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tert.-Butylation of *p*-Cresol with *tert.*-Butyl Chloride

Md. Shahruzzaman, Manoranjan Saha*, Nusrat Sharmin, Md. Kabir Hossain, Md. Tafsir Uddin Bhuyan, A. M. Sarwaruddin Chowdhury, Dipti Saha, Md. Zahangir Alam and Mohammad Ismail

Department of Applied Chemistry and Chemical Engineering, Dhaka University, Dhaka-1000, Bangladesh

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Abstract

2-*tert.*-Butyl-4-methylphenol was obtained in high yield by the alkylation of *p*-cresol with *tert.*-butyl chloride in the presence of anhydrous aluminium chloride. The effects of the variation of molar ratio of *p*-cresol to *tert.*-butyl chloride, temperature, amount of $AlCl_3$ and time of reaction have been studied on the reaction to find out an optimum condition.

I. Introduction

The outstanding antioxidants and multifunctional stabilizers for fuels, lubricating oils and polymeric materials are based on alkylphenols and cresols[1-3]. Alkyl cresols and some of their derivatives can also be used as herbicides, bactericides, insecticides etc.[3,4]. Alkylated cresols with an alkyl group of 9-12 carbon atoms are valuable intermediates for surfactants and nonionic detergents [2,3,5].

Alkylated cresols have been obtained by several authors by alkylation of isomeric cresols with olefins [6-15] and alcohols [16-25] using different catalysts. But no attempt has so far been made to investigate the reactions of *p*-cresol with *tert.*-butyl chloride in the presence of anhydrous aluminium chloride.

In the present work, attempt has been made to investigate the reaction of *p*-cresol with *tert.*-butyl chloride in the presence of anhydrous aluminium chloride as catalyst.

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. *p*-Cresol-$AlCl_3$ mixture was heated to the desired temperature and *tert.*-butyl chloride was introduced into the mixture gradually for a certain period of time (time of addition) with constant stirring. The reaction mixture was stirred for an extended period of time (time of stirring) at the same temperature after the complete addition of total amount of *tert.*-butyl chloride. 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) means.

III. Results and Discussion

The results of the reaction of *p*-cresol with *tert.*-butyl chloride in the presence of anhydrous aluminium chloride over the temperature range of 80 to 160°C are presented in Tables 1-4 and in Figs. 1-4. Molar ratio of *p*-cresol to *tert.*-butyl chloride was varied from 4:1 to 8:1, amount of $AlCl_3$ from 5 to 8% by wt. of *p*-cresol and reaction time from 1 to 4.5h. The *tert.*-butyl group substituted the aromatic ring to the *ortho*- position with respect to the –OH group and 2-*tert.*-butyl-4-methylphenol was obtained in good yield.

The effect of variation of molar ratio of *p*-cresol to *tert.*-Butyl chloride

The effect of variation of molar ratio of *p*-cresol to *tert.*-butyl chloride on the reaction of *p*-cresol with *tert.*-butyl chloride at temperature of 140°C, addition time of 2h and stirring time of 1h and in the presence of anhydrous aluminium chloride (5% by wt. of *p*-cresol**)** was studied when 62.1, 74.1 and 81.5% yield of 2-*tert.*-butyl-4-methylphenol were obtained at molar ratio of 4:1, 5:1 and 8:1, respectively. This showed that the yield of the product increased with the increase in molar ratio of *p*-cresol to *tert.*-butyl chloride. Thus the yield increased from 62.1 to 81.5% when the molar ratio of *p*-cresol to *tert.*-butyl chloride increased from 4:1 to 8:1, and it was maximum at a molar ratio of 8:1 (Fig. 1).

