STRUCTURE AND PROPERTIES OF 3-AMINO-1-VINYL-1,2,4-TRIAZOLE

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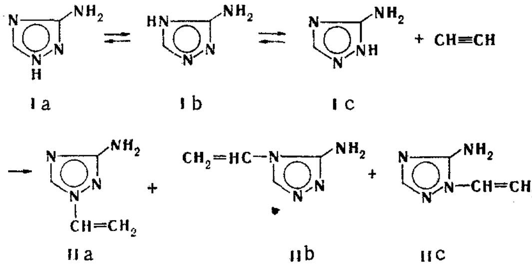
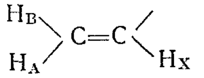
The reaction of acetylene with 3-amino-1,2,4-triazole forms two isomeric 3-amino-N-vinyl-1,2,4-triazoles. Their structures have been studied by PMR and IR spectroscopy and dipole moments. The high activity of the new vinyl compounds of the azole series in the addition of electrophilic reagents, in polymerization, and in complex formation has been shown.

Theoretically, 1,2,4-triazole and its derivatives can exist in tautomeric forms [1-3]. On this basis, in the reaction of 3-amino-1,2,4-triazole (I) with acetylene the formation of a mixture of N-vinyl isomers is possible:



1-Vinyl-1,2,4-triazole was first obtained by the transvinylation of 1,2,4-triazole with vinyl acetate [4]. We have previously developed a method for obtaining 1-vinylbenzotriazole with a high yield by the action on benzotriazole of acetylene in the presence of copper salts [5]. However, the best catalyst for the vinylation of benzotriazole, cuprous chloride, proved to be inactive for the synthesis of 3-amino-N-vinyl-1,2,4-triazoles (II). In this case, the mixture (II) was obtained with a yield of only 10-13%. The use as catalyst of metallic potassium, which has given a good result in the synthesis of vinyl derivatives of the pyrrole and phenothiazine series [6], led to the charring of the reaction mixture containing (I). Cadmium acetate did not catalyze the vinylation of (I) at all. It has been found that the reaction of (I) with acetylene under pressure takes place in 3 h in the presence of 30% caustic soda in an aqueous dioxane–ethanol medium at 170-175°C.

Investigations performed by PMR and IR spectroscopy and by gas–liquid chromatography have shown that the products of the vinylation of (I) contain two isomeric vinyl derivatives corresponding to the tautomeric forms of the starting material. The PMR spectrum of (II), taken in acetone, shows the presence of two isomers in the sample (Fig. 1, A). The H-5 proton is responsible for the appearance of two singlets in the weak field (δ 8.00 and 7.35 ppm). The protons of the vinyl group and of the NH_2 group also give two signals each, corresponding to two isomers. The amine protons resonate in the form of two broad singlets with δ 6.75 and 5.10 ppm. The signals of the protons of the vinyl group


$\begin{matrix}H_B\\H_A\end{matrix}\!>C=C<\!\begin{matrix}\\H_X\end{matrix}$

are represented

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by quartets due to the spin–spin coupling of the H_X protons with H_A and H_B (δ_A 4.69 and 4.73 ppm, δ_B 5.39 and 5.41 ppm; J_{AX} = 8.7 Hz, J_{BX} = 15.2 Hz, δ 7.04 ppm). In contrast to the H_A and H_B protons, the α-olefinic proton is shielded almost identically in the two isomers. The two quartets of this proton practically coincide. The PMR spectrum of (II) taken in deuteromethanol differs from the spectrum in acetone by the fact that the NH_2 signal is superposed on the signal of the solvent. In addition, the nonequivalence of the H_A protons decreases, and therefore the signals of these protons in the two isomers are superposed. The difference in the spectra taken in two solvents must be regarded as natural if the influence of various solvents on PMR spectra is taken into account.

