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E-mail: bjsir07@gmail.com

Synthesis of sec.-undecyl and sec.-dodecyl phenols as valuable intermediates of non-ionic surfactants

Dipti Saha*, Md Ashaduzzaman, Mithun Sarker, Partha Saha and Tahmina Siddiqui

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

Abstract

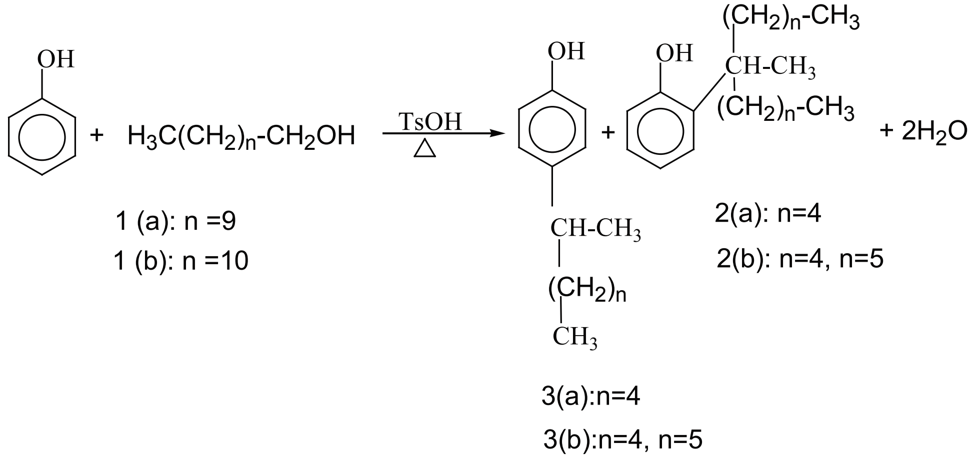
The reaction of phenol with undecan-1-ol and dodecan-1-ol respectively was investigated in the presence of *p*-toluenesulphonic acid to get the corresponding alkylated phenols. The effects of the variation of different reaction parameters viz. temperature, molar ratio of phenol to undecan-1-ol and dodecan-1-ol respectively, amount of *p*-toluenesulphonic acid, addition of time and stirring of time on the reaction were studied and optimum conditions of the reaction were determined.

Keywords: Alkylation; Phenol; Reaction time; Molar ratio; *P*-toluenesulphonic acid

Introduction

Alkylphenols with a long alkylgroup are intermediates for the production of surfactants and detergents. (Labedev 1984; Dimitriev et al. 1961; Saha, M. et al. 1994,1997, 2000; Belov et al. 1982; Anderson et al. 1972). Alkylphenols and their derivatives are important antioxidants for fuels, lubricating oils and polymeric materials (Babakhanov et al. 1968; Lebedev, 1984; Paul, 1950; Ravikovich, 1964; Shreve and Brink, 1977). Some of their derivatives are also strong herbicides, bactericides and insecticides (Melinikov et al. 1954; Nemetkin et al. 1951). Isomeric cresols have been alkylated with different olefins (Karim et al. 2005; Kharchenko and Zavgorodni, 1964; Palma et al. 2007; Saha & Roy, 1992; Saha et al, 1997, 1998, 2003; Shulov, 1969). Phenol has been alkylated with olefins, alkylhalides and alcohols with different catalysts (Clausen et al. 1978). Alkylphenols with long alkyl group are intermediates for surfactants and detergents. But no attempt has so far been made to investigate the reaction of phenol with undecanol-1 and dodecanol-1 respectively in the presence of *p*-toluenesulphonic acid.

p-Toluenesulphonic acid is milder in its action in phenol alkylation process and does not cause undesirable side reactions (Karim et al 2005). This could be one of the most suitable catalysts for the alkylation of phenol. In the present work, reactions of phenol with undecanol-1 and



1 (a): n =9
1 (b): n =10

2(a): n=4
2(b): n=4, n=5

3(a):n=4
3(b):n=4, n=5

Scheme-1

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*Corresponding authors: E-mail: dipti1993@yahoo.com do-decanol-1 respectively in the presence of *p*-toluenesulphonic acid have been investigated. The resulted products are sec.-undecyl phenol and sec.-dodecyl phenol respectively. (Scheme-1)

