



Indanylation of *o*-Cresol with Indene

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Abstract

Indanyl *o*-cresol has been obtained in high yield by the reaction of *o*-cresol with indene in the presence of *p*-toluenesulphonic acid as catalyst. The effects of variation of temperature, molar ratio of *o*-cresol to indene, time of reaction and amount of the catalyst have been investigated on the reaction. The yield of the product increased with the increase of each of the above mentioned parameters. Optimum conditions of the reaction for the production of indanyl *o*-cresol were temperature, 130°C; molar ratio of *o*-cresol to indene, 12:1; amount of catalyst, 8% by wt. of *o*-cresol; time of addition, 2h and time of stirring, 1h.

Key words: *o*-Cresol, Indene, *p*-Toluenesulphonic acid, Indanyl *o*-Cresol, Spectral analyses

Introduction

To protect synthetic fuels, lubricating oils and polymeric materials against thermal degradation due to heat, light, air, oxygen, ozone etc., use of antioxidant has become increasingly important. Alkylphenols and their derivatives are excellent antioxidants and multifunctional stabilizers in fuels, lubricating oils and polymeric materials (Babakhanov *et al.* 1968; Lebedev, 1984; Ravikovich, 1964). Moreover, derivatives of alkylphenols are also strong herbicides and bactericides (Melnikov *et al.* 1954; Nemetkin *et al.* 1951). Alkylated cresols with long alkyl group are intermediates for surfactants and detergents (Dritriev *et al.* 1961). Isomeric cresols have been alkylated by olefins in the presence of several different acidic catalysts (Babakhanov *et al.* 1965; Egidis *et al.* 1966; Gusev *et al.* 1969; Kharchenko and Zavgorodnii, 1964; Kharchenko and Zavgorodnii, 1964; Kharchenko and Zavgorodnii, 1964; Isagulayants and Belov, 1964; Saha and Ghosh, 1989; Saha *et al.* 1994; Saha *et al.* 1996; Saha *et al.* 1997; Saha *et al.* 1998; Saha *et al.* 2000; Saha *et al.* 2000; Shulov *et al.* 1969; Starkov *et al.* 1972; Vdovtsova and Fedorova, 1972; Viktorova *et al.* 1960; Yadav and Pala, 2000; Zavgorodnii and Kharchenko, 1963; Saha *et al.* 2003; Karim *et al.* 2005; Karim *et al.* 2007; Saha *et al.* 2008). Reports are also available on the reaction of cresols with indene (Saha *et al.* 2006; Palma *et al.* 2007). But no attempt has so far been made to study the reaction of *o*-cresol with indene in the presence of *p*-toluenesulphonic acid.

In the present work, reaction of *o*-cresol has been investigated with indene in the presence of *p*-toluenesulphonic acid.

Materials and Methods

The reactions were carried out in a three necked round bottomed flask fitted with a condenser, a thermometer, a dropping funnel and a stirrer. *o*-Cresol and catalyst were charged into the flask, heated to the temperature of the experiment, then indene was introduced into the mixture gradually over a certain period of time (time of addition) with constant stirring. The reaction mixture was stirred for another period of time (time of stirring) at the same temperature after the addition of the total amount of indene. The reaction mass was then cooled to room temperature, dissolved in diethylether or benzene and neutralized. The reaction mixture was then washed with distilled water several times and unreacted reactants and solvent were distilled off at atmospheric pressure. The product thus obtained was distilled and characterized by spectral analyses.

Results and Discussion

Reaction of *o*-cresol with indene was investigated in the presence of *p*-toluene sulphonic acid over the temperature range of 70 to 130°C. Molar ratio of *o*-cresol to indene was varied from 4:1 to 12:1, amount of *p*-toluene sulphonic acid was varied from 1 to 8% by wt. of *o*-cresol and time of reaction from 1 to 4h. *o*-Cresol with indene under the conditions studied gave indanyl *o*-cresol. The yield of the product increased from 59.0 to 64.7% with the increase in temperature from 70 to 130°C (Fig 1). The yield of the product depended also significantly on the molar ratio of *o*-cresol to indene (Fig 2). The yield increased from 52.1 to 80.9%, when the molar ratio of *o*-cresol to indene was varied from

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4:1 to 12:1. The yield of the product depended also on the amount of catalyst (Fig 3). Thus the yield increased from 78.5 to 80.9%, when the amount of catalyst was increased from 1 to 8% by wt. of o-cresol.

