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STUDY OF METHODS OF PREPARATION OF 1,4-DIGLYCIDYLTETRAZOLONE. NEW SYNTHESIS OF TRIGLYCIDYLISOCYANURATE

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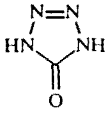
1,4-Diglycidyltetrazolone was synthesized for the first time by the reaction of tetrazolone and epichlorohydrin with subsequent treatment of the products of addition with a base. The basic directions of the reaction of carbamoyl azide with epichlorohydrin, which yields triglycidylisocyanurate and diglycidylcarbamoyl azide, were investigated. The features of the synthesis and properties of the substances obtained were described.

Of the epoxy heterocyclic monomers, glycidyl derivatives of high-nitrogen heterocycles, which are distinguished in polymers by a developed network of intermolecular interactions, are stimulating special interest [1, 2]. However, epoxy derivatives of tetrazoles have not been described up to now. For synthesizing promising monomers of the tetrazole series, it was expedient to use a bifunctional azolone structure similar to the skeletons of the popular glycidyl derivatives of cyclic ureas. Tetrazolone I, which is synthesized by diazotization of 5-aminotetrazole, could be such a structure [3, 4]. The last reaction involves the well-known difficulties caused by the hazard of explosion of the intermediate tetrazolediazonium salt in concentrations ≥ 2%. This situation stimulated our attempts to find another, less dangerous way of synthesizing 1,4-diglycidyltetrazolone based on semicarbazide derivatives. It is known that linear carbamoyl azide incapable of cyclization is obtained as a result of diazotization of semicarbazide [6, 7]. Nevertheless, the possibility of formation of a tetrazole system is possible for 4-monosubstituted semicarbazide thio analogs, which form the corresponding 2-amino-1,2,3,4-thiatriazoles in diazotization via intermediate 5-substituted thiocarbamoyl azides, and the thiatriazoles undergo Dimroth rearrangement in basic medium into tetrazole-5-thiones [8].

In addition to conducting glycidylation of tetrazolone with epichlorohydrin and bases, it was also interesting to study the possibility of cyclization of 5-substituted carbamoyl azide, which can be obtained during the reaction of unsubstituted carbamoyl azide with epichlorohydrin.

We found that in the reaction of tetrazolone I (60-100°C) with epichlorohydrin in a five- to tenfold excess of the latter in the presence of quaternary ammonium salts — tetraethylammonium chloride (TEAC) and bromide (TEAB) or tetraethylbenzylammonium chloride (TEBAC) — addition of oxirane to the tetrazolone ring in positions 1 and 4 and subsequent formation of chlorohydrin (II and III) and dioxirane (IV) derivatives is observed.



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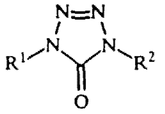
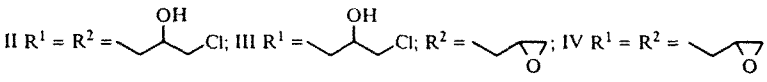


II–IV



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After the reaction is completed, the mixture primarily contains oxiranechlorohydrin III and only small amounts of dichlorohydrin II and dioxirane IV in the absence of basic agents. As a result of dehydrochlorination with bases, both intermediate compounds II and III are converted into crystalline dioxirane IV with a yield of 70-75%.

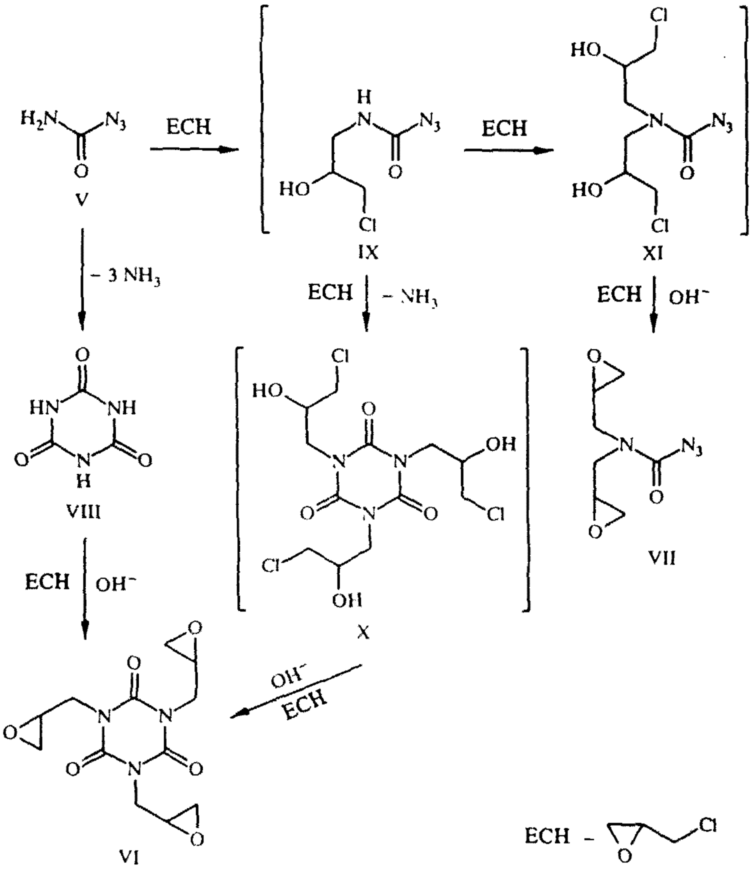
On the whole, the character of the reaction of tetrazolone I with epichlorohydrin is similar to the reaction known for transformations of related 1,2,4-triazol-5-ones [2, 5].