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 magnetic stirrer. Phenol (30g or 319 mmol) and p-toluenesulphonic acid (4.5 g or 26.1 mmol) mixture was heated to the desired temperature. Undecan-1-ol (5.49 g or 31.92 mmol) and dodecan-1-ol (5.94 g 31.92 mmol) was introduced separately into the mixture gradually over a certain period of time (time of addition) with constant stirring. After the complete addition of undecan-1-ol or dodecan-1-ol 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 a solvent, then washed with distilled water several times and distilled at atmospheric pressure Unreacted reactants and solvent were distilled off and the yield was expressed as a percentage of theory. The product was obtained as liquids yields incase of undecan-1-ol 5.52 g & yield 74.5% and incase of dodecan-1-ol 6.6 g & yield 84%. The residual product was finally distilled and its structure was elucidated by physico-chemical and spectral means (IR, UV ^{1}H NMR).

Results and Discussion

Alkylation of phenol with undecan-1-ol in the presence of, *p*-toluenesulphonic acid as catalyst has been carried out over the temperature range 140-160°C. Molar ratio of phenol to undecan-1-ol was varied from 5:1 to 10:1, amount of catalyst from 5 to 15% by wt. phenol and time of stirring was varied from 3 to 4h. Results of the reaction are presented in the Table I. The reaction gives *sec.*– undecyl phenol. The reaction scheme has been shown in scheme 1.Undecyl-1-ol reacting with the catalyst used, first produced undec-1-ene, which then reacts with phenol at ortho and para positions by the double bond. This is why, at both ortho and para positions *sec.*undecyl phenol formed. The yield of the product increases with the increase of the molar ratio of phenol to undecan-1-ol (Expt. no. 1 and 2, 4, 5 and 6), amount of catalyst (Expt. no. 2, 3 and 4), temperature (Expt. no. 4 and 7) and time of reaction (Expt. no. 4 and 8). The best yield of *sec.*-undecyl phenol in 74.5% is obtained under the following reaction conditions: temperature = 160^{o}C, molar ratio of phenol to undecan-1-ol = 10:1, amount of catalyst=15% by wt. of phenol, time of addition=2h and time of stirring = 2h (Expt. no. 4).

Characterisation of sec.-undecyl phenol

A mixture of *sec.*-Undecyl phenol has been obtained by the alkylation of phenol with undecan-1-ol. In the IR-spectrum of the product band at 750 cm $^{-1}$ indicates the

Table I. Alkylation of phenol with undecanol-1 in the presence of, *p*-toluenesulphonic acid catalyst.

	Reaction conditions					
Expt. No	Temp. ^{o}C	Molar ratio of phenol to undecanol-1	Amount of catalyst, %by wt. of phenol	Time of addition, h	Time of stirring, h	% yield of *sec.* – Undecyl phenol
1	100	8:1	10	2	2	62.7
2	160	10:1	10	2	2	72.3
3	160	10:1	5	2	2	45.9
4	160	10:1	15	2	2	74.5
5	160	5:1	15	2	2	30.0
6	160	8:1	15	2	2	67.5
7	140	10:1	15	2	2	37.0
8	160	10:1	15	2	1	70.8

presence of 1, 2- disubstituted aromatic ring and band at 830 cm^{-1} account for the 1, 4-disubstituted aromatic ring. The presence of –OH group is indicated by a broad absorption band at 3400-3,600 cm^{-1}. The presence of saturated cyclohexyl group (C-H stretch) and aromatic ring (C ...C) are indicated by the bands at 2850 - 3050 cm^{-1} and 1590 cm^{-1} respectively (Shaha et al. 2001).

^{1}H NMR-spectrum of *sec.*-undecylphenol shows multiplets at δ = 6.50-7.83 ppm for four protons of the aromatic ring. Signal for one proton on the –OH group is observed at δ =4.99-5.83 ppm. **δ** –Values for all the protons (-CH$_2$-) of the sec.-undecyl alkyl chain except one on the alpha-position relative to the aromatic ring and six protons from two methyl groups present at the end of the chain **δ** =1.1-2.2 ppm and **δ** = 0.73-1.1 ppm respectively. Furthermore peak at **δ** = 3.8-4.2 ppm represents the proton of the alpha position (-CH-) relative to the phenyl ring.

