Beckmann Rearrangement in Liquid Sulfur Dioxide. III. Rearrangement by Chlorine with Various Salts

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In a previous work¹⁾, it was shown that the Beckmann rearrangement may be carried out by bromine only or by chlorine with a small quantity of bromine at room temperature in liquid sulfur dioxide and a possible mechanism was discussed. When chlorine was used without a catalytic amount of bromine, the rearrangement could not be induced at all. This result led the authors to examine the effect of various inorganic substances, and it now has been found that the addition of small amounts of such substances to chlorine may effect the Beckmann rearrangement in liquid sulfur dioxide.

Four groups of compounds were examined.

(1) The bromine compounds (potassium bromide, *N*-bromosuccinimide and hydrogen bromide) were the most effective, yielding 75.6, 75.2 and 67.6% of the acid amide, respectively. (2) The chlorine derivatives were the least effective. (3) Red phosphorus, sulfur and iron powder gave a moderate yield of products. (4) The effect of potassium nitrate, nitrite and cyanide was similar to that of the chlorine compounds.

The rearrangement of cyclohexanone oxime in liquid sulfur dioxide was studied at 20°C. The molar ratio of chlorine to

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1) N. Tokura, R. Asami and R. Tada, *J. Am. Chem. Soc.*, **79**, 3135 (1957).

the promoter was 1 to 0.1. The results are listed in Table 1.

When compounds not easily soluble in liquid sulfur dioxide, such as phosphorus, were used, the reaction mixtures were occasionally shaken during the reaction. In the case of the bromine compounds, it was probable that the bromine liberated by the exchange reaction between chlorine and the bromine compounds promoted the rearrangement as in the previous case. The chlorine compounds were also likely to initiate the rearrangement but the yields of lactam were smaller than in the case of bromine compounds.

TABLE I

EFFECT OF CHLORINE AND INORGANIC MATERIALS OR SALTS ON THE REARRANGEMENT OF CYCLOHEXANONE OXIME IN LIQUID SULFUR DIOXIDE

Chlorine with	Yield of ε-caprolactam	
	g.	%
HBr	16.9	67.6
NaBr	6.9	27.6
KBr	18.9	75.6
N-bromosuccinimide	18.8	75.2
KI	4.1	16.4
KCl	3.2	12.8
PCl_5	5.5	22.0
S_2Cl_2	7.9	31.6
$SOCl_2$	2.9	11.6
$AlCl_3$	5.0	20.0
$FeCl_3$	2.9	11.6
$SnCl_4$	1.8	7.2
Phosphorus (red)	11.2	44.8
Sulfur	8.0	32.0
Iron powder	4.5	18.0
KNO_3	2.9	11.6
KNO_2	3.8	15.2
KCN	3.1	12.4

Cyclohexanone oxime, 25 g. (0.22 mole), liq. SO_2 200 ml., mole ratio of oxime: chlorine: salt=1 : 1 : 0.1, reaction temp. 20°C, reaction time, one hour.

Although the solubilities in liquid sulfur dioxide were very small, sulfur and iron powder gave 32.0 and 18.0% yields, respectively. These results well coincided with 31.6 and 11.6% obtained with sulfur chloride and ferric chloride, respectively, whereas it was expected that in liquid sulfur dioxide, sulfur and chlorine might combine to form sulfur chloride and iron and chlorine to form ferric chloride. The initiation of the rearrangement by chlorine and phosphorus was explicable by the formation of phosphorus chloride followed by the decomposition of the latter to phosphorus oxychloride and thionyl chloride in liquid sulfur dioxide.

The mixture of the oxime, chlorine and an added promoter salt in liquid sulfur dioxide turned blue or bluish green in color, indicating the formation of a chloro-nitroso compound, while, hydrogen bromide, potassium bromide, *N*-bromosuccinimide, sulfur chloride or sulfur gave a reaction mixture reddish brown to orange in color, showing the absence of the chloro-nitroso radical, and the rearrangement was more profound than in the cases using a salt. The rearrangement was not improved by the addition of potassium nitrate, nitrite or cyanide.

Experimental

Reagents.—Cyclohexanone oxime was prepared according to the description of " Organic Syntheses "[2], m.p. 89.5—90.5°C. The salts and the inorganic materials were of the commercial purest grade, and used without further purification. Commercial chlorine from a cylinder was treated with concentrated sulfuric acid and distilled. Liquid sulfur dioxide was dehydrated with concentrated sulfuric acid, but it brought about no difference upon the results whether it was dehydrated or not.

