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tert.-Methylcyclohexylation of *o*-Cresol with Methylcyclohexanol in the Presence of Sulphuric Acid

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Abstract

tert.-Methylcyclohexyl*o*-cresol has been produced in high yield by the alkylation of *o*-cresol with methylcyclohexanol in the presence of sulphuric acid. The effects of the variation of molar ratio of *o*-cresol to methylcyclohexanol, temperature, concentration and amount of sulphuric acid and reaction time have been studied on the reaction to find out an optimum condition.

I. Introduction

Alkylated cresols and their derivatives are the most effective antioxidants and multifunctional stabilizers in fuels, lubricating oils, polymeric materials and wide variety of oxygen sensitive materials[1-3]. Alkyl cresols and some of their derivatives can also be used as herbicides, bactericides, insecticides etc.[2,4]. Alkylated cresols with a long alkyl group are intermediates for surfactants and detergents [2,5].

Alkylated cresols have been obtained by several authors by alkylation of isomeric cresols with olefins [6-19] and alcohols [20-33] using different catalysts. But no attempt has ever been made to investigate the reaction of *o*-cresol with methylcyclohexanol.

In the present work, reaction of *o*-cresol with methylcyclohexanol in the presence of sulphuric acid has been investigated.

II. Experimental

The reactions were carried out in a three necked round bottomed flask fitted with a condenser, a thermometer, a dropping funnel and a magnetic stirrer. *o*-Cresol- sulphuric acid mixture was heated to the desired temperature and methylcyclohexanol (mixture of isomers) was introduced into the mixture gradually for a certain period of time (addition time) with constant stirring. The reaction mixture was stirred for an extended period of time (stirring time) at the same temperature after the complete addition of total amount of methylcyclohexanol. The reaction mass was then cooled to room temperature, dissolved in petroleum ether, neutralized with saturated $NaHCO_3$ solution followed by washing with distilled water and subjected to distillation. Unreacted reactants and solvent were distilled off at atmospheric pressure. The residual product was finally distilled and characterized by spectral (IR, ^{1}H NMR, UV and CMR) means.

III. Results and Discussion

The reaction of *o*-cresol with methylcyclohexanol in the presence of sulphuric acid over the temperature range of 80 to 140°C gave only *tert.*-methylcyclohexyl*o*-cresol. The results agree well with literature [34-36]. The *tert.*-methylcyclohexyl group substituted the aromatic ring to the *ortho*- or *para*- position with respect to the –OH group. Molar ratio of *o*-cresol to methylcyclohexanol was varied from 4:1 to 8:1, concentration of sulphuric acid from 80 to 94%, amount of the acid from 2 to 5% by wt. of *o*-cresol and reaction time from 1 to 3.5h.

The effect of the variation of molar ratio of *o*-cresol to methylcyclohexanol

The effect of the variation of molar ratio of *o*-cresol to methylcyclohexanol on the reaction of *o*-cresol with methylcyclohexanol at temperature of 100°C, addition time of 2h and stirring time of 1h and in the presence of 94% sulphuric acid (5% by wt. of *o*-cresol**)** was studied when 43.8, 46.3 and 71.0% yield of *tert.*-methylcyclohexyl*o*-cresol were obtained at molar ratio of 4:1, 6:1 and 8:1, respectively. This showed that the yield of the product increased with the increase in molar ratio of *o*-cresol to methylcyclohexanol. Thus the yield increased from 43.8 to 71.0% when the molar ratio of *o*-cresol to methylcyclohexanol was increased from 4:1 to 8:1, and it was maximum at a molar ratio of 8:1 (Fig. 1).

The effect of the variation of temperature

The effect of the variation of temperature on the reaction of *o*-cresol with methylcyclohexanol in molar ratio of 8:1, addition time of 2h, stirring time of 1h and in presence of 94% sulphuric acid (5% by wt. of *o*-cresol) was studied when 65.5, 71.0, 88.6 and 97.8% yield of *tert.*-methylcyclohexyl*o*-cresol were obtained at temperature of 80, 100, 120 and 140°C, respectively. This indicated that the yield of the product (*tert.*-methylcyclohexyl*o*-cresol) increased with the increase in temperature. The yield increased from 65.5 to 97.8% for the increase in temperature from 80 to 140°C and it was found maximum at 140°C (Fig. 2).

The effect of the variation of concentration of sulphuric acid

The effect of the variation of concentration of sulphuric acid on the reaction of *o*-cresol with methylcyclohexanol at temperature of 140°C, molar ratio of 8:1, addition time of 2h, stirring time of 1h was investigated when 92.2, 94.5 and 97.8% yield of *tert.*-methylcyclohexyl*o*-cresol were obtained using sulphuric acid (5%, based on 94% acid, by wt. of *o*-cresol) of concentration of 80, 90 and 94%, respectively. Thus the yield of the product increased also with the increase in the concentration of sulphuric acid. The yield increased from 92.2 to 97.8% when concentration of sulphuric acid was increased from 80 to 94% (Fig. 3).