The reaction of carbamoyl azide V with epichlorohydrin in conditions similar to the transformation of tetrazolone described above yields two types of compounds — crystalline substance A (mp = 90-150°C) and low-viscosity liquid B, characterized by a high concentration of epoxy groups (39-42.5%).

The crystalline substance, which was not identical to 1,4-diglycidyltetrazolone IV, was separated into two forms by fractional crystallization from methanol: α (mp = 106-107°C) and β (mp = 153-157.5°C). The same composition $(C_4H_5NO_2)_n$ corresponds to both forms, and the concentration of epoxy groups is 42-43.2%. Multiplet signals of protons from CH_2O (2.65, 2.80), CHO (3.22), and CH_2N (3.95, 4.02, 4.10, 4.17 ppm), belonging to glycidyl fragments of the molecules, are observed in the PMR spectra of the isomers. The IR spectra of compounds α and β exhibit absorption bands at 1688 belonging to vibrations of carbonyl groups and 978, 930, and 848 cm^{-1} from vibrations of oxirane C–O bonds.

Based on the data obtained and by direct comparison with two known isomeric forms of triglycidylisocyanurate (IR spectra and in samples from mixing), it was found that the α form separated here corresponds to *R,R,S/S,S,R*-triglycidylisocyanurate VI while the β form corresponds to *R,R,R/S,S,S*-isomer VI (see scheme), obtained from cyanuric acid according to the data in [10].

The second (resinous) compound is characterized by a 39-40% concentration of epoxy groups and one basic spot on the thin-layer chromatogram (R_f 0.66) resembling carbamoyl azide with respect to the position (R_f 0.68). Its PMR spectrum contains signals characteristic of glycidyl group protons alone (CH_2O, 2.65; CHO, 3.1; CH_2N, 3.6-3.9 ppm). Absorption bands of carbonyl (1705, 1750) and azide (2110) groups similar to those for carbamoyl azide are observed in the IR spectrum of the resin (cf. in the spectrum of carbamoyl azide ν C=O 1685, 1780, ν N_3 2120, 2180 cm^{-1}). The compound decomposes when heated to 100-110°C with liberation of gaseous substances. These factors, and the data from elemental analysis, suggest that



diglycidylcarbamoyl azide VII is the basic compound of mixture B. The resin contains a small amount of monomer VI which can be separated from it by treatment with methanol–ether mixtures, 1:1-5.

Formation of triazine ring VI and diglycidylcarbamoyl azide VII is thus observed in the reaction of carbamoyl azide V with epichlorohydrin.

The details of the chemistry of formation of the triazine ring are still unclear. However, since cyanuric acid VIII is obtained in small quantities (2-5%) in recrystallization of carbamoyl azide (from alcohols and especially from water), we can hypothesize that conversion of azide V into cyanuric acid VIII and then addition of epichlorohydrin to acid VII and epoxide formation in the presence of bases initially take place in epichlorohydrin (excess of epichlorohydrin, bases). Formation of cyanuric acid VIII form carbamoyl azide V can take place by nucleophilic substitution of the azide ion by an amide group or trimerization of the cyanic acid obtained in decomposition of carbamoyl azide. The last conversion of cyanuric acid with epichlorohydrin is well known and takes place via mono-, di-, and trichlorohydrin and the corresponding mixed epoxy–chlorohydrin substituted compounds [10, 11].

Moreover, it is also not possible to eliminate the possible formation of monomer VI from the intermediate monochlorohydrin derivative of carbamoyl azide IX due to its self-condensation. This path seems more probable, especially since thermal decomposition of carbamoyl azide in water or alcohols (80-100°C) takes place less intensely than in less polar and probably less preferred epichlorohydrin at 60-80°C. Trimerization should lead to trischlorohydrin X, which is converted into monomer VI under the effect of bases.

It is evident that azide monomer VII is only formed when the amino group of chlorohydrin IX can react with a second molecule of epichlorohydrin. For this reason, dichlorohydrin XI and the corresponding epoxy chlorohydrin derivative of isocyanuric acid are intermediate products of the transformation.

Diglycidylcarbamoyl azide VII is a previously unknown combination of epoxide, azide, and carbamide fragments in one structure.

