

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

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Abstract

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

Introduction

Alkyaromatic hydrocarbons can be used as lubricating oil, grease, transformer oil, lacquer resins, plasticizers, pour-point depressants and intermediates for detergents (Akhmedov 1987; Allison and Balack, 1953; Ashimov *et al*, 1966; Ashimov *et al*, 1969; Bataafsche de, 1952; Bataafsche de, 1952; B. Hydrocarbon Che. Ltd., 1963; Lebedev *et al*, 1960; Lebedev, 1984; Paul, 1950; Vol.-Epshtein *et al*, 1964). Reactions of xylenes have been investigated with olefins, alkylhalides and alcohols by several authors (Davtyan *et al*, 1971; Friedman *et al*, 1957; Guscinov *et al*, 1975; Mekhtiev *et al*, 1980; Pashaev *et al*, 1970; Rafique *et al*, 2006; Saha *et al*, 2001; Saha *et al*, 2006). But no attempt has so far been made to study the reactions with cyclohexene in the presence of *p*-toluenesulphonic acid.

In the present work, reactions of isomeric xylenes (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. xylene and *p*-toluenesulphonic 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*-xylene with cyclohexene

Table I records the results of the reaction of *o*-xylene with cyclohexene in the presence of *p*-toluenesulphonic acid. The reaction gave a mixture of isomeric cyclohexyl *o*-xylene. The yield of the product increased with the increase of temperature (Expt. No. 1,2,3,10

and 11), the molar ratio of *o*-xylene to cyclohexene (Expt. No. 4,5,6 and 10), time of reaction (Expt. No. 10 and 11) and the amount of catalyst (Expt. No. 7,8,9 and 10). But the change in the yield was insignificant when temperature was increased further ((Expt. No. 10 and 11). Thus the best yield of cyclohexyl *o*-xylene was obtained under the following reaction conditions: temperature = 130°C, molar ratio of *o*-xylene to cyclohexene = 10:1, time of addition = 2h, time of stirring = 1h and the amount of catalyst = 10 % by wt. of *o*-xylene.

B. Reaction of *m*-xylene with cyclohexene

Reaction of *m*-xylene with cyclohexene was investigated in the presence of *p*-toluenesulphonic acid over the temperature range of

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

Expt. No.	Reaction conditions					% Yield of cyclohexyl <i>o</i> -xylene
	Temp., °C	Molar ratio of <i>o</i> -xylene to cyclohexene	Time of addition, h	Time of stirring, h	Amount of catalyst, % by wt. of <i>o</i> -xylene	
1	100	10:1	2	1	10	62.7
2	110	10:1	2	1	10	77.1
3	120	10:1	2	1	10	88.5
4	130	3:1	2	1	10	16.2
5	130	6:1	2	1	10	49.4
6	130	8:1	2	1	10	89.6
7	130	10:1	2	1	5	25.3
8	130	10:1	2	1	7	65.2
9	130	10:1	2	1	9	90.8
10	130	10:1	2	1	10	97.4
11	135	10:1	2	1	10	97.5
12	130	10:1	2	0	10	78.7

120-130^o C, molar ratio of *m*-xylene to cyclohexene was varied from 6:1 to 10:1, time of reaction was varied from 2 to 3.5h and the amount of catalyst was varied from 5 to 10 % wt. of *m*-xylene. Table II records the results. The yield of product (cyclohexyl *m*-xylene) increased with the increasing temperature (Expt. No. 3, 6 and 8), molar ratio of *m*-xylene to cyclohexene (Expt. No. 1, 2 and 3), time of reaction (Expt. No. 3, 4 and 7; 2 and 9) and the amount of catalyst. (Expt No. 3 and 5). But a slight increase in the yield was observed when the temperature was increased from 130 to 135^o C (Expt No. 7 and 8). Thus the best yield of cyclohexyl *m*-xylene was obtained under the following conditions : temperature = 130^o C, molar ratio of *m*-xylene to cyclohexene = 8:1, the amount of catalyst = 10 % by wt. of *m*-xylene, time of addition = 2h and time of stirring = 3h.

