On the Beckmann Rearrangement in Liquid Sulfur Dioxide. I : Synthesis of ε-Caprolactam

On the Beckmann Rearrangement in Liquid Sulfur Dioxide. I Synthesis of ε-Caprolactam.

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(Received February 7, 1956)

Synopsis

The formation of ε-caprolactam from cyclohexanone oxime by the Beckmann rearrangement in liquid sulfur dioxide has been studied. When sulfuric anhydride SO_3 was used as a rearrangement reagent and the process was carried out at 20°C, the reaction proceeded stoichiometrically between the oxime and sulfuric anhydride, which approved of the mechanism of the Beckmann rearrangement proposed by Kuhara and Chapman, yielding 93.6 per cent of ε-caprolactam as maximum.

The preparative method of using a small amount of the reagent and being conducted at room temperature without stirring will enable the lactam industry more economical.

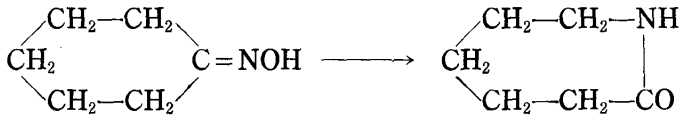
Other reagents for the rearrangement were also examined.

I. General

Liquid sulfur dioxide, as having special properties as a solvent, has recently been used in organic reaction(1), no report, however, on the application of the solvent in the Beckmann rearrangement has been found in the literature.

A method in which an oxime was subjected to the Beckmann rearrangement in good yield using sulfuric anhydride in liquid sulfur dioxide at about −10°C was described in a German patent(2), details of which were however not given.

In the former rearrangement process, for example, in the preparation of ε-caprolactam from cyclohexanone oxime, an excess of concentrated sulfuric acid was used at above 100°C. As the reaction was an exothermic one, special attention was needed for the regulation of the reaction temperature. And its yield was reported to be only 59–65 per cent by Marvel and Eck(3) and 75–78 per cent when conducted at industrial scale by Manase(4).



Cyclohexanone oxime → ε-Caprolactam (1)

The authors have conducted the Beckmann rearrangement of cyclohexanone oxime using liquid sulfur dioxide as a solvent at 20°C using a glass pressure-vessel.

(1) H. F. Johnstone, Ind. Eng. Chem., **34** (1942), 1017; L. F. Audrieth and J. Kleinberg, *Non-Aqueous Solvents*, (1953) p. 210. Cf. (6).

(2) Badische Anilin und Soda Fabrik, D. R. P. 858,397 (1952); C. A., **48** (1954), 12,810.

(3) C. S. Marvel and J. C. Eck, Org. Synth., **17** (1937), 60.

(4) K. Manase, Rev. of High Molecular Compounds, **6** (1952), 34.

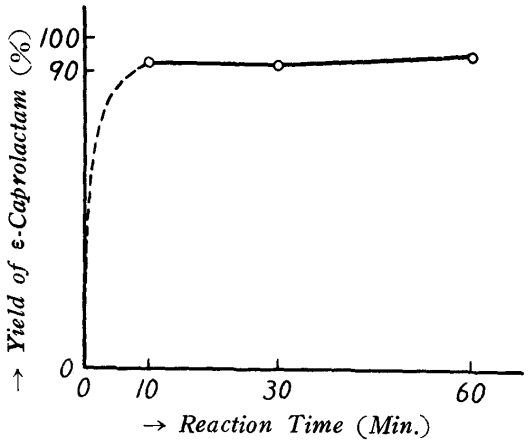
As the vapor pressure of sulfur dioxide at 20°C was about 3.2 atm/cm^2, the process was safely conducted in a glass pressure-vessel.

1. Blank test

To examine whether any reaction between cyclohexanone oxime and sulfur dioxide was caused or not, a blank test without the rearrangement reagent was conducted, obtaining unexpected results. When the oxime was kept in liquid sulfur dioxide for 1 hour, 77.2 per cent of the used oxime were recovered, but the remaining one was changed into a chloroform-insoluble substance and a chloroform-soluble high boiling substance. It is therefore necessary to carry out the present reaction with special care as far as a little part of the oxime reacts with liquid sulfur dioxide.

2. Reaction velocity and time

When an excellent rearrangement reagent was however used in the reaction, the rearrangement was completed in 10 minutes as shown in Fig. 1. As it is practically difficult to get experimental data of the reaction which will be completed within 10 minutes, it will be supposed that the rearrangement may be completed within 10 minutes or instantaneously. In this case, the change of the oxime by the action of sulfur dioxide described above may be neglected. However, when the action of the reagent is slow, the change of the oxime due to sulfur dioxide should be taken into consideration.



