

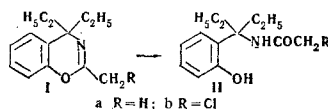
OPENING OF THE BENZOXAZINE RING IN 2-SUBSTITUTED 4,4-DIETHYL-4H-1,3-BENZOXAZINES

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We have previously shown [1] that the alkaline hydrolysis of benzoxazines leads to the formation in low yield of amides of type II, while acid hydrolysis is accompanied by far-reaching decomposition of the benzoxazine molecule. In contrast to this, the hydrolytic opening of the benzoxazine ring in compounds of type I takes place readily in the presence of salts of bivalent copper (for example, the acetate or nitrate) in ethanol or acetic acid containing water.



In the absence of copper salts, hydrolysis does not take place under the conditions studied. The structure of II was confirmed by IR spectroscopy. Thus, the spectrum of IIa has the following bands (cm^{-1}): 3360 (bound OH and NH groups), 1650 (amide I), 1540 (amide II).

N-Acetyl- α, α -diethyl-o-hydroxybenzylamine (IIa). A solution of 4 g (0.02 mole) of Ia [1] in 10 ml of 70% CH_3COOH was added to a solution of 3.9 g (0.02 mole) of $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$ in 10 ml of 70% CH_3COOH . The reaction mixture was stirred for 2 hr and poured into 50 ml of water, and the mixture was made alkaline with sodium carbonate and extracted with ether. The ether was evaporated off and the residue was triturated with petroleum ether. The yield of IIa was 1.75 g (40.7%), mp 131-132° C (from benzene and petroleum ether). The substance gave no depression of the melting point in admixture with the sample obtained previously [1] and the IR spectra of the two substances were identical. The petroleum ether solution yielded 1.5 g (37.5%) of the initial Ia, bp 85-88° C (3 mm), n_D^{20} 1.5160.

N-Chloroacetyl- α, α -diethyl-o-hydroxybenzylamine (IIb). A solution of 4.9 g (0.02 mole) of Ib in 20 ml of ethanol was added to a solution of 3.9 g (0.02 mole) of $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$ and 1.6 g (0.01 mole) of sodium acetate in 50 ml of 70% ethanol, and the mixture was treated as described above to give 2.6 g (50%) of IIb, mp 119-120° C (from benzene and petroleum ether). Found, %: C 60.73; H 7.06; N 5.52; Cl 13.79. Calculated for $\text{C}_{13}\text{H}_{18}\text{NO}_2\text{Cl}$, %: C 61.05; H 7.09; N 5.47; Cl 13.86. The amount of the initial Ib recovered was 1.3 g (26.5%), bp 106-107° C (1 mm), n_D^{20} 1.5320.

REFERENCE

1. V. A. Zagorevskii, K. I. Lopatina, S. M. Klyuev, and B. V. Lopatin, ZhOrKh, 4, 119, 1968.

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