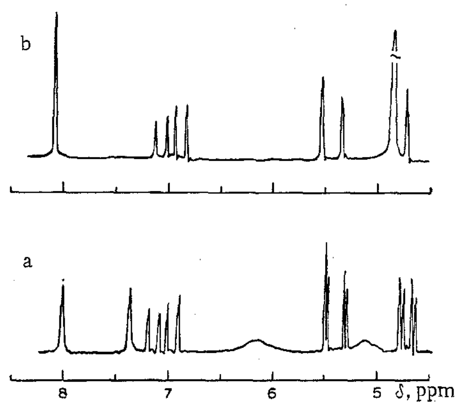

Fig. 1. PMR spectra of the mixture (II): a) taken in acetone; b) taken in deuteromethanol.

The existence of two compounds in (II) was also shown by GLC, two peaks appearing on the chromatogram. According to PMR and GLC, the ratio of the isomers in the product of the vinylation of (I) was 60 : 40. After additional purification by the recrystallization of this product, which had been isolated by vacuum distillation, the number of signals in the PMR spectrum fell to one half (Fig. 1, B). The positions and multiplicities of the signal in it are characterized by the following parameters: δ_5 8.05 ppm, δ_X 6.96 ppm, δ_B 5.43 ppm, δ_A 4.76 ppm, J_{AX} = 15.2 Hz, J_{BX} = 8.7 Hz, J_{AB} = 0.8 Hz, δ_{NH_2} 4.84 ppm. The results obtained show that the product isolated was fairly pure and enabled it to be assigned to one of the isomeric forms of the vinyl derivative of 3-amino-1,2,4-triazole. Its individuality was also confirmed by the GLC method – only one peak appeared on a chromatogram.

When the IR spectra of (II) were recorded in the solid state, the superposition of the frequencies of the formation vibrations of the NH_2 group and of the C = C stretching vibrations at 1640-1660 cm^{-1} was observed. To confirm the presence of a vinyl group, the IR spectra were taken in deuteroethanol and chloroform. In solutions, the intermolecular association of the NH_2 groups is disturbed, and δ_{NH_2} shifts to 1580 and 1650 cm^{-1}, respectively [7]. As a result, the bands at 1650 cm^{-1} can be assigned with great confidence to the vibrations of the vinyl group. In the IR spectrum of the individual product, in comparison with the IR spectrum of the mixture of isomers (II), a decrease in the number of bands in the 2600-2800 cm^{-1} region is found and also the disappearance of the absorption bands at 1530, 1290, and 1077 cm^{-1} connected with a definite position of the substituent in the ring. Furthermore, the presence in the spectrum of absorption in the region of the nonplanar deformation C–H vibrations of the ring (725, 766 cm^{-1}) similar to what has been described previously [4] for 1-vinyl-1,2,4-triazole, gives grounds for assuming that the main product of the vinylation of (I) corresponds to the structure of 3-amino-1-vinyl-1,2,4-triazole (IIa).

A confirmation of the correctness of the proposed structure of the isomer (IIa) is the coincidence of the experimental value of its dipole moment – 2.32 D – with that calculated vectorially – 2.35 D. For the isomers (IIc) and (IIb) the calculated values of the dipole moments are 3.71 and 5.60 D.† A comparison of these values with the values of the dipole moments for the phenyl-substituted promoters of 1,2,4-triazole [8] also shows the addition of the vinyl group to the nitrogen atom in position 1 of the triazole ring.

The new vinyl monomer (II) that we have synthesized possesses a high reactivity. It has been shown that the action of hydrogen chloride on it readily forms a hydrochloride. When an ethanolic solution of (II) was heated with methyl iodide, a quaternary salt was formed. Manganese, cobalt, and zinc chlorides give complexes with a 1 : 2 composition regardless of the ratio of the components taken for the reaction. In the IR spectra of the hydrochloride, the methiodide, and the complexes of (II) with metal halides, the absorption bands of the vinyl and amino groups are retained. The frequencies characteristic for the vibrations of the heterocycle shift in the short-wave direction (1563 → 1573, 1530 → 1545, 1344 → 1390, 1145 → 1165), the greatest displacement of these bands taking place in the case of the hydrochloride.

