

A NOBLE SYNTHESIS OF 1-ALKYL-2-NAPHTHOLS

Taketoshi KITO and Koki OTA

Department of Industrial Chemistry, Kyushu Institute of Technology,  
Tobata-ku, Kitakyushu-shi 804

It was found that the treatment of alkali 2-naphthoxide with alcohols easily afforded 1-alkyl-2-naphthols in good yields. The structures were determined by means of MS, NMR, and IR.

It is well-known that 1-alkyl-2-naphthols are useful as antibacterial substances and antioxidants. However, the syntheses of these compounds are generally performed in many steps and, as a result, the yields are low. For example, 1-alkyl-2-naphthols have been prepared by the acylation of 2-naphthol (the Friedel Crafts reaction) and the subsequent reduction of the carbonyl group<sup>1)</sup>; by the reaction of 1-benzylpyridium chloride and 2-naphthol<sup>2)</sup>; as a by-product of the Williamson ether synthesis of alkyl halide and sodium naphthoxide<sup>3)</sup>; by the dehydrogenation of 1-methyl-2-oxo-2,3,4,6,7,8-hexahydronaphthalene or of 1-propyl-2-hydroxy-5,8-dihydronaphthalene<sup>4)</sup>; by the hydrogenolysis of 2,2'-dihydroxy-1,1'-dinaphthylmethane<sup>5)</sup>; by the reaction of 2-naphthol with an excess of sodium methoxide in methanol<sup>6)</sup> or with formaldehyde and thiols ( $C_nH_{2n+1}SH$ ) in ethanol in the presence of triethylamine<sup>7)</sup>, etc. By those methods mentioned above, 1-methyl-, 1-ethyl-, 1-propyl-, 1-butyl-, 1-cyclohexyl-, 1-dodecyl-, 1-hexadecyl-, and 1-octadecyl-2-naphthols have been prepared.

The authors now found a noble method to synthesize 1-alkyl-2-naphthols by the one-step reaction of alkali naphthoxide and alcohol in the absence of catalyst in good yields.

A typical example is as follows. Potassium naphthoxide (10 g) and 1-pentanol (50 ml) were placed in a 300 ml autoclave with an electro-magnetic stirrer. After the air had been replaced by  $N_2$ , the autoclave was heated at 270°C for 5 hr. The inner pressure reached to 20 kg/cm<sup>2</sup>. The autoclave was cooled, and the reaction mixture was washed with 2 % aq. sodium hydroxide. Vacuum distillation of the mixture gave 1-pentyl-2-naphthol in a 68 % yield (mp 81.6°C, from  $C_6H_{12}$ . Found: C, 84.43 %; H, 8.44 %. Calcd for  $C_{15}H_{18}O$ : C, 84.07 %; H, 8.47 %).

When other alcohols were used, the corresponding 1-alkyl-2-naphthols were obtained. The results are listed in Table. No product was obtained when potassium naphthoxide was heated with 1-pentanol at 200°C for 5 hr. However, the best yield was obtained when heated at 270°C for 5 hr. Cornforth *et al.* reported that the reaction of 2-naphthol with excess sodium methoxide in methanol gave 1-methyl-2-naphthol in 16 % yield (200°C for 11 hr)<sup>6)</sup>. In the present reaction, however, alkylation did not occur in both methanol and ethanol. In consequence, aliphatic alcohols comprising the carbon atoms more than 3, cyclohexanol, and benzyl alcohol were effective.

Table Syntheses of 1-alkyl-2-naphthols

Alcohols	Alkyl group	Yield (mol%)
Ethanol	$\text{CH}_3\text{CH}_2$	0
1-Propanol	$\text{CH}_3(\text{CH}_2)_2$	2 5
1-Butanol	$\text{CH}_3(\text{CH}_2)_3$	7 7
1-Pentanol	$\text{CH}_3(\text{CH}_2)_4$	6 8
1-Hexanol	$\text{CH}_3(\text{CH}_2)_5$	7 3
1-Dodecanol	$\text{CH}_3(\text{CH}_2)_{11}$	6 0
Benzyl alcohol	$\text{C}_6\text{H}_5\text{CH}_2$	5 5

Reaction conditions : Temp., 270°C; Time, 5 hr.

the alkyl group does not isomerize in this reaction. A singlet peak appeared at  $\delta$  7.16 in the spectrum of 2-naphthol (the proton at the  $\alpha$ -position in acetone) disappeared thoroughly in the spectrum of 1-pentyl-2-naphthol. This fact indicates that pentyl group attaches to the  $\alpha$ -position adjacent to the hydroxyl group. The IR absorptions at  $806\text{ cm}^{-1}$  and  $742\text{ cm}^{-1}$  also support the presence of the 1,2-disubstituents. The structures of other products were also confirmed by the same method.

The structures of those products were determined by means of MS, NMR, and IR. As an example, the confirmation of 1-pentyl-2-naphthol will be mentioned here.

The molecular formula ( $\text{C}_{15}\text{H}_{18}\text{O}$ ) was obtained by the high resolution mass spectroscopy. The presence of two triplet peaks (2H protons at  $\delta$  2.92 and 3H protons at  $\delta$  0.87) suggested strongly that pentyl group attaches to the naphthalene nucleus; that is,

#### References

- 1) N. P. Buu-Hoi, D. Lavit, and J. Collard, *J. Org. Chem.*, **23**, 542 (1958); R. D. Desai and W. S. Waravdeker, *Chem. Abstr.*, **40**, 6456<sup>h</sup> (1946); C. R. Noller and R. Adams, *J. Amer. Chem. Soc.*, **46**, 1889 (1924).
- 2) V. N. Setkina and D. N. Kursanov, *Chem. Abstr.*, **46**, 458i (1952).
- 3) E. Wenkert, R. D. Youssefyeh, and R. G. Lewis, *J. Amer. Chem. Soc.*, **82**, 4675 (1960); V. A. Zagorevskii, *Chem. Abstr.*, **52**, 14572d (1958).
- 4) J. Szmuszkowicz and H. Born, *J. Amer. Chem. Soc.*, **75**, 3350 (1953); K. Takeda and H. Osaka, *J. Pharm. Soc. Japan*, **75**, 210 (1955).
- 5) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, **1949**, 626.
- 6) J. W. Cornforth, R. H. Cornforth, and R. Robinson, *J. Chem. Soc.*, **1942**, 682.
- 7) F. Poppelsdorf and S. J. Holt, *J. Chem. Soc.*, **1954**, 1124.

(Received July 30, 1975)