Bangladesh J. Sci. Ind. Res. **42(4)**, 499-502, 2007 **Short Communication**

Alkylation of *m*-Cresol with Cyclopentene in the Presence of *p*-Toluenesulphonic Acid

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Abstract

m-Cresol has been cycloalkylated with cyclopentene in the presence of *p*-toluenesulphonic acid as catalyst. The effects of the variation of temperature, molar ratio of *m*-cresol to cyclopentene, time of reaction and amount of catalyst have been investigated on the reaction and cyclopentyl *m*-cresol has been obtained in high yield.

Key words : Alkylation , *m*-Cresol, time frechtion, molar ration

Introduction

Alkylphenols and their derivatives are important antioxidants for fuels, lubricating oils and polymeric materials (Babakhanov *et al*. 1968; Lebedev, 1984; Paul, 1950; Ravikovich, 1964; Shreve & Brink, 1977). Some of their derivatives are also strong herbicides, bactericides and insecticides (Melinikov *et al*. 1954; Nemetkin *et al.* 1951).Isomeric cresols have been alkylated with different olefins (Karim *et al.*2005; Kharchenko & Zavgorodni, 1964; Palma *et al.*2007; Saha & Roy,1992; Saha *et al.*1997; Saha *et al.*1998; Saha *et al.*2003; Shulov, 1969). But no attempt has been made to study the reaction of m-cresol with cyclopentene in the presence of p-toluenesulphonic acid. p-Toluenesulphonic acid is a mild catalyst which does not give rise to undesirable side reactions. Moreover, it is less corrosive and hazardous.

In the present work, attempt has been made to investigate the reaction of *p*-cresol with cyclopentene in the presence of *p*-toluenesulphonic acid as catalyst.

Materials and Methods

Cresol-catalyst mixture was heated to the temperature of the experiment in a three necked round bottomed flask fitted with a stirrer, a condenser, a thermometer and a dropping funnel. Then cyclopentene was introduced into the mixture gradually over a certain period of time (time of addition) with constant stirring. After the addition of the total amount of cyclopentene, the reaction mixture was stirred for further period of time (time of stirring) at the same temperature. The reaction mass was then cooled to room temperature, dissolved in petroleum ether and neutralized. The reaction mixture was

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then washed with distilled water several times and unreacted reactants and solvent were distilled off at atmospheric pressure. The residual product was finally distilled and characterized by spectral means.

Results and Discussion

m-Cresol with cyclopentene in the presence of *p*-toluenesulphonic acid produced cyclopentyl m-cresol. Cyclopentyl group is substituted into the benzene ring to the ortho- or para-position with respect to the –OH group. The effects of the variation of parameters, viz. temperature, molar ratio of *m*-cresol to cyclopentene, time of reaction and amount of *p*-toluenesulphonic acid on the yield of the product were investigated. Results are presented in the Tables I-IV.

The yield of the product was increased from 46.4 to 79.7 % on increasing the temperature from 60 to 100^{O}C. At110^{O}C, the yield of the product slightly decreased. (Table I).

Table I. The effect of the variation of temperature on the reaction of *m*-cresol with cyclopentene in the presence of *p*-toluenesulphonic acid (molar ratio of *m*-cresol to cyclopentene = 4:1, time of addition = 2h, time of stirring = 1h, amount of *p*-toluenesulphonic acid = 10 % by wt. of m-cresol)

Temperature, ^{O}C	% Yield of cyclopentyl m-cresol
60	46.4
80	72.5
100	79.7
110	79.5

The yield of the product was also increased from 72.5 to 75.9 % by changing the molar ratio of m-cresol to cyclopentene from 4:1 to 6:1.But the increase in the yield was insignificant when the molar ratio was increased further (Table II).

Table II. The effect of the variation of molar ratio of *m*-cresol to cyclopentene on the reaction of *m*-cresol with cyclopentene in the presence of *p*-toluenesulphonic acid (temperature = 80^{O} C, time of addition = 2h, time of stirring = 1h, amount of *p*-toluenesulphonic acid = 10 % by wt. of *m*-cresol)

Molar ratio ofm-cresol to cyclopentene	% Yield of cyclopentyl *m*-cresol
4:1	72.5
6:1	75.9
8:1	76.0
10:1	76.1

Changing the amount of *p*-toluenesulphonic acid from 1 to10 % by wt. of m-cresol, the yield of the product was raised from 36.4 to72.5 %. The yield increased to a negligible value on increasing the amount of catalyst above 10% by wt. of *m*-cresol (Table III).

The effect of the variation of time of reaction (Table IV) was investigated by three sets of experiments with different time of addition and time of stirring. From the first set of experiments, it was observed that the yield of the product increased from 54.6 to 70.8 % when the time of addition varied form 1 to 3h. Second set of experiments showed that increasing the time of addition to a value greater than 2h, no significant effect on the yield was observed. Finally the third set of experiments showed that the yield increased by additional stirring. The yield increased

Table III. The effect of the variation of amount of *p*-toluenesulphonic acid on the reaction of *m*-cresol with cyclopentene in the presence of p-toluenesulphonic acid (temperature = 80^{O} C, molar ratio of *m*-cresol to cyclopentene = 4:1, time of addition = 2h, time of stirring = 1h)

Amount of *p*-toluenesulphonic acid, % by wt. of *m*-cresol	% Yield of cyclopentyl *m*-cresol
1	36.4
5	57.9
10	72.5
12	72.8

from 65.7 to 79.9 %, when the time of additional stirring was increased from 0 to 3 h . Increase in the yield was insignificant on further increase in the time of stirring.

Thus the product was obtained in 79.9 % yield under the following conditions: temperature = 80^{O} C, molar ratio of m-cresol to cyclopentene = 4:1, the amount of catalyst = 10 % by wt. of m-cresol, time of addition = 2h, time of stirring = 3h.

The UV-spectrum of cyclopentyl *m*-cresol in 0.01M petroleum ether solution strongly absorbed at λ_{max} = 293.4 nm.

IR-spectrum of the product showed absorption band at 730-770 cm^{-1} for the 1,2,3-trisubstituted aromatic ring. Bands near 800 - 900 cm^{-1} indicated the 1,2,4-trisubstituted aromatic ring. Band at 3400 cm^{-1} indicated the presence of –OH group.

The ^{1}H NMR-spectrum showed signals at = 6.30-7.06 ppm, 5.20 ppm and 2.13 ppm for benzene ring, -OH group and –CH_3 group

Table IV. The effect of the variation of time of reaction on the reaction of *m*-cresol with cyclopentene in the presence of *p*-toluenesulphonic acid (temperature = 80^{O} C, molar ratio of *m*-cresol to cyclopentene = 4:1, amount of *p*-toluenesulphonic acid = 10 % by wt. of *m*-cresol)

Set. No.	Time of addition, h	Time of stirring, h	Total time of reaction, h	% Yield of cyclopentyl *m*-cresol
1	1	0	1	54.6
	2	0	2	65.7
	3	0	3	70.8
	1	2	3	69.7
2	2	1	3	72.5
	3	0	3	70.8
	2	0	2	65.7
	2	1	3	72.5
3	2	2	4	77.5
	2	3	5	79.9
	2	4	6	80.1

protons respectively. Signals for all the protons of cyclopentyl ring except one on the α-position was observed at δ = 0.93-2.00 ppm. Signal for the hydrogen on the α-position was observed at δ = 2.67-3.34 ppm.

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Received : October, 31, 2005;
Accepted : August, 28, 2007