FORMATION OF 1,4- AND 1,5-REGIOISOMERS OF TRIAZOLINES IN REACTIONS OF 2-ETHOXYETHYL AZIDE WITH MONOSUBSTITUTED ETHYLENES

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The structural specificity of the reactions of 2-ethoxyethyl azide with alkenes RCH=CHR [R = CH2C6H5, CH2OC6H13, CH(OC2H5)2, C6H5] was studied. The formation of 1,4- and 1,5-substituted triazolines and the high stabilities of the latter were demonstrated by PMR spectroscopy, data from gas-liquid chromatography (GLC), and the kinetics of thermolysis.

The understanding of the structural possibilities of reactions involving the cycloaddition of azides to ethylene compounds CH2=CHR is far from complete. The formation of the 1,4- and 1,5-isomers that are possible in such reactions was demonstrated for the reactions of 4-nitrophenyl azide with styrene and 2-ethoxyethyl azide with alkenes [1, 2]. Only one isomer was described in the reactions of azides with vinyl ethers (1,5-isomers) and with methyl vinyl ketone, methyl acrylate, and acrylonitrile (1,4-isomers) (for example, see [3-5] and the literature cited therein).

In the present research we investigated the structural specificity of the reactions of 2-ethoxyethyl azide with four monosubstituted ethylenes with different polarities (see the scheme).

In syntheses with the use of allylbenzene, allyl hexyl ether, and acrolein diethylacetel the elementary compositions of the isolated compounds corresponded to disubstituted 1,2,3-Δ2-
triazolines Ia-IIIa and Ib-IIIb (Table 1). They could not be separated into individual isomers by fractionation or by means of column chromatography. The conclusions regarding the structure of the synthesized triazolines were drawn on the basis of the PMR spectra, data on the kinetic of thermal decomposition, and the determination of the compositions of the mixtures of thermolysis products.

The presence of 1,4- and 1,5-isomers of triazolines I and III is determined reliably from the PMR spectra. Two triplet signals of methyl groups of the OC2H5 radical of equal intensity with δ 1.05 and 1.11 ppm were observed in the spectrum of triazoline I. This result indicates unequivocally the presence in the mixture of isomers Ia and Ib in an equimolar ratio. The presence in the PMR spectrum of doublet signals of nonequivalent methyldiene protons of a diethylacetal group at 4.32 (J = 5.3 Hz) and 4.63 ppm (J = 4.7 Hz) constitutes evidence for the structural isomerism of triazoline III. After the labile isomer is removed from the mixture of triazolines by thermolysis, only the doublet with δ 4.32 ppm, which belongs to the stable isomer, is retained in the spectrum. We were unable to detect isomers in the PMR spectrum of triazoline II because of masking of the signals of the CH3 group in the OC2H5 radical by signals of the protons of the C2H5 group. The thermolysis of triazolines I-III was carried out at 170°C. The kinetics of decomposition were determined by gasometry, since, as we previously ascertained, triazolines liberate an equimolar amount of nitrogen. The kinetic dependences in the coordinates of a first-order equation included two rectilinear sections with different slopes (Fig. 1). The break on the graphical dependence for a monomolecular reaction constitutes evidence for the presence of two compounds that are characterized by different rates of decomposition. Consequently, the parallel formation of 1,4- and 1,5-substituted triazolines occurred during the synthesis. The kinetic data, like the PMR spectra of the triazolines, while demonstrating the presence of two isomers, do not make it possible to correlate the type of structure with its lability. The data necessary for such assignments were obtained in a study of the products of thermolysis of triazolines Ia-IIIa and Ib-IIIb, the labile and stable isomers. In analyzing the thermolytic mixtures we proceeded from the assumption that the decomposition of the triazolines obtained occurs as in the decomposition of 4(5)-alkyl-1-(2-ethoxethyl)-1,2,3-Δ2-triazolines, i.e., with the formation of nitrogen, identical aziridines Ic-IIIc, and different azomethines: aldimines Id-IIId from Ia-IIIa and ketimines Ie-IIIe from Ib-IIIb [2]. Thus the task of determining the structure of each of the isomers reduced to identification of the resulting azomethines. The time required for the complete decomposition of the triazolines at 170°C was determined from the kinetic dependences: 1h for I, 42 min for II, and 2 h for III. The stable isomer was isolated in the form of a residue after decomposition of the less stable isomer and removal of the products of its decomposition by distillation. The products that were removed by distillation were the thermolyzate of the labile isomer. The time necessary for decomposition of the bulk of the labile isomer was also found from kinetic data. For triazolines I-III the times were 1.5, 2.0, and 5.0 min. During these times the labile and stable isomers underwent decomposition to the extent of, respectively, 99% and 8% (Ia,b) 83% and 13% (IIa,b), and 81% and 13% (IIIa, b). The conditions of thermolysis of the stable isomers were the same as for mixtures of the isomers. The thermolysis products were identified from data from gas-liquid chromatography (GLC) and the PMR spectra.