EXCHANGE REACTION INVOLVING OLEFIN α-OXIDES AND DIETHYL-β-HYDROXYALKYLAMINES

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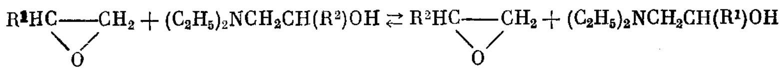
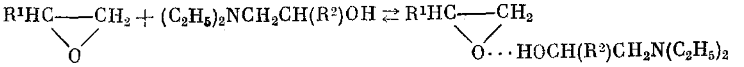
The exchange reactions studied earlier for the olefin oxide – R-β-hydroxyalkyl sulfide system [1-3] are characteristic for olefin oxides and amines having at least one β-hydroxyl group at the nitrogen atom. The scheme for the exchange reaction involving diethyl-β-hydroxyalkylamine is as follows:

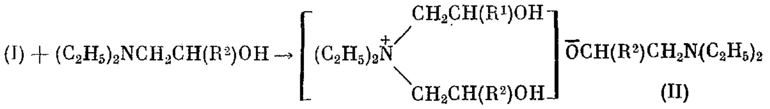

(1)

$R^1 = CH_3,\ C_2H_5,\ CH = CH_2,\ C_6H_5,\ CH_2OC_2H_5;\ R^2 = CH_3,\ C_6H_5.$

In all cases, the corresponding olefin oxide and aminoalcohol were found among the reaction products. The structure of the olefin oxide formed is determined by the structure of the β-hydroxyalkyl group of the starting amine. In addition, reaction (1) is reversible. Analogies in the literature would indicate the following mechanism for reaction (1). The first step is the formation of a hydrogen-bonding complex (I):


(2)

This type of complex was studied quantitatively in earlier work [4, 5]. The observed catalysis of the exchange reactions by acetic and benzoic acids and ethylene glycol is attributed to the formation of a more reactive hydrogen-bonded complex with the participation of the introduced proton donor. The formation of ammonium salt (II) with two different β-hydroxyalkyl groups is the result of the second step:

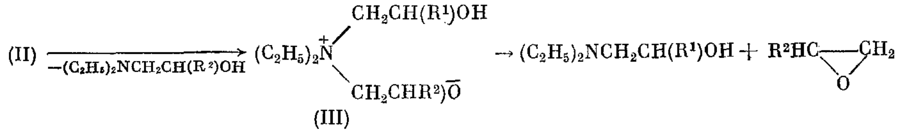

(3)

$$(I) + (C_2H_5)_2NCH_2CH(R^2)OH \rightarrow \left[(C_2H_5)_2\overset{+}{N}\begin{matrix} CH_2CH(R^1)OH \\ CH_2CH(R^2)OH \end{matrix}\right]\bar{O}CH(R^2)CH_2N(C_2H_5)_2 \qquad (3)$$

(II)

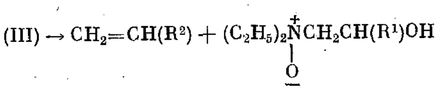
Ammonium salts formed by reaction of the olefin oxides in the presence of proton donors were obtained, for example, by Sorokin et al. [6]. These authors showed that the total reaction order for the olefin – amine – proton-donor system is 3: first-order in each component [7]. The total reaction order for reaction (1), in which step (3) is rate-limiting should also be 3: first order in olefin oxide and second order in the aminoalcohol; one aminoalcohol molecule acts as the proton donor in reaction (2).

The reaction is completed by the decomposition of zwitterion (III), which is formed by the loss of a proton by the OH group in salt (II) and the regeneration of the starting aminoalcohol molecule:


(III) (4)

The formation of a zwitterion of type (III) as an intermediate in the amine-epoxy compound–proton-donor system has been proposed, for example, by Tiger et al. [8].

This mechanism may be used to explain the reverse reaction. The formation of the olefins found among the reaction products is apparently related to another pathway for the decomposition of zwitterion (III)


(5)

$$(III) \rightarrow CH_2{=}CH(R^2) + (C_2H_5)_2\underset{\underset{\bar{O}}{|}}{\overset{+}{N}}CH_2CH(R^1)OH \qquad (5)$$

The N-oxide is hardly stable under the reaction conditions [9]. Reaction (5) does not permit the establishment of a dynamic equilibrium for the olefin oxide – aminoalcohol system.

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Reactions of type (1) are apparently characteristic for Group VA and VIA elements, which are capable of forming derivatives of onium bases by reaction with olefin oxides.

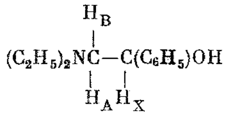
EXPERIMENTAL

The gas–liquid chromatographic analysis was carried out on a Tsvet chromatograph with a flame-ionization detector, nitrogen carrier gas, 1 m × 4 mm column packed with 15% PEGA on S-22. The PMR spectra were taken on a Varian HA-100 spectrometer at 29°C for 30-50% solutions in CCl_4. The chemical shifts are given in the δ scale, and the internal standard was HMDS.

Samples of the starting aminoalcohols were prepared according to Malinovskii [10] and their purity was checked by gas chromatography.

The experiments were run at 150°C with thermostatted glass ampuls and periodically analyzed by gas chromatography or in a metal autoclave without solvent.

Reaction of Styrene Oxide with 1-Diethylamino-2-propanol. A mixture of 3.12 g (0.026 mole) styrene oxide and 5.10 g (0.039 mole) 1-diethylamino-2-propanol was maintained for 12 h in a metal autoclave at 150°C. The conversion was about 50%. The structure of the propylene oxide formed which was distilled from the reaction mixture at 36°C and of 2-diethylamino-1-phenyl-1-ethanol which was distilled at 140°C (6 mm Hg) was determined by gas chromatography and PMR spectroscopy.



$$(C_2H_5)_2N\overset{H_B}{\underset{H_A}{C}}-\underset{H_X}{C}(C_6H_5)OH$$

PMR spectrum (δ, ppm, J, Hz): 0.83 t [6H, $(CH_3)_2$, J = 7.0], 2.21 q (1H, H_A, J = 14.0, 9.0), 2.23 q [4H, $(CH_2)_2N$, J = 7.0], 2.49 q (1H, H_B, J = 14.0, 4.5), 4.11 s (1H, OH), 4.46 q (1H, H_X, J = 9.0, 4.5), 7.11 m (5H, C_6H_5). Found: C 73.52; H 9.35%. Calculated for $C_{12}H_{19}ON$: C 74.61; H 9.84%.

CONCLUSIONS

The feasibility was demonstrated for an exchange reaction for the olefin oxide–β-hydroxyalkylamine system, and a mechanism was proposed involving the formation of an ammonium salt as an intermediate.

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