5-(γ-Hydroxypropyl)-1,2-dihydropyrrolizine (XII). A solution of 1.7 g (45 mmole) of $LiAlH_4$ 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 $LiAlH_4$ 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

1. I. M. Skvortsov, S. A. Kolesnikov, Yu. Yu. Samitov, and G. D. Shcherbakova, Khim. Geterotsikl. Soedin., No. 8, 1090 (1977).
2. S. A. Kolesnikov, I. M. Skvortsov, and Yu. Yu. Samitov, Zh. Org. Khim., 7, 1533 (1971).
3. A. A. Ponomarev, I. M. Skvortsov, and V. M. Levin, Khim. Geterotsikl. Soedin., No. 10, 1339 (1970).
4. I. M. Skvortsov, V. M. Levin, and I. Ya. Evtushenko, Khim. Geterotsikl. Soedin., No. 7, 995 (1971).
5. I. M. Skvortsov and S. A. Kolesnikov, Khim. Geterotsikl. Soedin., No. 4, 572 (1971).
6. A. A. Ponomarev, L. N. Astakhova, and V. N. Volkolupov, in: Methods for the Synthesis of Chemical Reagents and Preparations [in Russian], Vol. 26, Moscow (1974), p. 190.
7. R. A. Raphael et al. (editors), Advances in Organic Chemistry, Vol. 5, Wiley-Interscience (1965).
8. F. Dalton, G. D. Meakins, J. H. Robinson, and W. Zaharia, J. Chem. Soc., 1566 (1962).
9. M. Oki, H. Iwamaura, T. Onoda, and M. Iwamura, Tetrahedron, 24, 1905 (1968).
10. M. Oki and H. Iwamura, Bull. Chem. Soc. Jpn., 33, 717 (1960).
11. A. Weissberger, A. Proskauer, J. Riddick, and A. Toops, Organic Solvents [Russian translation], Inostr. Lit., Moscow (1958), pp. 25, 175.
12. I. M. Skvortsov, I. V. Antipova, Yu. A. Pentin, Hoan Tran Suan, and S. V. Vasil'kovskii, Khim. Geterotsikl. Soedin., No. 8, 1087 (1975).

REACTION OF PYRIDINE-2-THIONE WITH ACETYLENES

G. G. Skvortsova, D. G. Kim, and L. V. Andriyankova

UDC 547.825

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.

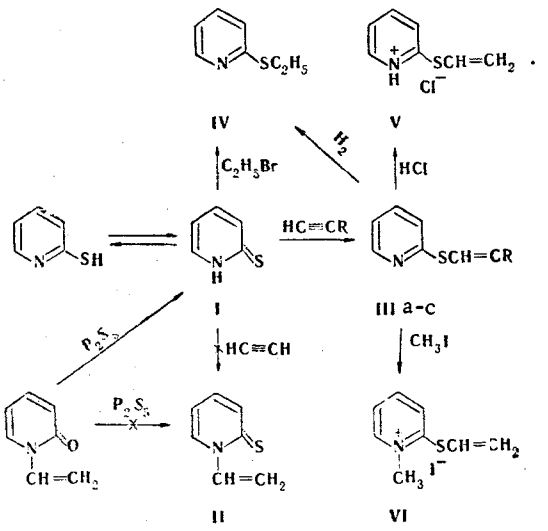
In the present research we studied the reaction of thione I with acetylene, phenylacetylene, and diacetylene under various catalytic conditions in order to search for methods for the synthesis of new N- and S-vinyl monomers of the pyridine series and to study their properties.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Irkutsk 664033.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 364-367, March, 1978. Original article submitted June 30, 1977.

0009-3122/78/1403-0297$07.50

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-vinylpyridine-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).



