

Short Communication

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PREPARATION OF SOME LONG CHAIN ALKYL NAPHTHYL ETHERS

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INTRODUCTION

Most of the methods for the preparation of alkyl naphthyl ethers reported in the literature require rather drastic conditions and involve relatively difficult procedures [1-4]. Recently, a relatively simple and convenient method of preparing alkyl-2-naphthyl ethers by acid catalyzed etherification of 2-naphthol has been reported [5]. This method was only applied for the preparation of relatively short chain alkyl-2-naphthyl ethers. The general applicability of the acid catalyzed etherification of naphthols remained to be established. A comparison of the reaction conditions and procedure for the preparation of alkyl-2-naphthyl ethers by this method with those of the previously reported methods tempted us to apply this method for the preparation of some longer-chain alkyl group containing 2-naphthyl as well as 1-naphthyl ethers. For this purpose acid catalyzed etherification of 1- and 2-naphthol with 1-decanol, 1-dodecanol and 1-octadecanol was attempted. As a result of these attempts, six long-chain alkyl naphthyl ethers, i.e. decyl-2-naphthyl ether, dodecyl-2-naphthyl ether, octadecyl-2-naphthyl ether, decyl-1-

naphthyl ether, dodecyl-1-naphthyl ether and octadecyl-1-naphthyl ether, were successfully prepared. The purity of each of the isolated ether was established by the use of thin layer chromatography technique; in three different solvent systems, *n*-hexane itself, ethyl acetate itself and petroleum ether (40-60°): ethyl acetate (4:1), on a silica plate, each prepared ether showed a single spot. Except for decyl-1-naphthyl ether which is a liquid, all the prepared ethers are relatively low-melting solids. The melting points observed for the five solid ethers and the boiling point of the liquid ether along with their %yields are summarized in Table 1.

The ethers obtained were identified and characterized on the basis of element analysis (Table 1), NMR spectral data (Table 1) and the characteristic strong C-O-C stretching absorption peaks [6] at 1250-1260 and 1035-1040 cm^{-1} in the IR spectrum (KBr) of each ether. In general, the etherification reaction was found to be slower and more difficult with 1-naphthol than with 2-naphthol. Furthermore, from the present studies, it appears that the acid catalyzed etherification reaction of 2-naphthol is relatively more facile with longer-chain aliphatic alcohols, e.g. the

Table 1. Preparation and characterization of some alkyl naphthyl ethers.

Ether	Reflux time(h)	M.P. obs. (c°)	%Yield	NMR data (CCl ₄)	Element analysis	
					%C	%H
Decyl-2-naphthyl	3	31-32	74	7.00-8.00(7H,m), 4.10 (2H, t) 1.40-2.30(16H,m), 1.20 (3H, t)	Found 84.40 Calcd. 84.51	9.95 9.86
Dodecyl-2-naphthyl	3	42-43	85	7.00-8.00(7H,m), 4.10 (2H, t) 1.35-2.35(20H,m), 1.20 (3H, t)	Found 84.44 Calcd. 84.62	10.35 10.26
Octadecyl-2-naphthyl	3	56-57	90	7.00-8.00(7H,m), 4.15 (2H, t) 1.35-2.45(32H,m), 1.20 (3H, t)	Found 84.98 Calcd. 84.85	11.00 11.11
Decyl-1-naphthyl	8	160-162/15mm*	62	7.10-8.10(7H,m), 4.20 (2H, t) 1.35-2.35(16H,m) 1.20 (3H, t)	Found 84.25 Calcd. 84.51	9.98 9.86
Dodecyl-1-naphthyl	8	30-31	68	7.10-8.10(7H,m), 4.20 (2H, t) 1.35-2.40(20H,m), 1.20 (3H, t)	Found 84.58 Calcd. 84.62	10.30 10.26
Octadecyl-1-naphthyl	8	43-45	82	7.15-8.15(7H,m), 4.25 (2H, t) 1.40-2.45 (32H,m) 1.20 (3H, t)	Found 84.67 Calcd. 84.85	11.20 11.11

reported reaction of methanol with 2-naphthol required seven hours of reflux of the reaction mixture to yield 65% of methyl-2-naphthyl ether, whereas in the present studies, decyl-2-naphthyl ether, dedecyl-2-naphthyl ether and octadecyl-2-naphthyl ether were obtained in much higher yields (74 - 90%) each requiring only 3 hr. reflux time.

