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Abstract

Full Text

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N-VINYLTHIOPYRROLIDONE

It is well known that N-vinyllactams of the general structure

$$CH_2{=}CHN(CH_2)_nC{=}O$$

are of theoretical and practical interest. The greatest importance among this group of compounds has been attained by N-vinylpyrrolidone ([1]). It was of interest to synthesize the sulfur-containing analogs of N-vinyllactams, namely N-vinylthiolactams, and to study their reactivity. N-vinylthiolactams have not been described in the literature. In order to develop a method for the synthesis of these compounds, we studied the reaction of acetylene with thiolactams in the presence of their alkali salts. It was found that under these conditions thiolactams react in the thiolactim form, as a result of which S-substituted derivatives are formed. The data obtained are the subject of a special communication.

Table 1

Effect of the amount of pyridine on the yield of N-vinylthiopyrrolidone

Vinylpyrrolidone, g-mol	Xylene, ml	Pyridine, ml	Yield, %	Resinous products, %
0.1	–	75	45	55
0.1	25	50	55	45
0.1	30	30	60	40

To obtain N-vinylthiolactams, in the present work we studied the interaction of phosphorus pentasulfide with N-vinyllactams. The process was investigated in greatest detail using N-vinylpyrrolidone as an example. By the action of phosphorus pentasulfide on N-vinylpyrrolidone in a solution of xylene and pyridine, N-vinylthiopyrrolidone was obtained in 60% yield. The yield of the product depends on the amount of pyridine (see Table 1).

$$CH_2{=}CHN(CH_2)_3C{=}O + P_2S_5 \rightarrow CH_2{=}CHN(CH_2)_3C{=}S + P_2O_5.$$

Figure 1 and Figure 2: ultraviolet spectra plots

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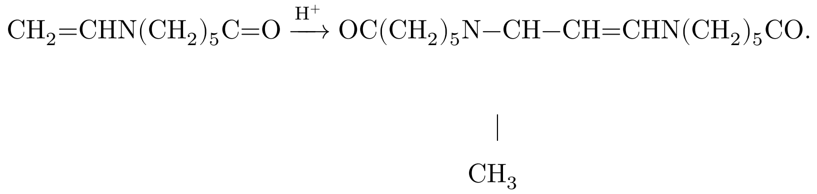
We did not succeed in obtaining N-vinylthiocaprolactam under these conditions, since dimerization of N-vinylcaprolactam occurred (^{2})



$$CH_2{=}CHN(CH_2)_5C{=}O \xrightarrow{H^+} OC(CH_2)_5N{-}\underset{\underset{CH_3}{|}}{CH}{-}CH{=}CHN(CH_2)_5CO.$$

A study of the IR spectrum of N-vinylthiopyrrolidone showed the presence of a characteristic absorption band for a terminal C=C bond at 1637 cm^{-1}. The UV spectrum of N-vinylthiopyrrolidone, in comparison with the spectrum of thiopyrrolidone (Fig. 1), is shifted considerably into the long-wavelength region (λ_{max} for thiopyrrolidone 266 $m\mu$, and for the N-vinyl derivative 302 $m\mu$). This effect is apparently due to conjugation of the C=S and C=C bonds through the lone pair of electrons of the nitrogen atom.

N-Vinylthiopyrrolidone, like *N*-vinylpyrrolidone (^{3}), is hydrolyzed in the presence of acid:

$$CH_2{=}CH\overline{N(CH_2)_3C}{=}S \xrightarrow[H_2O]{H^+} CH_3CHO + \overline{HN(CH_2)_3C}{=}S.$$

On the action of thiophenol on *N*-vinylthiopyrrolidone in the presence of azobisisobutyronitrile, α-phenylthioethylthiopyrrolidone was obtained.

$$CH_2{=}CH\overline{N(CH_2)_3C}{=}S + C_6H_5SH \rightarrow CH_3CH(SC_6H_5)\overline{N(CH_2)_3C}{=}S.$$

The addition of thiophenol to unsaturated compounds in accordance with Markovnikov' s rule, even in the presence of a free-radical initiator, has also been observed previously in the case of *N*-vinylpyrrolidone (^{4}). The structure of the sulfide obtained by us was established on the basis

Fig. 1. U.-v. spectra (in ethanol) of thiopyrrolidone *(1)* and *N*-vinylthiopyrrolidone *(2)*

Fig. 2. U.-v. spectra (in ethanol) of *N*-(β-phenylthioethyl)-thiopyrrolidone *(1)* and *N*-(α-phenylthioethyl)-thiopyrrolidone *(2)*

of the difference between the constants of this product and those of the sulfide having a known β-structure, synthesized by the following reaction:

$$C_6H_5SCH_2CH_2\overline{N(CH_2)_3C}{=}O + P_2S_5 \xrightarrow{H^+} C_6H_5SCH_2CH_2\overline{N(CH_2)_3C}{=}S$$

The u.-v. spectra of both sulfides are also different (see Fig. 2).

Of great interest is the polymerization reaction of *N*-vinylthiopyrrolidone. The polymerization was carried out under the action of DINITs at a temperature of 80°. A powdery polymer was isolated which, analogously to the starting monomer, differs sharply in solubility from the oxygen analogue, i.e., polyvinylpyrrolidone. The polymer of *N*-vinylthiopyrrolidone is soluble only in chloroform and dimethylformamide, in which respect it resembles the behavior of polyacrylonitrile.

