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SHORT COMMUNICATIONS

Importance of Acyl Rearrangement in the Acid-Catalyzed Reaction of ε-Caprolactam with Carboxylic Acids

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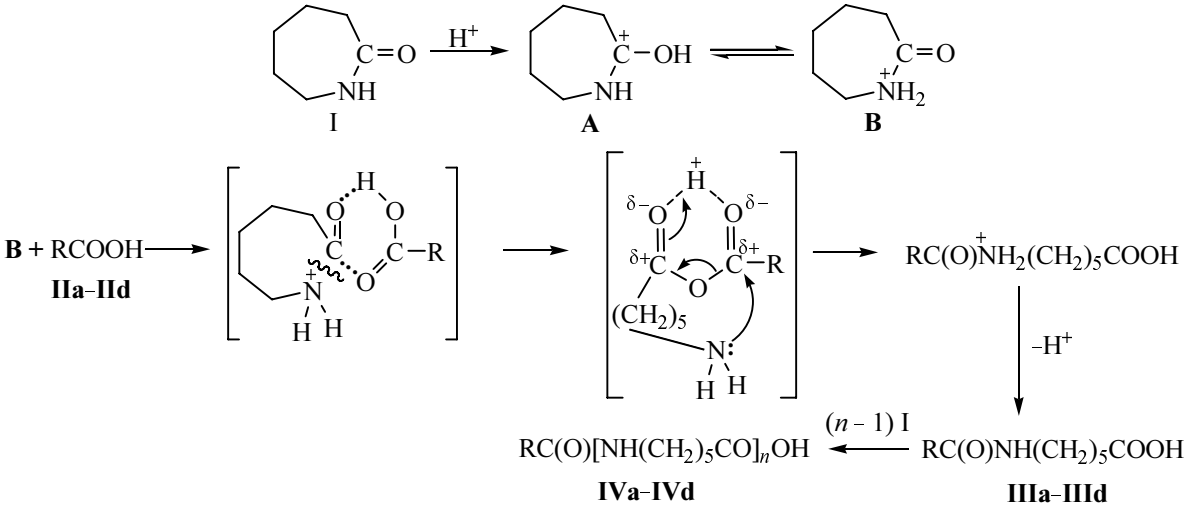
Reactions of ε-caprolactam (**I**) with carboxylic acids in the presence of acidic catalysts led to the formation of N-acyl derivatives of the ε-aminocaproic acid oligomers [1, 2].

We investigated the consumption of lactam **I** and carboxylic acid **II** [benzoic (**IIa**), *m*-nitrobenzoic (**IIb**), valeric (**IIc**), and stearic (**IId**) acids] in the temperature range 150–210°C under catalysis with p-toluenesulfonic acid (TsOH). Reaction products were identified, and the analysis of the elementary stages of the reaction was performed using quantum-chemical method AM1.

The quantum-chemical calculation showed that the anhydride formation under the acid catalysis occurred with an activation barrier of 134 kJ/mol through a stage of the ε-caprolactam intermediate protonated at the amide group **B**. The state **B** is close in the energy to the stage **A** where the proton adds to the carbonyl oxygen in compound **I**. However in the form protonated at the NH group the C–N bond (1.52 Å) is longer than in the protonated form **A** (1.33 Å). This fact favors the cleavage of the amide ring. The increase in the consumption of the *m*-nitrobenzoic acid and formation of *N*-*m*-nitrobenzoyl-ε-aminocaproic acid (isolated in a 65% yield) is well consistent with an acyl rearrangement favored by the presence of the electron-withdrawing nitro group. In reaction of the valeric acid we succeeded to isolate *N*-valeroyl-ε-aminocaproic acid in a 55% yield evidencing that the contribution from the acyl rearrangement was facilitated by smaller acid residue compared with stearic



R = Ph (**a**), $C_6H_4NO_2$-*m* (**b**), C_4H_9 (**c**), $C_{17}H_{35}$ (**d**); *n* = 1–10.

acid where only an oligomer with $n = 2$ and higher oligomers were obtained. The energy gain at the acyl rearrangement is no less than 83.8 kJ/mol.

