Reactions of 2-Naphthol with *N*-Piperidinomethyl and *N*-Morpholinomethyl Alkyl Ethers

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ONE PHASE of our study of the Mannich reaction (2) involves the reactivity of α-amino ethers as intermediates. These compounds are known to form readily under the conditions of the Mannich reaction (6, 8).

In this article we report several α-amino ethers of piperidine and morpholine prepared by the method of McLeod and Robinson (6). These compounds reacted with 2-naphthol to yield 1-piperidinomethyl-2-hydroxynaphthalene (8) and 1-morpholinomethyl-2-hydroxynaphthalene (5). Table I shows the properties of these aminoethers and analyses of those which are new. The fact that the two propargyl derivatives are not Mannich bases of formula $R_2NCH_2C \equiv CCH_2OH$ was confirmed by the infrared spectra which showed strong bands near 3300 cm.$^{-1}$ characteristic of the $\equiv CH$ group. NoOH band was observed.

All Mannich reactions were run in duplicate by allowing equimolar quantities (0.01 mole) of amino ether and 2-naphthol in 10 ml. of 1,4-dioxane to stand at room temperature for 72 hours. The product was precipitated with water and identified by melting point. For comparison, reactions were also run using the methylene bisamines in place of the amino ethers, and the secondary amine and formaldehyde in place of the α-aminoethers. In all cases yields were essentially quantitative. The basicities of the amines (Table I) did not seem to be important. Another series of runs employing the same conditions but 0.1*M* proportion of H_2SO_4 as catalyst also gave essentially quantitative yields.

It is assumed that the relative ease of rupture of the C—N and C—O bonds in the ethers will be related to the polar effect of the alkoxy group. Thus in the compound R_2NCH_2OX, where X is hydrogen or the alkoxy groups shown in Table I, the electron releasing effect of X = H lies between that of X = ethyl and X = propargyl (1). The C—O bond strength in R_2NCH_2OH should therefore be intermediate between that of R_2NCH_2OEt and $R_2NCH_2OCH_2C=CH$.

Reactions employing as intermediates the condensation products of the reaction of 2-naphthol with formaldehyde were carried out to study the role of these compounds as intermediates. Both the 1-hydroxymethyl-2-naphthol (7) and the methylene bis-2-naphthol (4) were reacted with piperidine and with morpholine in dioxane solution under conditions identical to those employed above. In each case the major material recovered was the original naphthol-formaldehyde intermediates identified by melting point and mixed melting point.

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Table I. Physical Properties of α-Amino Ethers

Amino Ether	d_{25}^{25}	n_d^{25}	pK_a^a	B.P. °C.	Mm. of Hg	Analysis, % C Calcd.	C Found	H Calcd.	H Found
$C_5H_{10}NCH_2OEt$			9.63	52-8	1[b]				
$C_5H_{10}NCH_2OC_2H_4OCH_3$	0.9539	1.4514	9.75	76-7	16	62.32	62.33	11.06	11.13
$C_5H_{10}NCH_2OCH_2CH=CH_2$	0.9150	1.4567	9.60	79-80	11	69.55	68.92	11.04	11.08
$C_5H_{10}NCH_2OCH_2C\equiv CH$	0.9899	1.4723	9.50	82.5-83	12	70.46	70.48	9.87	9.91
$OC_4H_8NCH_2OEt$			7.38	55-6	1[c]				
$OC_4H_8NCH_2OC_2H_4OCH_3$	1.0415	1.4501	7.43	111-3	36	54.84	54.94	9.77	9.85
$OC_4H_8NCH_2OCH_2CH=CH_2$			7.29	80	8[d]				
$OC_4H_8NCH_2OCH_2C\equiv CH$	1.0476	1.4698	6.95	65-8	1	61.91	60.65	8.44	8.68

[a] Determined from the half-neutralization point of the titration curve (3). [b] 176-178°/760 mm. (8); [c] 58-63°/6 mm. (6); [d] 82-83°/7 mm. (6). [e] 9.03% N(calcd.), 9.47%(found).