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The effect of the variation of the amount of sulphuric acid

The effect of the variation of amount of sulphuric acid on the reaction of *o*-cresol with methylcyclohexanol at temperature of 140°C, molar ratio of 8:1, addition time of 2h, stirring time of 1h, concentration of 94% was carried out when 90.5, 92.8 and 97.8% yield of *tert.*-methylcyclohexyl*o*-cresol were obtained using the catalyst in an amount of 2, 3 and 5% by wt. of *o*-cresol, respectively. Thus the yield of the product was found to increase with the increase in the amount of sulphuric acid. The yield increased from 90.5 to 97.8% when the amount of sulphuric acid was increased from 2 to 5% and it was observed to be maximum at 5% by wt. of *o*-cresol (Fig. 4).

The effect of the variation of reaction time

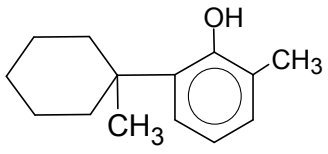
The effect of the variation of reaction time on the reaction of *o*-cresol with methylcyclohexanol (molar ratio of *o*-cresol to methylcyclohexanol = 8:1) at temperature of 140°C in the presence of 94% sulphuric acid (5% by wt. of *o*-cresol) was investigated by three sets of experiments with different addition time and stirring time (Fig. 5). From the first set of experiments, it was observed that the yield of the product increased from 90.2 to 95.1% when addition time was varried from 1 to 2.5 h (Fig. 5, Curve 1). Second set of experiments showed that the best yield was obtained when addition time was 2h (Fig. 5, Curve 2). Finally the third set of experiments showed that the yield increased with the increase in stirring time (Fig. 5, Curve 3).

Optimum conditions

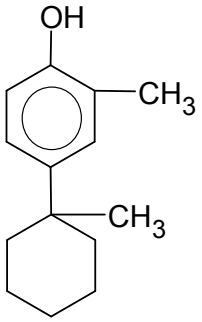
Thus the following conditions were considered as optimum for the production of *tert.*-methylcyclohexyl*o*-cresol: temperature = 140°C, molar ratio of *o*-cresol to methylcyclohexanol = 8:1, amount of 94% sulphuric acid = 5% by wt. of *o*-cresol, addition time = 2 h and stirring time = 1 h.

Spectral studies of *tert.*-methylcyclohexyl*o*-cresol:

The following two isomers (I and II) were obtained in the alkylation of *o*-cresol with methylcyclohexanol:



I



II

The IR spectrum of *tert.*-methylcyclohexyl*o*-cresol showed bands at **713 cm^{-1}** and **752 cm^{-1}** indicating the presence of 1, 2, 3 – trisubstituted benzene ring. Bands at **815 cm^{-1}** and **883 cm^{-1}** were the characteristics of 1, 2, 4 – trisubstituted benzene ring. The spectrum also showed absorption bands at **3409 cm^{-1}**, **3030 cm^{-1}** , **2925 cm^{-1}** and **1610 cm^{-1}** for -OH group, aromatic =C-H , aliphatic C-H and aromatic ring C-C stretching, respectively.

Table 1 shows the positions of signals of the protons in the ^{1}H NMR spectrum of *tert.*-methylcyclohexyl *o*-cresol. The product showed strong absorption at λ_{max} **= 275.8 nm** in 0.01M petroleum ether solution in the UV- spectrum.

^{13}C NMR ($CDCl_3$): δ 153.61- 151.04, 133.07- 114.66, 40.07- 15.67

Table 1. Signals of the protons in the ^{1}H NMR spectrum of *tert.*-methylcyclohexyl*o*-cresol.

Observed signals of the protons	Chemical shift in δ ppm
Aromatic ring protons	6.53 - 7.01
One proton on the **─OH** group	4.7
Three protons of **─CH_3** group	2.0 – 2.2
tert.-Methylcyclohexyl group protons	0.7 – 1.9

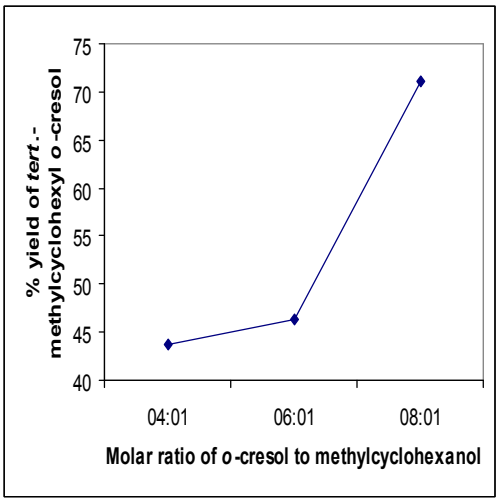


Fig. 1. The effect of the variation of molar ratio of *o*-cresol to methylcyclohexanol on the reaction of *o*-cresol with methylcyclohexanol in the presence of sulphuric acid (temperature = 100 °C, concentration of sulphuric acid=94%, amount of the acid = 5% by wt. of *o*-cresol, addition time = 2h and stirring time = 1h).

