MECHANISTIC STUDY ON ELECTROCHEMICAL GENERATION OF CHIRAL IMINIUM IONS FROM CHIRAL AMINO ACIDS

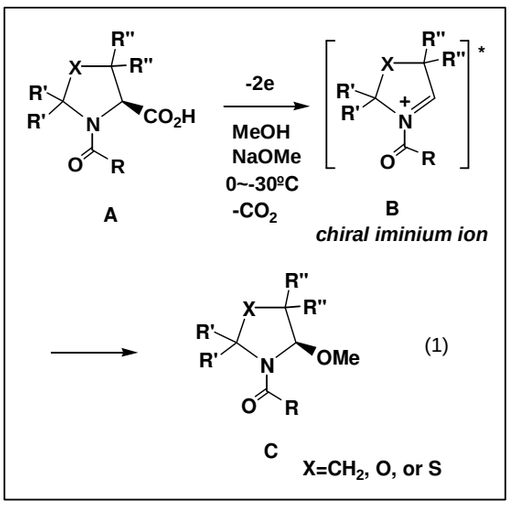
Yoshihiro Matsumura, George Ng'ang'a Wanyoike, Toshihide Maki, and Osamu Onomura

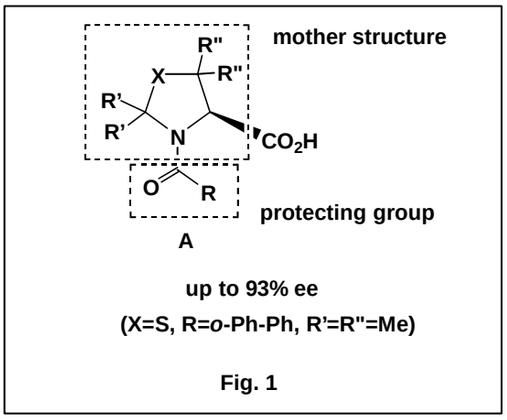
Department of Pharmaceutical Sciences, Graduate School of Biomedical Sciences, Nagasaki University, 1-14 Bunkyou-machi, Nagasaki 852-8521, Japan

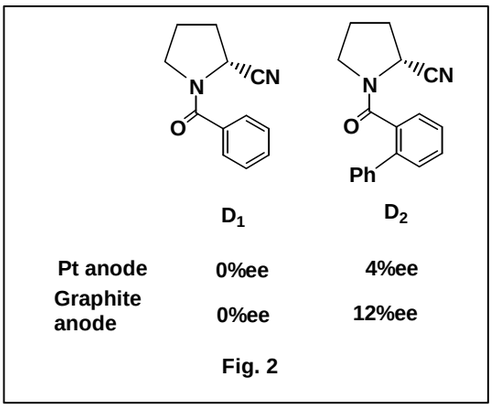
We have already reported a generation of chiral iminium ions **B** from chiral α-amino acids **A** using electrochemical oxidation (eq 1).[1)~3)] The %ee of the product **C** was dependent on the mother structure of **A**, the *N*-protecting group (COR), and the reaction temperature, the maximum %ee being 93%ee in a case where R was o-Ph-Ph, X was a sulfur atom, and both R' and R" were Me (Fig. 1).[4)] The use of the other chemical method than electrochemical oxidation resulted in a decrease of yields and %ee's. This report presents further some data suggesting the reaction mechanism.

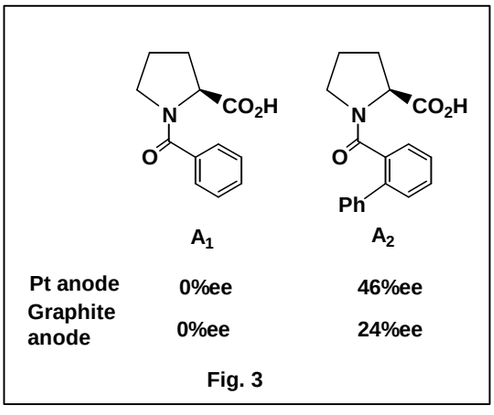
In order to give some insight into the mechanism, we prepared optically active α-cycanopyrrolidines $\mathbf{D_{1,2}}$ and tried their electrochemical oxidation under conditions similar to that for **A**. The result is shown in Fig. 2. For comparison, the %ee's for $\mathbf{A_{1,2}}$ are shown in Fig. 3.

Those results imply that the carboxyl group of **A** plays an important role for the generation of chiral iminium ions and the reaction mechanisms for the oxidation of **A** and **D** are different from each other. Also, we tried the electrochemical oxidation of **A** and **D** using a gold as an anode material, and observed some electrode effect on the %ee. On the basis of those results, the reaction mechanisms will be presented.









References:

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3) G. N. Wanyoike, O. Onomura, T. Maki, and Y. Matsumura, *Org. Lett.*, **4**(11), 1875-1877 (2002).

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