

## Alkylation of Phenol with *n*-Alcohols (C<sub>5</sub>-C<sub>7</sub>) in the Presence of Sulphuric Acid

Manoranjan Saha\*, Md. Kabir Hossain, Md. Ashaduzzaman, Mirza Galib, Dipti Saha,

A. M. Sarwaruddin Chowdhury, Md. Tafsir Uddin Bhuyan and Md. Shahruzzaman

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

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### Abstract

Alkylphenols have been obtained in high yield by the alkylation of phenol with *n*- alcohols (C<sub>5</sub>-C<sub>7</sub>) in the presence of sulphuric acid. The effects of the variation of temperature, molar ratio of phenol to *n*-alcohol, time of reaction, concentration and amount of sulphuric acid on the reactions have also been studied.

### I. Introduction

Alkylphenols and their derivatives are excellent antioxidants and stabilizers for fuels, lubricating oils and polymeric materials<sup>1-7</sup>. Moreover, some of their derivatives are also strong insecticides, herbicides and bactericides<sup>4,8-10</sup>. Alkylphenols are also utilized as plasticizers for polymeric materials and valuable intermediates for the manufacture of surfactants and detergents<sup>4,11,12</sup>. Derivatives of alkylphenols can also be used in paints and varnishes, dye, perfume and soap industries<sup>13-15</sup>. Alkylation of phenols with olefins<sup>16-20</sup>, alcohols<sup>21-25</sup> and alkylhalides<sup>26</sup> has been investigated in the presence of protic and aprotic acids by several authors. But studies on the reactions of phenol with *n*-alcohols (C<sub>5</sub>-C<sub>7</sub>) in the presence of sulphuric acid are absent.

In the present work, reactions of phenol with *n*-alcohols (C<sub>5</sub>-C<sub>7</sub>) have been investigated in the presence of sulphuric acid as catalyst.

### II. Experimental

Reactions were carried out in a three necked round bottomed flask fitted with a stirrer, a condenser, a thermometer and a dropping funnel. Phenol and sulphuric acid were charged into the flask and heated to the desired temperature and alcohol was introduced dropwise to the mixture for a certain period of time (time of addition) with constant stirring. After the addition of the total amount of alcohol, the reaction mixture was stirred for an extended period of time (time of stirring) at the same temperature. The reaction mass was then cooled to room temperature, dissolved in ether, neutralized with saturated NaHCO<sub>3</sub> solution, and washed with distilled water several times and subjected to distillation. Unreacted reactants and solvent were distilled off at atmospheric pressure. Products thus obtained were distilled and characterized by spectral means.

### III. Results and Discussion

#### A. Reaction of phenol with pentanol-1

**Table 1** showed the reaction of phenol with pentanol-1 in the presence of sulphuric acid over the temperature range of 140 - 160°C. Molar ratio of phenol to pentanol-1 was varied from 4:1 to 10:1, concentration of sulphuric acid from 80 - 94%, reaction time from 4 to 5 hours and the amount of catalyst from 5 to 8% by wt. of phenol. The reaction gave sec.-amylphenols. The yield of sec.-amylphenols increased with the increase in temperature (Expt. no. 3 and 4), molar ratio of phenol to pentanol-1 (Expt. no. 1-3), concentration of sulphuric acid (Expt. no. 4 and 6), amount of catalyst (Expt. no. 4 and 5) and time of reaction (Expt. no. 4 and 7). Thus the best yield (47.3%) of the sec.-amylphenols was

obtained under the following reaction conditions: temperature = 160°C, molar ratio of phenol to pentanol-1 = 10:1, concentration of sulphuric acid = 94%, amount of catalyst = 8% by wt. of phenol, time of addition = 2 hours and time of stirring = 3 hours.

The ultraviolet spectrum of sec.-amylphenols showed strong absorption at  $\lambda_{\max} = 300.0 \text{ nm}$  in 0.01M petroleum ether solution.

In the IR- spectrum, absorption bands near **750 cm<sup>-1</sup>** and **810 cm<sup>-1</sup>** accounted for 1, 2- and 1, 4- disubstituted benzene ring, respectively. Band at **3400 cm<sup>-1</sup>** showed the presence of -OH group in the product. The presence of aromatic ring C=C and saturated C-H group is indicated by the band at **1600 cm<sup>-1</sup>** and **2890-2940 cm<sup>-1</sup>**, respectively.

The signals of the protons in the <sup>1</sup>H NMR-spectrum of sec.-amylphenols have been recorded in **Table-2**.

