# THE REACTION OF MONOETHANOLAMINE WITH CYANOGEN BROMIDE

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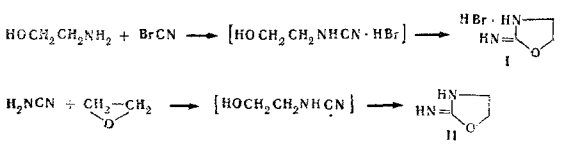
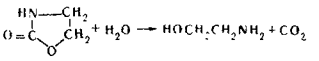
The reaction of monoethanolamine with cyanogen bromide has been studied. 2-Imino-1,3-oxazolidine has been obtained and its structure has been proved. It has been confirmed that the reaction of cyanamide or calcium cyanamide with organic oxides and their chlorohydrins forms, in the first stage, hydroxyalkyl derivatives of cyanamide which cyclize with the formation of the corresponding 2-iminooxazolidine derivatives. 2-Aminooxazone derivatives are obtained by the tautomerization of the 2-iminooxazolidine derivatives.

In the last decade and a half, oxazolidine and oxazoline derivatives have been widely used to obtain plastics, primary [2] and secondary [3] simple and mixed [4] amino alcohols, and dihydroxydiamines [5]. The most important method of obtaining oxazolidine and oxazoline derivatives is their synthesis from cyanamide and its substituted derivatives. However, the literature contains extremely contradictory information on the structure of the compounds so obtained. It is stated that these compounds are hydroxyalkyl derivatives of cyanamide [6, 7]. According to other results, they have a cyclic structure and are derivatives of oxazolidine [8-10] or oxazolidine or an unresolvable mixture of these tautomeric forms [11-13].

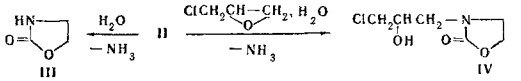
In continuation of investigations carried out earlier on the structure of oxazolidine and oxazoline derivatives [10] and also of the mechanism of their formation by the reaction of alkylene oxides and their chlorohydrins with cyanamide and calcium cyanamide, we have studied the reaction of monoethanolamine with cyanogen bromide. The reaction leads to 2-imino-1,3-oxazolidine hydrobromide (I), which, after treatment with an equivalent amount of freshly calcined calcium oxide in anhydrous methanol, gives 2-imino-1,3-oxazolidine (II) in the free state. The formation of β-hydroxyethylcyanamide by the reaction of the substances mentioned is possible. However, it is impossible to isolate it from the reaction mixture even under mild conditions. β-Hydroxyethylcyanamide is obviously very unstable and even at room temperature it cyclizes with the formation of **I**. It is probable that the synthesis of **II** from ethylene oxide and calcium cyanamide also takes place through the stage of the formation of β-hydroxyethylcyanamide.



On being heated above 100° C, **II** partially decomposes with the liberation of ammonia. In contrast to 5-alkyl- and 5-aryl-2-imino-substituted oxazolidines, **II** is very unstable to the action of water and on prolonged heating it hydrolyzes with the formation of oxazolid-2-one (**III**). Compound **III** is readily decomposed by a 3% solution of alkali with the formation of monoethanolamine and carbon dioxide, isolated in the form of barium carbonate:



The formation of **III** confirms the structure of **II**, since **III** can be obtained only by the incomplete hydrolysis of **II**; its formation from 2-aminooxazoline is impossible. The structure of **II** is shown no less convincingly by its reaction with epichlorohydrin in an aqueous medium. Under these conditions, as in the case of the reaction of **III** with epichlorohydrin [16], 3-(γ-chloro-β-hydroxypropyl)oxazolid-2-one (**IV**) is obtained:



Its structure was shown by alkaline cleavage, which gave β-hydroxyethyl(γ-chloro-β-hydroxypropyl)amine (**V**).

The results of the investigations performed show that the reaction of cyanamide [8] and calcium cyanamide [9] with alkylene oxides and their chlorohydrins [14] leads to the formation of **II** or 5-alkyl- or 5-aryl-2-imino-substituted oxazolidines. Aminooxazoline and its 5-alkyl- and 5-aryl-substituted derivatives [12] are probably obtained as a result of the tautomerization of **II**.

