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LETTERS TO THE EDITOR

Reaction of ε-Caprolactam with 1,1,3-Trihydroperfluoropropanol Catalyzed by Phosphorous Amide Copper Complexes

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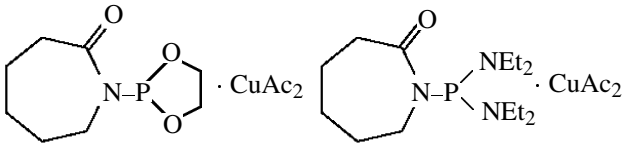
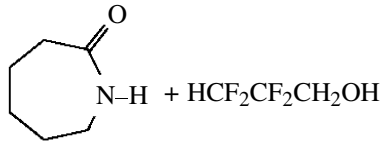
It was shown previously [1] that diacetatobis(ε-caprolactam)copper well catalyzes the reaction of ε-caprolactam with polyfluorinated alcohols.

We examined the catalytic activity of the complexes of copper diacetate with N-substituted phosphorous amides: diacetato[*N*-(1,3,2-dioxaphospholan-1-yl)-ε-caprolactam]copper **I** and diacetato[*N*-bis(diethylamino)phosphanyl-ε-caprolactam]copper **II**.



I **II**

We found that the copper complexes **I** and **II** derived from phosphorylated ε-caprolactam derivatives exhibit enhanced catalytic activity in oligomerization of caprolactam with 1,1,3-trihydroperfluoropropanol:



$$\xrightarrow{\text{Cat}} \text{H[HN(CH}_2)_5\text{C(O)]}_n\text{OCH}_2\text{CF}_2\text{CF}_2\text{H},$$

III, IV

Cat = **I, II**, n = 1 (**III**), 2 (**IV**).

With these complexes, the reaction temperature could be decreased from 250 to 165°C, and the reaction time, from 4 h to 60 min. With catalyst **I**, the yield of the oligomers was as follows: 56.8% of **III** and 43.2% of **IV**; the caprolactam conversion was 92%. With catalyst **II**, the yield was lower: 42.9% for **III** and 57.1% of **IV**; conversion 72%.

The higher activity of the catalyst **I** based on phosphorous acid monoamide can be attributed to higher polarity of the oxygen-containing copper complex formed by the lactam carbonyl group and oxygen of the five-membered phospholane ring.

The structure of the oligomers obtained was proved by IR spectroscopy, and their composition was determined by elemental analysis. The calculated molecular weights were confirmed by cryoscopy. The IR spectra were recorded on a Specord M-82 instrument as mulls in mineral oil.

Monomer III, 6-aminocaproic acid 1,1,3-trihydroperfluoropropyl ester, is a light grey powder, mp 126–129°C. It was purified by recrystallization from water. IR spectrum, ν, cm^{-1}: 1728 ($\nu_{C=O}$), 1635 (amide **I**), 1537 (amide **II**). Found, %: N 6.1; F 30.8. *M* 252 (acetic acid). $C_9H_{15}F_4NO_2$. Calculated, %: N 5.7; F 31.0. *M* 245.

Dimer IV, *N*-(6-aminocaproyl)-6-aminocaproic acid 1,1,3-trihydroperfluoropropyl ester, is a light grey powder, mp 153–157°C. It was purified by recrystallization from alcohol. IR spectrum, ν, cm^{-1}: 1724 ($\nu_{C=O}$), 1636 (amide **I**), 1540 (amide **II**). Found, %: N 7.86; F 23.0. *M* 360 (acetic acid). $C_9H_{15}F_4NO_2$. Calculated, %: N 7.82; F 21.2. *M* 358.

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