STEPS Students Report

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I had been a STEPS participant in the Laboratory of Professor Shu Kobayashi during two months. In this research group I was working at the field of catalytic asymmetric 1,4-addition reactions of diarylmethanes with the use of chiral crown ethers.

Firstly, I need to say that C-C bond formation at the α-position of carbonyl compounds is one of the most fundamental and frequently employed methodologies for the construction of complex molecules in organic synthesis. Many types of the reactions have been developed. Among them, reactions using only a catalytic amount of base are very efficient from a viewpoint of atom economy. However, the reaction is difficult to use substrates with less acidic hydrogen atoms as pro-nucleophiles. Therefore, the development of new methodologies to activate these less reactive substrates and their application to catalytic reactions are desired.

Recently, along with the tradition base catalytic mechanism product base mechanism has been investigated. Catalytic carbon-carbon bond forming reactions of less acidic pro-nucleophiles, such as esters and amides bearing no EWG group at the α-position, proceeded smoothly. The asymmetric direct 1,4-addition reactions of simple amides with α,β-unsaturated carbonyl compounds by using a catalytic amount of a novel chiral catalyst consisting of a potassium base and a macrocyclic chiral crown ether has been developed in the Prof. Kobayashi group. The desired compounds were obtained in high yields with excellent diastereo- and enantioselectivities.

The main purpose of my work included to try the racemic reaction of diarylmethanes, and the second point – to use the catalytic system of KHMDS (Potassium (**K**) **H**exa**M**ethyl**D**i**S**ilazide) and chiral crown ethers. To carry out our objective the first step was to check reproducibility of the asymmetric reaction procedure. Then we tried the conditions of asymmetric reaction with the use of chiral catalytic system of KHMDS. After it, we tried to put the diphenylmethane into the 1,4-addition reaction. At the beginning, we conducted this reaction in the racemic reaction conditions. We obtained the racemat in 86% isolated yield. We tried the reactions with three different chiral crown ethers. So, we obtained the product in medium yields. But, unfortunately, enantiomeric excess was very low.

To sum up the results of my work I would like to say that we found the diarylmethanes can be used in 1,4-addition reactions. But the yields and enantioselectivity are not very good. That is why I think that this reaction need to be optimized. We need to change the conditions and to try some other chiral catalytic systems.

In addition, I would like to express gratitude to STEPS committee and to all members of Prof. Kobayashi research group. It was the grate opportunity to learn how to work in such hard working scientific group on advanced science. I would like to thank Prof. Kobayashi and his research group for friendly and helpful attitude to me.