REACTION OF 1,2,4-TRIAZOLE-3-THIONE WITH ACETYLENE

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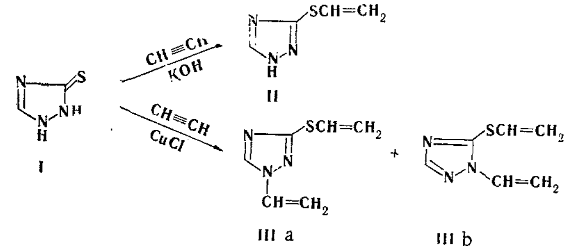
A mixture of 1,2,4-triazol-3-yl vinyl sulfide and N,S-divinyl derivatives is formed in the reaction of 1,2,4-triazole-3-thione with acetylene under pressure. The mixture of N,S-divinyl derivatives was separated into two isomers by gas–liquid chromatography. The hydrogenation, polymerization, and complexing of 1,2,4-triazol-3-yl vinyl sulfide were studied.

In the present research we set out to investigate the peculiarities of the behavior of 1,2,4-triazole-3-thione (I) on reaction with acetylene under pressure and to study some transformations of the synthesized vinyl derivatives.

1,2,4-Triazol-3-yl vinyl sulfide (II) in yields up to 70% and a small amount of derivatives with two vinyl groups were obtained when triazolethione I was heated up to 180 deg C with acetylene under pressure in the presence of potassium hydroxide. An increase in the reaction time leads to a decrease in the yield of sulfide II and a simultaneous increase in the yield of the divinyl derivatives. When cuprous chloride is used as the catalyst, in analogy with imidazolethiones [1, 2], sulfide II remains the principal reaction product. Divinyl derivatives in up to 43% yield in the form of a liquid fraction that distills at 93-122 deg C (3 mm) can be obtained only by doubling the amount of CuCl. This fraction was separated by gas–liquid chromatography (GLC) into 1-vinyl- (IIIa) and 2(4)-vinyl-3-vinylthio-1,2,4-triazole (IIIb), the ratio of which was 1 : 2.



The use of PMR spectroscopy made it possible to determine the locations of the vinyl groups in II and III. The chemical shifts of the signals and the spin–spin coupling constants (SSCC) of the olefinic protons are characteristic for double bonds attached to sulfur and nitrogen atoms [3] (Table 1). The IR spectra of IIIa and IIIb do not contain absorption bands of NH groups; the bands at 1593 and 1652 cm^{-1} are due to the stretching vibrations of C$=$C bonds attached, respectively, to the sulfur and nitrogen atoms. The absorption at 3100 cm^{-1}, which is due to vibrations of associated NH groups, is retained in the spectrum of sulfide II. The absorption band at 1550 cm^{-1} that is characteristic for the thioamide fragment in triazole systems [4, 5] vanishes in the IR spectra of both III and sulfide II.

The reactivity of thione I in the reaction with acetylene is somewhat reduced as compared with the reactivities of the previously investigated imidazole- and benzimidazolethiones [1, 2], as evidenced by the lower yields of the corresponding vinylation products under similar conditions. This can probably be explained by the decrease in the nucleophilicity of the sulfur atom due to the incorporation of a tertiary nitrogen atom in the five-membered ring.

An attempt to raise the yield of the vinyl compounds through a further increase in the temperature as in the vinylation of 1,2,4-triazole [6] was unsuccessful, since in this case we observed thermal polymerization of the resulting vinyl derivatives, which lowers the overall yield of the desired product to a considerable degree.

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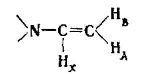
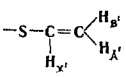
TABLE 1. Parameters of the PMR Spectra



$>N-C(H_X)=CH_AH_B$



$-S-C(H_{X'})=CH_{A'}H_{B'}$

Compound	Chemical shifts, δ, ppm							Spin-spin coupling constants, J, Hz					
	H_A	H_B	H_X	H_A'	H_B'	H_X'	H_{ring}	$H_A'\cdot H_X$	$H_B'\cdot H_X$	$H_A'\cdot H_B$	$H_A'\cdot H_X'$	$H_B'\cdot H_X'$	$H_A'\cdot H_B'$
II	—	—	—	5,45	5,50	6,76	8,18	—	—	9,8	16,7	0	—
IIIa	4,90	5.69	6,88	5,46	5,43	6,48	7,71	14,8	0,6	9,6	16,4	0,5	8,6
IIIb	4,90	5,65	6,89	5,35	5,42	6,95	7,98	15,0	1,0	9,2	16,5	0	8,6
V	—	—	—	5,62	5,67	6,75	9,20	—	—	8,8	16,4	0,8	—

The complete (100%) conversion to a polymer in 10 h under the influence of azobisisobutyronitrile (AIBN) constitutes evidence for the high activity of vinyl sulfide II in the polymerization reaction. Compound II readily undergoes copolymerization with vinylpyrrolidone via a radical mechanism to give a water-soluble copolymer.

In the presence of a nickel catalyst sulfide II undergoes hydrogenation to give 1,2,4-triazol-3-yl ethyl sulfide (IV), which was also obtained by alkylation of triazolethione I with ethyl bromide.

The corresponding hydrochloride (V) is formed in the reaction of sulfide II with hydrogen chloride. The shift in the bands of the ring stretching vibrations to the short-wave region (1474 → 1552 cm^{-1}) and the absorption at 2500-2600 cm^{-1} provide evidence for salt formation. The reaction of sulfide II with zinc chloride is evidently realized through the unshared electron pair of the nitrogen atom in the 4 position and the vacant d orbitals of the metal. Polymerization of the resulting complex, in which the ratio of the ligand and the salt is 2 : 1 and 3 : 1, proceeds simultaneously.