Mole Ratio of Cyclohexanone oxime and SO_3 was 1:1 and Reaction Temperature was 20°C.

Fig. 1. Effects of Reaction Time on the Beckmann Rearrangement.

From the above consideration and the manipulative convenience, the reaction time was arbitrarily taken as 1 hour.

3. The rearrangement due to sulfuric anhydride and the mechanism of the Beckmann rearrangement

When sulfuric anhydride was used as the rearrangement reagent, the result was excellent, giving maximum yield of 93.6 per cent as shown in Fig. 2. Moreover, the purity of the produced ε-caprolactam was high, the melting point of which being 65–67°C by mere vacuum distillation. And the mole amount of the oxime corresponding to that of sulfuric anhydride was just changed into the lactam. Although excess of sulfuric anhydride was present, the yield did not increased accordingly. Namely, the Beckmann rearrangement occured, in this case, stoichiometrically corresponding to the rearrangement reagent. When the amount of sulfuric anhydride was decreased against that of the oxime, the theoretical yield to sulfuric anhydride was kept at about 90 per cent. Namely, in the present reaction, sulfuric anhydride forms a compound (in this case a sulfuric ester) with the oxime

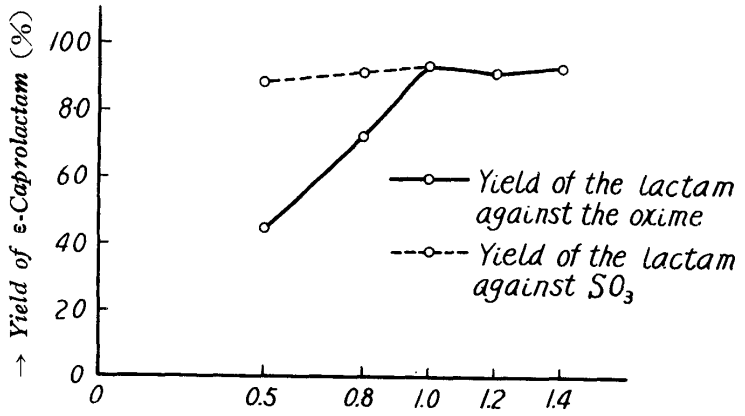


Fig. 2. Effects of SO_3 Moles on the Yield of Lactam.

in the mole ratio of 1 : 1, through which the rearrangement reaction is completed. Sulfuric anhydride does not react as a catalyst. This fact endorses the theory proposed by Kuhara and chapman[5].

When sulfuric anhydride is used in liquid sulfur dioxide as the rearrangement reagent, the minimum amount of the anhydride is sufficient for the reaction. Moreover, the reaction is conducted at room temperature without heating and agitation. This method has therefore important meaning in industry.

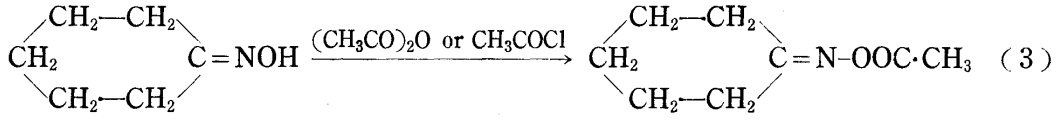
4. Action of various rearrangement reagents

Various reagents were used in the equimolar ratio to the oxime at the same condition, the results being shown in Table 2. The following compounds were used as rearrangement reagents, figures in the blackets being the yields in percentages: P_2O_5 (29.2), PCl_5 (54.8), $POCl_3$ (45.6), PCl_3 (41.6), PBr_3 (43.2), and $SOCl_2$ (60.0). Their yields were less than that obtained by using sulfuric anhydride. Reacting with 2 moles of water, bromine in liquid sulfur dioxide is known to form hydrogen bromide and sulfuric acid as shown in the following formula (2)[6].

$$Br_2 + 2H_2O + SO_2 = 2HBr + H_2SO_4 \qquad (2)$$

The resulting product or the product freed from sulfuric acid gave no rearrangement action. Also SO_2Cl_2 gave no lactam and the color of the reacting solution was changed blue, which was supposed to be due to chloro-nitroso reaction of the oxime.

When acetic anhydride or acetyl chloride was reacted with the oxime in liquid sulfur dioxide, only acetyl compound of the oxime was produced, which was clear from its infra red absorption spectrum or the result of its hydrolysis.



(3)

(5) B. Jones, Chem. Rev., **35** (1944), 335.

