NEW NITROGEN-CONTAINING α-OXIDES

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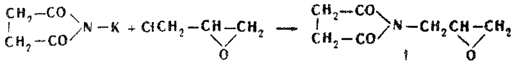
N-(2,3-Epoxypropyl)-α-pyrrolidone and N-(2,3-epoxypropyl)-α-succinimide have been obtained for the first time. It has been shown that N-(2,3-epoxypropyl)-α-pyrrolidone readily reacts with ammonia and diethylamine to form the corresponding amino alcohols.

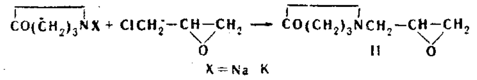
In the present work we studied the preparation of α-oxides containing a lactam ring or a succinimide grouping. α-Oxides with lactam rings have not been described in the literature. With the object of synthesizing N-epoxy amides and N-epoxy imides we investigated two reactions: the oxidation of vinyl and allyl derivatives of amides and imides and the reaction of epichlorohydrin with alkali-metal salts of amides and imides. When vinyl derivatives of cyclic amides, namely N-vinylpyrrolidone, N-vinylpiperidone, and N-vinylcaprolactam, were oxidized (under the conditions described in a patent [1]), we were unable to obtain α-oxides. Only the products of their further transformation, 1,4-dioxanes, were obtained [2]. Under the same conditions N-vinylphthalimide and N-vinylsuccinimide did not undergo oxidation. Hydrolysis yielded phthalimide and succinimide.

The oxidation of N-allylpyrrolidone and N-allylcaprolactam with 89% peracetic acid at temperatures of from −10° to +60° C and times of 3 hr–30 days did not give α-oxides either. The starting materials were recovered. Since the oxidation of unsaturated compounds under the conditions given did not lead to the synthesis of epoxy derivatives, we undertook a study of the reaction of alkali-metal salts of lactams and imides with epichlorohydrin.

It is known that when potassium phthalimide is heated with epichlorohydrin at 115–116° C, epoxypropylphthalimide is formed [3]. Under the same conditions, from potassium succinimide and epichlorohydrin we obtained epoxypropylsuccinimide (I). The isolation of the epoxypropylsuccinimide from the reaction mixture presented great difficulty. The epoxypropylsuccinimide was isolated in the pure state by chromatography on a column of alumina (elution with acetone).

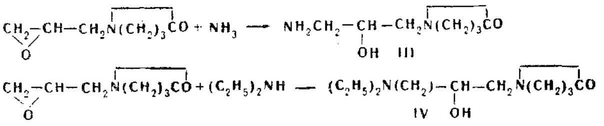


We were unable to obtain epoxypropylpyrrolidone under the conditions described by Weizmann and Malkowa [3]. In this case, low-molecular-weight polymers of epoxypropylpyrrolidone (trimers and tetramers) were formed. The IR spectrum of the polymers obtained had a band at 1100 cm^{-1} which is characteristic for the ether group and a band at 850 cm^{-1} corresponding to an epoxide group. Epoxypropylpyrrolidone (II) could be obtained only under milder conditions at temperatures from 40 to 80° C in solution in diethyl ether, methylene chloride, or benzene.



The reaction of epichlorohydrin with potassium pyrrolidone was carried out at a lower temperature (40° C) than that with sodium pyrrolidone (80° C). Heating the reaction mixtures at the temperatures given led to polymerization and resin formation with both the sodium and the potassium derivative of pyrrolidone. Under the conditions given, it was impossible to effect the synthesis of epoxy lactams with larger rings (piperidone and caprolactam). The basicity of the initial nitrogen-containing heterocycle is apparently of fundamental importance for this reaction.

The presence of an epoxy group is responsible for the high reactivity of epoxypropylpyrrolidone. Thus, even at room temperature it adds ammonia and amines with the formation [4, 5] of the corresponding amino alcohols III and IV.



EXPERIMENTAL

N-(2,3-Epoxypropyl)succinimide (I). A mixture of 6.8 g (0.05 mole) of potassium succinimide and 13.8 g (1.5 mole) of epichlorohydrin was boiled for 1 hr. The potassium chloride was filtered off and the epichlorohydrin was driven off in a vacuum at 15 mm. Chromatography on a plate showed that the reaction mixture consisted of succinimide and epoxypropylsuccinimide. Product I was isolated on a chromatographic column 1.2 m × 2.5 cm filled with alumina of activity grade II. This gave 2.66 g of I (yield 35%), mp 52° C, readily soluble in many organic solvents. Found, %: C 54.58; H 5.81; N 9.22; content of epoxy groups 23.11%; mol. wt. 154 (in benzene). Calculated for $C_7H_9NO_3$, %: C 54.14; H 5.80; N 9.03; content of epoxy groups 27.74%; mol. wt. 155.

