6. No ethyl chloride could be obtained by the action of diethyl sulfate or carbonate on aluminum chloride in ligroin.

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Syntheses from Ethanolamine. III. Synthesis of N-β-Chloroethyl Urethan and of β-Chloroethyl Isocyanate

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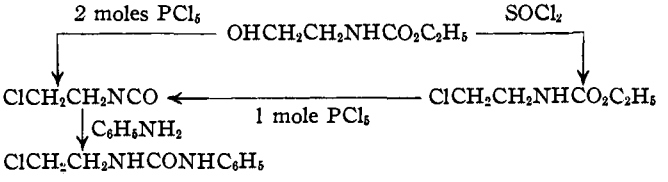
In extending a study of syntheses from enthanolamine, it has been found that N-β-oxyethyl urethan reacts with thionyl chloride to form N-β-chloroethyl urethan. Under the influence of phosphorus pentachloride, the latter compound yields β-chloroethyl isocyanate, which can also be prepared directly from the oxyurethan by using 2 moles of phosphorus pentachloride. The constitution of the isocyanate was confirmed by the preparation of the respective α-aryl-β-(β-chloroethyl) ureas from aniline and from *p*-phenetidine. The reactions involved are expressed by the formulas



Both compounds have not been described hitherto; their use for further syntheses is now being investigated.

Experimental

N-β-Chloroethyl Urethan.—One hundred and forty-three grams of thionyl chloride is added gradually to 133 g. of N-β-oxyethyl urethan. The reaction is finished by short heating on the water-bath and the product distilled *in vacuo*. With the exception of a small residue, all distilled from 128–130° at 13 mm. The yield was 138 g. or 91%.

Anal. Calcd. for $C_5H_{10}O_2NCl$: N, 9.3; Cl, 23.4. Found: N, 9.1; Cl, 23.2.

N-β-Chloroethyl urethan is a colorless, fairly mobile liquid possessing a slightly pungent odor. It dissolves readily in ethanol and ether, but not in water.

β-Chloroethyl Isocyanate.—Preparation from N-β-oxyethyl urethan: 133 g. of the urethan is dropped, under external cooling, on 420 g. of phosphorus pentachloride contained in a 2-liter flask. About one-half of the pentachloride remains undissolved, but heating on the water-bath soon produces a clear homogeneous solution. The product is then distilled very slowly, using an efficient fractionating column. Even so, there is a considerable intermediate fraction, until finally the pure isocyanate distils at 135°. The yield was 52 g. or 49%.

Anal. Calcd. for C_3H_4ONCl: N, 13.3; Cl, 33.6. Found: N, 13.0; Cl, 33.4.

The preparation from N-β-chloroethyl urethan is identical, except that for one mole of the urethan, or 151 g., one mole of pentachloride or 210 g. is used. The yield is the same as above.

β-Chloroethyl isocyanate is a colorless, mobile liquid, heavier than water and rapidly decomposed by it under evolution of carbon dioxide. The resulting solution is clear with silver nitrate, but on standing becomes cloudy. The isocyanate has an unpleasant odor and its vapor is very irritating on the eyes.

Ten and one-half grams of isocyanate was added to 9.3 g. of aniline dissolved in 50 ml. of ether. The solution boiled up spontaneously and a sludge of white crystals was formed. Crystallized from dilute ethanol, the product melted at 124°; the literature[1] gives 124° for α-phenyl-β-(β-chloroethyl) urea.

The isocyanate reacts similarly with *p*-phenetidine; the urea melts at 149°. It forms fine white crystals of silky luster.

Anal. Calcd. for $C_{11}H_{15}O_2N_2Cl$: N, 11.5; Cl, 17.9. Found: N, 11.2; Cl, 17.9.

Phosphorus pentoxide, which has been used successfully[2] for the preparation of phenyl isocyanate from phenyl urethan instead of the pentachloride,[3] was found to be unsuitable for the purpose of converting N-β-chloroethyl urethan into the isocyanate; upon heating decomposition with evolution of hydrogen chloride occurred.

Summary

N-β-Oxyethyl urethan reacts with thionyl chloride to form N-β-chloroethyl urethan; both urethans, the former with 2 moles, the latter with 1 mole of phosphorus pentachloride, yield β-chloroethyl isocyanate.

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(1) Gabriel and Stelzner, *Ber.*, **28**, 2937 (1895).
(2) Hofmann, *ibid.*, **3**, 655 (1870).
(3) Lengfeld and Stieglitz, *Am. Chem. J.*, **16**, 71 (1894).