(6) J. Ross, J. H. Percy, R. L. Brandt, A. I. Gebhart, J. E. Mitchell and S. Yolles, Ind. Eng. Chem., **34** (1942), 924.

II. Experimental

1. Samples

(i) Liquid sulfur dioxide

Commercial sulfur dioxide in a bomb was used after filtering through filter paper. Sulfur dioxide, distilled or distilled after drying with concentrated sulfuric acid and subsequently with phosphorous pentoxide was used for comparison but no difference was perceived.

(ii) Cyclohexanone oxime

This was prepared from cyclohexanone and hydroxylamine by the known method[7] in the yield of 82–86 per cent, m. p. 89.5–90.5°C.

(iii) Rearrangement reagents

The following extra pure commercial products were used : Sulfuric anhydride, concentrated sulfuric acid, phosphorous pentoxide, concentrated phosphoric acid, PCl_5, $POCl_3$, PCl_3, PBr_3, $SOCl_2$, SO_2Cl_2, Br_2, glacial acetic acid, $AlCl_3$, BF_3(etherate), chlorosulfonic acid.

2. Experimental apparatus and manipulation

A glass pressure-vessel (A) of 300 cc capacity shown in Fig. 3 was used. The upper part of (A) was connected to cock (B) through a metallic joint (a). Cyclohexanone oxime was taken into (A) and cooled with ice. Another pressure-vessel containing liquid sulfur dioxide was connected to a joint (b) and the cock (B) was opened. Thus liquid sulfur dioxide was introduced into (A) and the oxime in (A) was dissolved in a colorless transparent solution. A rearrangement reagent dissolved in liquid sulfur dioxide contained in a similar vessel was introduced into (A) under cooling. The whole was thoroughly shaken and kept for the reaction at 20°C.

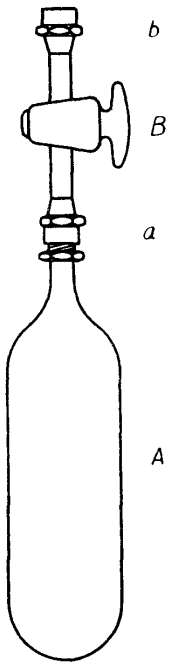


Fig. 3. Glass Reaction Vessel.

Among the reagents, as concentrated sulfuric and phosphoric acids, phosphorous pentoxide and phosphorous tribromide were difficultly soluble in liquid sulfur dioxide, a liquid sulfur dioxide solution of the oxime was added into a mixture of the reagent and liquid sulfur dioxide for reaction.

3. Experimental results

(i) Action of liquid sulfur dioxide to cyclohexanone oxime

As a blank test, the action of the solvent sulfur dioxide to the oxime without the rearrangement reagent has been examined. Twenty five grams (1/4.5 mole) of

(7) E. W. Bonsquet, Org. Synth., **11** (1931), 56.

the oxime were dissolved in 200 cc of liquid sulfur dioxide contained in a pressure-vessel and kept at 20°C for 1 hour. A colorless solution became turbid and then light yellow semi-transparent solution. Then liquid sulfur dioxide was evaporated off and the residue was extracted with chloroform, from which a fraction boiling at 95–115°C/10–11 mm was obtained by distillation under reduced pressure, which gave a substance melting at 89.5–90.5°C by recrystallizing from ligroin (b. p. 80–100°C), the yield being 19.3 grams (77.2 per cent). The substance was proved to be cyclohexanone oxime by mixed melting test with the known oxime.

By further vacuum distillation of 4 grams of the distillation residue, a fraction (1.1 grams; 4.4 per cent yield) boiling at 115–125°C/1–2 mm was obtained, which gave a solid melting at about 140°C by recrystallization from ligroin (b.p. 80–100°C). The chloroform insoluble part of the evaporation residue of liquid sulfur dioxide was 1.5 grams in weight (6.0 per cent). The examination results of these substances will be reported in future.

(ii) The Beckmann rearrangement

Twenty five grams (1/4.5 mole) of cyclohexanone oxime were dissolved in 100 cc of liquid sulfur dioxide (about 150 grams, 10 times moles against that of the oxime), to which the rearrangement reagent dissolved in 100 cc of liquid sulfur dioxide was added and kept for a definite time at 20°C. It was thoroughly cooled and then the whole was transferred into a beaker and the unreacted reagent and the reaction product were treated with water. After evaporating off liquid sulfur dioxide, the residue was neutralized with a 25 per cent sodium hydroxide solution and extracted with 500 grams of chloroform. Unreacted cyclohexanone oxime was recovered by vacuum distillation at 95–115°C/10–11 mm and subsequently ε-caprolactam was obtained as colorless crystals, melting at 65–67°C. When other reagents were used, the product (m. p. 40–60°C) was generally colored, which gave crystals of m. p. 67–68°C by recrystallizing from ether.

