5(4)-Methoxyimidazole-4(5)-thiocarbamide (IV). A 0.15-g (1.06 mmole) sample of methoxyimidazolecarboxamide VIII was suspended in 30 ml of absolute dioxane, 0.22 g (0.5 mmole) of P_4S_{10} was added, and the reaction mixture was refluxed with stirring for 5 h. It was then evaporated in vacuo to dryness, and the residue was refluxed in 80 ml of 0.1 N HCl with activated charcoal. The mixture was filtered, and the filtrate was evaporated in vacuo to dryness. The residue was dissolved in 2 ml of water, and the solution was neutralized with 10% sodium carbonate solution. The precipitate was removed by filtration to give 0.03 g (18%) of a product with mp 246-248°C and R_f 0.6 (1), 0.46 (2), and 0.17 (3). UV spectrum (water), λ_{max} (log ε): 272 (4.39) and 339 (3.76). Found: N 26.4; S 20.4%. $C_3H_7N_3OS$. Calculated: N 26.7; S 20.7%.

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REACTIONS OF IMIDAZOLETHIONES WITH PHENYLCYANOACETYLENE

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The reaction of phenylcyanoacetylene with imidazolethiones was studied. It is shown that in the presence of 5-10% KOH the addition of phenylcyanoacetylene is accompanied by intramolecular cyclization with the formation of imidazo-1,3-thiazines. An increase in the amount of catalyst to 20% leads to cleavage of the thiazine ring at the C-S bond and the formation of the corresponding acrylonitrile derivatives. Products of addition of 2 moles of phenylcyanoacetylene were obtained.

The existence of imidazolethiones in two tautomeric forms is responsible for their ability, depending on the conditions, to add acetylene to the sulfur or nitrogen atom. We have previously shown that azolyl vinyl sulfides are primarily formed in the reaction with acetylene as a consequence of the great nucleophilicity of sulfur [1, 2]. The reaction with acetylenic acid esters takes place at the same center [3, 4]. Information that activated acetylenes react at the nitrogen atom of the thioamide grouping was recently published [5].

In the present research we studied the reaction of 1-phenyl-2-cyanoacetylene (I) with benzimidazole-2-thione (II) and 4,5-diphenylimidazole-2-thione (III).

The addition of activated acetylene I to azolethiones II and III proceeds readily in the presence of 5-10% potassium hydroxide and is accompanied by intramolecular cyclization at the nitrile group. The investigated reaction proceeds with high regio- and stereospecificity, and, according to the PMR spectral data, the reaction mixture contains only one isomer. 2-Imino-

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4-phenylbenzimidazo[2,3-b]-1,3-thiazine (IV) and 2-imino-4,6,7-triphenylimidazo[2,3-b]-1,3-thiazine (V) were isolated in up to 80% yields



 $X = (CH)_4, 2C_6H_5$

The IR spectra of thiazines IV and V contain characteristic absorption bands of an N-C=CH group (1624 cm⁻¹) but do not contain bands of stretching vibrations of a nitrile group (2230 cm⁻¹). A singlet of the olefin proton of the thiazine ring at 6.64 ppm, a multiplet of aromatic protons at 7.49 ppm, and a signal of the proton of an imino group at 8.44 ppm are present in the PMR spectrum of IV.

Cleavage of the thiazine ring and the formation of, respectively, 1(3)-(1-phenyl-2-cyano-vinylene)benzimidazole-2-thione (VI) and $1(3)-(1-phenyl-2-cyanovinylene)-4,5-diphenylimida-zole-2-thione (VII) are observed in the reaction of thiazines IV and V with alkali (20% KOH). Identical VI and VII were obtained in the reaction of acetylene I with starting azolethiones II and III in the presence of 20% KOH. An absorption band at 2230 cm⁻¹ (CN) is present in the IR spectra of acrylonitriles VI and VII. The absorption at 1625 cm⁻¹ should be assigned to the N-C=CH group. The long-wave absorption in the UV spectra at 303 nm (log <math>\epsilon$ 4.32) corresponds to a $\pi-\pi^*$ transition of the chromophore thioamide group. The PMR spectrum of acrylonitrile VI contains signals of an olefin proton (6.88 ppm) and the proton of the NH group (11.90 ppm) and a multiplet of aromatic protons (7.46 ppm).

