VINYL DERIVATIVES OF THIOCAPROLACTAM

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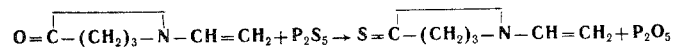
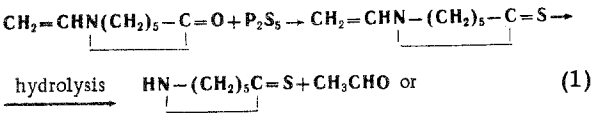
A study is made of the reaction of N-vinylcaprolactam with phosphorus pentasulfide. When the reaction is run in xylene, thiocaprolactam is isolated, when Na_2CO_3 is present, or pyridine, a dimer of N-vinylcaprolactam is formed. As a result of a study of the reaction of thiocaprolactam with acetylene under various conditions, a method is devloped for synthesizing new sulfur- and nitrogen-containing monomers of N-vinylthiocaprolactam and S-vinylthiocaprolactam.

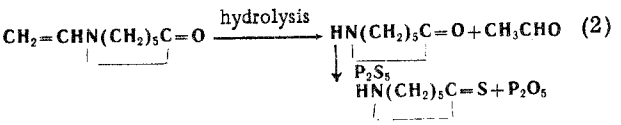
There is very little information in the literature about the chemistry of thiolactams. Hitherto unsaturated derivatives of thiolactams have generally been unknown. We have developed a method of preparing N-vinylthiopyrrolidone [1] by replacing the oxygen of the C=O group in N-vinylpyrrolidone with sulfur, by reacting it with phosphorous pentasulfide:



In the present work, to obtain large ring vinyl derivatives of thiolactams, an attempt was made to apply the above method to synthesizing N-vinylthiocaprolactam. However, reaction of phosphorus pentasulfide with N-vinylcaprolactam did not give the desired result. When the reaction was run in zylene, thiocaprolactam separated, which can be explained by one of the reaction schemes below:

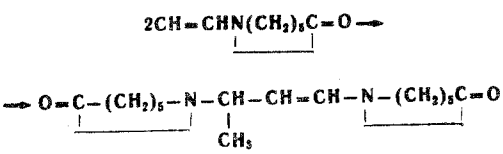


(1)



(2)

Since in the presence of moisture N-vinylcaprolactam is readily hydrolyzed by acid reagents [2], Na_2CO_3 or KOH was added to the reaction mixture to keep it neutral. In both cases the product was the previously described [3] dimer of N-vinylcaprolactam. When vinylcaprolactam was reacted with P_2S_5 in xylene or pyridine solution, at a ratio 1:1 or 2.5:1, the dimer of N-vinylcaprolactam was also found to be formed, the yield being up to 85%.



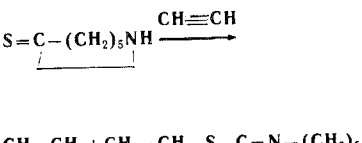
Because of the failure of an attempt to develop a synthesis of vinylthiocaprolactam using an indirect method which gave a good yield of N-vinylthiopyrrolidone [1], we paid special attention to investigating direct vinylation of thiocaprolactam, i.e. its reaction with acetylene.

The effects of catalyst nature, solvent, temperature, and reaction time on reaction products yield and composition were investigated. Vinyl derivatives of thiocaprolactam could not be obtained by using such catalysts as Na-thiocaprolactam, Na-pyrrolidone, Na-thiopyrrolidone, pyridine and triethylamine.

A detailed study of the process showed that vinylation of thiocaprolactam is effected in the presence of a potassium catalyst, and in this connection it is possible to use the previously prepared potassium salt of thiocaprolactam, and potassium hydroxide directly. Evidently the water separating through the action of potassium hydroxide on thiocaprolactam does not impede vinylation.

This property substantially differentiates thiolactams from their oxygen analogs, whose vinylation is retarded by even traces of water.

A second difference between vinylation of thiocaprolactam and vinylation of caprolactam is the high capacity of thiocaprolactam to react in two tautomeric forms [4, 6]. Because of this, two products were obtained, S-vinyl- and N-vinylthiocaprolactam.



With potassium hydroxide catalyst the total yield of sulfur and nitrogen vinyl compounds is 65–70%. The data of Table 1 show that as the catalyst concentration increases, the content of S-vinylthiocaprolactam increases. The optimum reaction temperature is 135°–155° C. At a lower temperature the starting materials are recovered unchanged, and at a higher one, there is much tar formation.