Oxidation of N-vinylphthalimide and N-vinylsuccinimide. The initial N-vinylphthalimide and N-vinylsuccinimide were obtained by the method of Nikolaev and Ushakov [6]. In drops, a solution of 5.5 g (0.055 mole) of 85% peracetic acid in 20 ml of methylene chloride was added to a solution of 8.6 g (0.05 mole) of N-vinylphthalimide in 40 ml of methylene chloride at −20° C. The reaction mixture was kept at −5 to −10° C for 3 hr and then at 18–22° C for two weeks. After the elimination of methylene chloride and repeated washing with diethyl ether, the reaction mixture gave phthalimide (yield 90%), mp 238° C.

Under analogous conditions, in the oxidation of N-vinylsuccinimide with peracetic acid succinimide was obtained (yield 90%, mp 125° C).

N-(2,3-Epoxypropyl)-α-pyrrolidone (II). a) At 20° C, 27.6 g (0.3 mole) of epichlorohydrin was added to 12.4 g (0.1 mole) of potassium pyrrolidone in 60 ml of absolute diethyl ether, and the mixture was heated to the boil for 3 hr. Then the potassium chloride was filtered off, the ether and epichlorohydrin were eliminated from the filtrate in vacuum, and the residue was distilled at 112.5–113° C (3 mm). This gave 9.6 g of II (yield 68%). When the reaction was carried out in methylene chloride, the yield was 56%. The constants were determined: d_4^{20} 1.1362; n_D^{20} 1.4877. Found, %: C 59.20; H 7.86; N 10.08; content of epoxy groups [5] 28.64%; mol. wt. (in benzene) 142; MR_D 35.71. Calculated for $C_7H_{11}NO_2$, %: C 59.63; H 7.85; N 9.95; content of epoxy groups 30.31; mol. wt. 141; MR_D 35.85. Readily soluble in water and many organic solvents. Insoluble in hydrocarbons.

b) At 20° C, 27.6 g (0.3 mole) of epichlorohydrin was added to 10.7 g (0.1 mole) of sodium pyrrolidone in 50 ml of absolute benzene. The mixture was heated to the boil for 5 hr, the potassium chloride was filtered off, the benzene and epichlorohydrin were eliminated from the filtrate in vacuum, and the residue was distilled at 112.5–113° C (3 mm). Yield 55%.

Reaction of N-(2,3-epoxypropyl)-α-pyrrolidone with ammonia. With stirring, 3.5 g (0.025 mole) of **II** was added at 18–20° C to 35 ml of an 18% aqueous ammonia solution. The temperature rose to 30° C. The reaction mixture was kept at 18–20° C for 70 hr, and then the water and ammonia were eliminated in vacuum to give N-(γ-amino-β-hydroxypropyl)pyrrolidone (**III**) in the form of a colorless mass. The IR spectrum had a band at 3200 cm^{-1} and lacked the band at 850 cm^{-1} that is characteristic for an epoxy group. Found, %: N 17.01; mol. wt. 154 (in dioxane). Calculated for $C_7H_{14}N_2O_2$, %: N 17.70; mol. wt. 158. Picrate of the amino alcohol **III**, mp 175° C. Found, %: N 16.75. Calculated for $C_7H_{14}N_2O_2 \cdot C_6H_3(NO_2)_3OH$, %: N 17.09.

Reaction of N-(2,3-epoxypropyl)-α-pyrrolidone with diethylamine. A mixture of 3 g (0.025 mole) of **II**, 2.5 ml (0.025 mole) of diethylamine, and 0.1 ml of water was stirred at 35–40° C for 3.5 hr. N-(γ-Diethylamino-β-hydroxypropyl)pyrrolidone (**IV**) separated out in the form of a viscous colorless liquid, bp 140–140.5° C (3 mm). Found, %: N 13.02; mol. wt. 212.5 (in benzene). Calculated for $C_{11}H_{22}N_2O_2$, %: N 13.07; mol. wt. 214.

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