5-(γ-Hydroxypropyl)-1,2-dihydropyrrolizine (XII). A solution of 1.7 g (45 mmole) of LiAlH₄ in 70 ml of absolute ether was placed in a three-necked 500-ml flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser, and a solution of 11 g (57 mmole) of VII in 70 ml of absolute ether was added with vigorous stirring in the course of 30 min. The reaction mixture was then refluxed for 1 h, after which the excess LiAlH₄ was decomposed by the successive addition of 10 ml of moist ether and 10 ml of water. The ether layer was separated, and the solid material was extracted three times with ether. The ether extract was dried with magnesium sulfate, the ether was removed, and the residue was distilled at reduced pressure to give 7.2 g (77%) of XII in the form of a moderately viscous colorless liquid.

Compounds XIII-XVI were similarly obtained.

LITERATURE CITED

REACTION OF PYRIDINE-2-THIONE WITH ACETYLENES

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In contrast to 2-pyridone, pyridine-2-thione reacts with acetylene with the participation of one reaction center — the sulfur atom. The reaction with phenylacetylene and diacetylene proceeds stereospecifically to give products with cis structures. The structures of the synthesized compounds were confirmed by chemical and spectroscopic methods.

The most stable tautomeric form of pyridine-2-thione, which is capable of prototropic transformations, is form I with a proton attached to the nitrogen atom [1]. In this connection, in the reaction with acetylenes one should have expected the formation of primarily N-vinyl derivatives; however, the possibility of the manifestation by thione I of dual reactivity with the formation of both N-substituted and S-substituted derivatives [2] is not excluded.

In the present research we studied the reaction of thione I with acetylene, phenylacetylene, and diacetylene under various catalytic conditions in order to search for methods for the synthesis of new N- and S-vinyl monomers of the pyridine series and to study their properties.
We have found that replacement of the oxygen atom in 2-pyridone by a sulfur atom changes the character of its reaction with acetylene. Regardless of the nature of the catalyst used, we were unable to obtain an N-vinyl derivative of thione I. We did not detect 1-vinlylpyrindine-2-thione (II) by analysis of the reaction mixture by means of thin-layer chromatography (TLC) and IR spectroscopy. In the presence of potassium hydroxide, cadmium acetate, and cuprous chloride thione I reacts with acetylene only at the sulfur atom. Thione I reacts similarly with phenylacetylene and diacetylene to give 2-styrylthiopyridine (IIIb) and 2-(2-ethynyl)vinylthiopyridine (IIIc). We were also unable to obtain thione II by thionation of 1-vinyl-2-pyridone with phosphorus pentasulfide in pyridine and without a solvent. Mainly the starting compound and a small amount of thione I are present in the reaction mixture at 80-85°C, and resinification occurs at higher temperatures (130-140°C).

![Chemical structures](image)

It should be noted that the reaction of thione I with acetylene under pressure proceeds under milder temperature conditions as compared with 2-pyridone. Thus vinyl sulfide IIIa is formed in 50% yield at 130-135°C in the presence of 0.6 mole of KOH. At lower concentrations cadmium acetate and cuprous chloride were found to be more active catalysts than potassium hydroxide. Thus the use of 0.1 mole of cadmium acetate or cuprous chloride leads to the formation of S-vinyl compound III in up to 70% yield. The yield of vinyl sulfide III is halved in the presence of the same catalytic amount (0.1 mole, 5%) of KOH. The high catalytic activity of cadmium acetate and cuprous chloride is probably due to their ability to form π complexes with acetylene [3].

The PMR and IR spectral data confirm the structures of the synthesized vinyl sulfides IIIa-c (Table 1). The spin-spin coupling constants of the protons of the vinyl group in IIIb,c are 10-11 Hz. This constitutes evidence that the addition of thione I to the triple bond of phenylacetylene and diacetylene proceeds stereospecifically to give products with cis-structures. According to the data in [4], the addition of 6-substituted pyridine-2-thiones to acetylenic carbonyl derivatives in the absence of a catalyst proceeds primarily with the formation of cis isomers.

The IR spectrum of vinyl sulfide IIIa in the region (1400-1650 cm⁻¹) of the frequencies of vibrations of the ring and vinyl group contains absorption bands at 1583, 1562, 1455, and 1415 cm⁻¹, whereas the spectrum of the starting thione I contains bands at 1616, 1581, 1500, and 1440 cm⁻¹. It is known that the frequencies of the vibrations of the C=C and C-H bonds of the thiopyridine group are characterized by bands at 3070, 1580, 1430, 1233, 960, and 870 cm⁻¹ [15]. However, the vibrations of the C=C, C=N, and C-H bonds of the pyridine ring appear at approximately the same frequencies, and this hinders a clear assignment of the bands.

Vinyl sulfides IIIa,c are high-boiling liquids, whereas IIIb is a solid with mp 48°C. The sulfides are soluble in ethanol, diethyl ether, and carbon tetrachloride. Hydrogenation of IIIa over Raney nickel gives 2-ethylthiopyridine (IV), which was also obtained by alternative synthesis by reaction of thione I with ethyl bromide in alkaline media. The frequencies of the ring vibrations in the IR spectrum of sulfide IV are characterized by absorption bands