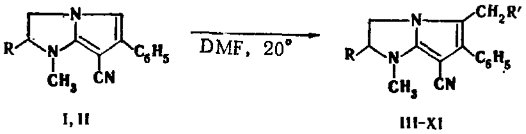

## EXPERIMENTAL

1-Methyl-6-phenyl- and 1-methyl-2-chloro-6-phenyl-7-cyanopyrrolo[1,2-a]imidazoles (I, II) were obtained by the method in [1].

5-Dialkylaminomethyl Derivatives of Pyrrolo[1,2-a]imidazole (III-XI, Table 1). A mixture of 0.05 mole of the secondary amine and 0.05 mole of a 37% solution of formaldehyde in 20 ml of dimethylformamide (DMF) was stirred at 20° for 30 min, after which 0.01 mole of the 7-cyano-derivative of pyrroloimidazole (I, II) was added, and the mixture was stirred for another 3 h. The precipitated V, VIII, X, and XI were removed by filtration and washed with aqueous alcohol. In the case of the remaining compounds, no precipitate formed; the reaction mixture was therefore cooled, and crystallization was induced by scratching a glass rod along the wall of the flask or by pouring in a twofold to threefold amount of water; the resulting oil began to crystallize on trituration with petroleum ether.

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# RADICAL ADDITION OF THIOLS TO VINYL DERIVATIVES OF 4,5-DIPHENYLIMIDAZOLE-2-THIONE

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UDC 547.786.9+547.268.1

It is shown that 2-vinylthio- and 1-vinyl-2-vinylthio-4,5-diphenylimidazoles readily add thiols to the double bond of the vinyl group attached to the sulfur atom. A vinyl group attached to the nitrogen atom undergoes only 7-15% thiylation; this is explained by the electron-acceptor effect of phenyl groups and also by steric factors.

In the present research we investigated the reaction of our previously synthesized [1] 2-vinylthio- (I) and 1-vinyl-2-vinylthio-4,5-diphenylimidazoles (II) with ethane-, butane-, and benzenethiols in order to study the reactivities of the double bonds of vinyl groups attached to different heteroatoms.

In contrast to benzimidazolyl vinyl sulfide, which reacts only with ethanethiol under homolytic conditions [2], imidazolyl vinyl sulfide I readily adds butanethiol and thiophenol, in addition to ethanethiol, to give stable 4,5-diphenyl-2-imidazolyl [$\beta$-alkyl(aryl)thioethyl] sulfides (III-V).

The synthesis of thiosulfides III-V in high yields is probably possible becuase of the high stability of the S−C bond due to the effect of two electron-acceptor substituents through the conjugated system of $\pi$, p bonds of the heteroring.

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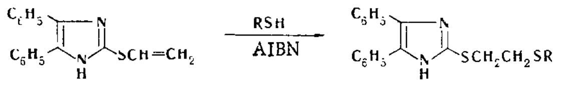


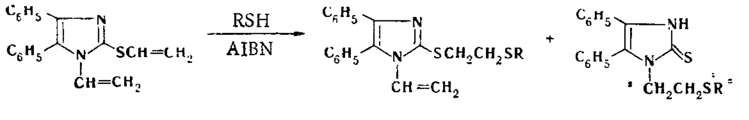
I III-V

III $R = C_2H_5$, IV $R = C_4H_9$, V $R = C_6H_5$

The absorption bands of a vinyl group attached to a sulfur atom (1590 $cm^{-1}$) vanish in the IR spectra of III-V, and new intense absorption bands, which characterize the stretching vibrations of methyl and methylene groups, appear at 2800-2970 $cm^{-1}$. The presence of the $-S-CH_2CH_2-$ fragment is characterized in the PMR spectra of III by a triplet at 2.56, 2.85, and 3.23 ppm, in the spectrum of IV by a quartet at 1.40, 2.45, 2.65, and 3.09 ppm, and in the spectrum of V by a singlet at 3.19 ppm.

Whereas 1-vinyl-2-vinylthiobenzimidazole under radical-initiation conditions reacts with thiols to give β-addition products at both vinyl groups [3], divinylmercaptoimidazole II adds alkanethiols mainly to the double bond of the vinyl group attached to the sulfur atom. As a result, new sulfur-containing N-vinyl derivatives VI and VII were synthesized.

The intense absorption band at 1642 $cm^{-1}$ due to the stretching vibrations of a vinyl group attached to a nitrogen atom is retained in their IR spectra. The absorption at 1590 $cm^{-1}$ ($-S-CH=CH_2$) vanishes completely, and bands affiliated with the stretching vibrations of $CH_2$ and $CH_3$ groups appear at 1380 and 2870-2970 $cm^{-1}$. The protons of the vinyl group attached to the nitrogen atom form an ABX spin system ($\delta_A$ 4.94, $\delta_B$ 5.10, $\delta_X$ 6.49 ppm; $J_{AB} = 1.2$ Hz, $J_{AX} = 7.2$ Hz, and $J_{BX} = 13.6$ Hz).



II VI, VII VIII

VI $R = C_2H_5$, VIII $R = C_4H_9$

An analysis of the side products in the thiylation of II showed that the vinyl group attached to the nitrogen atom undergoes 7-15% addition of the thioalkyl radical. Moreover, 1-β-ethylthioethyl-4,5-diphenylimidazole-2-thione (VIII) is formed in the reaction of imidazole II with ethyl mercaptan due to elimination of the ethylthio group attached to the sulfur atom in the 2 position of the five-membered ring. The structure of sulfide VIII is confirmed by the absence in its IR spectrum of absorption bands of both vinyl groups and by the presence of the absorption at 1510 $cm^{-1}$ characteristic for the thioamide fragment. In the reaction of divinylmercaptoimidazole II with butyl mercaptan, 1-β-butylthioethyl-2-butylthio-4,5-diphenylimidazole (IX) was isolated in small amounts along with disulfide VII.