The effect of variation of temperature

The effect of variation of temperature on the reaction of *p*-cresol with *tert.*-butyl chloride in molar ratio of 5:1, addition time of 2h, stirring time of 1h and in presence of anhydrous aluminium chloride (6% by wt. of *p*-cresol) was studied when 62.5, 74.6, 80.3 and 83.6% yield of 2-*tert.*-butyl-4-methylphenol were obtained at temperature of 80, 100, 140 and 160°C, respectively. This indicated that the yield of the product (2-*tert.*-butyl-4-methylphenol) increased with the increase in temperature. The yield increased from 62.5 to 83.6% for the increase in temperature from 80 to 160°C and it was found maximum at 160°C (Fig. 2).

The effect of variation of the amount of $AlCl_3$

The effect of variation of amount of anhydrous aluminium chloride on the reaction of *p*-cresol with *tert.*-butyl chloride at temperature of 140°C, molar ratio of 5:1, addition time of 2h, stirring time of 1h was carried out when 74.1, 80.3 and 84.9% yield of 2-*tert.*-butyl-4-methylphenol were obtained using the catalyst in an amount of 5, 6 and 8% by wt. of *p*-cresol, respectively. Thus the yield of the product was found to increase with the increase in the amount of $AlCl_3$. The yield increased from 74.1 to 84.9% when the amount of anhydrous aluminium chloride was increased from 5 to 8%

*Corresponding Author: E-mail: manoranjansaha2005@yahoo.com
Tel: +880-2-8621770, Fax: +880-2-8615583

and it was observed to be maximum at 8% by wt. of *p*-cresol (Fig. 3).

The effect of variation of reaction time

The effect of variation of reaction time on the reaction of *p*-cresol with *tert.*-butyl chloride (molar ratio of *p*-cresol to *tert.*-butyl chloride = 5:1) at temperature of 140°C in the presence of anhydrous aluminium chloride (6% by wt. of *p*-cresol) was investigated by three sets of experiments with different addition time and stirring time (Fig. 4). From the first set of experiments, it was observed that the yield of the product increased from 71.2 to 78.6% when addition time was varried from 1 to 2.5 h (Fig. 4, Curve 1). Second set of experiments showed that the best yield was obtained when addition time was 2.5h (Fig. 4, Curve 2). Finally the third set of experiments showed that the yield increased with the increase in stirring time (Fig. 4, Curve 3).

Optimum conditions

Thus the following conditions were considered as optimum for the production of 2-*tert.*-butyl-4-methylphenol:

temperature = 140°C, molar ratio of *p*-cresol to *tert.*-butyl chloride = 5:1, amount of anhydrous aluminium chloride = 6% by wt. of *p*-cresol, addition time = 2 h and stirring time = 2.5 h.

Spectral studies (IR, ^{1}H NMR) of 2-*tert.*-butyl-4-methylphenol

The IR spectrum of 2-*tert.*-butyl-4-methylphenol showed bands at 815.89 cm^{-1} and 877.61 cm^{-1} indicating the presence of 1, 2, 4 – trisubstituted benzene ring. The spectrum also showed absorption bands at 3387.00 cm^{-1}, 3018.60 cm^{-1}, 2924.09 cm^{-1} and 1606.70 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 2-*tert.*-butyl-4-methylphenol.

Table. 1. Signals of the protons in the ^{1}H NMR spectrum of 2-*tert.*-butyl-4-methylphenol

Observed signals of the protons	Chemical shift in δ ppm
Aromatic ring protons	6.55 - 7.24
One proton on the **─OH** group	4.76 – 5.01
Three protons of **─CH$_3$** group	2.06– 2.42
tert.-Butyl group protons	1.24 – 1.80

2-*tert.*-Butyl-4-methylphenol had b.p. = 237 °C, n_D^{20} = 1.5398 and d_4^{20} = 0.963.

