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Short Comuunication

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Alkylation of Cresols with Cyclohexene in the Presence of *p*-Toluenesulphonic Acid

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Abstract

Isomeric cresols have been cycloalkylated with cyclohexene in the presence of *p*-toluenesulphonic acid as catalyst. The effects of the variation of temperature, molar ratio of cresol to cyclohexene, time of reaction and amount of *p*-toluenesulphonic acid on the reactions have been studied and cyclohexyl cresols have been obtained in high yield.

Introduction

Alkylated phenols and their derivatives are outstanding antioxidants and stabilizers in fuels, lubricating oils and polymeric materials (Babakhanov *et al.* 1968; Lebedev, 1984; Paul, 1950; Ravikovich, 1964; Shreve and Brink, 1977).Some of their derivatives are also used as herbicides, bactericides and insecticides (Melinikov *et al.* 1954; Nemetkin *et al.* 1951). Cresols have been alkylated by different normal, iso- and cycloolefins (Karim *et al.*2005; Kharchenko and Zavgorodni, 1964; Saha and Ghosh, 1989; Saha *et al.*1994; Saha *et al*.1996; Saha *et al.* 1998; Saha *et al*.2000; Shulov, 1969). But no attempt has ever been made to investigate the reactions with cyclohexene in the presence of *p*-toluenesulphonic acid.

In the present work, reactions of isomeric cresols (ortho-, meta- and para-) have been investigated with cyclohexene in the presence of *p*-toluenesulphonic acid as catalyst.

Materials and Methods

Reaction was carried out in a flask fitted with a stirrer, a condenser, a thermometer and a dropping funnel for the addition of cyclohexene. Cresol and *p*-toluenesulphonic

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acid were charged into the flask and heated to desired temperature and cyclohexene was introduced into the mixture gradually over a certain period of time (time of addition) with constant stirring. After the addition of total amount of cyclohexene, the reaction mixture was stirred for another period of time (time of stirring) at the same temperature. Reaction mass was then cooled to the room temperature, dissolved in petroleum ether, neutralized and washed with distilled water several times. Unconverted reactants and solvent were distilled off by distillation at atmospheric pressure. The residual product was finally distilled and characterized by spectral means.

Results and Discussion

A. Reaction of *o*-cresol with cyclohexene:

Table I records the results of the reaction of *o*-cresol with cyclohexene in the presence of *p*-toluenesulphonic acid. The reaction gave the mixture of isomeric cyclohexyl *o*-cresols. The yield of the products increased with the increase of temperature (Expt. No. 1 - 5), molar ratio of *o*-cresol to cyclohexene (Expt. No. 6 - 8), time of reaction (Expt. No. 3 and 8) and the amount of catalyst (Expt. No. 3 and 9). But the increase in the yield was negligible when the temperature was raised from 130 to 160^{O}C (Expt No. 3 - 5). Thus cyclohexyl *o*-cresols could be obtained in 95.5% yield under the following reaction conditions: temperature = 130^{O}C, molar ratio of *o*-cresol to cyclohexene = 5:1, time of addition = 2h, time of stirring = 2h and the amount of catalyst = 10% by wt. of o-cresol.

B. Reaction of m-cresol with cyclohexene

Reaction of m-cresol with cyclohexene had been investigated in the presence of *p*-toluenesulphonic acid over the temperature range of 100-130^{O}C. Molar ratio of *m*-cresol to

Table I. Alkylation of *o*-cresol with cyclohexene in the presence of *p*-toluenesulphonic acid

Expt. No.	Reaction conditions					% Yield of cyclohexyl *o*-cresol
	Temp.,^{O}C	Molar ratio of *o*-cresol to cyclohexene	Time of addition, h	Time of stirring, h	Amount of catalyst, % by wt. of *o*-cresol	
1	70	5:1	2	2	10	28.3
2	100	5:1	2	2	10	70.1
3	130	5:1	2	2	10	95.5
4	155	5:1	2	2	10	95.9
5	160	5:1	2	2	10	96.0
6	130	3:1	2	1	10	72.0
7	130	4:1	2	1	10	80.2
8	130	5:1	2	1	10	89.4
9	130	5:1	2	2	5	81.0

cyclohexene was varied from 3:1 to 4:1, reaction time from 2 to 4h and the amount of catalyst was varied from 5 to 10% wt. of *m*-cresol. Table II records the results. The yield of products (cyclohexyl *m*-cresols) increased with the increasing temperature (Expt. No.1 and 2), molar ratio of *m*-cresol to cyclohexene (Expt. No. 3 and 4), time of reaction (Expt. No.2, 4 and 5; 6 and 7) and the amount of catalyst (Expt. No. 4 and 6). Thus the best yield of cyclohexyl *m*-cresols was obtained under the following conditions: temperature = 130^{O}C, molar ratio of m-cresol to cyclohexene = 4:1, the amount of catalyst = 10% by wt. of *m*-cresol, time of addition = 2h and time of stirring = 2h.

