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Alkylation of Phenol with Olefins in the Presence of Sulphuric Acid

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Abstract

Alkylphenols have been synthesised in high yield by the alkylation of phenol with olefins (C_6-C_8) in the presence of sulphuric acid. The effects of the variation of temperature, molar ratio of phenol to olefin, time of reaction, concentraction and amount of sulphuric acid have also been studied on the reactions.

Keywords: Alkylation, Phenol, Sulphuric Acid

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 stabilizers in such media (Lebedev, 1984; Ravikovich, 1964; Shreve and Brink 1977). They are also pour-point depressants for transmission fluid, corrosion inhibitors, plasticizers for polymeric materials (Egorov *et al.* 1978; Lebedev, 1984; Nelicova *et al.* 1974; Randell and Pickles,1978). Alkylphenols 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 nonionic detergents (Dritriev *et al.* 1961). Some of their derivatives are strong herbicides, insecticides, plant growth regulators, antiseptics etc (Akhmedov *et al.*1978; Belov and Isagulyants, 1964; Klarmann, 1938; Lebedev, 1984; Mills, 1940; Mills, 1941; Newman *et al.*1947; Okazaki *et al.* 1951). Derivatives of alkylphenols can also be used in paints and varnishes, dye, perfume and soap industries (Kheifits and Podberezina,1968; Topchiev *et al.* 1962).

Alkylation of phenols with olefins (Karim *et al.* 2005; Saha *et al.* 1996; Tesvetkov *et al.* 1970; Topchiev *et al.*1964;Topchiev *et al.* 1964), alcohols (Saha and Badruzzaman,

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1990; Saha *et al.* 2000; Saha and Roy,1992) and alkylhalides (Akhmedov *et al.*1978; Alieva and Akhmedov, 1983; Turaeva *et al.* 1976) has been investigated in the presence of protic and aprotic acids by severals authors. But the reactions have not been investigated in the presence of sulphuric acid as catalyst.

In the present work, attempt has been made to investigate the reaction of phenol with olefins (C_6-C_8) in the presence of sulphuric acid as catalyst.

Materials and Methods

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 olefins were introduced dropwise to the mixture for a certain period of time (time of addition) with constant stirring. After the addition of the olefins, 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 $NaHCO_3$ solution and washed with distilled water several times and then subjected to distillation. Unreacted reactants and solvent were distilled off at atmospheric pressure. Products thus obtained were distilled and characterized by IR- and ^{1}H NMR- spectroscopic methods.

Results and Discussion

A. Reaction of phenol with hexene-1 and cyclohexene

Results of the reaction of phenol with hexene-1 in the presence of sulphuric acid are recorded in Table I. The reaction gave sec.-hexylphenol. sec.- Hexylphenol were obtained in 65.8% yield under the following conditions: temperature = 140^{O}C, molar ratio of phenol to hexene-1 = 6:1, amount of 94% sulphuric acid = 8% by wt. of phenol, time of addition = 2 h and time of stirring = 2 h.

In the IR- spectrum of sec.-hexylphenol, band at 740 cm^{-1} was the characteristics of 1, 2- disubstituted benzene ring and band at 815 cm^{-1} showed the presence of 1, 4- disubstituted benzene ring. The presence of -OH group was indicated by band at near 3200-3600 cm^{-1} in the product. The signals of the protons in the ^{1}H NMR-spectrum of sec.-hexylphenol have been recorded in Table II.

Table I. Alkylation of phenol with hexene-1 in the presence of 94% sulphuric acid (temperature = 140° C, time of addition = 2h, time of stirring = 2h, amount of sulphuric acid = 8% by wt. of phenol)

Expt. No.	Molar ratio of phenol to hexene-1	% yield of sec.-hexylphenol
1	4:1	30.1
2	5:1	48.2
3	6:1	65.8

The reaction of phenol with cyclohexene in the presence of sulphuric acid was investigated over the temperature range of 50 - 140^{O}C (Table III). Molar ratio of phenol to cyclohexene was varied from 4:1 to 8:1, reaction time from 3 to 4 h and the amount of catalyst from 3 to 7% by wt. of phenol. The reaction gave cyclohexylphenol. The yield of cyclohexylphenols increased with the increase in temperature (Expt. no. 1 and 2; 4 and 7) molar ratio of phenol to cyclohexene (Expt. no. 3-5; 2 and 6), amount of catalyst (Expt. no. 2 and 3; 5 and 6). Thus the best yield (80%) of cyclohexylphenol was obtained under the following reaction conditions: temperature = 140^{O}C, molar ratio of phenol to cyclohexene = 6:1, amount of 94% sulphuric acid = 7% by wt. of phenol, time of addition = 2 h and time of stirring = 1 h.

