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Effect of the Allyl Group in Reactions of Allyl Alcohol and Its Derivatives with ε-Caprolactam

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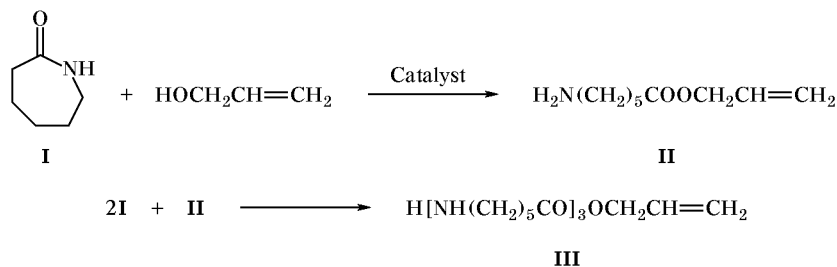*Institute of Chemical Problems of Ecology, Russian Academy of Natural Sciences*

Abstract—Unlike saturated alcohols, allyl alcohol reacts with ε-caprolactam under considerably milder conditions. Allyl esters react with ε-caprolactam to give the corresponding allyl ε-acylaminocaproates. The yield of the latter decreases in going from formyl to acetyl and propionyl derivatives. The observed effect of the allyl group is explained in terms of possible allylic rearrangement in the transition state.

Saturated monobasic alcohols react with ε-caprolactam (**I**) under conditions of heterogeneous [1] or homogeneous [2] catalysis, yielding mainly ε-aminocaproic acid trimer esters. The maximal conversion of lactam **I** in 20 h at 240°C, molar ratio **I**:BuOH:PbO (catalyst) = 1:10:0.1, is 44% [1]. Under homogeneous conditions (NEt$_3$, DMF) at 240°C, molar ratio **I**:BuOH = 1:1.2, the conversion of lactam **I** was raised to 60% [2]. The reaction of **I** with BuOH at 200°C is characterized by a low conversion. Under analogous conditions, lactam **I** does not react with esters derived from saturated alcohols. We have found that the reaction of **I** with allyl alcohol at a ratio of 1:1.2 at 220°C, catalyzed by DMF, yields mainly ε-aminocaproic acid trimer allyl ester **III** (Scheme 1). The reaction takes 4 h, the conversion of lactam **I** being 55%; the optimal DMF-to-**I** weight ratio is 0.0376:1. By carrying out the same reaction with NEt$_3$ as catalyst (optimal NEt$_3$-to-**I** weight ratio 1:10), other conditions being equal, we succeeded in reducing the temperature to 200°C and increasing the conversion of lactam **I** to 65% (reaction time 4 h).
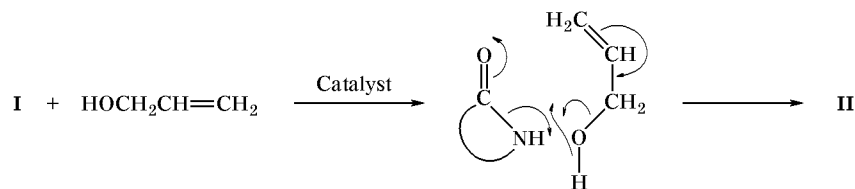
Allyl ε-aminocaproate (**II**), which is formed in the first stage, reacts with another molecule of lactam **I** to give the corresponding dimer and then trimer **III** in 60% yield. Propyl and butyl alcohols almost do not react with lactam **I** under analogous conditions. The elemental composition and molecular weight (determined in acetic acid) of the products are consistent with trimer structure **III**. Its structure was also confirmed by IR spectroscopy. The IR band at 1600 cm^{-1} belongs to stretching vibrations of the allyl C=C bond. This band is not observed in the IR spectrum of the homolytic phosphorylation product. The ester carbonyl group gives rise to absorption at 1770 cm^{-1}, and stretching vibrations of the NH$_2$ and NH groups appear as a strong band at 3356 cm^{-1}. The IR spectrum also contains amide I and amide II bands at 1640 and 1540 cm^{-1}, respectively.

The effect of the allyl group on the reactivity of allyl alcohol toward lactam **I** may be explained by the possibility for allylic rerrangement to occur in the transition state (Scheme 2). Provided that such a mechanism is really operative, allyl esters should
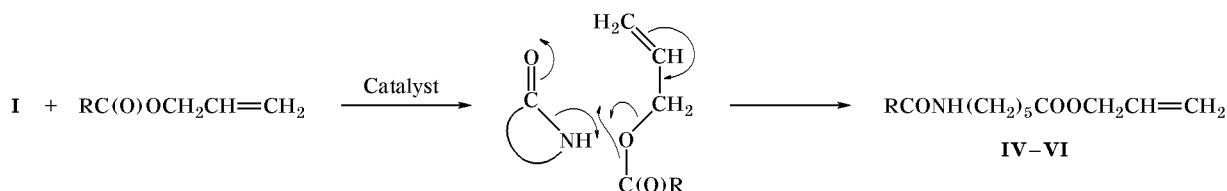
Scheme 1.