III a R = H; b R = C_6H_5; c R = C≡CH

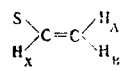
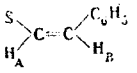
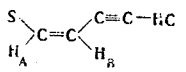
It should be noted that the reaction of thione I with acetylene under pressure proceeds under milder temperature conditions as compared with 2-pyridone. Thus vinyl sulfide IIIa is formed in 50% yield at 130-135°C in the presence of 0.6 mole of KOH. At lower concentrations cadmium acetate and cuprous 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 thiovinyl 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

TABLE 1. Data from the PMR Spectra

R	Chemical shift, δ, ppm	Spin–spin coupling constant, J, Hz
	H_A 5,44 H_B 5,40 H_X 7,16	AX 18 BX 11
	H_A 7,51 H_B 6,55	AB 11
	H_A 7,80 H_B 5,64 H_C 3,40	AB 10,3 BC 2,5 AC 0,7
—CH_2CH_3	CH_2 3,12 CH_3 1,44	8,0

at 1570, 1550, 1444, and 1406 cm^{-1}. Vinyl sulfide IIIa reacts with dry hydrogen chloride and methyl iodide to give, respectively, 2-vinylthiopyridine hydrochloride and methiodide (V and VI), which are soluble in water. We have shown that, in contrast to 2-vinyloxypyridine, vinyl sulfide IIIa is converted quantitatively to a chloroform-soluble polymer at 80°C under the influence of azobisisobutyronitrile.

EXPERIMENTAL

The PMR spectra of the compounds in CCl_4 were recorded with a BS487B spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of microlayers of the liquid compounds and of KBr pellets of the solid compounds were obtained with a UR-20 spectrometer.

2-Vinylthiopyridine (IIIa). A) A 0.5-liter rotating steel autoclave was charged with 11.1 g (0.1 mole) of pyridine-2-thione, 3.4 g (0.06 mole) of KOH, 90 ml of dioxane, and 3 ml of water, after which acetylene was fed in from a cylinder at 12-15 atm. The reaction mixture was heated at 175-185°C for 1 h, after which the autoclave was cooled, and the contents (a dark-brown liquid) were removed. The dioxane was removed from the mixture by distillation, and the residue was vacuum distilled to give 11 g (80%) of 2-vinylthiopyridine with bp 94°C (10 mm), d_4^{20} 1.1036, and n_D^{20} 1.6035. Found, %: C 61.0; H 5.1; S 22.8; MR_D 42.70. C_7H_7NS. Calculated, %: C 61.3; H 5.1; S 23.4; MR_D 42.12.

B) Similarly, 9.9 g (72%) of 2-vinylthiopyridine was obtained from 11.1 g of pyridine-2-thione in the presence of 1 g (0.01 mole) of CuCl.

C) Similarly, 9.3 g (68%) of 2-vinylthiopyridine was obtained in the presence of 2.7 g (0.01 mole) of $Cd(CH_3COO)_2 \cdot 2H_2O$.

2-Styrylthiopyridine (IIIb). An ampul was charged with 3.7 g (0.03 mole) of pyridine-2-thione, 1.8 g (0.03 mole) of KOH, 6.8 g (0.06 mole) of phenylacetylene, 35 ml of dioxane, and 3 ml of water, and the mixture was heated at 190-200°C for 1 h. The resulting precipitate was removed by filtration, the dioxane was removed by distillation, and the residue was vacuum distilled to give 3 g (40%) of 2-styrylthiopyridine with mp 48°C (from petroleum ether). Found, %: C 73.4; H 5.3; S 15.0. $C_{13}H_{11}NS$. Calculated, %: C 73.2; H 5.1; S 15.3.

2-(2-Ethynyl)vinylthiopyridine (IIIc). A three-necked flask equipped with a stirrer, a reflux condenser, and a gas-inlet tube was charged with 2.2 g (0.02 mole) of pyridine-2-thione, a solution of 0.7 g of KOH, in 15 ml of ethanol, and 30 ml of dioxane, and the mixture was heated on a water bath to 50°C during which diacetylene was bubbled through it for 4 h. The solution became darker during this period. The solvent was then removed by distillation, and the residue was extracted with chloroform. The chloroform was removed from the extract by distillation, and the residue was vacuum distilled to give 1.3 g (40%) of IIIc with bp 132°C (8 mm), d_4^{20} 1.1290, and n_D^{20} 1.6410. Found, %: C 66.1; H 4.4; S 19.3; MR_D 51.75. C_9H_8NS. Calculated, %: C 66.7; H 4.9; S 19.7; MR_D 49.35.