(a) Confirmation of ε-caprolactam

As ε-caprolactam is an isomer of cyclohexanone oxime, they are not distinguished each other by the elemental analysis. ε-Caprolactam was obtained in the yield of 93.6 per cent (23.4 grams) using 17.7 grams (1/4.5 mole) of sulfuric anhydride at 20°C for 1 hour. Seven tenths gram of the product was refluxed with 3.5 grams of 15 per cent sodium hydroxide solution for 30 minutes, to which 1 gram of benzoyl chloride was added drop by drop under cooling and agitation at about 20°C requiring about 20 minutes. It was diluted with 15 grams of water and made acidic by dropping hydrochloric acid (1:1) under agitation. The formed white oily product was set for 3 hours under cooling until crystals were produced. The crystal was thoroughly washed with water and dried in vacuo, m. p. 72–76°C; yield 1.2 grams (82.7 per cent). Recrystallizing from a mixture of ethanol-ligroin-ether, it gave crystals of m. p. 80–80.5°C (0.3 gram), which was proved to be benzoyl amino-caproic acid by mixed melting test with the authentic substance[8].

(8) A. Galat, J. Am. Chem. Soc., **69** (1947), 86.

Analysis of Nitrogen:

Found	Calculated as $C_{13}H_{17}O_3N$
5.99 %	5.95 %

(b) Effects of reaction time

One hour was arbitrarily selected as the reaction time. It was supposed that the reaction velocity was different according to the rearrangement reagent. When sulfuric anhydride was used, the reaction was completed within 10 minutes. In case 25 grams of the oxime and 17.7 grams of sulfuric anhydride were used (in 1 : 1 mole ratio), the yields of the product were 93.2 per cent after 10 minutes' reaction, 90.8 per cent after 30 minutes, and 93.6 per cent after 1 hour, respectively. In case a reagent by which the reaction velocity was very slow was used, it was not wise to have the oxime contacted with the solvent sulfur dioxide more than 1 hour from the result of the blank test, because the unreacting oxime would cause side reaction with sulfur dioxide in large degree.

(c) Action of sulfuric anhydride

When sulfuric anhydride was used as the rearrangement reagent in liquid sulfur dioxide, the lactam of high purity was obtained in good yield and no further recrystallization of the product was needed. Moreover, the Beckmann rearrangement proceeded stoichiometrically between the equimolar amount of sulfuric anhydride and the oxime. And the yield (rearrangement ratio) for the amount of sulfuric anhydride was about 90–93 per cent.

Table 1. Effects of SO_3 Moles on the Yield of Lactam.

SO_3 (g)	SO_3/Oxime (Mole Ratio)	ε-Caprolactam		Yield of the Lactam against the Mole Number of SO_3 (%)
		Amount (g)	Yield (%)	
23.7	1.4	23.1	92.4	—
21.2	1.2	22.7	90.8	—
17.7	1.0	23.4	93.6	93.6
14.1	0.8	18.1	72.4	90.5
8.8	0.5	11.2	44.8	89.6

The reaction was conducted at 20°C for 1 hour using 200cc of liquid SO_2 and 25 grams of the oxime.

(d) Action of various rearrangement reagents

Rearrangement reactions were conducted at 20°C for 1 hour using 25 grams (1/4.5 mole) of the oxime and 1/4.5 mole of a reagent, the results were shown in Table 2. When the reaction did not proceed smoothly, not only the oxime, but also cyclohexanone was recovered.

(e) Action of acetic anhydride and acetyl chloride

The rearrangement was conducted at the same condition described above using 25 grams of the oxime and the equimolar amount of acetic anhydride or acetyl chloride, respectively. By the vacuum distillation, cyclohexanone and then a fraction boiling at 127–128°C/16-17 mm were obtained in each case.

Table 2. Yield of the Lactam by Various Reagents.