EXPERIMENTAL

The PMR spectra were recorded on a Varian Gemini 200 spectrometer, and the IR spectra were recorded on a UR-20, slit program 4, 160 cm^{-1}/min recording speed. The concentration of epoxy groups was measured by direct titration of the samples with an acetic-acid solution of HBr with crystal violet indicator (compounds VI, VII) or back titration of samples treated with an acetone solution of hydrogen chloride (compound II) according to GOST 12497–78. The concentration of saponified chlorine was determined by treating the samples with a basic solution of potassium hydroxide with subsequent argentometric titration of chloride ions according to GOST 22457–77. The individuality of the substances was confirmed by the data from thin-layer chromatography on Silufol, chloroform–methanol mixture, 10:1 as eluent. Developer: iodine vapors.

1,4-Diglycidyltetrazolone (IV). Here 1 mmole of one of the catalysts (TEAC, TEAB, TEBAC) heated to 80°C was added to a mixture of 4.3 g (0.05 mole) of tetrazolone I and 78.4 ml (1 mole) of epichlorohydrin, mixed until the tetrazolone dissolved, and then for an additional 30 min. The solution was cooled to 40°C and 4.4 g (0.11 mole) of granulated sodium hydroxide was added over 30 min while stirring. Stirring was continued for 1 h in the same conditions. The sediment was filtered off, and the mother liquor was vacuum evaporated. The residue was a pale yellow, viscous resin which crystallized on cooling (–10°C) into an almost white crystalline mass. Yield of dioxirane IV of 7.1 g (72%). mp = 86-88°C (from toluene). R_f 0.70. Found, %: C 42.7; H 5.0; N 28.5. $C_7H_{10}N_4O_3$. Calculated %: C 42.4; H 5.1; N 28.3. PMR spectrum (in $CDCl_3$: 2.75 (2H, d.d, CH_2O), 2.85 (2H, d.d, CH_2O), 3.31 (2H, m, CHO), 4.13 ppm (4H, d, CH_2N). IR spectrum (in KBr), cm^{-1}: 3090 w (CH_2 ep.), 3020 w (CH ep.), 2950 w, 2870 w (CH_2), 1740 s (C=O), 1445 me, 1415 me, 1100 me.

Reaction of Carbamoyl Azide with Epichlorohydrin. Here 1395 ml (17.8 mole) of epichlorohydrin and 2.9 g (17.5 mmole) of TEAC were added to 76.3 g (0.89 mole) of carbamoyl azide. The temperature was slowly increased to 60°C and maintained for 30 min while stirring. Then stirring was continued at 70°C for 1.5 h and at 80°C for 3.5 h. The temperature was decreased to 40°C and 75.8 g (1.9 mole) of sodium hydroxide was added by portions over 30 min while stirring. Stirring was continued for 1 h in the same conditions. The sediment was filtered off, and the mother liquor was vacuum evaporated. Then 50 ml of ether–methanol mixture, 5:1, was added to the yellow resinous substance obtained, stirred, and the colorless sediment formed was left overnight with the mother liquor at –5°C. The sediment of triglycidylisocyanurate VI was filtered off and washed with ether. Yield of 37.5 g (43%). mp = 90-150°C. Concentration of epoxy groups of 41.0-42.5%, Cl 0.7-0.8%. The product was a mixture of α and β forms (mp = 105-106°C). Lit. 105°C [10] and 1.5-2 g of β form (mp = 153-

157.5°C. Lit. 156°C [10]. R_f 0.76. No depression of the melting point in samples of mixing and identical IR and PMR spectra to triglycidylisocyanurate prepared according to [10]. PMR spectrum (in $CDCl_3$): 2.65 (3H, m, CH_2O), 2.80 (3H, m, CH_2O), 3.22 (3H, m, CHO), 3.95, 4.02 (3H, d.d, CH_2N), 4.10, 4.17 ppm (3H, d.d, CH_2N). IR spectrum (in Nujol), cm^{-1}: 3070 w (CH_2 ep.), 1688 s (C=O), 1335 me, 1260 me, 978 me, 930 w, 882 w, 848 s, 800 s, 753 s.

The mother liquor was vacuum evaporated and 69 g (55%) of diglycidylcarbamoyl azide VII in the form of a pale yellow, low-viscosity resin was obtained. R_f 0.66. Found, %: N 26.4; SEG 39-40; Cl 1.1-1.3. $C_7H_{10}N_4O_3$. Calculated, %: N 28.3; SEG 43.8, Cl 0.

PMR spectrum (in $CDCl_3$): 2.65 (2H, m, CH_2O), 2.80 (2H, m, CH_2O), 3.10 (2H, m, CHO), 3.60-3.90 ppm (4H, m, CH_2N). IR spectrum (in thin layer) cm^{-1}: 3065 w (CH_2 ep.), 3000 me, 2965 me, 2930 me, 2875 w (CH_2CH), 2110 s (N_3, 1705 s, 1750 s (C=O), 1550 me, 1460 s, 1260 s, 1080 me, 970 me, 930 me, 860 s, 760 s.

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