## Catalytic Epoxidation with Molecular Oxygen Using Nickel Complex

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Abstract: Ni complex, [N,N'-bis[o-(p-tolucnesulfonylamino)benzylidene]ethylenediaminato]nickel(11) (1), was foundto be a good catalyst for the epoxidation of olefins with molecular oxygen in the presence of 2-methylpropanal(Mukaiyama's conditions).

Catalytic asymmetric epoxidation of olefins having no precoordinating functional group is of current interest in synthetic organic chemistry and many studies were focused on this field. Recently we and others reported chiral (salen)manganese(III) complexes of type i which carried stereogenic centers at C8(8') and/or C9(9') carbons, to be effective catalysts for the enantioselective epoxidation of unfunctionalized olefins with iodosylarene or sodium hypochlorite as a stoichiometric oxidant.<sup>1,2</sup>)



Asteriscs (\*) stand for stereogenic center

In generally, it is expected that the asymmetric induction of the catalyst becomes higher as stereogenic centers in the chiral catalyst become closer to the reaction center (that is, metal center). Therefore we thought



that complexes such as ii having asymmetric centers at asterisked positions would show higher asymmetric induction than i. But the introduction of asymmetric oxygen atoms into ii seemed to be extremely difficult. In order to overcome this problem, we chose the complex of type iii which carried asymmetric nitrogen atoms instead of oxygen atoms.

However, since catalytic activity of this type of complexes iii was totally unknown to our knowledge, we synthesized achiral  $[N,N'-bis[o-(p-toluenesulfonylamino)benzylidene]ethylenediaminato]nickel(II) (1)^{3,4})$  which had a basic structure of iii, and examined its reactivity as a catalyst for the epoxidation of olefins.

As shown in Scheme 1, the catalyst 1 was readily prepared from *o*-aminobenzyl alcohol (2). *N*-Tosylation of 2 and subsequent  $\gamma$ -MnO<sub>2</sub> oxidation afforded aldehyde 3. Treatment of 3 with Ni(OAc)<sub>2</sub> •4H<sub>2</sub>O and ethylenediamine in ethanol under reflux conditions gave Ni complex 1.<sup>5,6</sup>)

## Scheme 1



With complex 1 in hand, we first examined epoxidation of *trans*-stilbene. Contrary to the case of (salen)manganese(III) complexes,<sup>1</sup>) no epoxidation was observed when iodosylbenzene was used as a terminal oxidant. However, molecular oxygen in the presence of aldehyde (Mukaiyama's conditions<sup>7,8</sup>) was found to be an effective oxidant and the reaction proceeded smoothly at 50 °C to give corresponding epoxide in good yield. Epoxidation with aqueous sodium hypochlorite in the presence of molecular sieves 4Å also afforded the epoxide in good yield but substrates other than *trans*-stilbene were poorly epoxidized under these conditions.



Results obtained by using Mukaiyama's conditions are summarized in **Table 1**. Epoxidation of *trans*-diand trisubstituted olefins provided corresponding epoxides in good yields (entries 1, 2 and 5). Although epoxidation of *cis*- $\beta$ -methylstyrene also proceeded smoothly, it gave a mixture of *cis*- and *trans*-epoxides (entry 3).<sup>9)</sup> In the epoxidation of *cis*- and *trans*- $\beta$ -methylstyrenes, formation of a small amount of benzaldehyde was also observed (entries 2 and 3). To our surprise, the reaction of dihydronaphthalene was very sluggish (entry 4). The unusual behavior of dihydronaphthalene can not be rationalized at the present time.

Typical experimental procedure was exemplified with epoxidation of *trans*-stilbene: To a solution of *trans*-stilbene (21.2 mg, 0.12 mmol) in 1,2-dichloroethane (1.2 ml) were added 2-methylpropanal (17.4 mg,



Table 1. Epoxidation of Olefins Using 1 as a Catalyst.



a) Isolated yields unless otherwise mentioned.

b) Yield based on the amount of consumed trans-stilbene.

c) Only a trace amount of the epoxide was detected by TLC analysis and most of starting material was recovered intact.

0.24 mmol) and 1 (1.5 mg, 0.02 equiv.). The mixture was stirred at 50 °C for 8 h under oxygen atmosphere and concentrated *in vacuo*. The residue was chromatographed on alumina with pentane as an eluent to give *trans*-stilbene oxide as colorless crystals (18.4 mg, 79%).

As described here, we could show 1 to be an effective catalyst for the epoxidation with molecular oxygen. This result seems to suggest a potentiality of the complex of type iii as a catalyst for asymmetric epoxidation of olefins having no precoordinating functional group. The study on asymmetric epoxidation using chiral derivatives of 1 is under investigation in our laboratory.

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- Ni complex 1 was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-Hexane to give satisfactory spectroscopic and elementary analyses, prior to use. Mp 270°C (decompose). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.33 (s, 6H), 3.00 (m, 4H), 7.00 (dd, 2H, J=6.8Hz), 7.11 (d, 4H, J=7.8Hz), 7.15 (d, 2H, J=7.8Hz), 7.26-7.32 (m, 4H), 7.73 (s, 2H), 7.77 (d, 4H, J=7.8Hz). Anal. Calcd for C<sub>30</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Ni•0.4H<sub>2</sub>O: C, 56.42; H, 4.55; N, 8.77. Found: C, 56.42; H, 4.49; N, 8.77.
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- 9. This product distribution suggested the intervention of a radical intermediate in the epoxidation of  $cis-\beta$ -methylstyrene (references 1a and 10).
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