

THE INFLUENCE OF SUBSTITUENTS ON
POLYMERIZATION OF SEVEN-MEMBERED LACTAMS. IV.*
SYNTHESIS AND POLYMERIZATION
OF α -METHOXY- ϵ -CAPROLACTAM

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The polymerization of ϵ -caprolactam and its substituted derivatives is, at present, a subject of a considerable interest and reviews on the topic can be found elsewhere¹. To explain the influence of the position and character of substituents upon the polymerization of lactams, various isomers of C-alkyl derivatives of ϵ -caprolactam and their mixtures resp. have been studied. The above mentioned compounds are, however, relatively difficult to obtain in their pure form. Experimentally observed differences in the polymerization ability and the polymerization rate are believed to be caused both by varying distance of carbon-containing substituents from the amide group and by the size of the substituents themselves *i.e.* mainly by steric factors. It is to be expected that both the polymerization rate and the equilibrium concentration of monomer will also be influenced by the presence of polar substituents adjacent to the amide bond. These substituents can, according to their character, change the reactivity of this bond. This aspect, however, has not been sufficiently examined and as far as the literature data are concerned the paper of Ogata² is an exception. The work deals with the polymerization of perhydro-1,4-oxazepin-5-one and its C-methyl and phenyl derivatives, respectively. The change in the polymerization activity cannot, in this particular case, be accounted for only by the presence of the polar ether bond in the molecule. The fact that changing the methylene group by an oxygen atom causes a slight change in the ring strain should also be taken into account. Moreover, the induction effect of the ether oxygen is strongly suppressed by its relatively long distance from the amide bond (dimethylene bridge).

A maximum influence upon the activity of the amide bond can be expected in those cases where the substituent is attached to a geminal carbon atom *i.e.* in positions α - and ϵ -respectively. The selection of a suitable substituent is, however, considerably restricted because of relatively high temperatures at which polymerizations of lactams are carried out. It is obvious that the probability of side reactions is, under these conditions, considerably enhanced. It is the purpose of this work to examine both the possibility of α -methoxy- ϵ -caprolactam preparation and its polymerization ability.

α -Methoxy- ϵ -caprolactam was successfully prepared by a nucleophilic substitution reaction of sodium methoxide with α -bromo- ϵ -caprolactam in non-aqueous medium, the synthesis being analogous to that employed for preparation of alkoxy-compounds *via* their corresponding halogen derivatives³. The reaction of sodium methoxide with α -chloro- ϵ -caprolactam, prepared according to Tull and coworkers⁴, gave also positive results. The synthesis of N-benzoyl- ϵ -caprolactam in the presence of dry ϵ -caprolactam in great excess (see experimental) has many advantages as to its simplicity, easy separation and purity of the final product (compare⁴).

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Unsuccessful attempts to polymerize α -methoxy- ϵ -caprolactam in the presence of ϵ -aminocaproic acid can be accounted for by a low thermal stability of the monomer even at relatively low temperatures. The coloration of the reaction mixture together with the appearance of amine groups and transamide groups containing compounds on the one hand, and a complete disappearance of methoxy group in the liquid viscous product on the other hand, suggest a complicated course of the reaction. Destructive reactions that take place at 250°C cause, after 18 hours' exposure, the decomposition of almost fifty percent of all α -methoxy- ϵ -caprolactam molecules originally present. Analogous destructive reaction of α -alkoxybutyramide proceeding as low as at 100°C was reported by Duvilliere⁵. The presence of the *trans*-amide bond can be attributed to the process of monomer aminolysis by amino groups formed during the reaction. Because of the negative results of polymerization experiments no attempts were made to identify the reaction products.

Even more pronounced destructive reactions occur under similar conditions in the case of α -chloro- ϵ -caprolactam whose decomposition is accompanied by the evolution of hydrogen chloride. Insoluble carbon residue signifies the occurrence of considerable structural changes and complicated side reactions.

Both the above described cases shown that the amide group, containing polar substituents in its close vicinity, is prone to thermal destruction. With regard to the restricted selection of other suitable substituents it is very unlikely that the polymerization activity of ϵ -caprolactam can be significantly influenced by this means.

EXPERIMENTAL

Melting and boiling points are uncorrected. Infrared spectra were taken in chloroform using a Zeiss UR-10 spectrophotometer.