Alkylation by phenol with different long chain alkylating agent is available in literaures and this reaction is favorable to para-alkylation. We have not carried out HPLC experiment on the product.

The UV-spectrum of *sec*.-undecyl phenol in 0.001M methanol solution shows band at (λ_{max}=290.6nm) and sec.-*Undecyl* phenol had b.p. 330^{0}C, d_4^{20} 0.9063, n_D^{20} 1.485 (MRD, Found: 78.549, Calc.: 78.63).

*Characterisatation of **sec.**-dodecyl phenol*

The results of the alkylation of phenol with dodecan-1-ol in the presence of *p*-toluenesulphonic acid are presented in the Table II. The reaction gives only sec.-dodecyl phenol. The yield of the product increases with the increases of the molar ratio of phenol to dodecan-1-ol (Expt. no.1, 2 and 3), amount of catalyst (Expt. no.3, 4 and 8), temperature (Expt. no.3 and 5) and time of reaction (Expt. no.4 and 7). The best yield of *sec.*- dodecyl phenol is obtained, when the reaction is carried out under the following reaction conditions: temperature = 160°C, molar ratio of phenol to dodecan-1ol = 10:1, amount of catalyst 15% by wt. of phenol, time of addition = 2h and time of stirring = 2h (Expt, no. 4).

sec.-dodecyl phenol has been obtained by the alkylation of phenol with dodecan-1-ol. In the IR- spectrum of the product the presence of –OH group is indicated by absorption band at 3400 cm^{-1}. Band at 750 cm $^{-1}$ indicates the presence of 1, 2-disubstituted aromatic ring and band at 830 cm^{-1} accounts for the 1, 4-disubstituted aromatic ring. The bands at 1590 cm^{-1} and 2850-2905 cm^{-1} account for the aromatic ring (C ...C) stretch) and aliphatic C-H stretch respectively. (Shaha et al. 2001).

^{1}H NMR-spectrum of sec.-dodecylphenol shows signals at δ = 6.46-7.96 ppm for four protons on the aromatic ring. Signal for one proton on the –OH group is observed at δ = 5.30-5.96 ppm. δ –values for all the secondary protons (-CH$_2$-) of the *sec.*-dodecylalkyl chain except one on the alpha-position relative to the aromatic ring and six protons from two methyl groups present at the end of the chain δ = 3.76-4.40 ppm and δ = 3.8-4.2 ppm respectively. Furthermore peak at δ = 3.8-4.2 ppm represents the proton of the alpha position (-CH=) relative to the phenyl ring.

The UV-spectrum of *sec.*-dodecyl phenol in 0.001M methanol solution shows a band at λ_{max}=287.0 nm, *sec.*-dodecyl phenol had b.p. 339^{0}C, d_4^{20} 0.8991, n_D^{20} 1.482 (MRD, Found: 83.210, Calc.: 83.248).

Table II. Alkylation of phenol with dodecanol-1 in the presence of *P*-toluenesulphonic acid catalyst.

	Reaction conditions					
Expt. No	Temp. ^{o}C	Molar ratio of phenol to dodecanol-1	Amount of catalyst, %by wt. of phenol	Time of addition, h	Time of stirring, h	% yield of *sec.* – Dodecyl phenol
1	160	5:1	10	2	2	35.9
2	160	8:1	10	2	2	65.3
3	160	10:1	10	2	2	75.5
4	160	10:1	15	2	2	84.6
5	140	10:1	10	2	2	37.3
6	160	10:1	5	2	2	50.7
7	160	10:1	15	2	1	76.7

Conclusion

A mixture of *sec*. alkylated phenols in both *sec.*-Undecyl and *sec.*-Dodecylphenols have been synthesized in high yield by the alkylation of phenol with undecan-1-ol and dodecan-1-ol respectively in the presence of p-toluenesulphonic acid as catalyst. Monoalkylphenonls with an alkyl group of 5-8 carbon atoms are strong bactericides with longer alkylgroup upto 8-12 carbon atoms are valuable intermediates in the synthesis of nonionic surfactantants. The products can also be used as antioxidants. The reactivity of alcohols in the reactions depends on their ability to form length & degree of branching of the carbon chain. Among these alcohols dodecanol-1 was found to be most reactive.

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