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ZIRCONIUM AND DICHLOROTIN(IV) SALTS OF 3,4,5,6-TETRAHYDRO-2H-AZEPIN-7-OL HYDROGEN SULFATE, HIGHLY EFFECTIVE CATALYSTS FOR THE BECKMANN REARRANGEMENT OF CYCLOHEXANONE OXIME

M. Masaki, J. Kita, K. Fukui and S. Matsunami
Polymer Research Laboratory, Ube Industries
Minami-kaigan 8-2, Goi, Ichihara, Chiba 290, Japan

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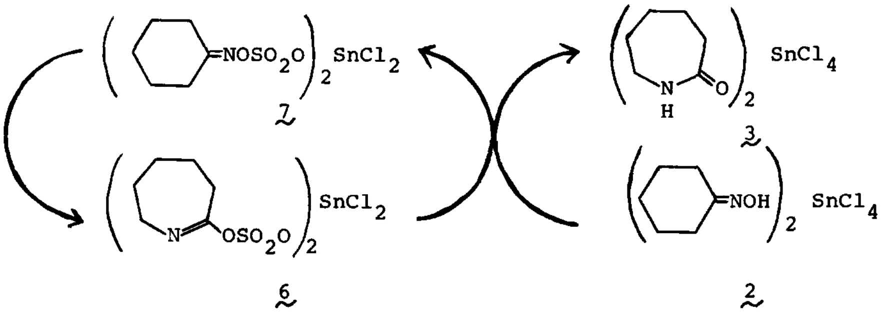
In the Beckmann rearrangement of ketoximes to amides using a rearranging agent containing sulfur trioxide moiety, *e.g.* such as sulfuric acid,[1)] oleum,[1)] or sulfur trioxide-Lewis base complex,[2)] it is well known that the agent is in need of at least an equimolar quantity to the ketoxime,[3)] and its recovery in any form which can be used for a repeated reaction is very difficult. Recently, we have found that a reaction of 3,4,5,6-tetrahydro-2H-azepin-7-ol hydrogen sulfate (**1**) with cyclohexanone oxime stannic chloride complex (**2**) in ethylene dichloride proceeds *via* sulfonyl group and ligand exchanges to give ε-caprolactam stannic chloride complex (**3**) and cyclohexanone oxime hydrogen sulfate (**4**), which rearranges to regenerate **1** in the reaction system.[4)]

We now wish to report syntheses of zirconium and dichlorotin(IV) salts of **1** and an unusually enhanced activity of the tin (IV) salt as a Beckmann rearrangement catalyst, which provides a new mode of recyclic system for the Beckmann rearrangement illustrated in Scheme I.

Scheme I



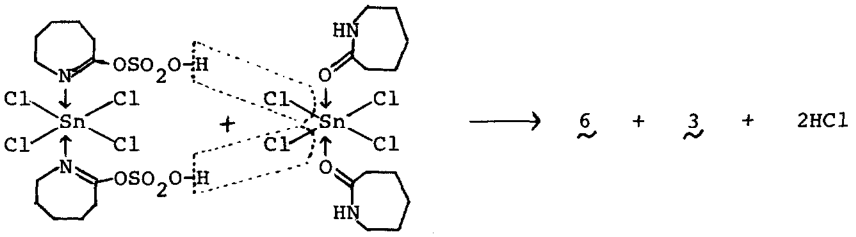
Zirconium tetrakis(3,4,5,6-tetrahydro-2H-azepin-7-ol sulfate) (5) was synthesized by heating a mixture of 4 equiv of 1 and 1 equiv of zirconium tetrachloride in ethylene dichloride for 4 hr, during which dry nitrogen gas was passed through a capillary into the mixture, in order to remove hydrogen chloride formed. Ninety four percent amount of hydrogen chloride based on 1 was removed, and 5 was obtained as colorless crystals insoluble in the solvent in 92.5% yield, which had mp 213° (decomp). Anal. Calcd. for $C_{24}H_{40}N_4O_{16}S_4Zr$: C, 33.51; H, 4.69; N,6.52; S, 14.91. Found: C, 32.94; H, 4.64; N, 6.66; S, 14.34. Ir-spectrum: $\nu_{C=N}$ 1560(s) and ν_{SO} 1340(m), 1210(s), 1195(m) and 1020 cm^{-1}(m).