The ether were prepared following the acid catalyzed etherification procedure of 2-naphthol [5] with slight modification. According to the modified procedure, a mixture of the required amount of naphthol (0.05 mole), the required alcohol (0.055 mole) and hydro-chloric acid (10 N, 15 ml) was heated under reflux, with continuous stirring for the desired period of time (Table 1). After the reflux period was over, the reaction mixture was cooled to room temperature (19-22^o) and neutralized with an aqueous sodium hydroxide solution (20%) till it was slightly basic to litmus. After this was achieved, 15 ml of aqueous sodium hydroxide solution (20%) was further added and the mixture was boiled vigorously for 15 min. to destroy any unreacted naphthol. The mixture was then cooled to room temperature and poured into about 400 ml of ice-cooled water. This resulted in the precipitation of a crude solid in each case, except in the case of decyl-1-naphthyl

ether. The crude ether was filtered and recrystallized from 50% aqueous ethanol. In the case of decyl-1-naphthyl ether, the alkaline aqueous mixture was extracted with diethyl ether (2 x 30 ml), solvent removed by evaporation and the residual liquid subjected to vacuum distillation to yield a liquid ether product, b. p. 160-162^o/15mm.

Key words: Alkyl-1-naphthyl ethers, Preparation of ethers.

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Alcohol	Yield (%)	Boiling Point (°C)
Methanol	65	35
Decyl alcohol	74	160-162
Dodecyl alcohol	85	175-178
Octadecyl alcohol	90	195-198

constant of butyric acid when compared to a weak propionic and butyric acids. Replacing the carboxylic hydrogen of butyric acid with a methyl group lowers the ionization constant by a factor of about ten. It appears that the methyl group as well as other alkyl groups is a slightly positive electron withdrawer than the hydrogen atom. This acid ionization constant is given in harmony with the thermodynamic data: ΔG° and ΔS° (Table 2). The values

Table 2. Thermodynamic parameters for the ionization of formic, acetic, propionic and butyric acids in aqueous solutions.

Acid	ΔG° (kJ/mol)	ΔS° (J/mol·K)
Formic acid	0.7883	4.39 ± 0.11
Acetic	1.2009	4.71 ± 0.16
Propionic	1.6498	4.87 ± 0.22
Butyric	2.1220	4.77 ± 0.26

is worthwhile that the standard state for acids is defined as the unit activity under similar conditions to show left and right comparisons. Hence, rather scattered and non-comparable measurements were carried out with conductivity meter model LHR, equipped with cell model L.A. 100. Temperature was maintained constant by circulating water in the cell compartment at temperature $\pm 0.01^\circ$. Measurements carried out at 25, 30, 40 and 50^o for formic, acetic, propionic and butyric acid solutions of concentration range from 5×10^{-3} to 2×10^{-2} mol/l.

All acids used in this study were analytical reagent grade and their solutions were made in distilled deionized water.

The ionization of a weak acid HA expressed as

$$H_2O + HA \rightleftharpoons H_3O^+ + A^- \quad (1)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad (2)$$

where C is the concentration (equivalent) and X is the degree of ionization. The classical ionization constant K_a is expressed in term of equation (2)

$$K_a = \frac{CX}{C(1-X)} = \frac{X}{1-X} \quad (3)$$

The magnitude of K_a gives an indication of the extent of the ionization of the acid strength (ionizing capacity).