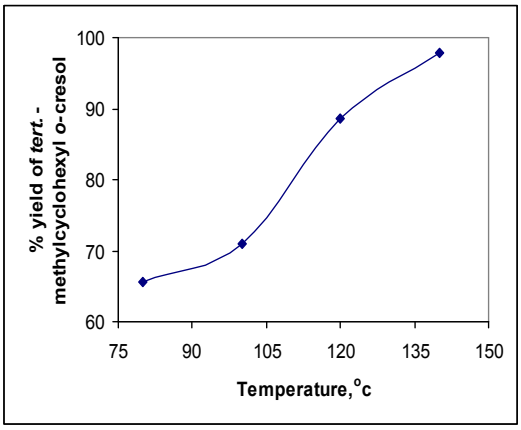


Fig. 2. The effect of the variation of temperature on the reaction of *o*-cresol with methylcyclohexanol in the presence of sulphuric acid (molar ratio of *o*-cresol to methylcyclohexanol = 8: 1, concentration of sulphuric acid=94%, amount of the acid = 5% by wt. of *o*-cresol, addition time = 2h and stirring time = 1h).

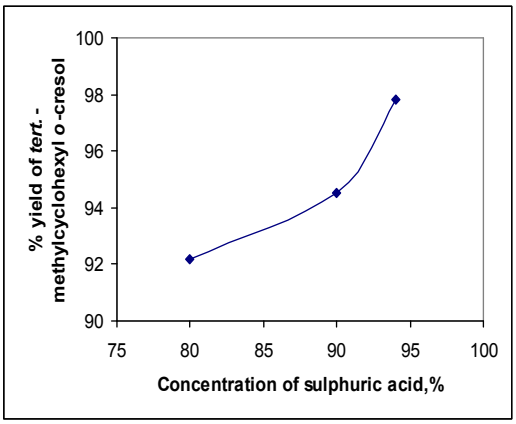


Fig. 3. The effect of the variation of the concentration of sulphuric acid on the reaction of *o*-cresol with methylcyclohexanol in the presence of sulphuric acid (temperature = 140°C, molar ratio of *o*-cresol to methylcyclohexanol = 8:1, amount of sulphuric acid (based on 94% acid) = 5% by wt. of *o*-cresol, addition time = 2h and stirring time = 1h)

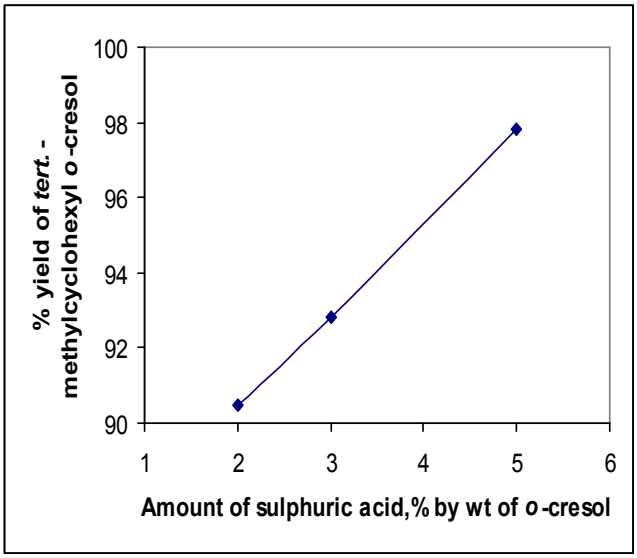


Fig. 4. The effect of the variation of the amount of sulphuric acid on the reaction of *o*-cresol with methylcyclohexanol in the presence of 94% sulphuric acid (temperature = 140°C, molar ratio of *o*-cresol to methylcyclohexanol = 8:1, addition time = 2h and stirring time = 1h).

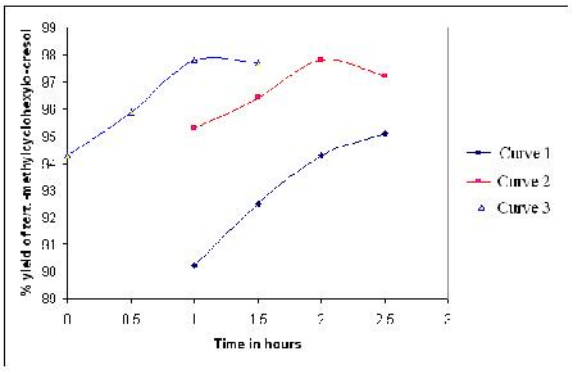


Fig. 5. The effect of the variation of reaction time on the reaction of *o*-cresol with methylcyclohexanol in the presence of sulphuric acid (temperature = 140°C, molar ratio of *o*-cresol to methylcyclohexanol =8:1 and amount of 94% sulphuric acid = 5% by wt. of *o*-cresol):
Curve 1 -The effect of the variation of addition time (stirring time = 0 h);
Curve 2 -The effect of the variation of addition time (reaction time = 3 h);
Curve 3 -The effect of the variation of stirring time (addition time = 2 h).

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