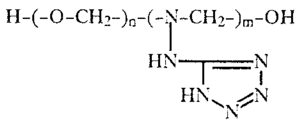
THE FORMATION OF TETRAZOLE AND AZIDO OLIGOMERS BY THE REACTION OF 5-HYDRAZINOTETRAZOLE WITH FORMALDEHYDE IN ACID MEDIA

A. G. Mayants, L. M. Tishchenko, V. N. Vladimirov,
and V. A. Shlyapochnikov

The reaction of 5-hydrazinotetrazole with formaldehyde in acid media was studied. Copolymers of these compounds are formed at pH ~6.0. In contrast, opening of the tetrazole ring and formation of a previously unknown copolymer of 1,3,4-aza-2-azido-1,4-pentene with formaldehyde occurs at pH ~3.0. The ratio of nitrogen-containing and oxymethylene units depends on the ratio of the starting reagents and solvent. The existence of terminal hydroxyl groups in the 1,3,4-aza-2-azido-1,4-pentene oligomer was demonstrated by acetylation.

Hydrazones of simple aldehydes, in particular, formaldehyde, dimerize readily upon formation to give hexahydro-1,2,4,5-tetrazines [1]. In contrast, hydrazone (II) formed in the reaction of the hydrochloride salt of 5-hydrazinotetrazole (I) and formaldehyde reacts further with excess formaldehyde to give copolymer (III) [2].



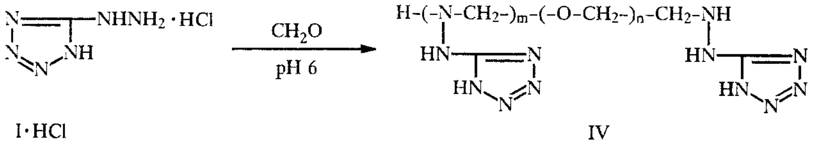
III

In the present work, we studied the effect of the pH of the medium, ratio of the starting reagents, and amount of solvent on the reaction of 5-hydrazinotetrazole with formaldehyde.

A solution of salt I·H_2SO_4 in dilute sulfuric acid formed upon the treatment of the disodium salt of azotetrazole with 3% sulfuric acid and removal of the precipitated diazido compound [3] was used as a starting reagent.

The experimental technique involved neutralization of the acid aqueous solution of I·H_2SO_4 by treatment with Na_2CO_3, addition of the catalyst for the formation of hydrazone II, namely, hydrochloric acid (to pH ~6.0 or ~3.0), addition of the calculated amount of an aqueous solution of formaldehyde, and subsequent removal of the solvent. The residual oligomer powder was washed with water to remove inorganic salts. The ratio of the starting reagents and major indices of oligomers (IV)-(X) obtained are given in Table 1.

Infrared analysis of the oligomers obtained at pH ~6.0 and ~3.0 showed that they differ significantly. Thus, the spectrum of oligomer IV obtained at pH ~6.0 has bands corresponding to the tetrazole fragment at 1000 and 1140 cm^{-1}. The corresponding bands for III are found at 990 and 1145 cm^{-1} [2]. This finding and the lack of bands for hydroxyl groups suggest that product IV is a tetrazole-containing oligomer with terminal NH groups.



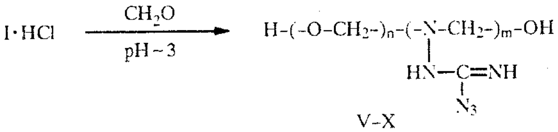
I·HCl

IV

V. V. Kuibyshev Samara State University, Samara 443010. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1064-1067, August, 1993. Original article submitted October 1, 1992.

The difference in the terminal groups in oligomers III (OH) and IV (NH) is probably a consequence of the different amounts of formaldehyde taken per mole of starting I (20 and 22 moles in the case of III [2] and 1.00 mole in the case of IV).

The IR spectra of products V-X obtained at pH ~3.0 lack tetrazole ring bands and display bands characteristic for the azide group (2150-2155 cm^{-1}) and the C=N group (1690-1698 cm^{-1}) [4]. These features unequivocally indicate that the tetrazole ring opens at pH ~3.0 to give the tautomeric imidazide form [5]. The results are in accord with the literature data on the greater stability of this form in strongly acidic media [6]. Hence, copolymers of 1,3,4-aza-2-azido-1,4-pentene with formaldehyde are formed at pH ~3.0.

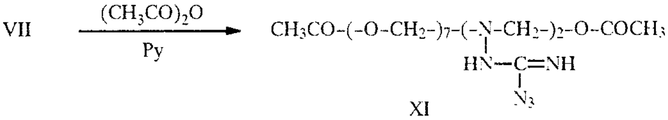


$$\mathrm{I\cdot HCl} \xrightarrow[\mathrm{pH}\sim 3]{\mathrm{CH_2O}} \mathrm{H{-}(-O{-}CH_2{-})_n{-}(-\underset{\substack{|\\ HN-\underset{\substack{|\\ N_3}}{C}=NH}}{N}{-}CH_2{-})_m{-}OH}$$

V-X

The data given in Table 1 show that the number of oxymethylene groups per nitrogen-containing monomer unit in oligomers V-X decreases with decreasing amount of formaldehyde and increasing amount of solvent (water).