2-Ethylthiopyridine (IV). A) A hydrogenation flask was charged with 2.5 g (0.02 mole) of 2-vinylthiopyridine, 1 g of Raney nickel, and 20 ml of absolute ethanol, and hydrogen from a gasometer was bubbled into the mixture for 48 h, during which the calculated amount (0.5 liter) of hydrogen was absorbed. The catalyst was then removed by filtration, the ethanol was removed by distillation, and the residue was vacuum distilled to give 1.3 g (50%) of 2-ethylthiopyridine with bp 67°C (3 mm), d_4^{20} 1.0801, and n_D^{20} 1.5725. Found, %: C 60.9; H 6.2; S 22.9; MR_D 42.36. C_7H_9NS. Calculated, %: C 60.4; H 6.4; S 23.0; MR_D 42.58.

B) A three-necked flask equipped with a stirrer, thermometer, and a reflux condenser was charged with 4.4 g (0.04 mole) of pyridine-2-thione, 4.75 g (0.043 mole) of ethyl bromide, 2.2 g (0.04 mole) of KOH, and 30 ml of ethanol, and the mixture was refluxed for 3 h. The ethanol was then removed by distillation, and the residue was treated with ether. The ether was removed by distillation, and the residue was vacuum distilled to give 3.9 g (70%) of 2-ethylthiopyridine.

2-Vinylthiopyridine Hydrochloride (V). Hydrogen chloride was passed into a solution of 0.45 g (0.003 mole) of 2-vinylthiopyridine in 15 ml of diethyl ether, and the white precipitate that formed immediately was removed by filtration, dissolved in ethanol, reprecipitated by the addition of ether, and vacuum dried to give 0.5 g (86%) of 2-vinylthiopyridine hydrochloride with mp 103°C. Found, %: S 17.9; Cl 20.6. $C_7H_7NS \cdot HCl$. Calculated, %: S 18.4; Cl 21.0.

2-Vinylthiopyridine Methiodide (VI). A three-necked flask equipped with a reflux condenser, stirrer, and thermometer was charged with 1.37 g (0.01 mole) of 2-vinylthiopyridine, 5.7 g (0.04 mole) of methyl iodide, and the mixture was heated at 45-50°C for 5 h. It was then treated with diethyl ether, and the precipitate was dissolved in ethanol and reprecipitated by the addition of ether to give 2.6 g (93%) of 2-vinylthiopyridine methiodide with mp 105°C. Found, %: S 11.7; I 44.8. $C_7H_7NS \cdot CH_3I$. Calculated, %: S 11.5; I 45.5.

Poly(2-vinylthiopyridine). A glass ampul was charged with 1.37 g (0.001 mole) of 2-vinylthiopyridine and 0.02 g (1.5%) of azobisisobutyronitrile, nitrogen was blown into the ampul, and the ampul was sealed and thermostatted at 80°C for 9 h, during which a dark-brown mass was formed. The mass was dissolved in chloroform and precipitated by the addition of petroleum ether. The precipitate was washed with diethyl ether and vacuum dried to give 1 g (73%) of poly(2-vinylthiopyridine) with mp 65-73°C. Found, %: C 61.2; H 5.3; S 22.7. C_7H_7NS. Calculated, %: C 61.3; H 5.1; S 23.4; M ~ 2000.

LITERATURE CITED

1. R. A. Jones and A. R. Katritzky, J. Chem. Soc., No. 10, 3610 (1958).
2. M. F. Shostakovskii, G. G. Skvortsova, S. M. Tyrina, Yu. L. Frolov, N. M. Deriglazov, V. K. Voronov, and N. A. Ivanova, Dokl. Akad. Nauk SSSR, 186, 620 (1969).
3. O. N. Temkin and R. M. Flid, Catalytic Transformations of Acetylene Compounds in Solutions of Complex Metals [in Russian], Nauka, Moscow, (1968), p. 11.
4. K. Undheim and L. A. Riege, J. Chem. Soc., Perkin Trans. I, No. 15, 1493 (1975).
5. L. J. Bellamy, New Data on the IR Spectra of Complex Molecules [Russian translation], Mir, Moscow (1971), p. 318.