SYNTHESIS AND SOME PROPERTIES OF N,S-DIVINYL-2-MERCAPTOBENZIMIDAZOLE

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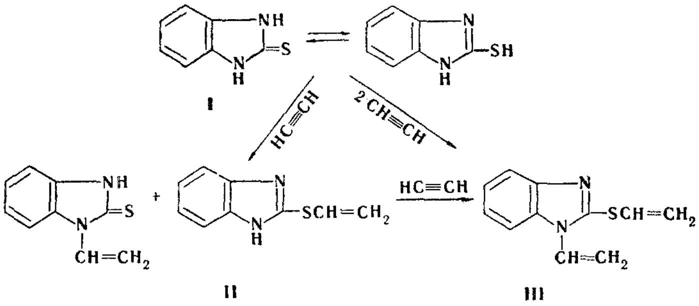
N,S-Divinyl-2-mercapto benzimidazole was obtained by reaction of 2-mercaptodimidazole with acetylene under pressure in the presence of heavy metal salts. N-Vinyl-S-ethyl-2-mercaptobenzimidazole was synthesized by hydrogenization of the product on a nickel catalyst. A high-melting polymer is obtained from N,S-divinyl-2-mercaptobenzimidazole under free-radical conditions.

Nitrogen-containing heterocyclic compounds with a mercapto group in the α or γ position with respect to the ring-nitrogen atom in a practical sense exist in the form of thione compounds with an $-NH-C=S$ grouping. In solutions under the influence of various reagents they display properties of both cyclic acid thioamides and mercaptans. In this connection, in the reaction of 2-mercaptobenzimidazole (I) with acetylene one might have expected the formation of several vinyl derivatives of I, which are presented in the following scheme:



Prilezhaeva and Shmonina [1] were able to synthesize only benzimidazolyl vinyl sulfide (II) via this reaction in the presence of potassium hydroxide. There is no information in the literature regarding the synthesis of N,S-divinyl-2-mercaptobenzimidazole (III) or other vinyl derivatives of I.

In the present research we have made a detailed study of the reaction of I with acetylene under pressure. Alkali hydroxides and some heavy metal salts were tested as catalysts. The studies showed that vinylation of I proceeds in a complex manner, and various vinyl derivatives of I are formed as a function of the conditions used. S-Vinyl compound II is formed most readily in the presence of potassium hydroxide. It was found that replacement of the alkaline catalyst by metal salts promotes reaction to favor the formation of divinyl derivative III; up to 40% II is obtained in the reaction mixture. The yields and ratios of products II and III are determined by the nature and

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concentration of the catalyst. It should also be noted that we detected III in very small amounts (5-7%) in the synthesis of II in the presence of potassium hydroxide. We assume that the synthesis of II or III proceeds to give maximum yields via different reaction mechanisms. S-Vinyl derivative I is probably formed initially and then reacts with a second molecule of acetylene through the labile hydrogen atom attached to the nitrogen atom to give III. This is in complete agreement with the facile formation of S-derivatives as a result of attack by an electrophilic agent on compounds with a thioamide grouping. A confirmation of this reaction direction is the result of our vinylation of II under the influence of cuprous chloride. In this case, III is obtained from II in 54% yield. Cuprous chloride and cadmium acetate proved to be the most effective catalysts for the preparation of III; the yield of III reaches 84%. We were unable to synthesize monovinyl N-substituted derivatives of I under the investigated conditions.

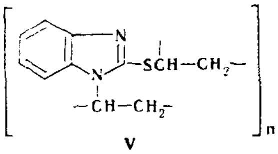
The structure of the isolated products of vinylation of I was proved by the results of elementary analysis and by IR and PMR spectroscopy.

The IR spectrum is characterized by absorption bands at 1632 and 1590 cm^{-1}, which are associated with the stretching vibrations of the C=C group attached to the nitrogen and sulfur atoms [2], and at 960 cm^{-1}, which is due to the deformation vibrations of the hydrogen atoms of the $=CH_2$ group. A terminal double bond adjacent to a heteroatom can also be identified from the weak vibrations at 3050 cm^{-1}. The complete disappearance of the frequencies of the vibrations of the NH (3300-3400) cm^{-1}) and $-HN-C=S$ (1515 cm^{-1}) groups in the spectrum of III as compared with the spectrum of benzimidazole I is also evidence for attachment of the vinyl groups to the nitrogen and sulfur atoms.

There is a difference in the chemical shifts and spin-spin coupling constants of the signals of the olefinic protons attached to the nitrogen and sulfur atoms in the PMR spectrum of III. The characteristics of the PMR spectrum are presented in Table 1.

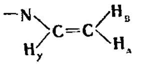
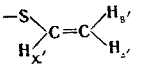
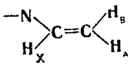
In addition, the structure of the synthesized N,S-divinyl-2-mercaptobenzimidazole is confirmed by its hydrolytic cleavage and hydrogenation. Under the influence of 4% sulfuric acid, III is hydrolyzed with the liberation of acetaldehyde (52.7%). When III is hydrogenated in the presence of a Raney nickel catalyst at room temperature and atmospheric pressure, hydrogen adds selectively only to the vinyl group attached to the sulfur atom. A new monomer — N-vinyl-S-ethyl-2-mercaptobenzimidazole (IV) — is isolated in 60% yield. In addition to this, desulfuration of III occurs, as a result of which the previously described N-vinyl- and N-ethylbenzimidazoles [3] were isolated. The absorption bands at 1635, 960, and 3050 cm^{-1} in the IR spectrum of IV are retained, while the absorption band at 1590 cm^{-1} vanishes. In addition, absorption bands at 2870-2970 cm^{-1}, which are characteristic for an ethyl group, appear. To establish the structure of IV, we recorded its PMR spectrum, from which it follows that it contains one vinyl and one ethyl group. It follows from a comparison of the chemical shifts and spin-spin coupling constants in the spectra of III and IV that the vinyl group in IV is bonded to a nitrogen atom, while the ethyl group is bonded to the sulfur atom (Table 1). It can be assumed that the formation of IV is associated with the specificity of the mechanism of hydrogenation on Raney nickel and also with the difference in the electronegativities of the nitrogen and sulfur atoms.

