

Cobalt(II) Complex Catalyzed Epoxidation of Olefins  
by Combined Use of Molecular Oxygen and Cyclic Ketones

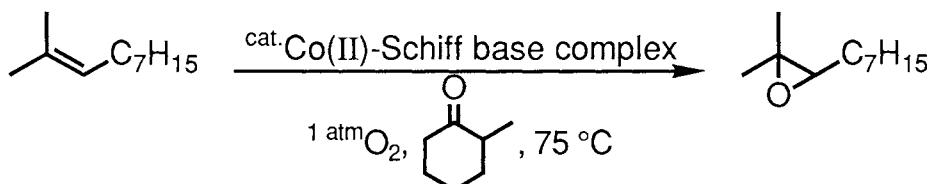
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In the presence of a catalytic amount of cobalt(II)-Schiff base complexes, various olefins are smoothly oxygenated into the corresponding epoxides in good to high yields by combined use of an atmospheric pressure of oxygen (oxidant) and cyclic ketones (reductant), such as 2-methylcyclohexanone, under mild conditions.

The selective monooxygenation of various organic compounds utilizing molecular oxygen (the most abundant oxidant) is one of the challenging topics in synthetic organic chemistry. Recently, much effort has been made toward monooxygenation reactions of olefins *via* single oxygen atom transfer by combined use of molecular oxygen and various organic reducing agents. For example, aerobic oxygenation of olefins into the corresponding alcohols by using cobalt(II)-Schiff base complexes in ethanol was reported.<sup>1,2)</sup> In the similar oxidation system, terminal olefins were also converted into the corresponding methyl ketones.<sup>3)</sup> Further, a new method for the selective hydration of olefins under neutral conditions was established by combined use of molecular oxygen and 2-propanol, a reductant, using bis(1,3-diketonato)cobalt(II) complexes as catalysts.<sup>4)</sup>

Of various monooxygenated compounds derived from olefins, epoxides are regarded as one of the most useful synthetic intermediates, and many trials have thus been reported. It was recently shown from our laboratory that bis(1,3-diketonato)nickel(II) complexes efficiently promoted monooxygenation of olefins into the corresponding epoxides by combined use of molecular oxygen and primary alcohols<sup>5)</sup> or aldehydes.<sup>6)</sup> In the latter reaction, aldehydes were considered to behave as reductants to accept one oxygen atom from molecular oxygen. Through our continuous study to find another reductant which could effectively accept an oxygen atom in aerobic oxygenation of olefins, it was revealed that cyclic ketones, such as 2-methylcyclohexanone, behaved as excellent reductants in epoxidation reaction.

In this communication, we would like to describe monooxygenation of olefins into the corresponding



Scheme 1.

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epoxides by combined use of an atmospheric pressure of oxygen and cyclic ketones in the presence of cobalt(II)-Schiff base complexes as catalysts (Scheme 1).

First, aerobic oxygenation of 2-methyl-2-decene was tried by using various ketones as a solvent in the presence of a catalytic amount of cobalt(II) complex. In the case of employing methyl ethyl ketone or pinacolone, the yields of epoxides were low (Entries 1 and 2 in Table 1), while by using cyclohexanone or 2-methylcyclohexanone, the yield of the epoxide increased up to 86% as shown in Entries 4 and 5. After the reaction,  $\alpha$ -hydroxyketone (2-hydroxy-2-methylcyclohexanone) was detected by GC analysis as a co-product.<sup>7)</sup> Therefore, it is reasonable to assume that the cyclic ketone behaves as a reductant to accept one oxygen atom of molecular oxygen on C-H group at  $\alpha$ -position of the carbonyl carbon to afford the corresponding  $\alpha$ -hydroxyketone. Thus, the above aerobic epoxidation of olefins revealed that cyclic ketones, especially 2-methylcyclohexanone, behaved as useful reductants.<sup>8)</sup>

Table 1. Epoxidation of 2-Methyl-2-decene in Ketones as a Solvent<sup>a)</sup>

Entry	Solvent	Conversion /% <sup>b)</sup>	
		Conversion /% <sup>b)</sup>	Yield /% <sup>b)</sup>
1		50	29
2		51	27
3		57	39
4		85	63
5		93	86

a) Reaction conditions; 2-methyl-2-decene 3.0 mmol, solvent 5.0 ml, bis(acetylacetone)cobalt(II) (= Co(acac)<sub>2</sub>) 0.06 mmol (2.0 mol%), 1 atm O<sub>2</sub>, 75 °C, 6 h. b) Determined by GC analysis.