To increase the yield, the known pre-prepared potassium salt of thiocaprolactam was used instead of KOH, after being dried by azeotropic distillation. This gave only an inconsiderable increase in products yield (to 70–75%). It proved quite useful to add a small amount (about 0.5 ml) of pyridine. This gave purer products, obviously because of prevention of side reactions. Research on the duration of the reaction showed that 2 hr to 2 hr 30 min sufficed for it to be completed.

Vinylation of Thiocaprolactam in the Presence of K Catalyst (reaction time 2–2 hr 30 min, solvent 35–40 ml dioxane)

Run number	Reaction temperature °C	Catalyst, % total weight	Run results			
			Starting thiosemicarbazone recovered, %	Products yield, %		Note
				N-vinylthiocaprolactam	S-vinylthiocaprolactam	
1	135—145	K salt, 10	15	36	36.5	
2	135—145	K salt, 20	—	—	42	Tar formation
3	140—145	K salt*, 10	14	38.0	39	—
4	145—150	K salt, 20	—	—	30	Marked tar formation
5	145—150	KOH, 10	—	34	36	—
6	150—155	KOH, 10	—	29	38	Tar formation
7	150—155	K salt, 10	—	35	37	" "
8	155—160	K salt, 10	—	28	33	Marked tar formation

*Reaction run in the presence of 0.5 ml pyridine.

Thus about 25 variations of the synthesis were tried, resulting in development of the method of making the new monomers, N- and S-vinyl-thiocaprolactams.

After two or three distillations N- and S-vinylthiocaprolactams were still not very pure. Thin-layer chromatography showed a number of impurities, which further distillation did not remove. Methods of purifying the compounds synthesized were worked out. N-Vinylthiocaprolactam was obtained pure by chromatography on alumina. Under those conditions S-vinylthiocaprolactam suffers chemical change. It can be obtained pure either by fractional distillation through an effective column, or else by chromatographing on an inert absorbent, e.g. active charcoal.

To confirm the structures of the N- and S-vinylthiocaprolactams, their IR and UV spectra were investigated.* The IR spectra of both preparations showed absorption bands characteristic of the double bond. In the case of N-vinylthiocaprolactam observed frequencies were 1630, 3080, 3040 and 3100 cm^{-1}. With S-vinylthiocaprolactam they were 1595 (C=C valence vibration in the SCH=CH_2 group), 3000, 3040, and 3085 cm^{-1}. The spectrum of N-vinylthiocaprolactam also had an absorption band at 1490 cm^{-1}, characteristic of the N—C=S group. The spectrum of S-vinylthiocaprolactam had bands at 1640 and 1675 cm^{-1}, due to C=N vibrations [7]. The UV spectrum of N-vinylthiocaprolactam showed intense absorption in the long wave region: λ_{max} = 304 mμ, ε_{max} = 18 500, values close to those found with the UV spectrum of N-vinylthiopyrrolidone, where λ_{max} = = 303 mμ, ε_{max} = 13 000 [1]. The absorption maximum of S-vinylthiocaprolactam is displaced towards the shorter wavelength region (λ_{max} = 254 mμ, ε_{max} = = 10 000).

To demonstrate the structures of the vinylation products chemically, the N- and S-vinylthiocaprolactam were hydrolyzed in the presence of acid. They were both found to give an aldehyde, characterized as the 2,4-dinitrophenylhydrazone. Mixed melting points, and thin-layer chromatography, showed the latter to be that of acetaldehyde.

The presence of an active double bond is also shown by polymerization. Heating the N- and S-vinylthiocaprolactams with 1% α, α'-azodiisobutyronitrile at 70° C gave polymers as powders, differing in respect of solubilities and color. It is noteworthy that N-vinylthiocaprolactam polymerizes more easily than S-vinylthiocaprolactam.

EXPERIMENTAL

Reaction of thiocaprolactam with acetylene in the presence of KOH. A 1 *l* rotating autoclave was charged with 12.9 g thiocaprolactam, 0.56 g KOH, and 40 ml dry dioxane. After saturating with acetylene, the contents were held for 2 hr at 145°–150° C. The reaction products formed a brown mass with a distinct sulfur-like odor. After vacuum-distilling (10–15 mm) off the solvent there remained a brown residue, which was fractionated at 1.5 mm, to give: 1) bp 70°–75° C; n_D^{20} 1.5500, 6 g, yield 38%; 2) bp 110°–123° C; n_D^{20} 1.6010, 6.3 g, 34%. The first cut was S-vinylthiocaprolactam, the second the N-vinyl compound. After redistilling, these compounds had the following properties: S-vinyl, bp 70°–73° C (1 mm); n_D^{20} 1.5460, 5.6 g; N-vinyl bp 108°–109° C (2 mm); n_D^{20} 1.6030, 4.5 g. The table gives the results of the other runs.

