The Reaction of Phenol with 1-Methylcycloalkenes in the Presence of Phosphorus-containing Zeolite Y

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Received February 7, 2007

Abstract—The results of cycloalkylation of phenol with 1-methylcyclopentene and 1-methylcyclohexene in the presence of phosphoric acid-impregnated zeolite are presented. Optimal conditions for the synthesis of 4(1-methylcycloalkyl)phenols were found. It was shown that the yield of the desired products under the optimal conditions is 86.4–89.6% of the theoretical value. The structure of 4(1-methylcycloalkyl)phenols was established by means of spectral and chemical analysis techniques.

DOI: 10.1134/S0965544107060059

Cycloalkylation of phenols with cyclic compounds in the presence of acetic acid, sulfuric acid, boron trifluoride, aluminum chloride, or the KU-2 or KU-23 ion exchange resin as a catalyst is characterized by a low yield of the desired product, the multistage character of the process, and the toxicity of the catalysts, in addition to other disadvantages [1–8].

In this paper, we report the results of cycloalkylation of phenol with 1-methylcyclopentene (1-MCP) and 1-methylcyclohexene (1-MCH) catalyzed by zeolite Y impregnated with phosphoric acid (zeolite-P).

EXPERIMENTAL

To prepare 4(1-methylcycloalkyl)phenols, freshly distilled reagent-grade phenol; 98% pure 1-methylcyclopentene with bp 74–75.5°C, n_D^{20} 1.4347, and ρ_4^{20} 0.7782; and 98.8% pure 1-methylcyclohexene with bp 110–111°C, n_D^{20} 1.4500 and ρ_4^{20} 0.8200 were used.

The orthophosphoric acid-based catalyst used in the cycloaddition reaction of phenol with methylcyclenes was prepared via thorough mixing alumina gel with a cracking catalyst (zeolite Y, SiO₂ : Al₂O₃ = 4 : 8; degree of ion exchange, 97%). The resulting material was shaped by forcing through a die (1.6 mm in diameter), pelletized, and calcined. Then, the catalyst was impregnated with 10% orthophosphoric acid (on P₂O₅ basis), heated to evaporate water, dried in an oven at 100°C, and calcined with a continuous temperature rise from 200 to 600°C.

The cycloaddition reaction of phenol with methylcyclenes was carried out in a laboratory batch reactor. The product was separated from the catalyst by means of hot filtration ($40-50^{\circ}$ C) and subjected to fractional distillation. First, unreacted methylcyclene was distilled off at atmospheric pressure; then, unreacted phenol and the desired product were collected under vacuum (10 mm Hg). The purity of the substances was determined by measuring their physicochemical parameters, and the structure was confirmed by spectral data.

The chromatographic analysis of the alkylate was performed on an LKhM-72 gas chromatograph with a thermal conductivity detector. The column length was 2 m; the solid support was Chromaton N-AW DMC (acid washed, silanized with dimethylchlorosilane), 0.2 ± 0.25 mm fraction; and the stationary phase was 5% SE-30 (methylsiloxane elastomer). The initial column temperature was 50°C; the final temperature, 280°C; the temperature programming rate, 10°C/min; the carrier-gas (helium) flow rate, 50 ml/min; the evaporator temperature, 355°C; and the detector temperature, 300°C. The internal standard method based on setting zero the total sum of peak areas was used for calculation.

Infrared spectra were recorded on an UR-20 spectrophotometer, and proton NMR spectra were measured with a Varian T-60 instrument in CCl_4 using tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

The reaction of phenol with 1-methylcyclopentene and 1-methylcyclohexene in the presence of the catalyst zeolite-P yields 4(1-methylcycloalkyl)phenols:



To find optimal conditions that ensure the maximal yield of 4(1-methylcycloalkyl)phenols, we studied the influence of temperature, reaction time, the phenol to 1-methylcycloalkene mole ratio, and the amount of the catalyst on the yield and composition of the products.

The reaction temperature was varied from 60 to 130° C; the reaction time, from 2 to 6 h; the phenol : 1-methycycloalkene molar ratio, from 2 : 1 to 1 : 2; and the amount of the catalyst, from 5 to 20 wt % (of feed-stock mass). The figure shows the results of experiments on the alkylation of phenol with 1-methylcyclopentene in the presence of the zeolite-P catalyst. At a temperature of 80°C, the highest yield of 4(1-methylcyclopentyl)phenol, 86.4%, is reached; an increase in temperature to 100°C leads to a decrease in the product yield to 79.3%. As the reaction time increases from 2 to 5 h, an increase in the yield of 4(1-methylcyclopen-



Yield of 4(1-methylcyclopentyl)phenol depending on (1) temperature, (2) reaction time, (3) reactants ratio, and (4) amount of catalyst.