To obtain additional evidence for the direction of primary addition of acetylene to azole thiones II and III we accomplished the reaction of 2-methylthiobenzimidazole (VIII) with phenylcyanoacetylene. Independently of this, we carried out the methylation of decyclization product VI. According to the PMR spectra, 2-methylthio-1(3)-(1-phenyl-2-cyanovinylene)benz-imidazole (IX) was obtained in both cases.



The PMR spectrum of product IX contained the following signals: 2.29 (CH₃), 6.11 (-C=-CH), and 6.87-7.83 ppm (C_6H_5).

The close reactivities of the NH and SH groups in the investigated imidazolethiones is confirmed by the fact that azolethione derivatives II and III, which have a vinyl group attached to the nitrogen or sulfur atom, react with acetylene under identical conditions and give, respectively, l-vinyl-2-[(l-phenyl-2-cyanovinylene)thio]benzimidazole (X) and 1(3)-(1-phenyl-2-cyanovinylene)-2-vinylthio-4,5-diphenylimidazole (XI). The IR spectra of the latter contain absorption bands of a C=C bond attached to the nitrogen atom at 1640 and 1624 cm⁻¹ for X and XI, respectively, and of a C=C bond attached to a sulfur atom at 1560 and 1590 cm⁻¹.

Thus the addition of acetylene I to imidazolethiones II and III takes place initially at the NH group and is accompanied by intramolecular cyclization at the exocyclic sulfur atom. An increase in the amount of catalyst (KOH) to 20% leads to cleavage of the resulting thiazines IV and V at the more labile C-S bond to give 1(3)-acrylonitriles VI and VII.

The use of excess acetylene I in the reaction with imidazolethiones II and III leads to the production of 1-(1-pheny1-2-cyanovinylene)-2-[(1-pheny1-2-cyanovinylene)thio]benzimidazole (XII) and 1-(1-pheny1-2-cyanovinylene)-2-[(1-pheny1-2-cyanovinylene)thio]-4,5-dipheny1imidazole (XIII) in quantitative yields. The addition of the first mole evidently proceeds through the formation of the corresponding thiazine and its subsequent decyclization.

The higher reactivity of the imino group in azolethiones II and III in their reaction with acetylene I is illustrated well by an experiment in which 1 mole of the latter was added at a high rate; signals of protons at 5.74 (S-C=CH) and 6.23 ppm (N-C=CH), which are characteristic for bis product XII, and a signal at 6.64 ppm, which is related to thiazine IV, were observed in the PMR spectrum of the reaction mixture.

In the reaction of thiazine IV with 1-phenyl-2-cyanoacetylene (I) in the presence of 5-10% KOH we were able to isolate 2-[(1-phenyl-2-cyanovinylene)imino]-4-phenylbenzimidazo[2,3b]-1,3-thiazine (XIV) as the principal product. At the same time, under the indicated conditions the reaction frequently terminated with the formation of bis derivative XII.



Bis product XIII was similarly synthesized from thiazine V.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Tesla BS-487B spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The UV spectra of solutions in dioxane were recorded with a Specord UV-vis spectrophotometer.

1-Phenyl-2-cyanoacetylene (I) was obtained by the method in [6], while 2-methylthiobenzimidazole (VIII) was obtained by the method in [7] and had mp 202°C.

2-Imino-4-phenylbenzimidazo[2,3-b]-1,3-thiazine (IV). A solution of 0.64 g (5 mmole) of 1-phenyl-2-cyanoacetylene (I) in dioxane was added with stirring at 20°C to a solution of 0.75 g (5 mmole) of benzimidazole-2-thione (II) and 0.1 g of KOH in 10 ml of dioxane. After 6 h, the dioxane was removed by distillation at reduced pressure, and the residue was recrystallized to give IV (Table 1).

2-Imino-4,6,7-triphenylimidazo[2,3-b]-1,3-thiazine (V). This compound was similarly obtained from 4,5-diphenylimidazole-2-thione (III).

1(3)-(1-Phenyl-2-cyanovinylene) benzimidazole-2-thione (VI). A mixture of 1.39 g (5 mmole) of thiazine IV and 0.28 g of KOH in 15 ml of dioxane was stirred at 20°C for 4 h, after which it was worked up as in the preceding experiments to give VI.

