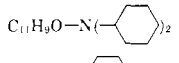
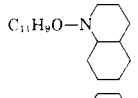
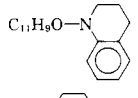
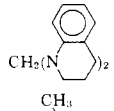
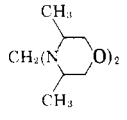
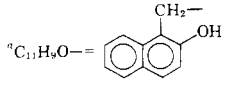
Synthesis of Methanediamines and Mannich Bases of 2-Naphthol

J. E. FERNANDEZ and JEANNE M. CALDERAZZO
University of South Florida, Tampa, Fla.

THE SYNTHESIS of several new compounds prepared in the course of work on the mechanism of the Mannich reaction (*2*) is reported. The Mannich bases of 2-naphthol were prepared by reacting 0.01 molar quantities of 2-naphthol, formalin, and the secondary amine in 10 ml. of dioxane for 24 hours at room temperature. The product was precipitated by adding water and recrystallized from ethanol. The methanediamines were prepared by mixing the secondary amine with formalin, warming for 1 hour, and salting out the organic layer with K_2CO_3. The organic layer was dried over $CaSO_4$ and distilled under reduced pressure. The Mannich bases and methanediamines are shown in Table I.

Attempts to prepare Mannich bases of 2-naphthol and 2,6-dimethylpiperidine, 3,5-dimethylmorpholine, and diisopropylamine resulted in impure products which, during purification, reacted to form 1,1′-methylenedi(2-naphthol). Similarly, attempts to prepare methanediamines of 2,6-dimethylpiperidine, diisopropylamine, dicyclohexylamine, and decahydroquinoline yielded impure compounds which, on the basis of elemental analyses and infrared spectra, are believed to be contaminated with the *N*-hydroxymethylamines with which they are in equilibrium (*1*). These mixtures could not be separated by distillation or chromatography.

Table I. Mannich Bases and Methanediamines

Compound[a]	Yield, %	M.P., °C.	B.P., °C.	Analysis, % C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
	25	111.5–2.5		81.9	81.9	9.25	9.03	4.15	3.88
	61	133.5		81.3	81.7	8.53	8.70	4.74	4.62
	17	206.5		83.0	83.7	6.62	6.19		
	91	60–61.5		82.0	81.6	7.97	7.86		
	26		126–7 @2.2 mm.	64.4	63.6	10.8	10.9	11.6	11.9
									

LITERATURE CITED

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(2) Fernandez, J.E., Powell, C., Fowler, J.S., J. CHEM. ENG. DATA 8, 600 (1963).

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