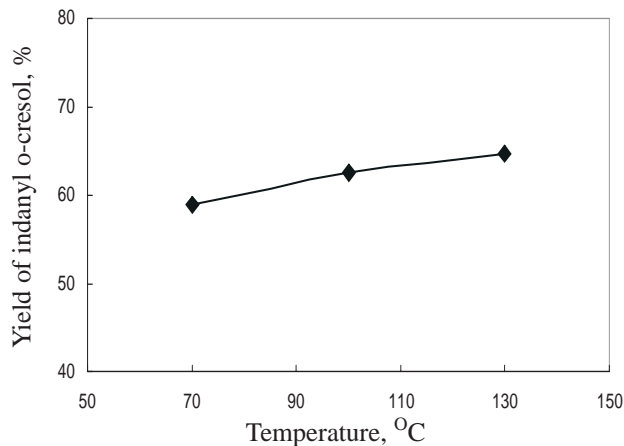


Fig. 1. The effect of the variation of temperature on the reaction of o-cresol with indene in the presence of p-toluenesulphonic acid (molar ratio of o-cresol to indene = 8:1, time of addition = 2h, time of stirring = 1h, amount of catalyst = 8% by wt. of o-cresol).

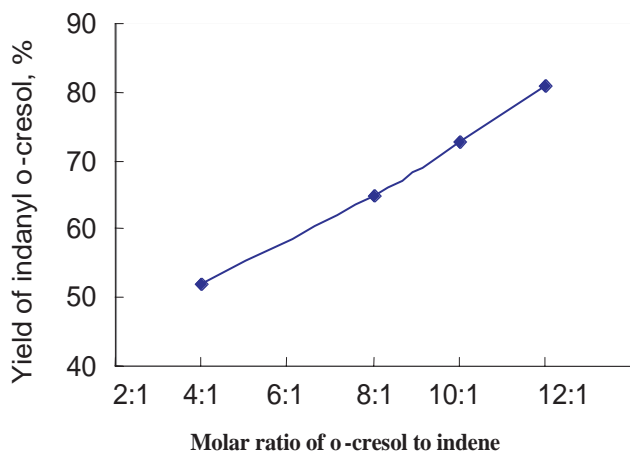


Fig. 2. The effect of the variation of molar ratio of o-cresol to indene on the yield of indanyl o-cresol (temperature = 130 °C, time of addition = 2h, time of stirring = 1h, amount of catalyst = 8% by wt. of o-cresol).

The effect of the variation of time of reaction was investigated by three sets of experiments with different time of addition and time of stirring (Fig 4). From the first set of experiments, it was seen that the yield of indanyl o-cresol increased from 69.5 to 78.2%, when the time of addition was

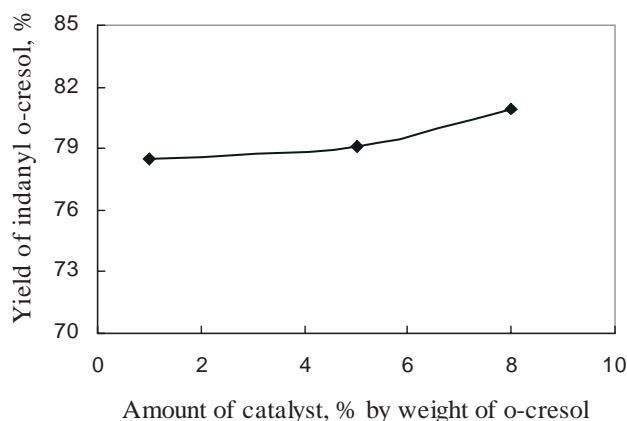


Fig 3. The effect of variation of the amount of p-toluenesulphonic acid on the reaction of o-cresol with indene (temperature = 130 °C, molar ratio of o-cresol to indene = 12:1, time of addition = 2h, time of stirring = 1h).

varied from 1 to 2.5h. From the second set of experiments it was seen that at constant total time of reaction (3h), 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 the effect of the variation of time of stirring at constant time of addition ($t_a = 2h$). On increasing the time of stirring from 0 to 2h, the yield increased from 75.4 to 81.2%. Thus the following conditions were considered as optimum for the production of indanyl o-cresol: temperature = 130°C, molar ratio of o-cresol to indene = 12:1, amount of catalyst = 8 % by wt. of o-cresol, time of addition = 2h and time of stirring = 1h.