A reaction of 1 with stannic chloride was attempted in a similar condition, but the dehydrochlorination was very slow and a prolonged heating caused some decomposition. Recently, Amaudrut and Devin described that the reactions of several carboxylic acids with stannic chloride afforded always disubstituted derivatives, whereas di- and trichloroacetic acids gave no substitution reactions.5) Stannic chloride is known to be hardly active to strong acids, such as sulfuric acid,6) perfluoroalkanecarboxylic acid,7) perfluoroalkanesulfonic acid8) or fluorosulfonic acid.9)

We succeeded in the dehydrochlorination between 2 equiv of 1 and 1 equiv of stannic chloride in the presence of 1 equiv of 3. Nearly quantitative amount (2 equiv) of hydrogen chloride was generated by refluxing in ethylene dichloride for 14 hr under passing dry nitrogen carrier gas into the solution. The formation of dichlorotin(IV) bis(3,4,5,6-tetrahydro-2H-azepin-7-ol sulfate) (6) in the solution was confirmed by disappearance of the acid proton of 1 at τ 12.77 in nmr-spectrum, and by a reaction of the product with ε-caprolactam hydrochloride giving 2 equiv of the parent sulfate (1) and 1 equiv of 3.

It is of interest and importance that the condensation does proceed smoothly in the presence of 3. Analogously, triphenylphosphine oxide stannic chloride complex could be successfully used in place of 3 as a catalyst for the dehydrochlorination reaction. This fact suggests that the dehydrochlorination occured between 1 coordinating on tin(IV) and stannic chloride activated by possessing the lactam as the ligand, as illustrated in Scheme II.

Scheme II



When **6** was treated with an equiv of **2** in ethylene dichloride at room temperature, an exothermic reaction occurred and the lactam complex (**3**) was obtained as a crystalline precipitate quantitatively.[10] Since **2** is estimated to be a N-coordinating complex,[11] this reaction can be rationalized by an initial nucleophilic attack of oxygen atom of **2** on sulfur atom of **6**, yielding ε-caprolactam and dichlorotin(IV) bis(cyclohexanone oxime sulfate) (**7**), nitrogen atom of which coordinates to stannic chloride, and affording **3** and **7** <u>via</u> the subsequent ligand exchange. The sulfate (**7**) rearranged to regenerate **6** under the reaction conditions. The regeneration of **6** was confirmed by a repeated reaction with **2**, which was performed by the following procedure.

A solution of **6** (24 mmole), prepared from **1** (48 mmole) and stannic chloride (24 mmole) in the presence of **3** (24 mmole) in ethylene dichloride (200 ml), was heated to 60°. To the stirred solution was added **2** (70.4 g, 144.6 mmole), in eight portions, at intervals of 10 min. An exothermic reaction occurred at each addition of **2**, whereby the temperature of the mixture rose by 2∼4°. After the eighth addition, the temperature of the mixture was maintained at 60° or above for 10 min. The mixture was then allowed to cool at room temperature, and filtered to give 70.6 g of **3** as colorless crystals, which were identified by ir-spectrum with an authentic sample.[4][12] The yield was quantitative, based upon **2** added.

The high yield in which **3** was obtained shows the high selectivity of the reaction. The selectivity appears to be based on that the susceptibility of the sulfur atom of **6** to a nucleophilic attack is enhanced by the electron withdrawing effect of dichlorotin(IV), and that the effect also makes the heterolytic fission of nitrogen-oxygen bond of **7** easy, which is the ratedetermining step in the Beckmann rearrangement.1)

The zirconium salt (5) was also confirmed to be an effective catalyst for a conversion of cyclohexanone oxime zirconium tetrachloride complex into the corresponding lactam complex.

References and Notes

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10) Although Lewis acids are known to promote the Beckmann rearrangement, a control experiment showed that 2 was recovered, when 2 was heated in ethylene dichloride in the presence of an excess of stannic chloride for 7.5 hr.

11) N-Coordinating structure has been estimated for an oxime boron trifluoride complex by C. R. Hauser and D. S. Hoffenberg [J. Org. Chem., 20, 1482 (1955)]. An examination of the ir-spectrum led also an N-coordinating structure for 2.

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