SYNTHESIS AND PROPERTIES OF VINYL DERIVATIVES OF 4,5-DIPHENYL-2-MERCAPTOIMIDAZOLE

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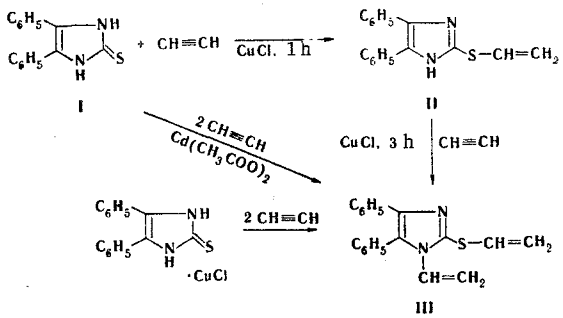
S-Vinyl-, N,S-divinyl-, and S-ethyl-N-vinyl-4,5-diphenyl-2-mercaptoimidazoles were synthesized by reaction of 4,5-diphenyl-2-mercaptoimidazole with acetylene under pressure. The reactivities of these monomers were investigated. It is shown that they have lower reactivities than S- and N,S-vinyl-2-mercaptobenzimidazoles in radical polimerization reactions and do not form complexes with transition metal salts.

2-Mercaptobenzimidazole, which has a thiomide fragment in its five-membered ring and is capable of tautomeric transformations, adds acetylene not only at the sulfur atom but also simultaneously at both heteroatoms [1]. The introduction, in place of the condensed benzene ring, of two phenyl substituents in the 4 and 5 positions of the imidazole ring causes redistribution of the electron density in the molecule and a change in the lability of the hydrogen atoms attached to the heteroatoms, and this may be reflected substantially in the behavior of this compound in vinylation reactions. In this connection, the aim of the present research was to investigate the reaction of 4,5-diphenyl-2-mercaptoimidazole (I) with acetylene and to study the reactivities of the synthesized vinyl derivatives in the case of reactions such as complexing, addition of vinyl groups to the double bond, polymerization, and oxidation, which we previously studied for vinyl derivatives of 2-mercaptobenzimidazole [1, 2].

We demonstrated that when mercaptoimidazole I is heated to 180° with acetylene in the presence of potassium hydroxide it forms only S-vinyl-4,5-diphenyl-2-mercaptoimidazole (II). Replacement of potassium hydroxide by cadmium acetate results in the formation of N,S-divinyl-4,5-diphenyl-2-mercaptoimidazole (III). The use of cuprous chloride as a catalyst makes it possible to direct the reaction, depending on its duration, to favor the formation of a monovinyl or a divinyl derivative.



Thus S-vinyl derivative II is obtained in almost quantitative yield when mercaptoimidazole I is heated with acetylene for 1 h. If the vinylation reaction is carried out for more than 2 h, mainly imidazole III is isolated.

It might be assumed that under the reaction conditions cuprous chloride reacts with the starting mercaptoimidazole I to give a complex, which reacts with acetylene to give vinyl derivatives. In fact, in some cases

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TABLE 1. PMR Spectral Parameters*

Compound	Chemical shifts, δ, ppm							Spin–spin coupling constant, J, Hz					
	H_A	H_B	H_X	$H_{A'}$	$H_{B'}$	$H_{X'}$	$H_{C_6H_5}$	H_A, H_X	H_B, H_X	H_A, H_B	$H_{A'}$, $H_{X'}$	$H_{B'}$, $H_{X'}$	$H_{A'}$, $H_{B'}$
II	—	—	—	5,35	5,36	6,60	6,95—7,83	—	—	—	9,1	16,2	0
III	4,94	4,99	6,53	5,37	5,39	7,01	6,88—7,53	8,0	16,4	1,2	9,4	17,0	0
IV	—	—	—	6,03	6,41	6,84	6,89—7,86	—	—	—	9,1	15,9	0
V	5,02	5,34	6,80	6,09	6,24	6,94	6,95—7,70	8,4	15,2	1,4	9,2	15,6	0
VI	—	—	—	5,54	5,55	†	6,86—7,61	—	—	—	9,0	15,5	0
VII	5,49	5,35	6,60	5,68	5,64	†	7,08—7,75	8,1	15,4	1,6	8,9	15,2	0,6
VIII	4,86	5,01	6,46	—	—	—	6,96—7,48	8,7	15,2	1,0	—	—	—

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*The signal of an NH group appears only in the spectrum of II (δ 14.75 ppm, broad singlet).