## EXPERIMENTAL

**2-Imino-1,3-oxazolidine hydrobromide (I).** A solution of 116.6 g (1.1 mole) of cyanogen bromide in 400 ml of ether was added over 1-1.5 hr with continuous stirring to 61 g (1 mole) of monoethanolamine cooled to 2-5° C. The reaction mixture was stirred at 30-32° C, the ether was distilled off, and compound I was obtained in the form of a viscous brown liquid. $n_D^{20}$ 1.5575; $d_4^{20}$ 1.5630. Found, %: N 16.01; $MR_D$ 32.10. Calculated for $C_3H_6N_2O \cdot HBr$, %: N 16.06; $MR_D$ 32.08; mol. wt. 168.01. The alkaline cleavage of 1.2634 g of I yielded 0.125 g of $NH_3$ and 1.443 g of $BaCO_3$. Calculated: $NH_3$ 0.128 g. $BaCO_3$ 1.479 g. Calculated: $NH_3$ 0.106 g; $BaCO_3$ 1.180 g.

**2-Imino-1,3-oxazolidine (II).** With stirring, a saturated solution of 56 g (1 mole) of calcined caustic potash in anhydrous methanol was added in small portions to 167.1 g (1 mole) of I, and the potassium bromide that deposited was filtered off. The methanol was distilled off from the filtrate (finally under vacuum), and II was obtained in the form of a viscous oil. Yield almost quantitative. $n_D^{20}$ 1.5436; $d_4^{20}$ 1.3639. Found, %: N 32.21; $MR_D$ 19.75; g-eq 85.87 (determined by nonaqueous titration [15]). Calculated for $C_3H_6N_2O$, %: N 32.56; $MR_D$ 20.13; g-eq 86.10. On alkaline cleavage, 1.149 g of II gave: $NH_3$ 0.211 g; $BaCO_3$ 2.343 g. Calculated: $NH_3$ 0.225 g; $BaCO_3$ 2.629 g. The hydrolysis of 1.245 g of II yielded: $NH_3$ 0.239 g; $BaCO_3$ 2.539 g. Calculated: $NH_3$ 0.243 g; $BaCO_3$ 2.848 g.

**Hydrolysis of II in a neutral medium.** A solution of 20 g (0.23) mole) of II in 50 ml of water was heated to the boil over 3 hr. Then

the water was distilled off from the solution (finally under vacuum), giving III in the form of a light brown viscous mass. Bp 156° C (0.005 mm); $n_D^{20}$ 1.5060; $d_4^{20}$ 1.3230. Found, %: N 16.60; $MR_D$ 19.55; g-eq 86.31. Calculated for $C_3H_5NO_2$, %: N 16.09; $MR_D$ 19.11; mol. wt. 87.08. On alkaline cleavage, 1.3043 g of III gave: $BaCO_3$ 2.79 g. Calculated: $BaCO_3$ 2.94 g. The hydrolysis of 0.89 g of III gave: $BaCO_3$ 1.97 g. Calculated: $BaCO_3$ 2.015 g.

**Cleavage of III in an alkaline medium.** A solution of 21.75 g (0.25 mole) of III in 150 ml of water and a solution of 34 g (0.6 mole) of potassium hydroxide in 450 ml of water were mixed and heated at 90–100° C for 4 hr, after which the water was distilled off. The resulting product was treated with 23.2 ml of sulfuric acid (d 1.835) and extracted with methanol to give ethanolamine. Bp 75–79° C (10 mm); $n_D^{20}$ 1.4538 (according to a handbook: $n_D^{20}$ 1.4539).

**Reaction of II with epichlorohydrin.** A mixture of 43 g (0.5 mole) of II, 95 ml of water, and 51 ml (0.55 mole) of epichlorohydrin was heated at 98–100° C for 4 hr, after which the water was distilled off and IV [16] was obtained in quantitative yield. The alkaline hydrolysis of IV gave an almost quantitative yield of V [16].

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