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CHEMISTRY

On the Preparation of Caprolactam from Cyclohexanone and Dinitroethane

by

T. URBAŃSKI and A. PIOTROWSKI

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Caprolactam is usually prepared by acting on cyclohexanone with hydroxylamine, followed by a Beckmann rearrangement of cyclohexanone oxime.

Novotný [1] discovered that the oxime formation can occur in presence of conc. sulphuric acid or oleum at a high temperature. Simultaneously, the rearrangement takes place and caprolactam is formed. As a further development of this method Novotný suggests [2], [3] the use of primary nitroparaffins as a source of hydroxylamine. According to his invention a primary nitroparaffin is added to conc. sulphuric acid at 120-125°. Then cyclohexanone is added to the resulting solution, and the temperature kept near 120°. After the reaction is completed the reaction mixture is neutralised with ammonia and an upper layer of caprolactam is separated and then purified by distillation under reduced pressure. The yield of caprolactam is 80 per cent of theoretical, calculated on the basis of cyclohexanone.

The authors of the present paper suggest a further development of Novotný's method, which consists in using 1,2-dinitroethane as the cheapest of all primary nitroparaffins. The trend of the reaction is much the same as that described by Novotný. The modification of the original method consisted in dissolving 1,2-dinitroethane in acetic acid prior to reacting it. This facilitated the uniformity and control of the reaction.

The solution was introduced into hot concentrated (120° C.) sulphuric acid. Isomerisation of 1,2-dinitroethane to oxalhydroxamic acid was followed by hydrolysis to hydroxylamine and oxalic acid. The latter was decomposed into carbon oxide, carbon dioxide and water. Acetic acid was distilled off during the reaction and could be recovered.

The yield of caprolactam was, in laboratory conditions, 70—75 per cent calculated on the basis of cyclohexanone.

An application for the patent has been filed at the Polish Patent Office [4].

Experimental

10 g. of 1,2-dinitroethane were dissolved in an equal weight of acetic acid. The solution was introduced dropwise during 20 minutes to 35 g. of conc. sulphuric acid, the temperature being maintained within the limits 120—125°C. The reaction flask was kept in a bath with calcium chloride solution boiling at 120°.

Next, 12.5 mg. cyclohexanone were added dropwise during 25 minutes to the reaction mixture, the temperature being still kept near 120°.

Acetic acid, was distilled off through a condenser.

After the reaction was completed (this was marked by a fall of temperature in the reaction flask), the reaction mixture was carefully neutralised by introducing it into cold aqueous 25 per cent solution of ammonia. The temperature was kept by cooling below 50°.

The mixture was separated into two layers: the lower was formed by an aqueous solution of ammonium sulphate with crystals of the latter, the upper was formed of caprolactam. The upper layer was dissolved in ether and dried over anhydrous sodium sulphate.

The product was purified by distilling under reduced pressure at 138—9°C. by 11—12 mm. Hg.

The yield was 10.5 g. of caprolactam, i. e., c. 72 per cent (calculated on cyclohexanone).

INSTITUTE OF ORGANIC SYNTHESIS, POLISH ACADEMY OF SCIENCES

REFERENCES

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[4] T. Urbański, A Piotrowski, Polish Patent application No. P 83,480 (1956).