†This is superimposed on the signals of the benzene ring.

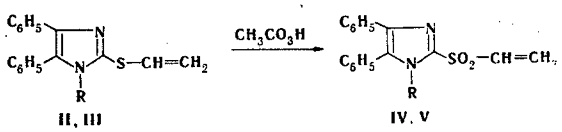
we were able to isolate a 1 : 1 complex of I with CuCl, by treatment of which with acetylene under pressure we obtained divinyl derivative III.

The high nucleophilicity of the sulfur atom in compounds with a thioamide grouping is responsible, in the vinylation of mercaptoimidazole I, for the formation initially of precisely S-vinyl derivative II, after which a second acetylene molecule reacts with the nitrogen atom in the 1 position. A confirmation of this sort of process is the fact that we were unable to isolate even traces of the mono-N-vinyl derivative of I. The presence of two phenyl substituents in the 4 and 5 positions of the imidazole ring facilitates easier vinylation of mercaptobenzimidazole, which we have previously studied in this reaction [1].

The structures of all of the compounds obtained in this study are confirmed by the PMR (Table 1) and IR spectroscopic data. The chemical shifts of the signals and the spin–spin coupling constants (SSCC) of the olefinic protons bonded to the sulfur and nitrogen atoms are characteristic [3]. An absorption band at 1593 cm^{-1}, which is characteristic for the S-vinyl group, appears in the IR spectrum of II, the absorption band of a thioamide fragment at 1510 cm^{-1} vanishes, and absorption at 3400 cm^{-1} due to NH vibrations is retained. The IR spectrum of divinyl derivative III is characterized by absorption at 1596 and 1646 cm^{-1} due to the stretching vibrations of vinyl groups bonded to sulfur and nitrogen heteroatoms [4] and by the absence of NH group vibrations.

Vinylmercaptoimidazoles II and III are polymerized under the influence of azobisisobutyronitrile (AIBN). In this case the degree of conversion of divinylimidazole III reaches only 40%, and this indicates the lower reactivity of the vinyl groups of this compound in radical polymerization as compared with divinylmercaptobenzimidazole.

The sulfur atoms of vinyl monomers II and III are capable of undergoing oxidation under mild conditions with acetyl hydroperoxide to give 4,5-diphenylimidazolyl vinyl sulfones (IV, V).



II, IV R = H; III, V R = $CH=CH_2$

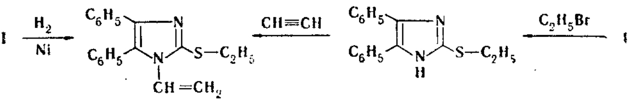
The appearance of intense absorption bands at 1140 and 1330 cm^{-1}, which are characteristic for the O=S=O group, is observed in the IR spectra of sulfones IV and V, and the signals of the α- and β-olefinic protons in their PMR spectra are shifted relative to their positions in the spectra of II and III (Table 1).

It is interesting to note that we were previously unable to obtain the corresponding sulfones for N,S-divinylmercaptobenzimidazole by oxidation because of its cleavage under the reaction conditions to N-vinyl-2-benzimidazolone [2]. The two phenyl substituents in the divinylmercaptoimidazole III molecule stabilize the conjugation system and make the sulfur–heteroring bond stronger, and it is probably for this reason that the formation and isolation of a sulfone with two vinyl groups become possible.

The introduction of two electron-acceptor substituents such as phenyl groups in the imidazole ring promotes a decrease in the electron density in the system, and this affects the magnitude of the negative charge on the nitrogen atom in the 3 position and the activity of II and III in complexing reactions. Whereas S- and N,S-vinylmercaptobenzimidazoles are capable of giving complexes with transition metal halides, our attempts to isolate complexes on mixing solutions of sulfides II and III with manganese, nickel, cobalt, and iron chlorides at various temperatures (20-70°) and under various time conditions were unsuccessful. Steric hindrance due to the presence of two bulky substituents may also play a decisive role in the case of vinyl derivatives of 4,5-diphenyl-2-mercaptoimidazole.

Dry hydrogen chloride adds quite readily to vinylmercaptoimidazoles II and III to give hydrochlorides VI and VII, which are unstable in water. An analysis of their IR spectra showed that the absorption bands of the vinyl groups at 1646 and 1596 cm^{-1} do not undergo any changes. Evidence for salt formation is also provided by the shift of the band of ring stretching vibrations to the shortwave region ($1493 \rightarrow 1512$ cm^{-1}), the appearance of new bands at 2400-2600 cm^{-1}, and the change in the δ and J values in the PMR spectra (Table 1).