The electronic absorption spectra of the complexes (II) with metal halides proved to be similar to the spectrum of their ligand (II): in water, λ_1 = 254 nm, λ_2 = 196 nm; in ethanol, λ_1 = 251 nm, λ_2 = 194 nm. Complex formation probably has no effect on the energy of the $\pi - \pi^*$ transitions in (II). It is not excluded that

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† The determination of the dipole moments was performed by V. B. Modonov for which the authors express their gratitude to him.

this may be connected with the dissociation of the complexes in the solvents mentioned. On the basis of information on the distribution of the π-electron density in the 1,2,4-triazole molecule, we assume that the center of coordination of (II) with the electron acceptors studied is the nitrogen in position 4. The absence of coordination at the nitrogen of the amino group, which bears a positive charge, is confirmed by the presence of the original frequencies of the N–H absorption in the IR spectra of the complexes. It has been shown that (II) reacts with aldehydes to form products of amino-aldehyde condensation.

The other reaction center – the vinyl group – proved to be fairly active and capable of polymerization. Under the influence of free-radical initiators, a water-soluble poly(aminovinyltriazole) was obtained from (II). The polymer can readily be modified by treating it with hydrogen chloride, methyl iodide, and halides of cobalt and of other metals. The introduction of an acceptor into the polymer chain is regulated by the ratio of the starting materials.

Compound (II) is hydrogenated by hydrogen in the presence of Raney nickel to 3-amino-1-ethyl-1,2,4-triazole. Bromine also adds mainly to the double bond of the vinyl group with the formation of 3-amino-1-(α,β-dibromoethyl)-1,2,4-triazole, as is confirmed by PMR and IR spectra. As in the bromination of 1-vinylbenzotriazole [9], the formation of complexes of (II) with bromine is also not excluded.

EXPERIMENTAL

The PMR spectra were recorded on a BS 487B spectrometer at room temperature with hexamethyldisiloxane as internal standard (δ scale). The IR spectra were recorded on a UR-20 spectrometer. Solid samples were prepared with KBr and in paraffin oil. The UV spectra were measured on a Unicam SP-8000 spectrophotometer at a concentration of 0.5-0.7 g/liter. GLC analysis was performed on a Khrom-3 chromatograph at a temperature of 100-300°C at a rate of heating of 4°C/min with a column 1.4 m × 4.4 mm containing silicone DS-550 (5%) on Chromaton.

The starting material used was imported 3-amino-1,2,4-trizole (I) of "pure" grade with mp 150°C.

3-Amino-1-vinyl-1,2,4-triazole. A rotating autoclave with a capacity of 0.5 liter was charged with 20 g (0.23 mole) of (I), 6 g (0.1 mole) of 30% KOH, 80 ml of dioxane, 40 ml of ethanol, and 6 ml of water. Acetylene was passed in under a pressure of 15 atm, and the autoclave was heated at 170-175°C for 3 h. The solvent was driven off from the reaction mixture, and vacuum distillation then yielded 17.1 g (65.7%) of (II) with bp 131-137°C (5 mm), white crystals with mp 95-96°C (from ethanol), soluble in water and in the majority of organic solvents. Found: C 43.3; H 5.5; N 51.1%. $C_4H_6N_4$. Calculated: C 43.6; H 5.5; N 50.9%. Picrate, mp 144-145°C (from ethanol). Found: C 36.0; H 3.0%. $C_4H_6N_4 \cdot C_6H_3N_3O_7$. Calculated: C 35.4; H 2.8%.