#### B. Reaction of phenol with hexanol-1

**Table 3** showed the reaction of phenol with hexanol-1 in the presence of 80-94% sulphuric acid over the temperature range of 140 - 160°C. Molar ratio of phenol to hexanol-1 was varied from 4:1 to 10:1, amount of catalyst from 5 to 8% by wt. of phenol and reaction time from 4 to 5 hours. The reaction gave sec.-hexylphenols. As can be seen from the result, the effects of the variation of parameters on the yield of products are similar to those of the reaction of phenol with pentanol-1. The yield of sec.-hexylphenols increased with the increase in temperature (Expt. no. 3 and 4), molar ratio of phenol to hexanol-1 (Expt. no. 1-3), concentration of sulphuric acid (Expt. no. 4 and 6), amount of catalyst (Expt. no. 4 and 5) and time of reaction (Expt. no. 4 and 7). It was observed that the best yield (57.2%) of the sec.-hexylphenols was obtained when the reaction was carried out under the following reaction conditions: temperature = 160°C, molar ratio of phenol to hexanol-1 = 10:1, concentration of sulphuric acid = 94%, amount of catalyst = 8% by wt. of phenol, time of addition = 2 hours and time of stirring = 3 hours.

sec.-Hexylphenols absorb strongly at  $\lambda_{\max} = 294.5 \text{ nm}$  in 0.01M petroleum ether solution in UV- spectrum.

In the IR- spectrum of the products, absorption bands at **740 cm<sup>-1</sup>** showed 1,2- disubstituted benzene ring. Band near **810 cm<sup>-1</sup>** accounted for 1, 4- disubstituted benzene ring. Bands at **3200-3600 cm<sup>-1</sup>** indicated the presence of -OH group in the product.

**Table 4** showed chemical shifts in ppm of the protons in the <sup>1</sup>H NMR-spectrum of sec.-hexylphenols.

\*Corresponding Author: E-mail: [manoranjansaha2005@yahoo.com](mailto:manoranjansaha2005@yahoo.com)

### C. Reaction of phenol with heptanol-1

The effect of the variation of parameters has been studied in detail in the example of alkylation of phenol with heptanol-1 in the presence of sulphuric acid from **Table 5** to **Table 9**. It can be seen from **Table 5** that the products (sec.-heptylphenols) depend significantly on the molar ratio of phenol to heptanol-1. Maximum yield is obtained at molar ratio of phenol to heptanol-1 = 10:1.

The yield of sec.-heptylphenols gradually increased upto 160°C. At 160°C, sec.-heptylphenols were obtained in 56.9%. Above 160°C, the reaction was difficult to carry out because of vapourisation of heptanol-1 (**Table 6**).

The yield of the products increased also with the increase of both the concentration (**Table 7**) and the amount of sulphuric acid (**Table 8**). Maximum yield was obtained when sulphuric acid of concentration 90-98% was used taking 5-8% by wt. of phenol. The effect of the variation of time of reaction can be observed from the following three sets of experiments with different time of addition and time of stirring:

1-time of stirring = 0, time of addition varied from 1 to 3 hours;

2-total time of reaction = 5 hours, time of addition varied from 1 to 3 hours;

3-time of addition = 2 hours, time of stirring varied from 0 to 4 hours.

It can be seen from the Table 9 that the yield of products increased with increasing time of addition (Set No. 1). No significant effect was observed when time of addition was increased to a value greater than 2 hours (Set No. 2). The effect of the variation of time stirring at constant time of addition showed that the best yield was obtained when time of stirring was  $\geq 3$  hours.

Thus the best yield of sec.-heptylphenols was obtained under the following conditions:

temperature = 160°C, amount of 94% sulphuric acid = 8% by wt. of phenol, time of addition of heptanol-1 = 2 hours and time of stirring = 4 hours.

Strong absorption was observed at  $\lambda_{\max} = 295.0 \text{ nm}$  in 0.01 petroleum ether solution in the UV-spectrum of sec.-hexylphenols.

In the IR-spectrum of sec.-heptyl phenols, absorption band at  $3400 \text{ cm}^{-1}$  showed the presence of -OH group. Band at  $750 \text{ cm}^{-1}$  was observed for 1,2-disubstituted benzene ring and band at  $810 \text{ cm}^{-1}$  accounted for the 1,4- disubstituted aromatic ring in the product.

Chemical shifts in ppm of the protons in the  $^1\text{H}$  NMR-spectrum of sec.-heptylphenols have been recorded in **Table 10**.