The behavior of the double bonds of the vinyl groups of monomers II and III in hydrogenation is unusual. Thus we were unable to obtain an ethyl derivative from S-vinylimidazole II by reduction with hydrogen by heating in the presence of a nickel catalyst even under pressure. In addition to the unchanged starting compound, we isolated only 4,5-diphenylimidazole, formed as a result of detachment of the S-vinyl group from sulfide II. The introduction of a second vinyl group in the II molecule at the nitrogen atom makes this bond stronger, and S-ethyl-N-vinyl-4,5-diphenyl-2-mercaptoimidazole (VIII) was obtained by hydrogenation of divinylimidazole III over Raney nickel.



VIII

In the IR spectrum of VIII the absorption band at 1596 cm^{-1} due to the stretching vibrations of the vinyl group attached to the sulfur atom vanishes, new bands appear at 1380 cm^{-1}, 2870, 2935, and 2980 cm^{-1} ($-CH_2CH_3$), and the band at 1646 cm^{-1} is retained. It was proved by PMR spectroscopy that the ethyl group is attached to the sulfur atom (δ_{CH_2} 3.28 ppm; δ_{CH_3} 1.44 ppm, $J_{CH_2CH_3} = 6.9$ Hz).

Compound VIII was also obtained by reaction of mercaptoimidazole I with ethyl bromide and subsequent condensation with acetylene under pressure.

EXPERIMENTAL METHOD

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of $CDCl_3$ solutions were recorded with a BS487B spectrometer at room temperature with hexamethyldisiloxane as the internal standard (δ scale). The starting 4,5-diphenyl-2-mercaptoimidazole was obtained by condensation of benzoin with thiourea [5].

S-Vinyl-4,5-diphenyl-2-mercaptoimidazole (II). A 1-liter steel rotating autoclave was charged with 10 g (40 mmole) of mercaptoimidazole I, 0.5 g (5 mmole) of Cu_2Cl_2 and 100 ml of dioxane. Acetylene was fed into the autoclave from a cylinder at an initial pressure of 15 atm. The reaction mixture was heated at 180° for 1 h. At the end of the reaction the black precipitate was removed by filtration, and the dioxane was removed from the filtrate at reduced pressure. The solid residue was recrystallized from aqueous acetone to give 9.9 g (90%) of a white crystalline powder with mp 178° (from benzene). Found: C 73.3; H 5.2; N 10.1; S 11.4%. $C_{17}H_{14}N_2S$. Calculated: 73.3; H 5.1; N 10.1; S 11.4%.

The vinylation of I in the presence of KOH and the isolation of II were carried out similarly. The maximum yield (70%) was obtained in the presence of 0.02 mole of KOH. The reaction time was 2 h.

N,S-Divinyl-4,5-diphenyl-2-mercaptoimidazole (III). A) A mixture of 10 g (40 mmole) of imidazole I, 0.8 g (8 mmole) of Cu_2Cl_2, and 100 ml of dioxane was saturated with acetylene and heated in an autoclave at 180° for 2.5 h. The dioxane was removed, and the solid residue was recrystallized from aqueous acetone to give 11.4 g (95%) of a product with mp 71°. Found: C 75.1; H 5.3; N 9.2; S 10.1%. $C_{19}H_{16}N_2S$. Calculated: C 75.0; H 5.3; N 9.2; S 10.5%.

B) The reaction of 3 g (0.01 mole) of the mercaptoimidazole I complex with cuprous chloride at 180° for 1 h gave 2 g (76%) of III.

C) The vinylation of 3 g (12 mmole) of II in the presence of 0.15 g (1.5 mmole) of CuCl at 180° for 1 h gave 2.62 g (80%) of III.

Radical Polymerization of Vinyl Derivatives (II, III) of 4,5-Diphenyl-2-mercaptoimidazole. An ampul containing a mixture of 1.0 g (3 mmole) of III, 0.04 g (4%) of AIBN, and 10 ml of absolute benzene was allowed to stand in a thermostat at 80° for 100 h. At the end of this time the solvent was removed, and the resulting polymer was purified by reprecipitation from chloroform solution by the addition of hexane to give 0.4 g (40%) of a product with mp 220-237°. Found: C 74.8; H 5.2; S 10.3%. $(C_{19}H_{16}N_2S)_n$. Calculated: C 75.0; H 5.3; S 10.5%. A polymer of mercaptoimidazole II was similarly obtained in 75% yield and had mp 120-134°. Found: C 73.1; H 5.2; S 11.2% $(C_{17}H_{14}N_2S)_n$. Calculated: C 73.4; H 5.0; S 11.5%.