We have previously proposed [3] a method for the synthesis of N-vinylbenzimidazole-2-thione by heating the divinyl derivative of benzimidazole-2-thione with a thiol without a catalyst. Under similar conditions, we were unable to obtain N-vinyl-4,5-diphenylimidazole-2-thione (X) from divinylmercaptoimidazole II; this is due to the high stability of the resulting sulfide. We isolated disulfide VI instead of the expected thione X.

Thus the vinyl derivatives of 4,5-diphenylimidazole-2-thione are characterized by higher stability of the C−S bond as compared with the corresponding vinyl derivatives of benzimidazole-2-thione. The double bond of the vinyl group attached to the nitrogen atom in II has lower activity in radical addition reactions; this apparently should be explained by the electron-acceptor effect of two phenyl groups and also by steric hindrance created by a bulky substituent in the 5 position of the imidazole ring. The indicated peculiarities in the structure of II make it possible to obtain new N-vinyl derivatives of imidazole that have a disulfide grouping in the 2 position.

## EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of $CCl_4$ solutions of the compounds were recorded at room temperature with a BS487B spectrometer and hexamethyldisiloxane as the internal standard. Compounds I and II were obtained by the method in [1].

4,5-Diphenyl-2-imidazolyl [β-Alkyl(aryl)thioethyl] Sulfide (III). An ampul was charged with 1.56 g (6 mmole) of I, 1.32 g (22 mmole) of ethyl mercaptan, and 0.01 g (~0.5% of the weight of the mixture) of azobisisobutyronitrile (AIBN), and the ampul was sealed and heated in a thermostat at 80° for 24 h. It was then cooled, and the excess mercaptan was removed by distillation. The crystalline residue was purified by reprecipitation from chloroform solution by the addition of hexane to give 1.4 g of product.

TABLE 1. Physical Characteristics of the Synthesized Compounds

| Compound | mp, °C | Empirical formula | Found, % |  |  | Calc., % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | C | H | S | C | H | S |  |
| III | 132—134 | $C_{19}H_{20}N_2S_2$ | 67,0 | 5,9 | 18,7 | 67,0 | 5,9 | 18,8 | 77 |
| IV | 124—126 | $C_{21}H_{24}N_2S_2$ | 68,2 | 6,6 | 17,4 | 68,4 | 6,5 | 17,4 | 85 |
| V | 141—143 | $C_{23}H_{20}N_2S_2$ | 70,8 | 5,0 | 16,1 | 71,1 | 5,2 | 16,5 | 61 |
| VI | 79—80 | $C_{21}H_{23}N_2S_2$ | 68,8 | 5,8 | 17,7 | 68,8 | 6,0 | 17,5 | 72 |
| VII | Oil | $C_{23}H_{26}N_2S_2$ | 70,3 | 6,4 | 16,2 | 70,1 | 6,6 | 16,2 | 57 |
| VIII | 121—124 | $C_{19}H_{20}N_2S_2$ | 67,4 | 6,1 | 18,4 | 67,1 | 5,9 | 18,8 | 15 |
| IX | 74—76 | $C_{25}H_{32}N_2S_2$ | 70,3 | 7,3 | 15,0 | 70,6 | 7,6 | 15,1 | 7,5 |

Sulfides IV and V were similarly obtained. The physical characteristics of the synthesized compounds are presented in Table 1.

1-Vinyl-4,5-diphenyl-2-imidazolyl β-Ethylthioethyl Sulfide (VI). A mixture of 1.5 g (4.9 mmole) of imidazole II, 2.1 g (35 mmole) of ethyl mercaptan, and 0.02 g of AIBN was heated in a sealed ampul at 80° for 24 h, after which the excess mercaptan was removed by distillation, and the residue was dissolved in chloroform and separated with a column filled with $Al_2O_3$ (elution with $CHCl_3$) to give 1.3 g of sulfide VI ($R_f$ 0.76) and 0.3 g of thione VIII ($R_f$ 0.25). Sulfides VII ($R_f$ 0.81) and IX ($R_f$ 0.2) (Table 1) were similarly obtained.

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# REDUCTION OF 4H-IMIDAZOLE N-OXIDES WITH SODIUM BOROHYDRIDE

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The reduction of derivatives of 4H-imidazole N-oxides with sodium borohydride leads, depending on the presence and position of an N-oxide group, to 1-hydroxyimidazoline or imidazolidine derivatives. Under the same conditions 4H-imidazole N,N'-dioxides form 1,3-dihydroxyimidazolidines. The reduction of 1-hydroxy-2,4,5,5-tetramethyl-3-imidazoline 3-oxide leads to N-(3-oximino-2-methyl-2-butyl)ethylhydroxylamine. It was observed by UV spectroscopy that 1-hydroxy-2-imidazolines exist in a tautomeric equilibrium with 2-imidazoline 3-oxides.

Continuing our study of the properties of 4H-imidazole derivatives, we have observed that, in contrast to covalent hydration [1, 2], the direction of their reduction depends on the presence and position of an N-oxide oxygen atom.

The literature contains information regarding the reduction of the nitrone grouping by alkali metal borohydrides. It is known, for example, that pyrroline N-oxide is reduced to N-hydroxypyrrolidine [3], and that hexamethyl-2,3-dihydropyrazine 1,4-dioxide is reduced to 1,4-dihydroxyhexamethylpiperazine [4]. The reduction of derivatives of 1-hydroxyimidazole 3-oxides leads to 1-hydroxyimidazoles [5]. Depending on the reaction conditions, open nitrones (azomethine N-oxides) may form azomethines or secondary amines [6]. The reaction

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