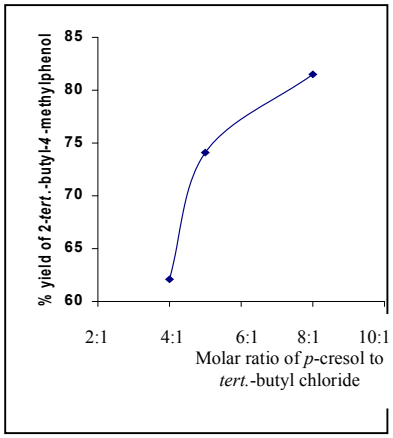

Fig. 1. The effect of variation of molar ratio of *p*-cresol to *tert.*-butyl chloride on the reaction of *p*-cresol with *tert.*-butyl chloride in the presence of anhydrous aluminium chloride (temperature = 140 °C, amount of anhydrous aluminium chloride = 5% by wt. of *p*-cresol, addition time = 2h and stirring time = 1h).

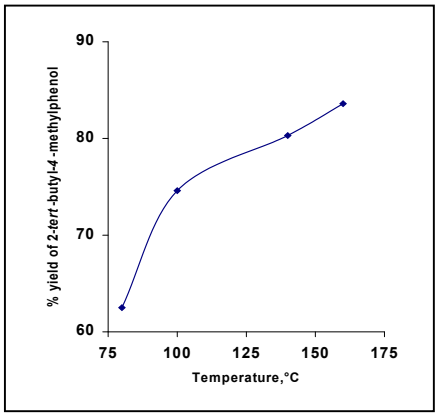

Fig. 2. The effect of variation of temperature on the reaction of *p*-cresol with *tert.*-butyl chloride in the presence of anhydrous aluminium chloride (molar ratio of *p*-cresol to *tert.*-butyl chloride = 5: 1, amount of anhydrous aluminium chloride = 6% by wt. of *p*-cresol, addition time = 2h and stirring time = 1h).

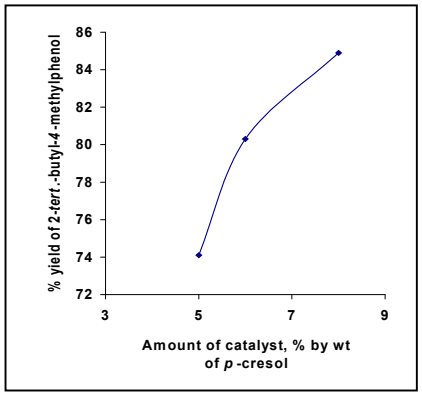

Fig. 3. The effect of variation of the amount of $AlCl_3$ on the reaction of *p*-cresol with *tert.*-butyl chloride in the presence of anhydrous aluminium chloride (temperature = 140°C, molar ratio of *p*-cresol to *tert.*-butyl chloride = 5:1, addition time = 2h and stirring time = 1h).

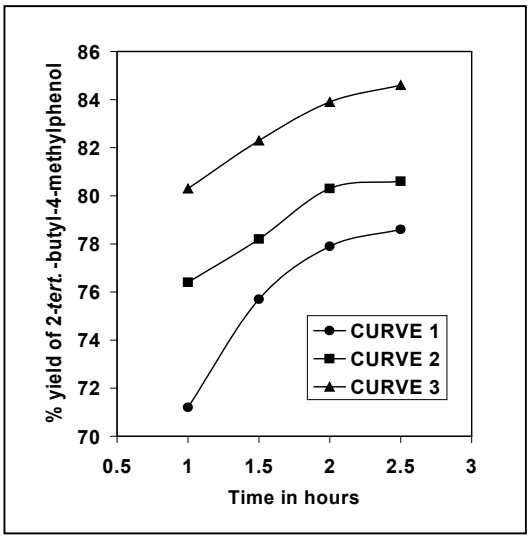

Fig. 4. The effect of variation of reaction time on the reaction of *p*-cresol with *tert.*-butyl chloride in the presence of anhydrous aluminium chloride (temperature = 140°C, molar ratio of *p*-cresol to *tert.*-butyl chloride =5:1 and amount of $AlCl_3$ = 6% by wt. of *p*-cresol):
Curve 1 -The effect of variation of addition time (stirring time = 0 h);
Curve 2 -The effect of variation of addition time (reaction time = 3 h);
Curve 3 -The effect of variation of stirring time (addition time = 2 h).

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