tyl)phenol from 47.5 to 86.4% is observed during the first three hours of the reaction; then, the yields drops to 76.6%. The decline in the yield indicates that a long residence of para-substituted phenol in the reaction zone creates conditions for the introduction of another cyclene molecule to form the di- and trisubstituted product, a fact that is corroborated by experimental data. The yield of 4(1-methylcyclopentyl)phenol was 86.4% at the 1 : 1 phenol : 1-MCP molar ratio; an increase in the amount of phenol or cyclene did not produce a favorable effect and the yield remained at the same level. The study of the dependence of the yield of the cycloalkylation product on the amount of the catalyst showed that the use of the catalyst at the 10 wt %(of phenol mass) level is optimal; even a considerable increase in the amount of the catalyst had no substantial effect on the yield of the product.

Thus, the optimal conditions for the preparation of 4(1-methylcyclopentyl)phenol are the reaction temperature of 80°C, the reaction time of 3 h, the phenol : 1-MCP molar ratio of 1 : 1, and the amount of the catalyst of 10% (of mass of phenol fed); the yield of the desired product is 86.4% (of theoretical value).

Similar results were obtained for 4(1-methylcyclohexyl)phenol; under the optimal conditions, the yield of 4(1-methylcyclohexyl)phenol was 89.6 of the theoretical yield. The physicochemical characteristics of 4(1-methylcycloalkyl)phenols are given in the table.

The products were identified by means of ¹H NMR and IR spectroscopy. The ¹H NMR spectrum of 4(1-methylcyclopentyl)phenol displays a singlet due to CH₃ group at 1.22 ppm; a broad singlet due to the saturated hydrocarbon ring (δ 1.77 ppm); a singlet in the OH region at 5–6 ppm, which is shifted upfield by dilution; and a multiplet of the 1,4-disubstituted benzene ring, which approximately resembles a type AB spectrum with an average chemical shift of 6.87 ppm and a coupling constant of v = 8.5 ± 0.5 Hz. The intensity ratio of these four signals is 3 : 8 : 1 : 4, respectively.

The IR spectrum of 4(1-methylcyclopentyl)phenol contains absorption bands at 825, 1240, 1510, and 1592–1610 cm⁻¹ characteristic of the *para*-substituted benzene ring and a band at 3220 cm⁻¹ (associated OH group).

The *gem*-substituted five-membered cycle is characterized by absorption bands at 2920 and 1859 cm⁻¹ (stretching vibrations of OH groups) and 1440 cm⁻¹

Structural formula	Bp, °C/10 mm Hg	Mp, °C	Molecular mass		Elemental composition, %			
					calculated		found	
			calculated	found	C	Н	С	Н
HO-CH3	145–148	90	176	176	81.8	9.1	82.3	8.4
HO-CH3	161–164	96	190	190	82.1	9.5	82.4	8.8

Physicochemical characteristics of 4(1-methylcycloalkyl)phenols

(bending vibrations of CH_2 groups). The bands at 1365 and 2940 cm⁻¹ correspond to the methyl group.

The proton NMR spectrum of 4(1-methylcyclohexyl)phenol exhibits four signals with an intensity ratio of 3 : 10 : 1 : 4. The singlet at 1.12 ppm is due to the protons of the CH₃ group attached to the quaternary carbon atom. The multiplet with a large peak (δ 1.77 ppm) is characteristic of the saturated hydrocarbon cycle; the OH group yields a signal at 5–6 ppm. The 1,4-substituted benzene ring (multiplet) corresponds to a type AABB spectrum or, approximately, an AB spectrum with an average chemical shift of 6.90 ppm and a spin–spin coupling constant of 8.5 ± 0.5 Hz.

The IR absorption spectrum of 4(1-methylcyclohexyl)phenol exhibits bands at 1505 and 1592–1610 cm⁻¹ (benzene ring), 3010 and 3030 cm⁻¹ (=CH₂ stretching), and 825 cm⁻¹ (out-of-plane =CH₂ bending); the OH group is determined by the band at 1240 cm⁻¹ and absorption in the region 3100–3500 cm⁻¹. The gem-substitution on the cyclohexane ring is confirmed by the C–H stretching bands at 2920 and 2845 cm⁻¹, as well as the bands at 1108 and 1345 cm⁻¹, which characterize δ_{CH_2} in the cycle. The methyl group is characterized by bending vibration bands at 1370 and 1460 cm⁻¹.

As is seen from the data presented in the table, the found molecular mass and elemental composition of the products agree with the calculated values.

On the basis of the experimental data, it may be concluded that zeolite-P is a more effective catalyst for the cycloalkylation reaction of phenol with 1-methylcyclopentene and 1-methylcyclohexene as compared with the known catalysts.

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