In order to ascertain the capacity of III with respect to polymerization, we studied its behavior under homolytic and heterolytic conditions. 2,2-Azobisisobutyronitrile (AIBN), hydrogen peroxide, and boron trifluoride etherates, $SnCl_4$, and $SnCl_4 \cdot 5H_2O$ catalysts and mineral acids were tested as polymerization initiators. It was found that III undergoes 90% conversion to a glassy solid polymer (mp 260-290°, insoluble in organic solvents) at 60° in the course of 50 h in the presence of 4% AIBN; this makes it possible to propose a reticular structure for polymer V:



V

TABLE 1. PMR Spectra of Vinyl Derivatives of 2-Mercaptobenzimidazole

R	δ, ppm	J, Hz
	Compound III	
	5,04 (H_A) 5,40 (H_B) 6,81 (H_X)	1,2 (AB) 9,0 (AX) 15,6 (BX)
	5,43 ($H_{A'}$) 5,45 ($H_{B'}$) 7,21 ($H_{X'}$)	0 (A′B′) 9,6 (A′X′) 17,1 (B′X′)
	Compound IV	
	4,95 (H_A) 5,36 (H_B) 6,80 (H_X)	1,2 (AB) 9,0 (AX) 15,6 (BX)
$-S-CH_2-CH_3$	3,26 (CH_2) 1,38 (CH_3)	7,3 (CH_2CH_3)

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*Ring δ 6.87-7.65 ppm.

When cationic polymerization catalysts were used, the formation of stable complexes was always observed.

Thus, new sulfur-containing vinyl monomers of the benzimidazole series were obtained as a result of our investigations. Our investigation of the reactivities of the vinyl derivatives of I is continuing.

EXPERIMENTAL

The PMR spectra of CCl_4 solutions of the compounds were recorded with a BS487B spectrometer at room temperature with hexamethyldisiloxane as the internal standard.

N,S-Divinyl-2-mercaptobenzimidazole. A 0.25-liter steel rotating autoclave was charged with 3 g (0.02 mole) of I, 0.15 g (0.0015 mole) of CuCl, and 30 ml of dioxane. Acetylene was fed into the autoclave from a cylinder with an initial pressure of 17 atm. The reaction mixture was heated and maintained at 180° for 3 h. The product obtained from the autoclave consisted of a mobile brown liquid and a black precipitate. The precipitate was removed by filtration, and the dioxane was removed by distillation at reduced pressure. The brown oil was dissolved in benzene. Compound II, which was insoluble in benzene, was removed by filtration, the benzene was removed from the benzene solution by distillation, and the residue was vacuum distilled in a nitrogen atmosphere. Two vacuum distillations gave 3.38 g (84%) of III, which was a light-yellow oily liquid with bp 150° (2 mm), d_4^{20} 1.1938, n_D^{20} 1.6553 and ΔMR_D 0.418. Found:C 65.5; H 5.0; N 13.8; S 15.8%. $C_{11}H_{10}N_2S$. Calculated: C 65.3; H 5.0; N 13.9; S 15.9%.

Pure III can be stored for a long time and is quite soluble in organic solvents. The vinylation of I in the presence of $Cd(CH_3COO)_2 \cdot 2H_2O$ and workup of the reaction products were carried out similarly. Compound III was obtained in maximum yield (81%) in the presence of 5.6 mmole of cadmium acetate under the same vinylation conditions.

Vinylation of Benzimidazolyl Vinyl Sulfide (II). The reaction of 3 g (17 mmole) of II in the presence of 0.05 g (0.5 mmole) of CuCl at 180° for 3 h gave 3.44 g (54%) of III.

Hydrogenation of N,S-Divinyl-2-mercaptobenzimidazole (III). Reduction of III in the presence of Raney nickel by the method described in [4] gave N-vinyl-S-ethyl-2-mercaptobenzimidazole (IV) with bp 122-124° (1 mm), d_4^{20} 1.1507, n_D^{20}1.6247, and ΔMR_D 0.5.

Hydrolysis of N,S-Divinyl-2-mercaptobenzimidazole (III). A 100-ml ampul containing 0.155 g of III and 20 ml of 4% H_2SO_4 was heated in a thermostat at 80° for 30 h. The contents of the ampul were then transferred quantitatively to a cooled volumetric flask. The amount of acetaldehyde was determined by the Ripper method [5] by titration of the excess bisulfite with a 0.1 N solution of iodine. The yield of acetalydehyde was 52.7%.

Radical Polymerization of N,S-Divinyl-2-mercaptobenzimidazole (III). A 0.08-g (4%) sample of AIBN was added to an ampul containing 2.02 g (0.01 mole) of III. The ampul was then sealed and placed in a thermostat at 60° for 50 h. The resulting polymer was then ground in a mortar and washed out from the monomer and initator with ethanol. The product was dried to constant weight in a vacuum desiccator to give 1.8 g (90%) of a polymer with mp 260-290°. Found: C 64.8; H 5.1; N 13.2; S 15.9% $(C_{11}H_{10}N_2S)_n$. Calculated: C 65.3; H 5.0; N 13.9; S 15.9%.

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