Reagent	Lactam		Recovered	
	Amount (g)	Yield (%)	Cyclohexanone (g)	Cyclohexanone oxime (g)
SO_3	23.4	93.6	0	0
96–97% H_2SO_4	0	0	1.3	19.7
P_2O_5	7.3	29.2	2.2	6.5
85–86% H_3PO_4	0	0	10.5	7.1
PCl_5	13.7	54.8	Trace	2.7
$POCl_3$	11.4	45.6	1.0	5.4
PCl_3	10.4	41.6	1.0	3.7
PBr_3	10.8	43.2	1.3	1.2
$SOCl_2$	15.0	60.0	5.8	0
SO_2Cl_2	0	0	1.3	12.8
HBr	0	0	5.9	10.2
$HBr+H_2SO_4$	0	0	4.6	13.2
CH_3COOH	0	0	11.8	3.6
$AlCl_3$	0	0	0.1	19.0
$BF_3{\cdot}O(C_2H_5)_2$	0	0	8.4	12.6
$SO_2(OH)Cl$	0	0	3.8	12.3

	Reagent	B.P.	n_D^{22}	N (%)	Acetate amount (g)	Acetate yield (%)	Cyclohexanone (g)
I	Acetic anhydride	127–128°C/16–17mm	1.4792	9.26	27.5	79.9	1.6
II	Acetyl chloride	126–128°C/16–17mm	1.4800	9.34	19.3	56.1	3.5

As it was difficult to identify the obtained liquid to be cyclohexanone oxime acetate[9] or N-acetyl-ε-caprolactam[10], they were subjected to infra red absorption and hydrolysis.

	Physical constants of the Authentic Compounds in the Literatures[9),10)]		Calculated	
		B.P.	n_D^{22}	N% as $C_8H_{13}O_2N$
III	Cyclohexanone oxime acetate	127–128°C/16–17mm	1.4790	9.03 (9)
IV	N-Acetyl-ε-caprolactam	124–125°C/16–17mm	1.4860	9.03 (10)

Comparison of Infra Red Absorption Spectra

The infra red absorption spectra were measured using a Perkin-Elmer 21 B double beam spectrometer.

The maximum absorptions of the infra red absorption spectra in the case of I and II were found as follows:

I	2940 cm^{-1}	1750 cm^{-1}	1640 cm^{-1}
II	2940 cm^{-1}	1750 cm^{-1}	1640 cm^{-1}

(Prism: NaCl, Thickness: 0.025 mm)

The maximum absorptions of III and IV synthesized according to the literature description were found as follows:

(9) Z. Csürös, K. Zech, G. Dely and E. Zalay, C. A., **46** (1952), 5003.
(10) H. A. Offe, C. A., **42** (1948), 4548.

III	2940 cm^{-1}	1750 cm^{-1}	1640 cm^{-1}
IV	2940 cm^{-1}	1680 cm^{-1}	

(Prism : NaCl, Thickness : 0.025 mm)

The absorption curves of I and II coincided well with that of III.

The absorptions 1750 cm^{-1} and 1640 cm^{-1} were assigned to the presence of ester combination and azometin radical (-N : C<), the reaction product was therefore cyclohexanone oxime acetate.

Hydrolysis

Five grams of the sample was heated for 3 hours on a boiling water bath with 10 grams of concentrated hydrochloric acid, then the product was cooled with ice, neutralized with 100 cc of ether. The extract was evaporated to dryness under reduced pressure and the residue was recrystallized from ligroin (b. p. 80–100°C) obtaining cyclohexanone oxime in the yield of 74.1 per cent (2.7 grams) and melting at 89.5–90.5°C. A mixture of the crystal and the known oxime gave no lowering of melting point.

Summary

(1) The Beckmann rearrangement in liquid sulfur dioxide was studied, obtaining ε-caprolactam from cyclohexanone oxime.

(2) The reaction was conducted at room temperature (20°C), without heating and agitation. When the equal moles of sulfuric anhydride and the oxime were used, the maximum yield of the lactam was 93.6 per cent.

(3) When sulfuric anhydride was used as the rearrangement reagent, the reaction was completed in a very short period and the lactam was formed stoichiometrically corresponding to the amount of sulfuric anhydride used. Namely, the fact endorsed the theory on the Beckmann rearrangement proposed by Kuhara and Chapman.

(4) It was made clear from the present experiment that the manufacture of ε-caprolactam might be more economically conducted than the former method.

(5) The reaction was also conducted in liquid sulfur dioxide using other various rearrangement reagents. Phosphorous-pentoxide, -pentachloride, -oxychloride, -trichloride, -tribromide, and thionyl chloride were effective and their yields being about 50–60 per cent.

Acknowledgement:

Liquid sulfur dioxide used in the experiment was donated by Befu Chemical Industrial Company. Infra red absorption spectra were taken by Mr. Y. Ikegami of this Institute, Tôhoku University. The authors should like to express their thanks for them.

(The paper was read at the Joint Meeting of the Kantô and Tôhoku Branches of the Chemical Society, Japan, held at Yamagata City in October 6, 1955).