With the aim of modifying the properties of the polymer, copolymerization of *N*-vinylthiopyrrolidone with other monomers was studied. Copolymers of *N*-vinylthiopyrrolidone with *N*-vinylpyrrolidone were obtained at two ratios of the monomers in the initial mixture. The synthesized copolymers differ from one another in the nature of their solubility and in color. Copolymerization of *N*-vinylthiopyrrolidone with acrylonitrile, methyl acrylate, and vinyl acetate was carried out. All the copolymers are solid powdery substances, almost colorless. The physical properties of these copolymers are given

Table 2

Characteristics of copolymers

Comonomer	Amount of vinylthiopyrrolidone in the initial mixture, mol. %	Amount of vinylthiopyrrolidone in the copolymer, mol. %	Yield, %	Softening point, °C	Solubility	Purification method: solvent	Purification method: precipitant
Vinylthiopyrr.	100	100	56	230	DMF, $CHCl_3$	DMF	Diethyl ether
Vinylpyrrolid.	50	55.38	57.1	230	DMF, DCE, $CHCl_3$	$CHCl_3$	Same

Comonomer	Amount of vinylthiopyrrolidone in the initial mixture, mol. %	Amount of vinylthiopyrrolidone in the copolymer, mol. %	Yield, %	Softening point, °C	Solubility	Purification method: solvent	Purification method: precipitant
Vinylpyrrolid.	25	27.36	49	210	DMF, DCE, $CHCl_3$, CH_3OH, C_2H_5OH, C_6H_6, acetone	$CHCl_3$	» »
Acrylonitrile	50	20.2	56	220	DMF, $CHCl_3$	DMF	Methyl alcohol
Methyl acrylate	50	33.75	58.4	190	DMF, DCE, $CHCl_3$, C_6H_6	$CHCl_3$	Same
Vinyl acetate	50	43.80	57.4	240	DMF, DCE, $CHCl_3$	$CHCl_3$	» »

Note. DMF—dimethylformamide, DCE—dichloroethane.

in Table 2. Further study of the reactivity of N-vinylthiopyrrolidone using ionic and free-radical reactions is continuing.

Experimental Part

N-Vinylthiopyrrolidone. To a solution of 11.1 g (0.1 mole) of N-vinylpyrrolidone in 30 ml of xylene and 30 ml of pyridine, 9 g of phosphorus pentasulfide was added in portions with stirring. The reaction mixture was heated to boiling for one hour. After cooling, the liquid phase was separated by decantation, and the solvents were removed in vacuum at 20-30 mm. The viscous residue was precipitated with diethyl ether and recrystallized from it three times. The yellow crystals that separated, 7 g (yield 60%), were N-vinylthiopyrrolidone, m.p. 60-61°.

Found, %:	C 55.98, 55.97;	H 7.01, 6.81;	S 24.64, 24.92
C_6H_9NS. Calculated, %:	C 56.60;	H 7.08;	S 25.18

N-Vinylthiopyrrolidone is insoluble in water, hydrocarbons, and petroleum ether.

Hydrolysis of N-vinylthiopyrrolidone. 0.2 g of N-vinylthiopyrrolidone was dissolved with heating in 8 ml of water, and a hot solution of 0.15 g of 2,4-dinitrophenylhydrazine in 5 ml of 5% HCl was added. The crystals that separated after recrystallization from ethyl alcohol had m.p. 159–160°. A mixed sample with 2,4-dinitrophenylhydrazone, known to have been obtained from acetaldehyde, gave no depression of the melting point. Identification was also carried out by thin-layer chromatography.

Addition of thiophenol to N-vinylthiopyrrolidone. 4.3 g (0.4 mole) of freshly distilled thiophenol, 5 g (0.4 mole) of N-vinylthiopyrrolidone, and 0.09 g (1% of the total weight) of DINITs (recrystallized from methanol) were heated in an ampoule for 18 h at 80–81°. The reaction mixture was dissolved in 20 ml of diethyl ether and precipitated with heptane (25 ml). The viscous mass obtained was treated again with heptane, giving white crystals with m.p. 47–47.5°, which were N-(α-phenylthioethyl)-thiopyrrolidone. Yield 3.7 g (~40% of theory).

Found, %:	C 60.64, 60.75;	H 6.40, 6.32;	S 27.49, 27.53
$C_{12}H_{15}NS_2$. Calculated, %:	C 60.70;	H 6.32;	S 27.00

Preparation of N-(β-phenylthioethyl)-thiopyrrolidone. The reaction was carried out according to the procedure described in experiment 1. Taken: 4 g of N-(β-phenylthioethyl)-pyrrolidone (5), 2.5 g of phosphorus pentasulfide, 25 ml of xylene, 25 ml

pyridine. After removal of the solvents, a viscous mass was obtained; it was treated with heptane to give 4.2 g (yield 95%) of a white crystalline substance with m.p. 67°, which was N-(β-phenylthioethyl)thiopyrrolidone. A mixed sample of the α- and β-substituted compounds melted at 28–35°.

Found, %: C 60.36, 60.33; H 6.00, 6.14; S 26.76, 26.65
$C_{12}H_{15}NS_2$. Calculated, %: C 60.70; H 6.32; S 27.00

Polymerization of N-vinylthiopyrrolidone under the action of DINIZ. Into an ampoule were placed 3 g of N-vinylthiopyrrolidone and 0.03 g (1% of the amount of N-vinylthiopyrrolidone) of DINIZ, and the ampoule was heated for 8.5 h in a thermostat at 80–81°. The resulting polymer was purified by reprecipitation with diethyl ether from a dimethylformamide solution (10 ml). This gave a powdery polymer—1.75 g (56% of theory), with decomposition temperature 230°.

Copolymerization of N-vinylthiopyrrolidone with vinylpyrrolidone, vinyl acetate, methyl acrylate, and acrylonitrile was carried out in the presence of 1% DINIZ in sealed ampoules at 80° for 4.5 h. The isolation and purification of the copolymers are given in Table 2.

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