Hydrochloride of (II). Dry HCl was passed to saturation into a solution of 1 g (9 mmole) of (II) in 15 ml of ethanol. The white precipitate formed was filtered off, giving 0.96 g (73.9%) of the hydrochloride of (II), mp 137-139°C. Found: C 32.3; H 4.6; Cl 24.1%. $C_4H_6N_4 \cdot HCl$. Calculated: C 32.7; H 4.7; Cl 24.3%.

Methiodide of (II). A mixture of 0.5 g (4 mmoles) of (II), 0.63 g (4 mmoles) of methyl iodide, and 5 ml of ethanol was kept at 40-45°C for 10 h. Then it was dissolved in ethanol, and precipitation with ether gave 0.47 g (39.1%) of yellow crystals with mp 134-136°C. Found: I 49.9%. $C_5H_9N_4I$. Calculated: I 50.3%.

Complex of (II) with $CoCl_2$. A solution of 0.6 g (2 mmoles) of $CoCl_2 \cdot 6H_2O$ was added to 0.5 g (4 mmoles) of (II) in 10 ml of ethanol, and the mixture was stirred for 40 min with a magnetic stirrer. The lilac-colored precipitate that deposited was filtered off, giving 0.77 g (98%) of the complex of (II) with $CoCl_2$, mp 338-340°C. Found: C 27.5; H 3.5; Cl 20.3%. $(C_4H_6N_4)_2 \cdot CoCl_2$. Calculated: C 27.4; H 3.4; Cl 20.2%.

The complexes of (II) with $MnCl_2 \cdot 4H_2O$ [yield 83.3%, mp 343-344°C. Found: Cl 20.6%. $(C_4H_6N_4)_2 \cdot MnCl_2$. Calculated: Cl 20.5%] and with $ZnCl_2$ [yield 85%, mp 199-200°C. Found: Cl 19.5%. $(C_4H_6N_4)_2 \cdot ZnCl_2$. Calculated: Cl 19.9%] were obtained similarly.

Poly[3-amino-N-vinyl-1,2,4-triazole]. A tube was charged with 1 g (9 mmoles) of (II) and 0.02 g (2%) of azoisobutyronitrile in 2 ml of ethanol and was kept in a thermostat for 1 h. The block formed was treated with ethanol, giving 0.95 g (95% by weight) of a white powder with mp above 400°C. Found: C 42.9; H 5.9%. $(C_4H_6N_4)_n$. Calculated: C 43.6; H 5.4%.

Under conditions analogous to those used for (II), the poly(aminovinyltriazole) forms complexes with $CoCl_2$, CH_3I, and HCl. Found, respectively: Cl 6.3%. $[(C_4H_6N_4)_9 \cdot CoCl_2]_n$. Calculated: Cl 6.3%; I 49.6%. $[(C_4H_6N_4) \cdot CH_3I]_n$, I 50.3%; Cl 24.5%. $[(C_4H_6N_4) \cdot HCl]_n$, Cl 24.2%.

3-Amino-1-ethyl-1,2,4-triazole. In the presence of Raney nickel, 3 g (0.027 mole) of (II) in 50 ml of absolute ethanol was hydrogenated until the absorption of hydrogen ceased, and then 2.42 g (79.2%) of white crystals with mp 81-82°C were isolated. Found: C 42.9; H 7.2; N 50.2%. $C_4H_8N_4$. Calculated: C 42.8; H 7.1; N 50.0%.

3-Amino-1-(α,β-dibromoethyl)-1,2,4-triazole. With stirring, a solution of 0.75 g (4 mmoles) of bromine in 10 ml of ethanol was added over 30 min to a solution of 0.5 g (4 mmoles) of (II) in 10 ml of ethanol. The reaction mixture was kept for 5 h, and then the solvent was evaporated off and the crystals that deposited were washed with acetone and dried. Yield 0.53 g (40.7%) of white crystals with mp 148-149°C. Found: Br 58.5%. $C_4H_6Br_2N_4$. Calculated: Br 59.0%.

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