Synthesis of ε-Caprolactam from Cyclohexanecarboxylic Acid by Using Liquid Sulfur Dioxide*

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Recently two attractive ways of ε-caprolactam syntheses have been disclosed by research groups, one being the synthesis of cyclohexanone oxime via the photonitrosochlorination of cyclohexane,[1] and the other the so-called SNIA process.[2] The latter process consists of the production of ε-caprolactam from cyclohexanecarboxylic acid and a related compound by the action of nitrosylsulfuric acid;

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* The Beckmann Rearrangement in Liquid Sulfur Dioxide, Part XII. Part XI: N. Tokura, K. Shiina and T. Terashima, This Bulletin, 35, 1986 (1962).

[1] A. E. Müller, *Angew. Chem.*, **71**, 229 (1959); *Chem. Ber.*, **90**, 1179 (1959); ibid., **92**, 63 (1959). B. M. Ito, *J. Soc. Org. Synth. Chem., Japan*, **21**, 160 (1963).

[2] SNIA Viscosa, Ital. Pat. 603606 (1960); *Chem. Abstr.*, **59**, 11273 (1963); Belg. Pat. 582793 ((1960).

the mechanism has also been discussed.[3] Cyclohexane derivatives other than cyclohexanecarboxylic acid, such as cyclohexyl aryl ketones and cyclohexanesulfonic acid, have also been suggested as possible starting materials.[2]

This paper will present a simpler method for converting cyclohexanecarboxylic acid into ε-caprolactam, using liquid sulfur dioxide as the solvent as well as the reagent. When cyclohexanecarboxylic acid was stirred into a mixture of liquid sulfur dioxide, nitric acid and sulfuric acid and the reaction was carried out at a moderate temperature for an appropriate time, ε-caprolactam could be prepared in a fair yield. In the procedure described above, it seems likely that nitrosylsulfuric acid or a reagent which could behave like nitrosylsulfuric acid may be prepared in situ in the reaction mixture from nitric acid and liquid sulfur dioxide.

Experimental

Materials.—Liquid sulfur dioxide was dried with phosphorus pentoxide and distilled. Commercial fuming nitric acid (sp. gr. 15°, 1.50) was used without further purification. Cyclohexanecarboxylic acid was distilled in vacuo; m. p. 31°C, b. p. 232—233°C. Sulfur trioxide was used after one distillation. Sulfuric acid (100% or sulfur trioxide monohydrate) was prepared from 95% sulfuric acid and sulfur trioxide. Chloroform and ether were purified by the ordinary recipes.

A Typical Procedure.—Two hundred milliliters of sulfur dioxide was distilled while being stirred into a three-necked flask cooled to −20°C, placed in a dry ice bath and equipped with a deep-freezing cooler. To this solution, 18.9 g. (0.30 mol.) of fuming nitric acid was added slowly; the white crystals which separated in the bottom of the flask dissolved again upon the addition of fuming sulfuric acid. After the dropping of nitric acid was over, fuming sulfuric acid, prepared by mixing 39.2 g. (0.4 mol.) of 100% sulfuric acid and 11.2 g. (0.14 mol.) of sulfur trioxide, was added. To this mixture, 25 g. (0.20 mol.) of cyclohexanecarboxylic acid was added slowly. The temperature was gradually raised to 68—70°C, while the excess sulfur dioxide was purged through the top of the cooler. The mixture was stirred for one more hour, cooled, and poured into ice-water.

The resultant solution was extracted with ether several times to recover the unchanged cyclohexanecarboxylic acid. The aqueous layer was neutralized with a sodium hydroxide solution, and the separated crystal of sodium sulfate was filtered off. Then the solution was repeatedly extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate and distilled. ε-Caprolactam distilled under reduced pressure at 120—130°C/5.6 mmHg and solidified to white needles, m. p. (recrystallized from petroleum ether) and mixed m. p. 68—70°C. The infrared spectrum of this sample was superimposable on that of the authentic ε-caprolactam; yield, 12.7 g. (60%, based on the consumed carboxylic acid; 3.7 g. of cyclohexanecarboxylic acid was recovered).

Below 30°C the reaction does not take place. Among the factors which may affect the yield, the reaction temperature seems to be most important.

Results and Discussion

The process employed here for the synthesis of ε-caprolactam is similar to that employed in the SNIA process except that the former uses liquid sulfur dioxide with fuming nitric acid instead of nitrosylsulfuric acid. It was obvious that, by adding fuming nitric acid to chilled sulfur dioxide, either nitrosylsulfuric acid or a reagent which would behave like nitrosylsulfuric acid was produced in the mixture. A number of methods for preparing nitrosylsulfuric acid have been published.[4] Among them, the introduction of sulfur dioxide gas into nitric acid is the most popular.[4b] However, the present authors believe that the method described in this article is without doubt a simpler method for the conversion of the carboxylic acid to the lactam.

Though the structure of the white crystals formed in the reaction mixture when fuming nitric acid was added to liquid sulfur dioxide have not yet been confirmed, it is believed to be nitrosylsulfuric acid, since the decomposition temperature of the crystal was 68—73°C (literature; [4a] 73.5°C) and the solubility (soluble in sulfuric acid and insoluble in liquid sulfur dioxide) resembled that of nitrosylsulfuric acid. An experiment was carried out using nitrosylsulfuric acid synthesized by the method of Ref. 4b to find out whether the yield was comparable to the above case. In part, a complex formed in situ from sulfur dioxide and nitric acid or a precursor of nitrosylsulfuric acid may also be the effective reagent for the reaction, since the separated crystals were small in amount and since the heat of reaction seemed to be very little.

At the beginning of this project the present authors expected a smooth running of the reaction at below-zero temperatures, since the process is thought to be a combination of nitrosation and the Beckmann rearrangement, which can occur even at −70°C. However, the reaction cannot be carried out below +30°C. This means that the nitrosation needs a somewhat higher energy of activation. A yield of 26% was recorded by the reaction at 30°C. The yield much improves at 68—70°C which

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[3] Y. Ogata, Y. Furuya and M. Ito, *J. Am. Chem. Soc.*, **85**, 3649 (1963).

[4] a) L. Vanino, "Preparative Chem.," Band I, F. Enke, Stuttgart (1923), pp. 99, 106; b) H. S. Booth, "Inorganic Synth.," Vol. I, 55 (1939).

is near the decomposition temperature (73.5°C) of nitrosylsulfuric acid. In such a temperature range the concentration of the effective nitrosonium ion (NO^+) may become higher. A search for better conditions and an elucidation of the reaction mechanism is now under way.

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