Apparatus and the general procedure.—Glass pressure bottles, 300 ml. capacity, were used. Liquid sulfur dioxide (100 ml.) was added to the oxime (25 g., 0.22 mole) with cooling and a solution (100 ml.) containing chlorine (15.8 g., 0.22 mole) with a small definite amount (0.022 mole) of a promoter (one of the inorganic substances) was added. In experiments with a sparingly soluble material such as sulfur or sodium bromide, the cyclohexanone oxime solution was added to the chlorine solution. The mixture was allowed to stand, with occasional shaking when the mixture was not homogeneous or the reagent was difficultly soluble, for one hour at 20°C. Then the mixture was added to water with cooling and the solvent was allowed to evaporate. The residue was neutralized with diluted sodium hydroxide solution and the products were extracted with chloroform. After removal of the solvent, the residue was distilled under a reduced pressure to yield cyclohexanone (b.p. 55∼65°C/35∼36 mm.), unchanged oxime (b.p. 95∼115°C/10∼11 mm.) and ε-caprolactam (b.p. 120∼130°C/7∼8 mm.). The ε-caprolactam was recrystallized from ether, m.p. 67∼68°C. It was identified as ε-benzoylamino-caproic acid, m.p. and mixed m.p. 80∼80.5°C.

Rearrangement by chlorine with various reagents.—*Hydrogen bromide.* Liquid sulfur dioxide solution of anhydrous hydrogen bromide (0.022 mole) was prepared by separating the upper layer of the reaction mixture from 1.8 g. (0.011

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[2] E. W. Bonsquet, "Org. Synth.", **11**, 56 (1931).

mole) of bromine, 0.4 g. (0.022 mole) of water and 100 ml. of liquid sulfur dioxide. When chlorine mixed with the solution was added to the oxime solution, the reddish-orange reaction mixture produced 16.9 g. of ε-caprolactam. Yield 67.6% of the theory.

Sodium bromide. To a mixture of 15.8 g. of chlorine and 2.3 g. of sodium bromide in liquid sulfur dioxide a solution of cyclohexanone oxime in liquid sulfur dioxide was added. The reaction mixture turned blue in color and an insoluble powder precipitated. Treatment as described above gave 6.9 g. of ε-caprolactam. Yield 27.6%.

Potassium bromide. Chlorine and 2.7 g. of potassium bromide in liquid sulfur dioxide afforded 18.9 g. of ε-caprolactam (75.6%). The sulfur dioxide solution was reddish orange in color with fine fibrous precipitates.

N-Bromosuccinimide. This reagent (4.0 g.) gave a transparent solution pale reddish-orange in color with fine white precipitates, which afforded 18.8 g. of ε-caprolactam. Yield 75.2%.

Potassium iodide. ε-Caprolactam (4.1 g., 16.4%) was obtained from the reaction mixture of green emulsion by using 3.7 g. of potassium iodide.

Potassium chloride. By the use of 1.7 g of potassium chloride the reaction mixture became blue in color and gave a small amount of a powder and yielded 3.2 g. (12.8%) of ε-caprolactam.

Phosphorus pentachloride. From the blue reaction mixture from 4.7 g. of phosphorus pentachloride, 5.5 g. of ε-caprolactam (22.0%) was obtatined.

Sulfur chloride. By the use of 3.0 g. of sulfur chloride, the pale blue, turbid, reaction mixture afforded 7.9 g. of ε-caprolactam (31.6%).

Thionyl chloride. To the solution of the oxime in liquid sulfur dioxide, chlorine with 2.7 g. of thionyl chloride in liquid sulfur dioxide was added and the resulting pale blue reaction mixture gave 2.9 g. (11.6%) of ε-caprolactam.

Aluminum chloride. By the use of 3.0 g. of aluminum chloride, the blue reaction mixture afforded 5.0 g. of ε-caprolactam. Yield 20.0%.

Ferric chloride. The pale green reaction mixture from 3.7 g. of ferric chloride produced 2.9 g. of ε-caprolactam, yield 11.6%.

Stannic chloride. From a pale blue reaction mixture from 5.8 g. of stannic chloride and chlorine, 1.8 g. (7.2%) of ε-caprolactam was obtained.

Phosphorus. The pale blue reaction mixture, in which 2.8 g. of red phosphorus had been added in suspension, gave 11.2 g. (44.8%) of ε-caprolactam.

Sulfur. A dark reddish brown reaction mixture was obtained from 5.7 g. of sulfur which was difficultly soluble and afforded 8.0 g. of ε-caprolactam in 32.0% yield.

Iron. Iron powder (1.3 g.) was mixed and occasionally shaken with the reaction mixture to afford 4.5 g. (18.0%) of ε-caprolactam.

Potassium nitrate. When 2.5 g. of potassium nitrate was used, 2.9 g. (11.6%) of ε-caprolactam was obtained from the blue reaction mixture with a small white precipitate.

Potassium nitrite. ε-Caprolactam 3.8 g., 15.2% was obtained from the pale blue reaction mixture with chlorine and 2.4g. of potassium nitrite.

Potassium cyanide. By the use of 1.5 g. of potassium cyanide, the bluish green reaction mixture gave 3.1 g. of ε-caprolactam, yield 12.4%.

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