Preparation of α -Methoxy- ϵ -caprolactam

N-Benzoyl- ϵ -caprolactam. The mixture of ϵ -caprolactam (565 g, 5 mol) with freshly distilled benzoylchloride (140.5 g, 1 mol) was left standing for seven days at room temperature. The ϵ -caprolactam hydrochloride and the excessive ϵ -caprolactam were removed by repeated extraction with the mixture of water and ice. The raw product was washed on the sintered glass⁶ with ice water, 5% water solution of sodium bicarbonate and then again with the ice water till neutralization and after that it was dried *in vacuo* at room temperature. 142 g (65.5% theory) of *N*-benzoyl- ϵ -caprolactam was obtained. M.p. 68–69°C (ether; ref.⁴ 68–70.5°C). Improved product yields (up to 85%) and shortening of the time needed for the reaction were achieved when the temperature of the reaction mixture, during the addition of benzoyl chloride into the ϵ -caprolactam and during the 3 hours' standing that followed, was kept at 90–95°C.

N-Benzoyl- α -chloro- ϵ -caprolactam was prepared according the method described by Tull and coworkers⁴ through the reaction of *N*-benzoyl- ϵ -caprolactam with sulfurylchloride, the yield being 85.5% (m.p. 118°C).^{*} By treating the product with sulfuric acid α -chloro- ϵ -caprolactam was obtained in 83.5% yield (m.p. 92–93°C); α -bromo- ϵ -caprolactam was prepared in 38% yield (m.p. 111–112°C) by the reaction of distilled ϵ -caprolactam with bromine in the presence of phosphorous pentachloride and iodine⁶.

α -Methoxy- ϵ -caprolactam. A solution of α -bromo- ϵ -caprolactam (19.2 g, 0.1 mol) in 100 ml of dry benzene was added dropwise, excluding moisture, to a solution of sodium methoxide prepared by dissolving 4.85 g (0.21 mol) of sodium in 140 ml of absolute methanol. The reaction mixture was refluxed for 16 hours. The separation of sodium bromide started after two hours.

* Raw product.

The solvents were then distilled off, the sodium bromide was dissolved in water and the mixture was neutralised by an aqueous solution of acetic acid prior to extraction with chloroform. The raw product was isolated from the dry extract by fractionation collecting a 120–130°C/1 Torr fraction (3.7 g, 25.9%); The same yields were obtained when α -chloro- ϵ -caprolactam was employed. The product was then redistilled at 126–128°C/0.9 Torr and further purified by four-times repeated crystallisation from ether. The final product had m.p. 54–55°C. Infrared spectrum: 2830 and 1100 cm^{-1} (CH_3O), 1670 cm^{-1} (CO amide), 3200 cm^{-1} (NH). For the empirical formula $\text{C}_7\text{H}_{13}\text{NO}_2$ it was calculated (143.2): 58.68% C, 9.15% H, 9.78% N, 21.62% CH_3O —; found: 58.63% C, 9.22% H, 10.14% N, 21.47% CH_3O —.

Polymerization

α -Methoxy- ϵ -caprolactam, was dried at room temperature and 1 Torr pressure for twelve hours. The experiments were carried out conventionally in sealed glass tubes⁷, using 2 mol% of ϵ -aminocaproic acid as a catalyst. No polymerization occurred within the time interval from 19–66 hours and at temperatures 150, 220 and 250°C. A substantial change in the colour of the reaction mixture was observed together with the evolution of a considerable amount of basic volatile products. In all samples examined no methoxy groups were detected spectroscopically at 250°C. The infrared spectrum suggested the presence of *cis*- as well as *trans*- amide group (1670 and 1540–1580 cm^{-1} resp.). The contents of the basic products, both gaseous and those obtained by successive distillation at 100°C and normal pressure, were determined in the samples heated for 18 hours at 250°C. The gaseous products were absorbed in an excess of 0.1M-HCl and the basic compounds contents then determined by titration with 0.1M-NaOH using methylorange as an indicator (0.226 mol base per mol of the original lactam); conductometric titration with 0.1M-HCl was employed to determine the basic compounds contents in the remaining liquid phase (0.170 mol per mol of the original lactam). The overall basic groups concentration was found to be 0.396 mol/mol of the original lactam.

The attempts to polymerize α -chloro- ϵ -caprolactam carried out under similar conditions were negative. Moreover, a considerable amount of hydrogen chloride was formed during the reaction together with a charred porous residue.

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