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 streching 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 Calcd.	84.40 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 Calcd.	84.44 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 Calcd.	84.98 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 Calcd.	84.25 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 Calcd.	84.58 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, m)	Found Calcd.	84.67 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°) 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°/15mm.

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