Scheme 2.

$$\mathbf{I} \ + \ HOCH_2CH{=}CH_2 \xrightarrow{\text{Catalyst}} \qquad \longrightarrow \ \mathbf{II}$$

Scheme 3.

$$\mathbf{I} \ + \ RC(O)OCH_2CH{=}CH_2 \xrightarrow{\text{Catalyst}} \qquad \longrightarrow \ RCONH(CH_2)_5COOCH_2CH{=}CH_2$$

$$\mathbf{IV{-}VI}$$

IV, R = H; **V**, R = CH$_3$; **VI**, R = C$_2$H$_5$.

react with lactam **I** to give the corresponding *N*-acyl derivatives of ε-aminocaproic acid. In fact, by reaction of **I** with allyl formate, allyl acetate, and allyl propionate at 200°C we obtained *N*-acyl derivatives **IV–VI** (Scheme 3).

The reaction time and the product yield depend on the nature of R radical. In the reaction with allyl formate, the yield of compound **IV** was 53% in 8.5 h. The reaction of allyl acetate with **I** gave only 14% of product **V** over the same period. The yield of ester **VI** was 15.1% in 17 h (6% in 8.5 h). These data are explained on the assumption that alkyl groups hinder formation of transition state. The conditions are the most favorable in the case of formyl group.

Esters **IV–VI** are colorless high-boiling liquids. Their density decreases in the series **IV** > **V** > **VI**, i.e., in parallel with increase of the length of the hydrocarbon radical in the *N*-acyl group. The structure of compounds **IV–VI** was proved by the IR spectra and elemental analyses. The properties of product **V** were consistent with those reported in [3]. The IR spectra of **IV–VI** contain a strong absorption band at 1732 (**IV**, **VI**) or 1736 cm^{-1} (**V**), corresponding to stretching vibrations of the ester carbonyl group. The amide I band (1640 cm^{-1}) appears as a shoulder to the ester C=O bond. Amide II band is also present (1540 cm^{-1}). Stretching vibrations of the NH group are observed at 3284 (**IV**) or 3296 cm^{-1} (**V**, **VI**).

EXPERIMENTAL

The IR spectra were recorded on a Specord M-82 spectrometer from samples dispersed in mineral oil. ε-Caprolactam of analytical grade was used without additional purification. Allyl alcohol, allyl formate, allyl acetate, and allyl propionate were distilled in the presence of hydroquinone (0.1 g per 100 ml).

Allyl 6-[6-(6-aminohexanoylamino)hexanoylamino]hexanoate (III). *a.* A mixture of 9.04 g of lactam **I**, 7.04 g of allyl alcohol, and 0.34 g of DMF was heated in a sealed ampule for 4 h at 220°C. The mixture was treated with chloroform, and the precipitate of product **III** was filtered off. Yield 6.35 g (60%). The product was recrystallized from boiling ethanol and then from a 10:2 ethanol–benzene mixture. mp 199–200°C. Found, %: C 63.51; H 9.94; N 10.70. C$_{21}$H$_{39}$N$_3$O$_4$. Calculated, %: C 63.44; H 9.89; N 10.57.

b. A mixture of 10 g of compound **I**, 6.16 g of allyl alcohol, and 1 g of triethylamine was heated in a sealed ampule for 4 h at 200°C. The product was isolated as described above in *a.* Yield 7.49 g (64%).

Allyl 6-formylaminohexanoate (IV). A mixture of 9.77 g (0.0865 mol) of lactam **I**, 8.93 g (0.104 mol) of allyl formate, and 0.508 g (0.005 mol) of triethylamine was heated in a sealed ampule for 8.5 h at 200°C. The mixture was then distilled under reduced pressure to isolate 9.09 g (53%) of compound **IV** with bp 188–191°C (1 mm); $n_D^{20} = 1.4698$, $d_4^{20} = 1.0381$; $MR_D = 53.55$ (found), 53.96 (calculated according to Vogel). Found, %: C 60.83; H 8.98; N 7.12. C$_{10}$H$_{17}$NO$_3$. Calculated, %: C 60.36; H 8.59; N 7.24.

Allyl 6-acetylaminohexanoate (V). A mixture of 3.7 g (0.0327 mol) of lactam **I**, 3.3 g (0.033 mol) of allyl acetate, and 0.15 g (0.00146 mol) of triethylamine was heated in a sealed ampule for 8.5 h at

200°C. The mixture was then distilled under reduced pressure to isolate 1.01 g (14%) of product **V**; bp 187–188°C (1 mm), $n_D^{20} = 1.4650$, $d_4^{20} = 1.0235$, $MR_D = 57.60$ (found), 57.56 (calculated according to Eisenlor). Found, %: C 62.01; H 9.14; N 6.65. $C_{11}H_{19}NO_3$. Calculated, %: C 61.94; H 8.98; N 6.57.

Allyl 6-propionylaminohexanoate (VI). A mixture of 10.0 g (0.0885 mol) of lactam **I**, 12.6 g (0.106 mol) of allyl propionate, and 0.5 g (0.00494 mol) of triethylamine was heated in a sealed ampule for 17 h at 200°C. The mixture was distilled under reduced pressure to isolate 3.04 g (15%) of compound **VI**, bp 187–191°C (1 mm), $n_D^{20} = 1.4691$, $d_4^{20} = 1.0135$, $MR_D = 62.46$ (found), 62.18 (calculated

according to Eisenlor). Found, %: C 63.84; H 9.52; N 6.28. $C_{12}H_{21}NO_3$. Calculated, %: C 63.41; H 9.31; N 6.16.

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