cresol with cyclohexene has been shown in Table III. The reaction gave only 2-cyclohexyl-4-methylphenol. The yield of the product increased with the increasing temperature (Expt. No. 1 - 3), molar ratio of *p*-cresol to cyclohexene (Expt. No. 4, 5 and 6), time of reaction (Expt. No. 2, 4 and 7 ; 8 and 9) and the amount of catalyst (Expt. No. 4 and 8). But the increase in the yield was insignificant when the temperature was increased above 130^{O}C (Expt No. 2 - 3). At a molar ratio of *p*-cresol to cyclohexene = 4:1, the maximum yield could be obtained by increasing the time of additional stirring (Expt No. 2).The best yield of the product was obtained when the reaction was carried

Table II. Alkylation of *m*-cresol with cyclohexene in the presence of *p*-toluenesulphonic acid

Expt. No.	Reaction conditions					% Yield of cyclohexyl *m*-cresol
	Temp.,^{O}C	Molar ratio of *m*-cresol to cyclohexene	Time of addition, h	Time of stirring, h	Amount of catalyst, % by wt. of *m*-cresol	
1	100	4:1	2	2	10	61.2
2	130	4:1	2	2	10	96.4
3	130	3:1	2	1	10	82.3
4	130	4:1	2	1	10	86.0
5	130	4:1	2	0	10	72.5
6	130	4:1	2	1	5	75.1
7	130	4:1	2	3	5	87.5

C. Reaction of *p*-cresol with cyclohexene:

The influence of variation of the parameters, viz. temperature, molar ratio of *p*-cresol to cyclohexene, time of reaction and amount of *p*-toluenesulphonic acid on the reaction of *p*-

out under the following conditions: temperature = 130^{O}C, molar ratio of *p*-cresol to cyclohexene = 4:1, the amount of catalyst = 10% by wt. of *p*-cresol, time of addition = 2h and time of stirring = 2h.

Table III. Alkylation of *p*-cresol with cyclohexene in the presence of *p*-toluenesulphonic acid

Expt. No.	Reaction conditions					% Yield of 2-cyclohexyl-4-methylphenol
	Temp., ^{O}C	Molar ratio of *p*-cresol to cyclohexene	Time of addition, h	Time of stirring, h	Amount of catalyst, % by wt. of *p*-cresol	
1	100	4:1	2	2	10	64.5
2	130	4:1	2	2	10	96.6
3	160	4:1	2	2	10	96.7
4	130	4:1	2	1	10	88.7
5	130	5:1	2	1	10	95.9
6	130	6:1	2	1	10	96.2
7	130	4:1	2	0	10	76.1
8	130	4:1	2	1	5	76.9
9	130	4:1	2	3	5	95.2

Table IV. ^{1}H NMR-spectrum of cyclohexyl cresols

Products	Observed signals of the protons	Chemical shift δ in ppm
Cyclohexyl *o*-cresol	Three protons on the aromatic ring	6.01 - 7.0
	One proton on the -OH group	4.06
	Three protons on the $-CH_3$ group	2.0 - 2.02
	All the protons (10) on the cyclohexane ring except one on the α-position relative to the aromatic ring	1.05 - 2.16
	One proton on the cyclohexane ring on the a-position relative to the aromatic ring	2.4 - 2.8
Cyclohexyl *m*-cresol	Three protons on the aromatic ring	6.06 - 7.1
	One proton on the -OH group	4.6 - 5.3
	Three protons on the $-CH_3$ group	2.05 - 2.5
	All the protons (10) on the cyclohexane ring except one on the a-position relative to the aromatic ring	1.06 - 2.0
	One proton on the cyclohexane ring on the α-position relative to the aromatic ring	2.5 - 3.1
2-Cyclohexyl-4-methylphenol	Three protons on the aromatic ring	6.3 - 7.1
	One proton on the -OH group	4.5
	Three protons on the $-CH_3$ group	2.233
	All the protons (10) on the cyclohexane ring except one on the a-position relative to the aromatic ring	1.20 - 2.17
	One proton on the cyclohexane ring on the α-position relative to the aromatic ring	2.633

Cyclohexyl group is substituted into the aromatic ring to the ortho- or para-position with respect to the -OH group. Therefore, the reaction of *p*-cresol with cyclohexene gave only one product, while the reactions of ortho- and meta-cresols gave mixtures of isomeric cyclohexyl cresols.

In the IR-spectrum of cyclohexyl *o*-cresol bands at 740-770 cm^{-1} accounted for the 1,2,3-trisubstituted benzene ring, while bands near 800-900 cm^{-1} were the characteristics of the 1,2,4-trisubstituted benzene ring. Bands near 3400 cm^{-1} indicated the presence of -OH group.

Absorption band at 3400 cm^{-1} in the IR-spectrum of cyclohexyl *m*-cresols showed the presence of -OH group. Bands near 800-900 cm^{-1} were the characteristics of the 1,2,4-trisubstituted benzene ring. Bands at 740-780 cm^{-1} accounted for the 1,2,3-trisubstituted benzene ring.

IR-spectrum of 2-cyclohexyl-4-methylphenol showed absorption band at 3350 cm^{-1} (-OH). Bands at 800-900 cm^{-1} accounted for the 1,2,4-trisubstituted benzene ring.

The ^{1}H NMR-spectrum of cyclohexyl cresols Table IV.

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