Additional evidence for the existence of terminal hydroxyl groups in oligomers V-X is found in the preparation of the diacetate (XI) from VII.



$$\mathrm{VII} \xrightarrow[\mathrm{Py}]{\mathrm{(CH_3CO)_2O}} \mathrm{CH_3CO{-}(-O{-}CH_2{-})_7{-}(-\underset{\substack{|\\ HN-\underset{\substack{|\\ N_3}}{C}=NH}}{N}{-}CH_2{-})_2{-}O{-}COCH_3}$$

XI

The IR spectrum of XI has bands for the C=O group at 1710, 1715, and 1733 cm^{-1} in addition to bands for the azide group at 2155 cm^{-1} and C=N group at 1693 cm^{-1}.

The thermal stability of oligomers IV and VII-IX was studied by derivatography. These results showed significant differences between the oligomer with low nitrogen content IX, in which there is no exo effect upon decomposition, and oligomers IV, VII, and VIII, which contain more nitrogen and undergo decomposition with heat evolution. The temperature for the onset of the exo effect for oligomer IV is 180°C (corresponding to 14.7% mass loss) and the temperature for rapid decomposition is 190°C. The temperature for the onset of the endo effect for oligomer VII is 90°C (10.3% mass loss) and the temperature for the maximum endo effect is 135°C (16.2% mass loss). The temperature for the exo effect onset for this oligomer is 175°C and the explosion point is 210°C (the mass loss at 200°C is 35.0%). The temperature for the onset of the endo effect for oligomer VIII is 55°C and the temperature for the maximal endo effect is 95°C (4.4% mass loss). The temperature for the onset of the exo effect for this oligomer is 158°C and the explosion temperature is 195°C (the mass loss at 185°C is 11.0%). Only an endo effect is observed in the decomposition of low-nitrogen oligomer IX. The temperature for the onset of the endo effect for this oligomer is 88°C (2.3% mass loss) and the temperature for the maximum endo effect is 168°C (66.7% mass loss). The endo effect presumably corresponds to decomposition of the oxymethylene fragments, while the exo effect corresponds to destruction of the nitrogen-containing fragments of the oligomers. We should note that oligomers VII and VIII containing azide groups decompose explosively. Such behavior is not noted for oligomer IV, which contains tetrazole groups.

EXPERIMENTAL

The IR spectra were taken for KBr pellets on UR-20 and Specord M-80 spectrometers. The derivatograms were taken on a Paulik—Paulik—Erdey derivatograph in air at a heating rate of 5°C/min. The hydroxyl group content in the oligomers was determined by acetylation using the technique of Avvakumova et al. [7], with the exception that the reaction was carried out for 20 h at 20°C.

TABLE 1. Ratio of Formaldehyde and 5-Hydrazinotetrazole I and Characteristics of Oligomers IV-X

Compound	Chemical formula	Moles formaldehyde per mole comp. 1, mole	Number of units		Amount of hydroxyl groups, %	Molecular mass		Yield, %
			m	*n*		found rel. to OH group content	calc. from chem. formula	
IV	$C_{10}H_{22}N_{24}O_2$	1,00	3	2	0,0	—	510	12,3
V	$C_{17}H_{36}N_{36}O_6$	2,02	6	5	4,18	840	840	34,6
VI	$C_{23}H_{48}N_{42}O_{10}$	9,84	7	9	3,31	1027	1072	39,7
VII	$C_{11}H_{24}N_{12}O_8$	20,09	2	7	7,79	436	452	34,9
VIII*	$C_{20}H_{42}N_{42}O_7$	20,31	7	6	3,72	914	982	37,3
IX	$C_{49}H_{100}N_6O_{48}$	40,18	1	47	—	—	1540	16,6
X	$C_{55}H_{112}N_6O_{54}$	66,89	1	53	—	—	1720	20,4

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*Oligomer VIII was obtained using a tripled amount of water solvent.

**Nitrogen-containing (*m*) and oxymethylene units (*n*).

Satisfactory elemental analysis data for C, H, and N were obtained for oligomers IV-XI.

Copolymers of 5-(1,2-Diaza-2-propene)tetrazole and Formaldehyde (IV). A suspension of 3 g (10.00 mole) I·HCl in 50 ml water with 32 ml 3% sulfuric acid was carried out analogously to the reported procedure for the preparation of 5-azodiazomethanotetrazole hydrate [3]. Na_2CO_3 was added to the filtrate containing $I \cdot H_2SO_4$, obtained after the removal of this tetrazole, to pH 7.0-7.3. Concentrated hydrochloric acid (0.5 ml) was then added to bring the solution to ~6.0 and the calculated amount of 38% aqueous formaldehyde was introduced (the amount of starting salt $I \cdot H_2SO_4$ in the filtrate was determined relative to the yield of I). After evaporation of the solvent in the air at 20°C, the product was mixed with 25 ml water. Crystalline IV was filtered off and washed with three 25-ml portions of water.

Copolymers of 1,3,4-Aza-2-azido-1,4-pentene and Formaldehyde (V-VII, IX, and X). Oligomers V-VII, IX, and X were obtained according to a technique described for the synthesis of oligomer IV except that concentrated hydrochloric acid was added to pH ~3.0 and then an additional 0.25 ml concentrated hydrochloric acid was added.

Copolymer of 1,3,4-Aza-2-azido-1,4-pentene and Formaldehyde (VIII). Oligomer VIII was prepared by the procedure described above for V-VII, IX, and X except that 90 ml water was added to the residue after evaporation of most of the solvent. Then, evaporation followed by water addition was carried out three times.

Product of the Acetylation of Oligomer VII at the Terminal Hydroxyl Groups (XI). The acetylation of oligomer VII carried out according to the method for determining hydroxyl group content gave a precipitate, which was filtered and washed with water and then ethanol. The yield of diacetate XI was 43%.

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