrogen, flow rate 30 ml/min; oven temperature programming from 80 to 200°C at a rate of 8 deg/min.

Alkylation of phenol and its derivatives with cyclohexanol. Cyclohexanol, 100.16 g, was added over a period of 1 h to a mixture of 141.17 g of phenol (**I**) and 411.6 g of 85% phosphoric acid, maintaining the temperature at 130°C. The mixture was kept for 2 h at that temperature, and the organic phase (upper layer) was separated. The acid layer (bottom) was extracted at ~100°C with three portions

Scheme 1.

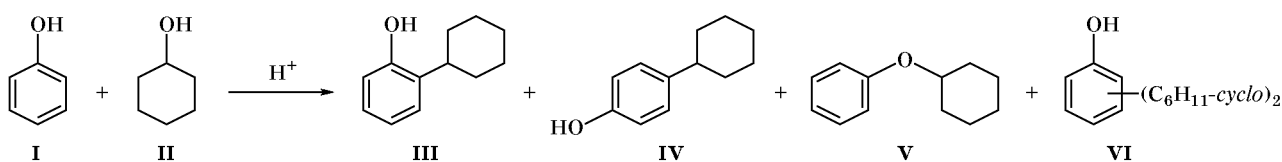


Table 1. Alkylation of phenol (**I**) with cyclohexanol (**II**) (reaction time 2.5 h)

Catalyst	Conditions		Conversion of phenol, %	Composition of the reaction mixture, %			
	temperature, °C	molar ratio I : II :catalyst		III	IV	V	VI
AlCl ₃	110	20 wt % of I + II		No reaction			
H ₂ SO ₄	30	1.5:1:1		Tarring			
H ₃ PO ₄	105	1.5:1:4.20	78	43	29	28	–
H ₃ PO ₄	115	1.5:1:4.20	84	47	37	16	–
H ₃ PO ₄	130	1.5:1:0.85	68	33	26.5	40.5	–
H ₃ PO ₄	130	1.5:1:2.50	90	49.5	37	13.5	–
H ₃ PO ₄	130	1.5:1:4.20	97	54	42	4	–
H ₃ PO ₄	145	1.5:1:4.20	98	46	38	1	15
KU-2	110		93	55	33	10	2
KU-23	120	40 wt % of I + II	91	56	29	15	–
KU-2-FPP	130		95	69	25	5	2

Table 2. Melting points and IR and ¹H NMR spectral parameters of cyclohexylphenols

Initial phenol	Product	mp, °C	IR spectrum, ^a cm ⁻¹	¹ H NMR spectrum, δ, ppm
Phenol	<i>o</i> -Cyclohexylphenol (III)	46–47 (50–55)	755, 3480 (OH)	8.95 s (1H, OH), 7.04 d.d (<i>J</i> = 8, 1.75 Hz), 6.83 t (1H), 6.75 d.d (<i>J</i> = 7.8, 1.8 Hz), 6.70 t (1H), 2.90–2.80 m (1H), 1.85–1.70 m (5H), 1.40–1.20 m (5H)
	<i>p</i> -Cyclohexylphenol (IV)	126–128 (132–133)	821, 3200 (OH)	9.1 s (1H, OH), 7.16 d (2H, 2-H, <i>J</i> = 8 Hz), 7.98 d (2H, 1-H, <i>J</i> = 7.8 Hz), 7.56–7.45 m (2H, 3-H), 7.30–7.22 m (3H, 4-H, 5-H)
	Cyclohexyl phenyl ether (V)		bp 128°C (15 mm), <i>d</i> = 1.007 g/cm ³ , <i>n</i> _D ²⁰ = 1.5288	
Hydroquinone	2-Cyclohexyl-1,4-benzenediol	84–86	860, 800; 3300–3470 (OH)	8.30–8.56 s (OH), 6.45 d (2H), 6.37 d (3H), 6.39 s (4H)
Resorcinol	4-Cyclohexyl-1,3-benzenediol	119–121	800, 840, 870; 3300 (OH)	8.00 s (1H, OH), 8.06 s (1H, OH), 3.06–2.58 m (1H, CH), 6.32 (1H, 6-H), 6.35 (1H, 2-H); 6.86 d.d (1H, 5-H, <i>J</i> _{5,6} = 8.0, <i>J</i> _{2,6} = 2.4 Hz)
	2-Cyclohexyl-1,3-benzenediol	64.6–65.5	710, 767; 3410 (OH)	5.72 s (2H, OH), 3.28–2.84 m (1H, CH), 6.16 (2H, 4-H, 6-H, <i>J</i> = 8.0 Hz), 6.78 t (1H, 5-H, <i>J</i> = 8.0 Hz)
Pyrocatechol	4-Cyclohexyl-1,2-benzenediol	102–103	810, 845, 870; 3340 (OH)	8.40 s (1H, OH), 8.30 s (1H, OH), 6.60–6.50 m (3H), 2.34–2.25 m (1H, CH), 1.80–1.65 m (5H), 1.40–1.20 m (5H)
	3-Cyclohexyl-1,2-benzenediol	138–139	720, 770; 3360, 3470 (OH)	8.9 s (1H, OH), 7.7 s (1H, OH), 6.63–6.50 m (2H, 1-H, 2-H), 6.40 d (1H, 3-H, <i>J</i> = 8 Hz), 2.90–2.80 m (1H, CH), 1.80–1.65 m (5H), 1.40–1.20 m (5H)
<i>p</i> -Cresol	2-Cyclohexyl-4-methylphenol	45–47	805–870; 3470 (OH)	2.13 s (CH ₃), 8.87 s (OH), 6.47 d (3H), 6.73 d (4H), 6.75 s (5H)

^a Other absorption bands, ν, cm⁻¹: 1610, 1570, 1500 (C=C_{arom}); 2917, 2846, 1446 (cyclohexyl ring).

of toluene. The hot toluene extracts were combined with the organic phase and washed with distilled water to pH 5. After cooling, cyclohexylphenol **IV** separated from the toluene solution. The precipitate was filtered off, washed with toluene, and analyzed. The filtrate was subjected to fractional distillation under reduced pressure (~20 mm). The first fraction was toluene (bp 55°C), the second fraction was unreacted phenol (bp 135–169°C), the third fraction was cyclohexyl phenyl ether (bp 165–205°C), and the fourth fraction was cyclohexylphenol **III** (bp 205–210°C). Cyclohexylphenols **III** and **IV** were purified as follows. The product was dissolved in petroleum ether (bp 40–70°C) at ~100°C,* the solution was cooled to room temperature (or below), and the precipitate was filtered off and washed with a small

amount of petroleum ether (bp 40–70°C) and dried at 100°C (**IV**) or 30°C (**III**) in a drying box.

The alkylation of *p*-cresol, hydroquinone, pyrocatechol, and resorcinol with cyclohexanol was carried out in a similar way.

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