In the IR- spectrum of cyclohexylphenol, band at 750 cm^{-1} was the characteristic of 1, 2- disubstituted benzene ring and band at 815 cm^{-1} showed the presence of 1, 4- disubstituted benzene ring. The presence of -OH group was indicated by band near at 3150 - 3600 cm^{-1} in the product.

Table II. Signals of the protons in the ^{1}H NMR-spectrum of sec.-hexylphenol

Observed signals of the protons	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

B. Reaction of phenol with heptene-1 and cycloheptene

sec.- Heptylphenol was obtained in 73.8% yield by the alkylation of phenol with hep

Table III. Alkylation of phenol with cyclohexene in the presence of 94 % sulphuric acid

Expt. No.	Reaction conditions (Time of addition, 2h; time of stirring,1h)			% yield of cyclohexylphenol
	Temp., ^{0}C	Molar ratio of phenol to cyclohexene	Amount of sulphuric acid, % by wt. of phenol	
1	50	4:1	3	40.8
2	100	4:1	3	61.4
3	100	4:1	7	73.6
4	100	6:1	7	75.5
5	100	8:1	7	78.3
6	100	8:1	3	65.9
7	140	6:1	7	80.00

tene-1 in the presence of sulphuric acid under the following conditions: temperature = 140^{O}C, molar ratio of phenol to heptene-1 = 6:1, amount of 94% sulphuric acid = 8% by wt. of phenol, time of addition = 2 h and time of stirring =2 h.

The IR-spectrum of sec.-heptylphenol showed the absorption band at 750 cm^{-1} for the 1, 2- disubstituted benzene ring and band at 820 cm^{-1} for the 1, 4- disubstituted benzene ring. Band at 3400 cm^{-1} accounted for the presence of -OH group in the product.

The signals of the protons in the ^{1}H NMR-spectrum of sec.-heptylphenol have been represented in Table IV.

Sulphuric acid catalysed reaction of phenol and cycloheptene gave cycloheptylphenol in 88.6% yield under the following conditions: temperature = 140^{O}C, molar ratio of phenol to cycloheptene = 6:1, amount of catalyst = 8% by wt. of phenol, concentration of sulphuric acid = 94%, time of addition = 2 h and time of stirring =2 h.

In the IR- spectrum of these products, the presence of -OH group was indicated by band at 3400 cm^{-1}. Band at 750 cm^{-1} indicated the presence of 1, 2- disubstituted ben zene ring and band near 810 cm^{-1}accounted for 1, 4- disubstituted benzene ring in the product.

Table V showed the values of chemical shift in ppm of the protons in the ^{1}H NMR- spectrum of cycloheptylphenol.

C. Reaction of phenol with octene-1

Results of the reaction of phenol with octene-1 in the presence of 94% sulphuric acid have been shown in Table VI. The reaction gave sec.-octylphenol in 94.7% yield under the following conditions: temperature 140^{O}C, molar ratio of phenol to octene-1 = 10:1, amount 94% sulphuric acid = 8% by wt. of phenol, time of addition = 2 h, time of stirring = 2 h. The presence of -OH group was indicated by band at 3350 cm^{-1} in the IR-spectrum of sec.-octylphenol. Band at 750 cm^{-1} accounted for the presence of 1, 2- disubstituted benzene ring and at 810 cm^{-1} for the 1, 4- disubstituted benzene ring in the product.

Chemical shifts in ppm of the protons in the ^{1}H NMR- spectrum of sec.-octylphenol have been recorded in Table VII.

Table IV. Signals of the protons in the ^{1}H NMR-spectrum of sec.-heptylphenol

Observed signals of the protons	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 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

Table V. Signals of the protons in the ^{1}H NMR- spectrum of cycloheptylphenol

Observed signals of the protons	Chemical shift in ppm
Four protons on the aromatic ring	6.33 - 7.33
One proton on the -OH group	5.93
All the protons on the cycloheptane ring except one on the α-position relative to the aromatic ring	1.63
One proton on the α-position	2.17 - 3.27

Table VI. Alkylation of phenol with octene-1 in the presence of 94% sulphuric acid (temperature = 140° C, time of addition = 2h, time of stirring = 2h, amount of sulphuric acid = 8% by wt. of phenol)

Expt. No.	Molar ratio of phenol to octene-1	% yield of sec.-octylphenol
1	6:1	81.4
2	8:1	85.8
3	10:1	94.7

Table VII. Signals of the protons in the ^{1}H NMR- spectrum of sec.-octylphenol

Observed signals of the protons	Chemical shift in ppm
Four protons on the aromatic ring	6.33 - 7.17
One proton on the -OH group	5.07-5.83
All the protons of sec.-octyl group except one on the α-position relative to the aromatic ring	0.6-1.83
One proton on the α-position	3.33

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