Tetrahedron Letters No. 2, pp 195 - 197, 1974. Pergamon Press. Printed in Great Britain.

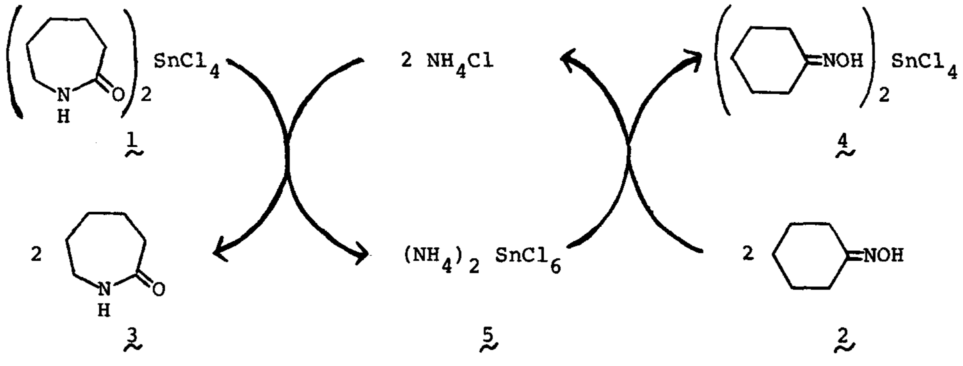
A TWO STEPS LIGAND EXCHANGE REACTION OF ε-CAPROLACTAM STANNIC CHLORIDE COMPLEX WITH CYCLOHEXANONE OXIME MEDIATED BY AMMONIUM CHLORIDE

M. Masaki, I. Uchida, H. Yasuno and N. Morimoto
Polymer Research Laboratory, Ube Industries
Minami-kaigan 8-2, Goi, Ichihara, Chiba 290, Japan

(Received in Japan 5 November 1973; received in UK for publication 3 December 1973)

Although much interest in coordination complexes of amides with stannic chloride has been directed to the structure and the behavior in solution,[1)] reports concerned with the reactivity have scarcely appeared as far as we are aware. We report here a two steps ligand exchange reaction of ε-caprolactam stannic chloride complex (**1**) with cyclohexanone oxime (**2**), in which ammonium chloride was used as a medium carrying stannic chloride. An overall representation of the reaction, which is available for an ε-caprolactam synthesis, is illustrated in Scheme I.

Scheme I.



It has been known that alcohols[2)] or enolizable ketones[3)] condense easily with stannic chloride to give dehydrochlorinated products. However, the reaction of **1** with 2 equiv of pyridine in isopropanol gave ε-caprolactam (**3**) and pyridine stannic chloride coordination complex (two to one in molar ratio) in yields of 95 and 97%, respectively, and dehydrochlorination reaction was not observed.

When **1** (10 mmole) was heated with **2** (20 mmole) in benzene (50 ml) for 30 min, a ligand exchange reaction occured, and **3** and cyclohexanone oxime stannic chloride complex (**4**) were formed in yields of 73 and 74%, respectively. The reaction mixture consisted of the solution of **3** (14.7 mmole) and **2** (5.3 mmole) in benzene and the precipitates of **4** (7.4 mmole) and **1** (2.6 mmole). The reaction was elucidated to be an equilibrium state (eq. 1) by a treatment of **4**

$$\mathbf{1} + 2\,\mathbf{2} \rightleftharpoons 2\,\mathbf{3} + \mathbf{4} \qquad (1)$$

with 2 equiv of **3** in a similar condition giving the same mixture. A reaction of **1** with **2** in isopropanol refluxed for 1 hr afforded **3** and **4** in 86% yields. The yields were confirmed to be the limited value by the reverse reaction. Under these conditions, all reaction were heterogeneous. The different yields between the reaction in benzene and in isopropanol are apparently due to a difference of the equilibrium states, which should be depending conclusively on each concentration of four components in the solutions. The difference could be ascribed to the different solubility ratios of **4** to **1** in these solvents.

When **1** (25 mmole) was heated with ammonium chloride (50 mmole) in isopropanol (100 ml) for 4 hr, ammonium hexachlorostannate (**5**) was obtained as a precipitate in a yield of 99%, and **3** was recovered in a yield of 99% from the solution.4) The stannate (**5**) was found to react with **2** giving **4** and ammonium chloride. When **5** (25 mmole) was treated with **2** (50 mmole) in water (5 ml)-isopropanol (60 ml) at room temperature for 4 hr, **4** was obtained as a precipitate in a yield of 97%. However, the same reaction in anhydrous isopropanol gave **4** only in a yield of 14% after stirring for 16 hr at room temperature, and in a yield of 36% after refluxing for 4 hr. The reaction of **2** with **5** was also performed successfully by contacting an aqueous solution of **5** with a solution of **2** in benzene or ethylene dichloride, thereby **4** was formed as a product insoluble in both phases in a yield of 97% in benzene or of 93% in ethylene dichloride.

In a combination of the reaction of **1** and ammonium chloride with that of the stannate (**5**) and **2**, the overall reaction can be regarded as a ligand exchange reaction of **1** with **2** mediated by ammonium chloride. This reaction is the first example of a ligand exchange reaction mediated by an inorganic salt. This method has two advantages over the direct reaction of **1** with **2**. The first is to overcome the limitation in yield of the products, which is depending on the equilibrium state of the direct reaction, while the second consists in that a contamination of the product (**3**) with the reactant (**2**) can be avoided and a separation of the product is easy.

An application of this novel method provides a new route for an ε-caprolactam synthesis accompanied with no by-product,5) since 4 has been found to be readily convertible into **1**.6)7)

References and Notes

1) R. C. Paul, "New Pathways in Inorganic Chemistry", E. A. V. Ebsworth et al., Ed., Cambridge Univ. Press, Cambridge, 1968, p 233.

2) R. K. Multani, Indian J. Chem., 2, 335 (1964); D. C. Bradley, E. V. Caldwell and W. Wardlaw, J. Chem. Soc., 3039 (1957).

3) Y. I. Baukov and I. F. Lutsenko, Organometal. Chem. Rev., A, 6, 355 (1970); A. L. Allred and D. W. Thompson, Inorg. Chem., 7, 1196 (1968).

4) S. S. Sandhu and J. C. Bhatia [J. Inorg. Nucl. Chem., 31, 2445 (1969)] reported that pyridine stannic chloride complex reacted with hydrogen chloride, thionyl chloride, or acyl chlorides to form conducting complexes in nitrobenzene, whose conducting character was ascribed to the formation of hexachlorostannate ion in the solution. In a reaction of **1** with hydrogen chloride, we could isolate ε-caprolactam hexachlorostannate as a very hygroscopic crystals, for which a satisfactory elemental analytical result was obtained. The stannate lost hydrogen chloride gradually at room temperature and rapidly on being heated under dry conditions, yielding **1** again.

5) Since it is still now a major theme in an industrial chemistry to produce ε-caprolactam avoiding by-products, searchs for new fundamental chemical reactions, in order to resolve the problem, are being done by many groups: Chem. Eng. News, 51, (15), 14 (1973).

6) M. Masaki, K. Fukui, M. Uchida, K. Yamamoto and I. Uchida, Bull. Chem. Soc., Japan, 46, 3179 (1973).

7) M. Masaki, J. Kita, K. Fukui and S. Matsunami, Tetrahedron Letters,