Oligomers of *N*-benzoyl-ε-aminocaproic acid (IVa). Sealed ampules charged with a reaction mixture containing 1.9 g (16 mmol) of compound **I**, 2 g (16 mmol) of compound **IIa**, and 0.3 g (1.6 mmol) of TsOH were heated at constant temperature 150°C. At equal intervals (15 min) one of the ampules was opened, the reaction mixture was treated with chloroform which dissolved compounds **I** and **IIa**, the precipitate was filtered off. The precipitate was composed of oligomers **IVa** of *n* monomer units ($n = 9, 10$). The separation of the oligomers was performed with the use of ethanol: the oligomers mixture was boiled in ethanol, the solution was filtered and cooled. The oligomer of $n = 10$ precipitated on cooling and was filtered off; the mother liquor contained oligomer of $n = 9$ which was obtained by evaporating the solvent and recrystallization of the residue. Yield of compound **IVa**, $n = 9$, 0.66 g (35%), mp 165–167°C. IR spectrum, ν, cm^{-1}: 1570 (C=O), 1642 (C=O), 3320 (NH). ^1H NMR spectrum, δ, ppm: 8.22 s (9H, NH), 2.99 m (18H, CH_2N), 2.22 m [18H, $CH_2C(O)$], 7.08–7.89 m (5H, Ph), 1.16–1.98 m (54H, CH_2). Found, %: N 10.92. $C_{61}H_{105}N_9O_{11}$. Calculated, %: N 11.05. Yield of compound **IVa**, $n = 10$, 0.85 g (45%), mp 188–190°C. IR spectrum, ν, cm^{-1}: 1553 (C=O), 1636 (C=O), 3295 (NH). Found, %: N 11.20. $C_{67}H_{116}N_{10}O_{12}$. Calculated, %: N 11.27.

***N*-*m*-Nitrobenzoyl-ε-aminocaproic acid (IIIb)**. The reaction was performed as described above; the reaction mixture was treated with ether which dissolved lactam **I** and acid **IIb**, the precipitate was filtered off and recrystallized from chloroform. Yield 1.2 g (65%), mp 98–100°C. IR spectrum, ν, cm^{-1}: 1540 (C=O), 1660 (C=O), 3310 (NH_2). ^1H NMR spectrum, δ, ppm: 8.57 s (1H, NH), 3.03 m (2H, CH_2N), 2.99 m [2H, $CH_2C(O)$], 7.08–8.41 m (4H, Ph), 1.24–2.98 m [6H, $(CH_2)_3$]. Found, %: N 9.90. $C_{13}H_{16}N_2O_5$. Calculated, %: N 9.96.

***N*-Valeroyl-ε-aminocaproic acid (IIIc)**. In a sealed ampule was heated to 150°C a mixture of 2.2 g (19 mmol) of lactam **I**, 1.9 ml (19 mmol) of acid **IIc**, and 0.34 g (1.9 mmol) of TsOH. Then the reaction mixture was treated with ether to dissolve unreacted initial lactam **I** and acid **IIc**. The residue insoluble in ether was recrystallized from ethanol. Yield 0.63 g (55%), mp 110–112°C. IR spectrum, ν, cm^{-1}: 1550 (C=O), 1650 (C=O), 3340 (NH). ^1H NMR spectrum, δ, ppm: 8.10 s (1H, NH), 3.2 m (2H, CH_2N), 2.2–2.30 m [4H, $CH_2C(O)$], 0.9 t (3H, CH_3) 1.24–2.98 m [10H, $(CH_2)_5$]. Found, %: N 6.60. $C_{11}H_{21}NO_3$. Calculated, %: N 6.51.

Oligomers of *N*-stearyl-ε-aminocaproic acid (IVd). In a sealed ampule was heated to 150°C a mixture of 2 g (8 mmol) of caprolactam **I**, 2 g (8 mmol) of acid **IId**, and 0.14 g (0.8 mmol) of TsOH. Then the reaction mixture was treated with ether to dissolve lactam **I** and acid **IId**. The precipitate was filtered off and recrystallized from ethanol. Yield of compound **IVd**, $n = 2$, 0.52 g (40%), mp 135–137°C. IR spectrum, ν, cm^{-1}: 1565 (C=O), 1670 (C=O), 3360 (NH). ^1H NMR spectrum, δ, ppm: 8.02 s (2H, NH), 3.15 m (4H, CH_2N), 2.17–2.22 m [8H, $CH_2C(O)$], 0.86 t (3H, CH_3), 1.29–2.55 m [40H, $(CH_2)_{20}$]. Found, %: N 5.42. $C_{30}H_{58}N_2O_4$. Calculated, %: N 5.50. Oligomers of higher molecular weight were also obtained.

IR spectra were recorded on a spectrophotometer Specord-M82, from thin films (liquids) and from mulls in mineral oil (solids). ^1H NMR spectra were registered on a spectrometer Varian Mercury Plus (300 MHz) in DMSO-d_6, internal reference TMS.

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