4,5-Diphenyl-2-imidazolyl Vinyl Sulfone (IV). A 2.75-g (15 mmole) sample of 70% acetyl hydroperoxide was added dropwise at 20° to a solution of 1.4 g (5 mmole) of II in 75 ml of diethyl ether, and the mixture was allowed to stand for 48 h. Workup gave 0.8 (51%) of sulfone IV with mp 191°. Found: C 65.7; H 4.8; S 10.5%. $C_{17}H_{14}N_2O_2S$. Calculated: C 65.8; H 4.6; S 10.3%.

N-Vinyl-4,5-diphenyl-2-imidazolyl Vinyl Sulfone (V). This compound was obtained by oxidation of 1.5 g (5 mmole) of III for 24 h under conditions similar to those in the preceding experiment. The yield of product with mp 142° was 0.8 g (50%). Found: C 68.2; H 5.0; S 9.7%. $C_{19}H_{16}N_2O_2S$. Calculated: C 67.9; H 4.8; S 9.5%.

S-Vinyl-4,5-diphenyl-2-mercaptoimidazole Hydrochloride (VI). Dry hydrogen chloride was bubbled into a solution of 1.5 g (6 mmole) of sulfide II in 15 ml of diethyl ether at room temperature. Workup gave 1.33 g (80%) of a product with mp 186-190°. Found: S 11.3; Cl 10.1%. $C_{17}H_{14}N_2S \cdot HCl$. Calculated: S 11.3; Cl 10.2%.

N,S-Divinyl-4,5-diphenyl-2-mercaptoimidazole Hydrochloride (VII). This compound was similarly obtained from 1.5 g of sulfide III. The yield of product with mp 135-137° was 1.0 g (60%). Found: S 10.4; Cl 9.0%. $C_{19}H_{16}N_2S \cdot HCl$. Calculated: S 10.4; Cl 9.4%.

Hydrogenation of S-Vinyl-4,5-diphenyl-2-mercaptoimidazole (II). A 0.25-liter steel rotating autoclave was charged with 3.0 g (12 mmole) of II, 30 ml of ethanol, and 8.0 g of a Raney nickel catalyst. Hydrogen was fed into the autoclave from a cylinder at an initial pressure of 95 atm. The reaction mixture was heated at 45° for 5 h. The resulting precipitate was removed by filtration and treated with acetone, from which 0.6 g (26%) of 4,5-diphenylimidazole, with mp 228-230° (from alcohol), was isolated. Removal of the alcohol from the filtrate gave 1.55 g (51.3%) of starting II.

S-Ethyl-N-vinyl-4,5-diphenyl-2-mercaptoimidazole (VIII). A) A hydrogenation flask was charged with 2.0 g (6 mmole) of sulfide III, 30 ml of ethanol, and 1.0 g a Raney nickel catalyst. The reaction was carried out at 20° with constant stirring. At the end of the reaction, the catalyst was removed by filtration, and the alcohol was removed from the filtrate by distillation to give 1.6 g (80%) of a product with mp 77° (from alcohol). No melting-point depression was observed for a mixture of this product with a compound obtained by alternative synthesis. Found: C 74.9; H 5.8; N 9.9; S 9.8%. $C_{19}H_{18}N_2S$. Calculated: C 74.5; H 5.9; N 9.1; S 10.4%.

B) A stirred mixture of 6.0 g (24 mmole) of mercaptoimidazole I, 7.0 g (64 mmole) of ethyl bromide, 1.42 g (36 mmole) of NaOH, 10 ml of water, and 100 ml of dioxane was heated at 35-40° for 5 h. The solvent was removed from the organic layer by distillation, and the residue was washed with ether to give 4.5 g (67%) of S-ethyl-4,5-diphenyl-2-mercaptoimidazole (IX) with mp 190-191°. Found: C 72.7; H 5.4; S 11.3%. $C_{17}H_{16}N_2S$. Calculated: C 72.8; H 5.7; S 11.4%. Vinylation of 1.4 g of ethyl derivative IX in an autoclave at 180° for 1 h in the presence of 20% Cu_2Cl_2 gave 1.0 g (65%) of VIII with mp 77-78°.

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