**Table 1. Alkylation of phenol with pentanol-1 in the presence of sulphuric acid for 2 hours addition time**

Expt. No.	Reaction Conditions					% yield of sec.- amyl phenols
	Temp., °C	Molar ratio of phenol to pentanol-1	Time of stirring, h	Concentration of sulphuric acid, %	Amount of sulphuric acid, % by wt. of phenol	
1	140	4:1	2	94	8	18.2
2	140	8:1	2	94	8	22.8
3	140	10:1	2	94	8	38.4
4	160	10:1	2	94	8	44.4
5	160	10:1	2	94	5	37.7
6	160	10:1	2	80	8	21.2
7	160	10:1	3	94	8	47.3

**Table 2. Signals of the protons in the  $^1\text{H}$  NMR-spectrum of sec.-amylphenols**

Observed signal	Chemical shift in ppm
Four protons on the aromatic ring	6.43-7.50
One proton on the -OH group	5.70
All the protons of sec.-amyl group except one on the $\alpha$ -position relative to the aromatic ring	0.56-2.20
One proton on the $\alpha$ -position	2.61-3.86

**Table 3.** Alkylation of phenol with hexanol-1 in the presence of sulphuric acid for 2 h addition time.

Expt. No.	Reaction conditions					% yield of sec.-hexyl phenols
	Temp., °C	Molar ratio of phenol to hexanol-1	Time of stirring, h	Concentration of sulphuric acid, %	Amount of sulphuric acid, % by wt. of phenol	
1	140	4:1	2	94	8	25.3
2	140	8:1	2	94	8	35.2
3	140	10:1	2	94	8	45.3
4	160	10:1	2	94	8	50.4
5	160	10:1	2	94	5	42.2
6	160	10:1	2	80	8	31.4
7	160	10:1	3	94	8	57.2

**Table 4.** Signals of the protons in the <sup>1</sup>H NMR-spectrum of sec.-hexylphenols.

Observed signal	Chemical shift in ppm
Four protons on the aromatic ring	6.36-7.43
One proton on the -OH group	5.46
All the protons of the sec.-hexyl group except one on the α-position relative to the aromatic ring	0.56-2.73
One proton on the α-position	3.00-3.83

**Table 5.** The effect of the variation of molar ratio of phenol to heptanol-1 on the alkylation of phenol with heptanol-1 in the presence of sulphuric acid (temperature = 140°C, time of addition = 2 h, time of stirring 2 h, amount of 94% sulphuric acid = 8% by wt. of phenol).

Molar ratio of phenol to heptanol-1	% yield of sec.-heptylphenols
6:1	33.8
8:1	38.4
9:1	47.2
10:1	52.9

**Table 6.** The effect of the variation of temperature on the alkylation of phenol with heptanol-1 in the presence of sulphuric acid (molar ratio of phenol to heptanol-1 = 10:1, time of addition = 2h, time of stirring = 2 h, amount of 94% sulphuric acid = 8% by wt. of phenol).

Temperature, °C	% yield of sec.-heptylphenols
100	21.7
120	35.5
140	52.9
160	56.9

**Table 7.** The effect of the variation of concentration of sulphuric acid on the alkylation of phenol with heptanol-1 (temperature = 160°C, molar ratio of phenol to heptanol-1 = 10:1, time of addition = 2 h, time of stirring = 2 h, amount of sulphuric acid, based on 94% acid = 8% by wt. of phenol).

Concentration of sulphuric acid, %	% yield of sec.-heptylphenols
80	40.2
85	45.9
90	53.8
94	56.9
98	57.2

**Table 8.** The effect of the variation of amount of sulphuric acid on the alkylation of phenol with heptanol-1 (temperature = 160°C, molar ratio of phenol to heptanol-1 = 10:1, concentration of sulphuric acid = 94%).

Amount of sulphuric acid, % by wt. of phenol	% yield of sec.-heptylphenols
2	45.1
5	50.5
6.5	52.2
8	56.9

**Table 9.** The effect of the variation of time of reaction on the alkylation of phenol with heptanol-1 in the presence of sulphuric acid (temperature = 160°C, molar ratio of phenol to heptanol-1 = 10:1, amount of 94% sulphuric acid = 5% by wt. of phenol).

No.	Time of addition (ta),h	Time of stirring (ts),h	Total time of reaction (ta+ts), h	Yield, %
1	1	0	1	28.7
	2	0	2	37.1
	3	0	3	49.4
2	1	4	5	63.5
	2	3	5	68.4
	3	2	5	68.1
3	2	0	2	37.1
	2	1	3	50.8
	2	2	4	56.9
	2	3	5	68.4
	2	4	6	69.7

**Table 10.** Signals of the protons in the <sup>1</sup>H NMR-spectrum of sec.-heptylphenols

Observed signal	Chemical shift in ppm
Four protons on the aromatic ring	6.43-7.33
One proton on the -OH group	5.7
All the protons of sec.-heptyl group except one on the α-position relative to the aromatic ring	0.63-2.00
One proton on the α-position	3.78-4.0

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