In the IR-sepectrum, absorption bands at 710-750 cm^{-1} accounted for 1,2,3- trisubstituted aromatic ring, while bands near 800-900 cm^{-1} indicated the presence of 1,2,4-trisubstituted aromatic ring. Band at 3400 cm^{-1} accounted for the -OH group, while bands at 2910 cm^{-1} and 1590 cm^{-1} showed the C-H stretch and C = C stretch, respectively.

Chemical shifts of the protons are shown in Table I

Table I. Signals of the protons in the ^1H NMR-spectrum of indanyl o-cresol.

Observed signals of the protons	Chemical shift in the δ ppm
Aromatic ring protons	6.91-7.59
-OH group proton	6.89
All the protons on the indanyl group except four on the aromatic ring	3.1-3.56
Three protons on the -CH ₃ group	2.3

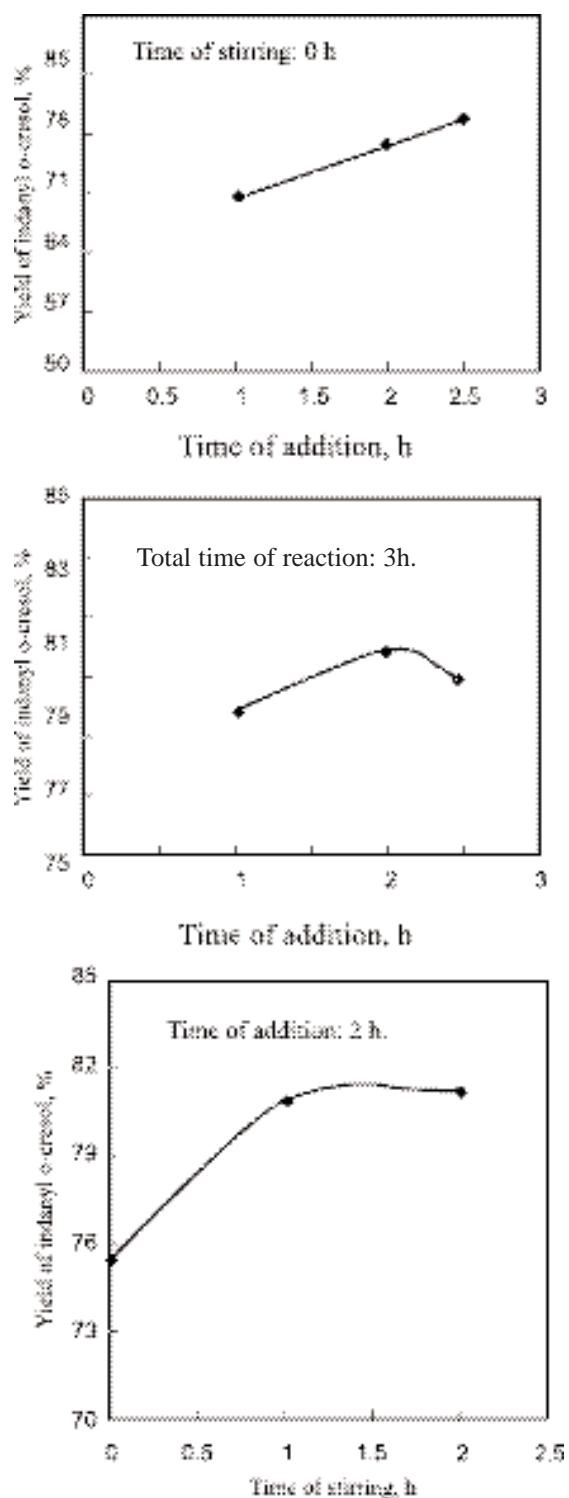


Fig. 4. The effect of variation of time of reaction on the yield of indanyl o-cresol (temperature = 130 °C, molar ratio of o-cresol to indene =12:1, amount of catalyst = 8% by weight of o-cresol).

The UV-spectrum of the product showed strong absorption at $\lambda_{\max} = 298.5$ nm in 0.01M methanol solution.

The product had b.p. 290°C, n_D^{20} 1.5471, d_4^{20} 1.042.

Conclusion

The influence of variation of different parameters was investigated on the reaction of o-cresol with indene in the presence of p-toluenesulphonic acid as catalyst. The yield of indanyl o-cresol was found to increase with the increase in temperature, molar ratio of o-cresol to indene, time of reaction and amount of catalyst. The optimum yield of the product was 80.9% obtained under the following conditions: temperature, 130°C; molar ratio of o-cresol to indene, 12:1; amount of catalyst, 8% by wt. of o-cresol; time of addition, 2h; time of stirring, 1h.

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