28 h as in the preparation of VI. The yield was 1.47 g (61%). The yellow crystals had mp 133-134°C (from alcohol). IR spectrum: 1680 cm^{-1} (C=O). Found: C 64.8; H 4.2; N 11.7%. $C_{13}H_{10}N_2OS$. Calculated: C 64.4; H 4.2; N 11.6%.

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BROMINATION OF VINYL DERIVATIVES OF BENZIMIDAZOLE-2-THIONE

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The reaction of vinyl derivatives of benzimidazole-2-thione with bromine was investigated. It is shown that the principal reaction is the addition of the halogen to the double bond of the vinyl group. Depending on the structure of the starting vinyl derivative, elimination of hydrogen bromide or halogenation at the heteroring nitrogen atom, which leads to the formation of hydrohalides, is subsequently possible.

The data available on the reaction of N-vinylazoles with bromine are limited and constitute evidence for the peculiar course of this reaction [1-3]. Thus complexing at the pyridine nitrogen atom and partial addition of the halogen to the vinyl group are primarily observed in the bromination of 1-vinylbenzimidazole.

We have studied the reaction of bromine with 1-vinyl-2-vinylthiobenzimidazole (I), 2-vinylthiobenzimidazole (II), and 1-vinylbenzimidazole-2-thione (III) in CCl_4 at –20 to 20°C.

We found that I readily adds bromine to give a difficult-to-separate mixture of products, the composition of which depends on the ratio of the starting components (Table 1). In the case of small amounts of bromine (1:0.5) poly[1-vinyl-2-(β-bromovinyl)thiobenzimidazole hydrobromide) (IV) is formed in low yield. Its IR spectrum contains the absorption band of a C=C bond attached to a nitrogen atom (1632 cm^{-1}). Under the influence of excess bromine the principal reaction product is poly[1-(α,β-dibromoethyl)-2-(β-bromovinyl)-thiobenzimidazole hydrobromide] (V).

The product of the initial addition of bromine to the vinyl group attached to the sulfur atom (VI) evidently readily splits out hydrogen bromide, which gives rise to instantaneous polymerization of the resulting 1-vinyl-2-(β-bromovinyl)thiobenzimidazole. The liberated HBr coordinates with the aza group to give hydrohalide IV. A second molecule of bromine adds to the N-vinyl group. To prove the structure of tetrabromo derivative V we accom-

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TABLE 1. Bromination of Vinyl Derivatives of Benzimidazole-2-thione (I-III)

Starting compound	Molar amt. of Br_2*	Reaction product	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
				Br	S		Br	S	
I	0,5	IV	75—103	43,5	8,3	$C_{11}H_{10}Br_2N_2S$	44,2	8,8	18
I	2	V	75—120	62,0	6,0	$C_{11}H_{10}Br_4N_2S$	61,3	6,1	25
I	3	V	85—125	62,3	5,9	$C_{11}H_{10}Br_4N_2S$	61,3	6,1	42
II	1	VIII	180—181	57,5	7,5	$C_9H_8Br_3N_2S$	57,6	7,7	41
II	2	VIII	181	57,8	7,6	$C_9H_8Br_3N_2S$	57,6	7,7	72
III	1	X	206	47,6	9,5	$C_9H_8Br_2N_2S$	47,6	9,5	72
III	2	X	206	47,7	9,4	$C_9H_8Br_2N_2S$	47,6	9,5	95
III†	1	XI	148	26,4	10,3	$C_{11}H_{13}BrN_2OS$	26,5	10,6	84

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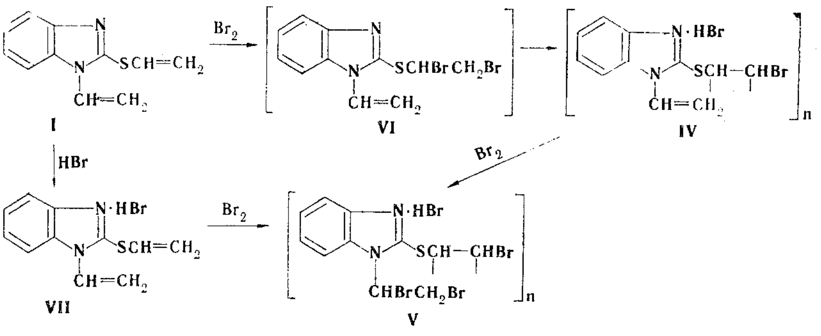
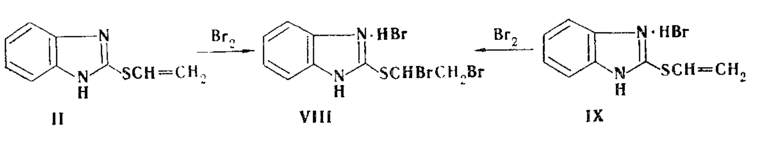
*The bromination of I was carried out at —20°C, while the bromination of II and III was carried out at 20°C.