Vinylation of thiocaprolactam in the presence of K-thiocaprolactam as catalyst. a) Preparation of K-thiocaprolactam. 1.12 g thiocaprolactam was dissolved in hot xylene (25 ml), and 0.56 g KOH added. The water formed in the reaction was completely distilled off with xylene. The residue was white, amorphous K salt.

b) A 1 *l* autoclave was charged with 12.9 g thiocaprolactam, 1.29 g of the above K salt (10% of total weight), 35 ml dry dioxane, 0.1 ml pyridine, and the necessary amount of acetylene introduced. The autoclave was rotated and held at 140°–145° C for 1 hr 30 min. The products were removed from the autoclave, distilled, first to remove solvent,

*The spectroscopic work was done by a colleague in the optics laboratory of the Institute of Organic Chemistry, B. V. Lopatnyi, whom the authors wish to thank.

and then at 1.5 mm to give 1) S-vinyl compound 70°–72° C; n_D^{20}, 1.5460, 6.2 g, 39% yield; 2) N-vinyl compound 110°–120° C; n_D^{20} 1.5960, 6 g, 38.7%; 3) starting thiocaprolactam, bp 135°–150° C 2 g. The table gives the results of the rest of the runs.

Purification of N-vinyl- and S-vinylthiocaprolactam. Thin-layer chromatography was carried out on a plate, using a mobile layer and alumina (AR). Solvent: ether–n-heptane. Visualizer: iodine vapor. Thin-layer chromatography of N-vinyl- and S-vinylthiocaprolactam showed them to contain impurities which further distillation did not remove. a) The N-vinylthiocaprolactam was purified by column chromatography of an ether–n-heptane (5:1) solution on alumina. After distilling, the pure N-vinylthiocaprolactam had bp 104°–105° (1.5 mm); n_D^{20} 1.6130 (viscous liquid). R_f 0.725 in the system Et_2O–n-heptane 5:1, and 0.545 in Et_2O–n-heptane 1:1. Found: C 61.70; 61.58; H 8.36; 8.23; S 20.70; 20.44%. Calculated for $C_8H_{13}NS$: C 61.95; H 8.39; S 20.64%.

b) The S-vinylthiocaprolactam was chromatographed on active charcoal, using Et_2O–heptane (1:1). Pure S-vinylthiocaprolactam was a colorless mobile liquid with a sulfurous odor, bp 70° (2mm); d_4^{20} 1.0458, n_D^{20} 1.5480.

Found: C 61.88; 62.09; H 8.51; 8.48; S 20.69; 20.54%; MR_D 47.06. $C_8H_{13}NS$. Calculated for: C 61.95; H 8.39; S 20.64%; MR_D 46.907; R_f 0.741

Hydrolysis of N- and S-vinylthiocaprolactam. a) 0.2 g N-vinylthiocaprolactam was heated with water (solution was incomplete), and to the hot solution 0.14 g was 2,4-dinitrophenylhydrazine in 5 ml 5% HCl added. The yellow crystals which separated were filtered off, and recrystallized from EtOH, mp 163°–164°, mixed mp with the 2,4-dinitrophenylhydrazone of authentic acetaldehyde 162°–164° C. The same acetaldehyde derivative obtained through hydrolysis of the N-vinyl compound had R_f 0.913 with Et_2O–n-heptane 1:2, while an authentic derivative had R_f 0.911.

b) Under the same conditions the S-vinyl compound was hydrolyzed, to give acetaldehyde 2,4-dinitrophenylhydrazone mp 161° C, undepressed mixed mp, R_f 0.911.

Polymerization of N- and S-vinylthiocaprolactams. Ampuls were charged separately with 2 g of the N-vinyl and S-vinyl compounds, and 0.02 g (1% total mass) azodiisobutyronitrile, and the whole heated for 5 hr (at 70° C with the N compound, at 80° C with the S one). The N compound polymer was soluble in dimethylformamide and $CHCl_3$ only, and it was purified by precipitation with ether from dimethylformamide solution (yield 60%). The S compound polymer was purified by precipitating with petrol ether from benzene solution (40% yield). The polymer was soluble in benzene, $CHCl_3$, dimethylformamide, dichloroethane, and insoluble in acetone, ether, MeOH, EtOH, and hydrocarbons.

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