

Indanylation of Phenol with Indene in the presence of Benzenesulphonic Acid

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Received on 12. 04. 2011. Accepted for Publication on 20.08.2011

Abstract

Indanylphenol has been obtained in high yield by the reaction of phenol with indene in the presence of benzenesulphonic acid. The effects of variation of temperature, molar ratio of phenol to indene, time of reaction and amount of benzenesulphonic acid have been studied on the reaction. The optimum conditions for the production of indanyl phenol have been determined.

I. Introduction

Alkylated phenols and their derivatives are the excellent antioxidants and multifunctional stabilizers in fuels, lubricating oils and wide variety of oxygen sensitive polymeric materials¹⁻³. They are also pour point depressant for transmission fluid, corrosion inhibitors and plasticizers for polymers⁴⁻⁶. Alkyl phenols with an alkyl group of 5-8 carbon atoms are strong bactericides and with an alkyl group of 9-12 carbon atoms are valuable intermediates for non-ionic detergents^{2,3,7,8}. They are also used in paint and varnishes, dye, perfume, adhesives and soap industries^{3,9-11}. Moreover, some of their derivatives have strong herbicidal, bactericidal and insecticidal activities^{3,12-14}.

Phenol has been alkylated by different cycloalkenes in the presence of various catalysts¹⁵⁻²⁵. Reports are also available on the reaction of phenol with indene in the presence of cation exchange resin and sulphuric acid²⁶⁻²⁸. Benzenesulphonic acid is milder in its action in phenol alkylation process and does not cause undesirable side reactions. This could be one of the most suitable catalysts for the indanylation of phenol. But no attempt has so far been made to investigate the reaction in the presence of this catalyst.

In the present work, reaction of phenol with indene in the presence of benzenesulphonic acid has been investigated.

II. Experiment

The reactions were carried out in a three necked round bottomed flask fitted with a condenser, a thermometer, a dropping funnel and a stirrer. Phenol-catalyst mixture was 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 petroleum ether 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 residual product was finally distilled and characterized by spectral means.

III. Result and Discussion

Reaction of phenol with indene was investigated in the presence of benzenesulphonic acid over the temperature range of 70 to 140°C. Molar ratio of phenol to indene was varied from 4:1 to 10:1, reaction time 1 to 5h and the amount of catalyst was varied from 3 to 8% by wt.% of phenol. The reaction of phenol with indene gave indanyl phenol. The indanyl group substituted the aromatic ring to the ortho- or para- position with respect to the -OH group. The yield of the product increased with increasing temperature, molar ratio of phenol to indene, time of reaction and amount of benzenesulphonic acid.

The effects of the variation of parameters in the reaction have been shown in the Tables 1-4. The variation of temperature showed that the yield of the product increased from 23.7 to 79.5% with the increase of temperature from 70 to 140°C (Table 1).

The yield of the product also increased significantly with the increase of the molar ratio of phenol to indene (Table 2). The yield of the product increased from 38.6 to 75.7% when the molar ratio of phenol to indene was increased from 4:1 to 10:1.

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Table 3 shows the effect of variation of the amount of benzenesulphonic acid on the reaction of phenol with indene in the presence of benzenesulphonic acid. The yield was increased from 53.3 to 75.3% by charging the amount of catalyst from 3 to 8%.

The effect of the variation of time of addition and stirring can be seen from Table 4. The yield of the product increased

from 47.9 to 73.6% when the time of addition was varied from 1 to 3 h. By increasing the time of addition to a value greater than 2h, no significant effect on the yield was observed. The yield also increased by additional stirring. The best yield was obtained when the time of stirring was 3h.

Table. 1. The effect of the variation of temperature on the reaction of phenol with indene in presence of benzenesulphonic acid (molar ratio of phenol to indene = 8:1, time of reaction = 2h, time of stirring = 1h, amount of benzenesulphonic acid = 8% by wt. of phenol).

Temperature, °C	% yield of indanyl phenol
70	23.7
100	41.8
140	79.5

Table. 2. The effect of the variation of molar ratio of phenol to indene on the reaction of phenol with indene in the presence of benzenesulphonic acid (temperature = 140°C, time of addition = 2h, time of stirring = 1h, amount of benzenesulphonic acid = 5% by wt. of phenol).

Molar ratio of phenol to indene	% yield of indanyl phenol
4:1	38.6
5:1	45.9
8:1	65.5
10:1	75.7

Table. 3. The effect of the variation of the amount of benzenesulphonic acid on the reaction of phenol with indene in the presence of benzenesulphonic acid (temperature = 140°C, molar ratio of phenol to indene = 8:1, time of addition = 2h, time of stirring = 1h).

Amount of benzenesulphonic acid, % by wt. of phenol	% yield of indanyl phenol
3	53.3
5	65.5
8	75.3

Table. 4. The effect of the variation of the reaction time on the reaction of phenol with indene in the presence of benzenesulphonic acid (temperature = 140°C, molar ratio of phenol to indene = 8:1 and amount of benzenesulphonic acid = 8% by wt. of phenol).

Set No.	Time of addition, h	Time of stirring, h	Total time of reaction, h	% yield of indanyl phenol
1	1	0	1	47.9
	2	0	2	61.2
	3	0	3	73.6
2	1	2	3	72.5
	2	1	3	75.3
	3	0	3	73.6
3	2	0	2	61.2
	2	1	3	75.3
	2	2	4	77.5
	2	3	5	79.9

The UV-spectrum of indanyl phenol showed strong absorption at $\lambda_{\max} = 299.0$ nm in 0.01 M methanol solution.

In the IR-spectrum of the product, absorption band at 750 cm^{-1} accounted for the 1,2-disubstituted aromatic ring. Band at 815 cm^{-1} showed the 1,4-disubstituted aromatic ring.

Absorption band at 3355 cm^{-1} indicated the presence of –OH group in the product.

Table 5 shows the signals of the protons in the $^1\text{H-NMR}$ -spectrum of indanyl phenol.

Table 5. $^1\text{H-NMR}$ spectrum of indanyl phenol

Observed signals of the protons	Chemical shift in the δ ppm
All the protons of the indanyl group except four on the aromatic ring	3.2-3.7
-OH group proton	6.1
Aromatic ring protons	6.9-7.7

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