EXPERIMENTAL

The IR spectra of KBr pellets and mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a BS487B spectrometer with hexamethyldisiloxane as the internal standard. Preliminary GLC was realized with a Khrom-3 chromatograph with 15% polyphenyl ether on Chromaton as the stationary phase and a 2.5 m by 10 mm column; the column temperature was 180 deg C, the vaporizer temperature was 200 deg C, and the carrier gas was helium. The starting 1,2,4-triazole-3-thione (I) was obtained by condensation of thiosemicarbazide with formic acid and subsequent cyclization by the method in [7].

1,2,4-Triazol-3-yl Vinyl Sulfide (II). A 0.5-liter rotating steel autoclave was charged with 10 g (0.1 mole) of triazolethione I, 2.0 g (0.04 mole) of KOH, and 100 ml of dioxane. Acetylene was fed into the autoclave from a cylinder at an initial pressure of 14 atm. The reaction mixture was heated at 180 deg C for 1 h, after which it was cooled to room temperature, and the solid material was removed by filtration. The dioxane was removed from the filtrate by distillation at reduced pressure, and the solid residue was recrystallized from ether–hexane to give 8.2 g (66%) of white crystals with mp 103-104 deg C. Found: C 37.9; H 3.8; N 33.1; S 24.8%. $C_4H_5SN_3$. Calculated: C 37.9; H 3.9; N 33.0; S 25.2%.

N-Vinyl-3-vinylthio-1,2,4-triazoles (IIIa, b). A mixture of 5 g (50 mmole) of triazole I, 0.5 g (8 mmole) of CuCl, and 75 ml of dioxane was saturated with acetylene and heated in an autoclave at 180 deg C for 3 h. The dioxane was then removed, and the residue was vacuum distilled in a nitrogen atmosphere with collection of 3.3 g (43%) of a fraction with bp 93-122 deg C (3 mm). Preparative GLC yielded 36% isomer IIIa and 64% isomer IIIb. Isomer IIIa polymerized rapidly and had n_D^{20} 1.5760. Isomer IIIb had d_4^{20} 1.1849, n_D^{20} 1.5832, and ΔMR_d 0.3. Found: C 46.8; H 4.7; S 20.6%. $C_6H_7SN_3$. Calculated: C 47.0; H 4.6; S 20.9%.

Polymerization of 1,2,4-Triazol-3-yl Vinyl Sulfide (II). An ampul containing 0.5 g (4 mmole) of II, 0.005 g (1%) of AIBN, and 12 ml of absolute benzene was heated in a thermostat at 80 deg C for 10 h, after which the precipitated polymer was removed by filtration, washed with hot absolute benzene, and dried in a vacuum desiccator to give 0.5 g (100%) of a product with mp 253-276 deg C. Found: C 38.2; H 4.1; S 25.3%. $(C_4H_5N_3S)_n$. Calculated: C 37.9; H 3.9; S 25.2%.

Copolymerization of 1,2,4-Triazol-3-yl Vinyl Sulfide with Vinylpyrrolidone. A 0.003-g (1%) sample of AIBN was added to an ampul containing 0.25 g (2.3 mmole) of II and 0.26 g (2.3 mmole) of vinylpyrrolidone in 7 ml of benzene, and the ampul was sealed and heated in a thermostat at 80 deg C for 24 h. The resulting precipitate was removed by filtration and reprecipitated from ethanol by the addition of ether. It was then dried in vacuo to give 0.4 g (73%) of the copolymer with mp 90-120 deg C. Found: C 50.3; H 6.2; S 13.6%. $C_4H_5N_3S \cdot C_6H_9NO$. Calculated: C 50.4; H 5.9; S 13.5%. IR spectrum: 1485 (C=N), 1710 (CO), 2960 (CH_2), and 3450 cm^{-1} (NH).

1,2,4-Triazol-3-yl Ethyl Sulfide (IV). A hydrogenation flask was charged with 0.5 g (4 mmole) of vinyl sulfide II, 10 ml of ethanol, and 4.0 g of Raney nickel catalyst, and the reaction was carried out at 20 deg C with constant stirring. At the end of the process, the catalyst was removed by filtration, and the alcohol was removed from the filtrate by distillation to give 0.24 g (47%) of a product with mp 65-67 deg C. No melting-point depression was observed for a mixture of a sample of this product with a sample of the compound obtained by alternative synthesis. Found: C 37.5; H 5.7; N 32.8; S 25.3%. $C_4H_7N_3S$. Calculated: C 37.2; H 5.5; N 32.6; S 24.8%.

1,2,4-Triazol-3-yl Vinyl Sulfide Hydrochloride (V). Dry hydrogen chloride was bubbled into a solution of 1 g (8 mmole) of sulfide II in 40 ml of ether at room temperature, and the resulting precipitate was removed by filtration and washed with ether to give 1.2 g (94%) of a product with mp 118-119 deg C. Found: Cl 21.7; S 19.6%. $C_4H_5N_3S \cdot HCl$. Calculated: Cl 21.7; S 19.6%.

Poly[bis(1,2,4-triazol-3-yl vinyl sulfide)zinc dichloride]. A solution of 0.3 g (2.5 mmole) of $ZnCl_2$ in 10 ml of ether was added to a solution of 0.62 g (5 mmole) of sulfide II in 25 ml of ether, and the mixture was stirred for 5 h. The solvent was then evaporated, and the residue was washed repeatedly with ether. The yield of product with mp 200-240 deg C was 0.8 g (87%). Found: Cl 17.5; S 16.0%. $[(C_4H_5N_3S)_2 \cdot ZnCl_2]_n$. Calculated: Cl 18.1; S 16.6%. IR spectrum: 1505 cm^{-1} (C=N).

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