 $\frac{1(3)-(1-\text{Phenyl-2-cyanovinylene})-4,5-\text{diphenylimidazole-2-thione (VII)}. A mixture of 1.26 g (5 mmole) of thione III, 0.38 g of KOH, and 0.64 g (5 mmole) of acetylene I was stirred at 20°C for 6 h, after which it was worked up as in the preceding experiments to give VII. A similar product was obtained by decyclization of thiazine V.$

 $\frac{2-\text{Methylthio-1(3)-(1-phenyl-2-cyanovinylene)benzimidazole (IX).}{\text{mmole} of 2-methylthiobenzimidazole (VIII), 0.08 g of KOH, and 0.31 g (2.5 mmole) of acetylene I in dioxane was stirred at 20°C for 6 h. Chromatography with a column filled with Al₂O₃ [chloroform-benzene-ethanol (20:4:1)] gave IX.$

1-Vinyl-2-[(1-phenyl-2-cyanovinylene)thio]benzimidazole (X). A solution of 0.64 g (5 mmole) of acetylene I in 5 ml of dioxane was added dropwise to 0.88 g (5 mmole) of 1-vinyl-benzimidazole-2-thione and 0.15 g of KOH in 10 ml of dioxane, and the mixture was stirred at 20°C for 6-8 h. Workup as in the preceding experiments gave X.

<u>1(3)-(1-Pheny1-2-cyanoviny1ene)-2-viny1thio-4,5-diphenylimidazole (XI).</u> This compound was similarly obtained from 2-viny1thio-4,5-diphenylimidazole..

Com- pound	mp, * °C	Found, %			Empirical	Calc., %			Yield,
		С	Н	S	formula	С	Н	s	%
IV V VI IX XI XII XII XIII XIII XIV	$\begin{array}{c} 183 - 184 \\ 195 - 197 \\ 254 - 256 \\ 257 - 258 \\ 133 - 135 \\ 85 - 86 \\ 131 - 132 \\ 175 - 176 \\ 199 - 201 \\ 232 - 233 \end{array}$	69,4 75,9 69,2 75,9 70,0 71,6 77,1 74,4 78,1 74,1	3,84,64,14,54,54,24,93,94,23,94,23,9	11,58,611,68,311,110,27,97,96,38,0	$\begin{array}{c} C_{16}H_{11}N_3S\\ C_{24}H_{17}N_3S\\ C_{16}H_{11}N_3S\\ C_{24}H_{17}N_3S\\ C_{24}H_{17}N_3S\\ C_{17}H_{13}N_3S\\ C_{18}H_{13}N_3S\\ C_{26}H_{19}N_3S\\ C_{26}H_{19}N_3S\\ C_{25}H_{16}N_4S\\ C_{33}H_{22}N_4S\\ C_{25}H_{16}N_4S \end{array}$	69,3 76,0 69,3 76,0 70,1 71,3 77,0 74,2 78,2 74,2	$\begin{array}{r} 4,0\\ 4,5\\ 4,0\\ 4,5\\ 4,5\\ 4,5\\ 4,3\\ 4,7\\ 4,0\\ 4,4\\ 4,0\end{array}$	$ \begin{array}{c} 11,6\\8,5\\11,6\\8,5\\11,0\\10,6\\7,9\\7,9\\6.3\\7,9\end{array} $	80 63 75 80 56 53 88 79 82 85

TABLE 1. Characteristics of the Synthesized Compounds

*Compounds IV and IX were crystallized from benzene, and V-VII and XII-XIV were crystallized from ethanol. Compounds X and XI were reprecipitated from solution in benzene by pouring the solutions into hexane.

1-(1-Pheny1-2-cyanovinylene)-2-[(1-pheny1-2-cyanovinylene)thio]benzimidazole (XII). A mixture of 0.75 g (5 mmole) of thione II, 0.1 g of KOH, and 1.27 g (10 mmole) of acetylene I in dioxane was stirred at 20°C for 6 h, after which the dioxane was removed by distillation to give XII.

<u>1-(1-Phenyl-2-cyanovinylene)-2-[(1-phenyl-2-cyanovinylene)thio]-4,5-diphenylimidazole</u> (XIII). This compound was similarly obtained from thione III.

2-[(1-Pheny1-2-cyanoviny1ene)imino]-4-pheny1benzimidazo[2,3-b]-1,3-thiazine (XIV). A solution of 0.64 g (5 mmole) of acetylene I in dioxane was added to a solution of 1.39 g (5 mmole) of thiazine IV and 0.1 g of KOH in dioxane, and the mixture was stirred at 20°C for 6 h. Workup as in the preceding experiments gave XIV.

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