C. Reaction of *p*-xylene with cyclohexene

The influence of the variation of different parameters, viz. temperature, molar ratio of *p*-xylene to cyclohexene and time of reaction on the reaction of *p*-xylene with cyclohexene has been shown in Table III. The reaction gave only 2-cyclohexyl-4-methylbenzene. The yield of the product increased with the increasing temperature (Expt. No. 2, 3 and 6, 7), molar ratio of *p*-xylene to cyclohexene (Expt. No. 4 - 6) and time of reaction (Expt. No. 1 and 2; 4 and 8). The increase in the yield was insignificant when the temperature was raised from 135 to 140^o C (Expt No. 2 and 3). The best yield of the product was obtained under the following conditions : temperature = 135^o C, molar ratio of *p*-xylene to cyclohexene = 10:1, the amount of catalyst = 10 % by wt. of *p*-xylene, time of addition = 2h and time of stirring = 1h.

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

Expt. No.	Reaction conditions					% Yield of cyclohexyl <i>m</i> -xylene
	Temp., ^o C	Molar ratio of <i>m</i> -xylene to cyclohexene	Time of addition, h	Time of stirring, h	Amount of catalyst, % by wt. of <i>m</i> -xylene	
1	130	6:1	2	1	10	45.7
2	130	8:1	2	1	10	80.8
3	130	10:1	2	1	10	90.2
4	130	10:1	2	0	10	73.8
5	130	10:1	2	1	5	24.5
6	120	10:1	2	1	10	87.1
7	130	10:1	2	1.5	10	97.6
8	135	10:1	2	1.5	10	97.8
9	130	8:1	2	3	10	98.9

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

Expt. No.	Reaction conditions					% Yield of 2-cyclohexyl-4-methylbenzene
	Temp., °C	Molar ratio of <i>p</i> -xylene to cyclohexene	Time of addition, h	Time of stirring, h	Amount of catalyst, % by wt. of <i>p</i> -xylene	
1	135	10:1	2	0	10	89.5
2	135	10:1	2	1	10	97.8
3	140	10:1	2	1	10	97.9
4	130	10:1	2	1	10	81.6
5	130	6:1	2	1	10	41.9
6	130	4:1	2	1	10	37.7
7	100	4:1	2	1	10	15.1
8	130	10:1	2	3	10	87.9

Table IV. ¹H NMR-spectrum of cyclohexyl xylenes

Products	Observed signals of the protons	Chemical shift δ in ppm
Cyclohexyl <i>o</i> -xylene	Three protons on the aromatic ring	6.43 - 6.96
	Six protons on the two -CH ₃ groups	2.03 - 2.33
	All the protons (10) on the cyclohexane ring except one on the α -position relative to the aromatic ring	0.83 - 2.03
	One proton on the cyclohexane ring on the α -position relative to the aromatic ring	3.53
Cyclohexyl <i>m</i> -xylene	Three protons on the aromatic ring	6.37 - 6.93
	Six protons on the two -CH ₃ groups	2.03 - 2.67
	All the protons (10) on the cyclohexane ring except one on the α -position relative to the aromatic ring	1-2
	One proton on the cyclohexane ring on the α -position relative to the aromatic ring	2.77
2-Cyclohexyl-4-methylphenol	Three protons on the aromatic ring	6.46 - 7.10
	Six protons on the two -CH ₃ groups	2.3
	All the protons (10) on the cyclohexane ring except one on the α -position relative to the aromatic ring	0.93 - 2.00
	One proton on the cyclohexane ring on the α -position relative to the aromatic ring	3.36

Cyclohexyl group is substituted into the aromatic ring to the ortho- or para-position with respect to the $-\text{CH}_3$ group. Therefore, the reaction of p-xylene with cyclohexene gave only one product, while the reactions of ortho- and meta-xylenes give mixture of isomeric cyclohexyl xylenes.

IR-spectrum of cyclohexyl o-xylene showed absorption bands at $720\text{-}780\text{ cm}^{-1}$ for the 1,2,3-trisubstituted benzene ring. Bands near $800\text{-}900\text{ cm}^{-1}$ were the characteristics of the 1,2,4-trisubstituted benzene ring.

In the IR-spectrum of cyclohexyl m-xylene, absorption bands near $800\text{-}900\text{ cm}^{-1}$ were the characteristics of the 1,2,4-trisubstituted benzene ring. Bands at $700\text{-}780\text{ cm}^{-1}$ accounted for the 1,2,3-trisubstituted benzene ring.

IR-spectrum of 2-cyclohexyl-4-methylbenzene showed absorption band at $800\text{-}900\text{ cm}^{-1}$ for the 1,2,4-trisubstituted benzene ring.

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