

Reaction of p-Cresol with Indene in the presence of Benzenesulphonic Acid

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Abstract

Reaction of p-Cresol with indene in the presence of benzenesulphonic acid as catalyst produced only 2-indanyl-4-methylphenol over the temperature range of 100-140°C. The yield of the product increased with the increase in temperature, molar ratio of p-cresol to indene, amount of catalyst and reaction time. The optimum yield of the reaction product was 94.1% of theory.

Keywords: p-Cresol, Indene, Benzenesulphonic acid, Spectrum, 2-indanyl-4-methylphenol

Introduction

Production and uses of synthetic fuels, lubricating oils and polymers have been increasing day by day. But these compounds tend to undergo thermal degradation in the presence of heat, light, air, ozone etc. The most effective antioxidants and multifunctional stabilizers in such media and in wide variety of oxygen sensitive materials are based on alkylphenols and cresols. Alkylated cresols and some of their derivatives also have herbicidal, bactericidal and insecticidal activities. Alkyl cresols with long alkyl group are intermediates for surfactants and detergents. They have been obtained by different authors by the alkylation of isomeric cresols with olefins in the presence of several acidic catalysts. Reactions of cresols with indene have also been reported¹⁻³. But no attempt has so far been made to investigate the reaction of p-cresol with indene in the presence of benzenesulphonic acid⁴⁻⁶. Benzenesulphonic acid is milder in its actions in phenol alkylation process and does not cause undesirable side reactions. This could be one of the most suitable catalysts for the indanylation of cresols.

The aim of the present investigation is to study the reaction of p-cresol with indene in the presence benzenesulphonic acid.

Experimental

Reactions were carried out in a three necked round bottom flask fitted with a condenser, a thermometer and a dropping funnel. Stirring was made by a magnetic stirrer and temperature was controlled by the temperature regulator. Cresol- benzenesulphonic acid mixture was heated to the desired temperature and indene added to it gradually during certain period of time (addition time) with constant stirring. The reaction mixture was continued to stir at that temperature for extended period of time (stirring time) and then cooled to room temperature. For the isolation of the product, reaction mass was dissolved in ether, neutralized and washed with distilled water several times. Unconverted reactants and solvent were distilled off at atmospheric pressure. The product was finally distilled to give 2-

indanyl-4-methylphenol which was confirmed by spectral means. The yield was expressed as percent of theory.

Results and Discussion

The reaction of p-cresol with indene in the presence of benzenesulphonic acid as catalyst over the temperature range of 100-140°C gave only 2-indanyl-4-methylphenol. The influence of the variation of temperature, molar ratio of p-cresol to indene and amount of benzenesulphonic acid has been recorded in Table 1 and reaction time in Table 2.

The effect of the variation of temperature on the reaction of p-cresol with indene in molar ratio of 8:1, addition time of 2 h, stirring time of 1 h and in presence of benzenesulphonic acid (8% by wt. of p-cresol) was studied when 71.0, 89.6 and 94.1% yield of 2-indanyl-4-methylphenol were obtained at temperature of 100, 120 and 140°C, respectively. This showed that the yield of the product increased with the increase in temperature and it was observed to be maximum of 140°C (Table 1, Expt No. 1, 2 and 3)

The effect of the variation of molar ratio of p-cresol to indene on the reaction of p-cresol with indene at temperature of 140°C, addition time of 2h, stirring time of 1h and in presence of benzenesulphonic acid (8% by wt. of p-cresol) was carried out when 56.9, 73.3 and 94.1% yield of 2-indanyl-4-methylphenol were obtained at molar ratio of 4:1, 6:1 and 8:1, respectively. The yield of the product also increased with the increase in molar ratio of p-cresol to indene and it was maximum at a molar ratio of 8:1 (Table 1, Expt. No. 3,4 and 5).

The effect of the variation of the amount of benzenesulphonic acid on the reaction of p-cresol with indene at temperature of 140°C, molar ratio of 8:1, addition time of 2h and stirring time of 1h was investigated when 67.0, 81.7 and 94.1% yield of 2-indanyl-4-methylphenol were obtained using benzenesulphonic acid as catalyst in an amount of 1, 5 and 8% by wt. of p-cresol, respectively. Thus the yield of the product increased with the increase in amount of catalyst and it was found to be maximum at 8% by wt. of p-cresol.(Table 1, Expt. No. 3,6 and 7).

The effect of the variation of reaction time on the reaction of p-cresol with indene (molar ratio 8:1) at 140°C in

presence of benzenesulphonic acid (8% by wt. of *p*-cresol) was studied by the following three sets of experiments with different addition and stirring time (Table 2): (I) addition time was varied from 1 to 3 h stirring time, 0 h (Set No. 1); (II) addition time was varied from 1 to 3 h, total reaction time, 3 h (Set No. 2); (III) stirring time was varied from 0 to 2 h, addition time, 2 h (Set No. 3). On increasing the addition time from 1 to 3 h, the yield of the product increased from 62.7 to 92.6%. When the addition time was

increased more than 2h, there was no significant effect on the yield. The yield increased also by additional stirring but the increase in yield was negligible after 1 h.

Thus for the production of 2-indanyl-4-methylphenol, the following conditions were optimum: temperature, 140°C; molar ratio of *p*-cresol to indene, 8:1; amount of benzenesulphonic acid, 8% by wt. of *p*-cresol; addition time, 2 h and stirring time, 1 h.

Table 1: Alkylation of *p*-cresol with indene in the presence of benzenesulphonic acid

Expt. No.	Reaction conditions (addition time, 2h; stirring time, 1h)			% yield of 2-indanyl-4-methylphenol
	Temp., °C	Molar ratio of <i>p</i> -cresol to indene	Amount of benzenesulphonic acid, % by wt. of <i>p</i> -cresol	
1	100	8:1	8	71
2	120	8:1	8	89.6
3	140	8:1	8	94.1
4	140	4:1	8	56.9
5	140	6:1	8	73.3
6	140	8:1	1	67.0
7	140	8:1	5	81.7

Table 2: The effect of the variation of time of reaction on the reaction of *p*-cresol with indene in presence of benzenesulphonic acid (temperature = 140°C, molar ratio of *p*-cresol to indene = 8:1 and amount of benzenesulphonic acid = 8% by wt. of *p*-cresol).

Set No.	Addition time, h	Stirring time, h	Total reaction time, h	% yield of 2-indanyl-4-methylphenol
1	1	0	1	62.7
	2	0	2	84.5
	3	0	3	92.6
2	1	2	3	86.9
	2	1	3	94.1
	3	0	3	92.6
3	2	0	2	84.5
	2	1	3	94.1
	2	2	4	94.8

Signals of the ¹H NMR spectrum of 2-indanyl-4-methylphenol were recorded as : δ 7.02-7.72 (phenyl-H), 5.99 (-OH), 3.15-3.61 (indanyl protons other than phenyl-H), 2.55(s, Me).

The UV-spectrum of the product showed strong absorption at λ max= 297.0nm in 0.01M methanol solution.

The presence of 1,2,4-trisubstituted aromatic ring, -OH group and aromatic ring

C C was identified by the bands at 800-900 cm⁻¹, 3400 cm⁻¹, 1600 cm⁻¹, respectively, in the IR-spectrum of the product. Bands at 2870-2910cm⁻¹ accounted for the saturated C-H stretch.

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