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Abstract

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REARRANGEMENTS IN THE SERIES OF S-ALLYLTHIOLACTAMS

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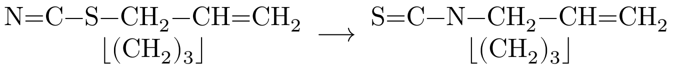
Previously, a method was developed for the synthesis of N-allyl- and S-allylthiolactams (13). In the preceding communication it was shown that N-allylthiolactams, under certain conditions, can undergo an isomerization reaction (14). It was of interest to investigate the capacity for isomerization in the series of S-allylthiolactams.

It is known that compounds containing systems of bonds $C = C - C - O - C = C$ (1) or $C = C - C - O - C = N$ (2) are capable of undergoing the Claisen rearrangement. There are several examples of rearrangement of compounds in which the double bond $C = N$ is part of a heterocyclic nucleus (3,4). The Claisen rearrangement has been described for systems in which the oxygen atom is replaced by sulfur (5–7); in this case the tendency toward rearrangement is somewhat reduced.

In the present work, we studied the capacity for Claisen rearrangement of compounds containing the bond grouping $-N = C - S - CH_2 - CH = CH_2$, using S-allylthiolactams with five- and seven-membered rings as examples. It is known that in the Claisen rearrangement heterolytic cleavage of bonds occurs; in connection with this, the rate of this process increases with increasing solvent polarity (8–10).

We studied the isomerization of S-allylthiolactams in chlorobenzene and diethylaniline solution. It was found that on heating S-allylthiopyrrolidone in chlorobenzene, a Claisen rearrangement takes place. In this process the allyl radical migrates from the sulfur atom to nitrogen, as a result of which N-allylthiopyrrolidone is formed (yield 50.5%).



$$\underset{\lfloor (CH_2)_3 \rfloor}{N{=}C{-}S}{-}CH_2{-}CH{=}CH_2 \longrightarrow \underset{\lfloor (CH_2)_3 \rfloor}{S{=}C{-}N}{-}CH_2{-}CH{=}CH_2$$

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The physical properties, as well as the UV and IR spectra of the isolated N-allylthiopyrrolidone, completely coincide with the properties of the compound synthesized previously (13).

When S-allylthiopyrrolidone was heated in diethylaniline solution, an unexpected phenomenon was observed. A new product was obtained which, according to elemental analysis, corresponded to allylthiopyrrolidone; however, in its physical properties it did not correspond to the N-allyl

Fig. 1. Ultraviolet spectra of allylthiolactams. 1 —N-allylthiopyrrolidone, 2 —C-allylthiopyrrolidone, 3 —S-allylthiopyrrolidone, 4 —S-allylthiocaprolactams, 5 —N-allylthiocaprolactams, 6 —C-allylthiocaprolactams

Figure 1: Fig. 1. Ultraviolet spectra of allylthiolactams. 1 —N-allylthiopyrrolidone, 2 —C-allylthiopyrrolidone, 3 —S-allylthiopyrrolidone, 4 —S-allylthiocaprolactams, 5 —N-allylthiocaprolactams, 6 —C-allylthiocaprolactams

derivative. It could be assumed that, under the reaction conditions, the N-allylthiopyrrolidone formed undergoes a prototropic transformation with formation of N-propenylthiopyrrolidone:

$$CH_2{=}CH{-}CH_2{-}N\lfloor(CH_2)_3\rfloor{-}C{=}S \longrightarrow CH_3{-}CH{=}CH{-}\underset{\text{III}}{N}\lfloor(CH_2)_3\rfloor{-}C{=}S$$

However, the physical constants and the UV and IR spectra of the isomerization product do not correspond to the N-propenyl derivative, synthesized and characterized by us earlier (11). Consequently, S-allylthiopyrrolidone, when heated in diethylaniline solution, isomerizes in a different direction than in chlorobenzene. In this case the allyl radical migrates from the sulfur atom not to the neighboring nitrogen atom, but to the neighboring carbon atom.

$$\text{S-allylthiopyrrolidone} \longrightarrow \text{IV}$$

An analogous rearrangement of the Claisen type, in which the allyl radical attacks not only the heteroatom but also the neighboring carbon atom, was described quite recently using allyloxypyridines as an example (12)

$$\text{allyloxypyridine} \xrightarrow{C_6H_5N(C_2H_5)_2} \text{allyl pyridone} + \text{N-allyl pyridone} + \text{pyridone}$$

The structure of product IV is confirmed by the following data. In the IR spectrum, bands at 1640, 3080, 3040, 3010, and 1420 cm^{-1}, characteristic of a terminal double bond, and bands at 3168 and 3442 cm^{-1}, inherent to an NH group, were found. The first of these (3168 cm^{-1}) is characteristic of a bound amino group, and the second of a free amino group. The presence in the spectrum of an absorption band at 1500 cm^{-1} indicates the presence of the group N—C=S (11), while the band characteristic of the C=N bond is absent. The UV spectrum of IV is similar in character to

Fig. 1. Ultraviolet spectra of allylthiolactams. 1 —N-allylthiopyrrolidone, 2 —C-allylthiopyrrolidone, 3 —S-allylthiopyrrolidone, 4 —S-allylthiocaprolactams, 5 —N-allylthiocaprolactams, 6 —C-allylthiocaprolactams.

the spectrum of N-allylthiopyrrolidone. In both cases, the absorption maximum lies in the region 265-275 mµ (Fig. 1). Obviously, the removal of the double bond from the thiolactam ring to the methylene group and the disruption of conjugation with the free electron pair of the nitrogen atom causes the same-

the degree of absorption of UV light both of the N-allyl and of the C-allyl derivatives. As a result of the analysis it was found that the substance (IV) isolated in the isomerization of S-allylthiopyrrolidone contains one active hydrogen*.

