Epoxidation of Alkenes Catalyzed by Cobalt(II) calix[4]pyrrole

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Introduction

The epoxidation of unfunctionalized as well as funtionalized olefins is still one of current interest and intensive researches in organic synthesis. since epoxides are widely utilized as intermediates in the laboratory and chemical manufacturing. Generally, epoxidation is mainly carried out with various peracids and peroxide such as MCPBA and H_2O_2. However, these two reagents are still suffered from the disadvantage of producing of unwanted by products. Recently, cobalt(II) Schiff base complexes, cobalt(II) complex, cobalt-containing polyoxotungstate and $Co(thd)_2$ are those examples to be effective catalysts to furnish epoxides. We disclose that cobalt(II) calix[4]pyrrole catalysts in the presence of certain aldehydes and O_2 exhibit an interesting chemoselectivity during the oxidation of alkenes at room temperature. Calix[4]pyrroles (*meso*-octaalkylporphyrinogens) are stable tetrapyrrolic macrocycles first synthesized in the 19th century by Baeyer *via* acid-catalyzed condensation of pyrrole with acetone in the presence of methanesulfonic acid as a catalyst to produce *meso*-octamethyl calix[4] pyrrole **1**. The discovery of these species acting as receptors for anions and neutral molecules has been utilized in the production of fluorescent, colorimetric, and electrochemical sensors for anions, in addition to new solid supports capable of separating mixtures of anions.

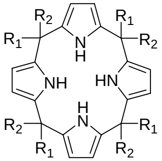
Materials and Methods

General procedure for epoxidation reaction

The epoxidation was carried out in toluene containing alkene, 2-ethylbutyraldehyde under O_2 atmosphere, and cobalt(II) calix[4]pyrrole complex at room temperature (30°C). The mixture was stirred for 24 h. After the reaction was finished, 1 mL of the reaction mixture was taken and extracted with Et_2O containing saturated $NaHCO_3$. The combined extracts were washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and analyzed by gas chromatograph with the addition of an exact amount of an appropriate internal standard.

Results and Discussion

Six cobalt calix[4]pyrroles **1-6** were synthesized and investigated on alkene epoxidation. Cobalt(II) calix[4]pyrrole complex **4** was disclosed to be the most suitable catalyst in cyclohexene epoxidation. CH_3CN and toluene gave superior yield to other mixed solvents. This developed epoxidation system was further explored for a variety of alkenes as presented in Table. The comparative kinetic study on the epoxidation of cyclohexene, 1-dodecene and 1-methylcyclohexene revealed that the rate of the epoxidation of 1-methylcyclohexene was faster than those of cyclohexene and 1-dodecene, respectively. The details of regioselectivity study were observed from the epoxidation of 4-vinylcyclohexene. The isolation of epoxide isomers from the epoxidation reaction of 4-vinylcyclohexene catalyzed by cobalt(II) complex of **4** yielded 1,2-oxide (86% composition) and 7,8-oxide (14% composition). The stereoselectivity study of the reaction was carefully examined employing *cis*- and *trans*-stilbenes. The detection of *cis*- and *trans*-epoxide could be accomplished by ^1H-NMR. The mechanism was believed to take place in the same fashion as that has been proposed for the metal complex-catalyzed oxygenation of substrates by O_2 and aldehydes.



1 R_1, R_2 = Me
2 R_1, R_2 = Et
4 R_1 = Me R_2 = 4-methoxyphenyl
5 R_1 = Me R_2 = C_6H_5
6 R_1, R_2 = C_6H_5

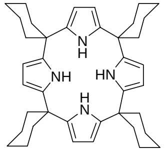


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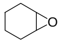
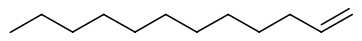
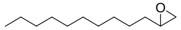
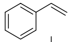
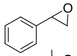
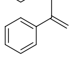
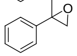
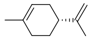
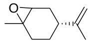
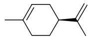
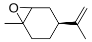
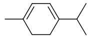
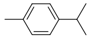
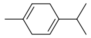
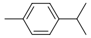
Figure Six synthesized of calix[4]pyrroles

Table The epoxidation of alkenes catalyzed by Co(II) calix[4]pyrrole **4**

entry	substrate	product (%)	
1			86
2			39, 74[a]
3			34, 68[a]
4			52, 76[a]
5			93
6			82
7			36
8			43

reaction conditions: alkene (5 mmol), catalyst (0.05 mmol), toluene (36 mL), O_2 and 2-ethylbutyraldehyde (10 mmol), reaction time (24 hr). [a]2-ethylbutyraldehyde (20 mmol)

Significance

A new and practical catalytic system for the epoxidation of alkenes catalyzed by cobalt [4]pyrrole has been successfully developed.

References

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