†The reaction was carried out in ethanol.



plished its alternative synthesis by bromination of 1-vinyl-2-vinylthiobenzimidazole hydrobromide (VII). The product of this reaction is identical to derivative V. The IR spectrum of the latter does not contain the absorption bands of vinyl groups (1590 and 1632 cm^{-1}), but absorption bands of an ammonium cation (2400-2800 cm^{-1}) and a methylene group (2940 cm^{-1}) do appear in the spectrum. In addition, a shift of the band of the stretching vibrations of the heteroring to the short-wave region as a result of complexing is observed.

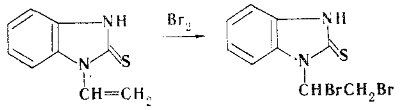
The addition of bromine to the S-vinyl group with retention of the α,β-dibromoethyl group was observed when II was treated with bromine. According to the results of elementary analysis, a tribromo derivative is formed. The absence in the IR spectrum of a free terminal C=C bond and the appearance of a broad band at 2700-3000 cm^{-1} ($\overset{+}{\mathrm{N}}\mathrm{H}$), as well as changes in the region of the stretching vibrations of the heteroring, constitute evidence in favor of the formation of 2-(α,b-dibromoethyl)thiobenzimidazole hydrobromide (VIII). We assume that replacement of hydrogen by bromine at the nitrogen atom with HBr evolution occurs along with the addition of halogen to the double bond. The resulting N—Br bond is



unstable, and bromine is readily eliminated with restoration of the N—H bond. The liberated HBr reacts with the aza group. The identical tribromo derivative VIII was obtained by the action of bromine on 2-vinylthiobenzimidazole hydrobromide (IX). The α,β-dibromoethyl group in VIII differs with respect to its greater stability as compared with derivative VI. The lability of the bromine atom in the α position is associated with the magnitude of the resulting positive charge on the α-carbon atom. The presence of a vinyl group attached to the nitrogen atom evidently favors elimination of hydrogen bromide in bromo derivative VI.

A further increase in the amount of bromine used in the reaction with I and II promotes the production of complex products with a higher percentage of halogen.

Vinyl derivative III reacts with bromine most unambiguously. It actively adds bromine to the double bond of the vinyl group to give 1-(α,β-dibromoethyl)benzimidazole-2-thione (X) in 95% yield. The protons of the α,β-dibromoethyl group of X form an ABX system and give signals in the PMR spectrum with chemical shifts δ_A 3.90, δ_B 4.50, and δ_X 6.60 ppm and coupling constants J_{AB} = 12.5, J_{AX} = 2.5, and J_{BX} = 7.0 Hz. The spin–spin coupling constants (SSCC) constitute evidence for the existence of retarded rotation relative to the carbon–carbon bond; this is evidently due to steric hindrance. Replacement of the bromine atom in the α position by an ethoxy group to give 1-(α-ethoxy-β-bromo)ethylbenzimidazole-2-thione (XI) is observed in the case of bromination of III in ethanol. The IR spectrum of bromoacetal XI is characterized by intense absorption at 1080 cm^{-1} (C–O–C). The PMR spectrum contains the following signals (CD_3OD): δ_A 4.22, δ_B 4.67, δ_X 6.48, δ_{CH_2O} 3.52, and δ_{CH_3} 1.30 ppm.



III X

The characteristics of the synthesized substances are presented in Table 1. They are white crystalline substances that are quite soluble in water.

Thus, in contrast to 1-vinylbenzimidazole, benzimidazole-2-thione derivatives I-III do not form complexes with bromine. Their principal reaction is the addition of halogen to the double bond of the vinyl group. Depending on the structure of the starting compound, elimination of hydrogen bromide or N-halogenation in the heteroring to give hydrobromides is subsequently possible.

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 DMSO or CD_3OD were recorded with a BS 487B spectrometer with DMSO or hexamethyldisiloxane as the internal standard.

Starting vinyl derivatives I-III were obtained by the methods in [4, 5].

The bromination of vinyl derivatives of benzimidazole-2-thione I-III was carried out in the cold or at 20°C in CCl_4. The products that precipitated were removed from the reaction mixture by filtration, washed with CCl_4 and ether, and reprecipitated from solution in acetone by pouring into ether (hydrobromides IV, V, and VIII) or recrystallized from benzene (X and XI).

1-Vinyl-2-vinylthiobenzimidazole Hydrobromide (VII). A stream of dry HBr was passed into a solution of 2.02 g (0.01 mole) of I in CCl_4 until absorption ceased, after which the resulting white precipitate was removed by filtration, washed repeatedly with CCl_4 and ether, and dried to give 2.52 g (89%) of VII with mp 182°C. Found: Br 28.4; S 11.2%. $C_{11}H_{11}BrN_2S$. Calculated: Br 28.2; S 11.3%.

2-Vinylthiobenzimidazole Hydrobromide (IX). This compound, with mp 183°C, was similarly obtained in 80% yield from II. Found: Br 31.0; S 12.5%. $C_9H_9BrN_2S$. Calculated: Br 31.1; S 12.5%.

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