A similar isomerization was also observed in the case of S-allylthiocaprolactam. However, in contrast to the derivative with a five-membered ring, in this case migration of the allyl group from the sulfur atom to the carbon atom occurred both on heating in diethylaniline and in chlorobenzene.

The rearrangement of S-allylthiolactams into C-allylthiolactams observed in the present work belongs to the Claisen type. In this case, in parallel with migration of the allyl group, transfer of a hydrogen atom from carbon to nitrogen occurs according to a triad type.

The mechanism of isomerization of S-allylthiolactams into N-allyl and C-allyl derivatives may be represented as follows:

[scheme: five-membered imino-thioether ring]$-S-CH_2-CH=CH_2 \longrightarrow$ [scheme: cyclic transition structure

[scheme: five-membered imino-thioether ring with two H atoms]$-S-CH_2-CH=CH_2 \longrightarrow$ [scheme: NH ring

Experimental Part

1. Isomerization of S-allylthiopyrrolidone in chlorobenzene.

A solution of 5 g of S-allylthiopyrrolidone in 50 ml of chlorobenzene was heated for 6 h at 130°. After removal of the solvent, the residue, a dark-yellow mass with n_D^{20}1.5640, was distilled in vacuo and the fractions were collected: fraction I, b.p. 46-50°/1 mm, n_D^{20}1.5290, 2.13 g (42%), is unchanged S-allylthiopyrrolidone; fraction II, b.p. 100-103°/1.5 mm, n_D^{20}1.5720, 2.6 g (yield 50.5%), is N-allylthiopyrrolidone (13).

2. Isomerization of S-allylthiopyrrolidone in diethylaniline.

A solution of 8 g of S-allylthiopyrrolidone in 50 ml of diethylaniline was heated at reflux for 6 h. After removal of the solvent, the residue was fractionated in vacuo and 4.2 g of a substance with b.p. 116-120°/1 mm was obtained, which quickly crystallized (yield 52%). M.p. 65.5-67° (after two recrystallizations from petroleum ether). Mixed samples with thiopyrrolidone, and also with N-propenylthiopyrrolidone, give a depression of the melting point.

Found, %: C 59.07, 59.23; H 8.17, 8.14; S 22.52, 22.57
$C_7H_{11}NS$. Calculated, %: C 59.57; H 7.83; S 22.64

The number of active hydrogens found was 1.06, 0.87. The substance obtained is C-allylthiopyrrolidone.

3. Isomerization of S-allylthiocaprolactam in chlorobenzene.

The reaction was carried out analogously to experiment 1.

A solution of 8 g of S-allylthiocaprolactam in 50 ml of chlorobenzene was heated at reflux for 6 h. After removal of the solvent, a reaction mass with n_D^{21}1.5520 was obtained. This product was distilled in vacuo and gave: fraction I (1 g) with b.p. 78–83°/1 mm, n_D^{21} 1.5450. Fraction II (0.8 g) with b.p. 85–100°/1 mm, n_D^{21} 1.5720, and fraction III (2.6 g) (yield 32.5%) with b.p. 127–129°/1 mm, n_D^{21} 1.5830, which crystallized on standing and, after two recrystallizations from *n*-heptane, had m.p. 60–60.5° and was C-allylthiocaprolactam.

4. **Isomerization of S-allylthiocaprolactam in diethylaniline.** The experiment was carried out analogously to experiment 2.

A solution of 8 g of S-allylthiocaprolactam in 50 ml of diethylaniline was heated for 6 h. After the indicated treatment, it was fractionated in vacuo to give: fraction I (2–3 drops) with b.p. 117–120°/1 mm, and fraction II, 3.6 g (yield 45%), with b.p. 125–129°/1 mm, n_D^{20} 1.5810; on standing, the substance crystallized and, after the third recrystallization from *n*-heptane, had m.p. 60–60.5° and was C-allylthiocaprolactam. A mixed sample with the product obtained in the preceding experiment had m.p. 60–60.5°; mixed samples with thiocaprolactam and N-propenylthiocaprolactam gave a depression of the melting point.

Found, %: C 64.05, 63.79; H 9.05, 8.76; S 19.16, 19.12
$C_9H_{15}NS$. Calculated, %: C 63.91; H 8.87; S 18.98

The number of active hydrogens found was 1.02, 1.00.
The purity of the isolated isomerization products was checked by thin-layer chromatography on alumina.

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Note: Figure translations are in progress. See original paper for figures.