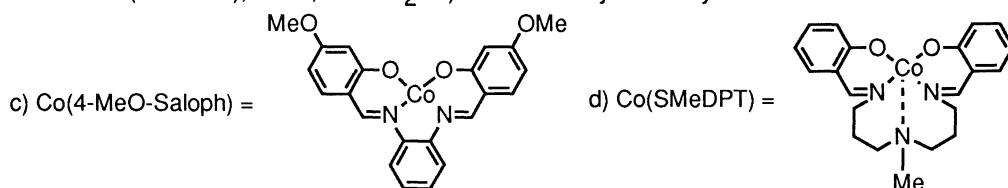
Next, various cobalt(II) complexes were examined in the above epoxidation reaction in 2-methylcyclohexanone solvent. Of various ligands screened, cobalt(II)-Schiff base complexes, such as [N, N'-bis(4-methoxy-salicylidene)-o-phenylenediaminato]cobalt(II)<sup>9)</sup> (= Co(4-MeO-Saloph)) having an electron-donating substituent on ligand or [N, N'-bis(salicylidene- $\gamma$ -iminopropyl)methylaminato]cobalt(II)<sup>10)</sup> (= Co(SMeDPT)) which had pentadentate ligand, were found as excellent catalysts to afford the epoxide in high yields (Entries 2 and 3 in Table 2).

The above procedure of using Co(4-MeO-Saloph) or Co(SMeDPT) as a catalyst was successfully applied to various olefins as shown in Table 3. Trisubstituted or *exo*-terminal olefins and norbornene analogues were smoothly monooxygenated into the corresponding epoxides in high yields (Entries 1 - 3).  $\alpha$ -Pinene also afforded epoxide in 67% yield (Entry 4). Trisubstituted olefins having ester or ether functions were converted into the corresponding epoxides in good yields without accompanying undesirable decomposition of these functional groups (Entries 5 - 8).

Table 2. Epoxidation of 2-Methyl-2-decene Catalyzed by Various Co(II) Complexes<sup>a)</sup>

	$\xrightarrow[2\text{-methylcyclohexanone,}]{1\text{ atm O}_2, \text{cat. Co(II) complex}}$	
75 °C, 6 h		
Entry	Catalyst	Time /h
1	Co(acac) <sub>2</sub>	6
2	Co(4-MeO-Saloph) <sup>c)</sup>	3
3	Co(SMeDPT) <sup>d)</sup>	6

a) Reaction conditions; 2-methyl-2-decene 3.0 mmol, 2-methylcyclohexanone 5.0 ml, catalyst 0.06 mmol (2.0 mol%), 75 °C, 1 atm O<sub>2</sub>. b) Determined by GC analysis.

Table 3. Co(II)-Schiff Base Catalyzed Epoxidation of Various Olefins in 2-Methylcyclohexanone Solvent<sup>a)</sup>

Entry	Olefin	Catalyst <sup>b)</sup>	Time /h	Epoxide	Yield /%
1		A	3		98 <sup>c)</sup>
2		A	11.5		87 <sup>c)</sup>
3		B	5		92 <sup>c)</sup>
4		B	6		67 <sup>c)</sup>
5		B	6		81 <sup>c)</sup>
6		A	7		70 <sup>d)</sup>
7		A	6		85 <sup>c)</sup>
8		A	6		77 <sup>c)</sup>

a) Reaction conditions; olefin 3.0 mmol, 2-methylcyclohexanone 5.0 ml, catalyst 0.06 mmol (2.0 mol%), 75 °C, 1 atm O<sub>2</sub>. b) Catalyst; A = Co(4-MeO-Saloph), B = Co(SMeDPT). c) GC yield. d) Isolated yield.

A typical procedure for epoxidation of citronellyl benzoate (Entry 6 in Table 3) was described as follows; citronellyl benzoate (780 mg, 3.0 mmol), Co(4-MeO-Saloph) (24 mg, 0.06 mmol, 2.0 mol%) in 2-methylcyclohexanone (5.0 ml) was stirred at 75 °C for 6 h under an atmospheric pressure of oxygen. Then solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 5 / 1) to afford the corresponding epoxide (577 mg, 70% yield).

It is noted that, in the presence of a catalytic amount of cobalt(II)-Schiff base complexes such as Co(4-MeO-Saloph) or Co(SMeDPT), various olefins are smoothly oxygenated into the corresponding epoxides in good to high yields by combined use of an atmospheric pressure of oxygen and 2-methylcyclohexanone.

Further investigation on the epoxidation of olefins catalyzed by cobalt(II)-Schiff base is now under way.

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- 7) When epoxidation of 2-methyl-2-decene was carried out in 2-methylcyclohexanone catalyzed by Co(4-MeO-Saloph), *ca.* 1 equiv. of 2-methylcyclohexanone was consumed against formed epoxide and formation of 2-hydroxy-2-methylcyclohexanone (*ca.* 0.2 equiv.) was detected by GC analysis together with 6-oxoheptanoic acid (*ca.* 0.6 equiv.). Thus, it is reasonable to assume that further oxidation of  $\alpha$ -hydroxyketone into  $\epsilon$ -ketocarboxylic acid has occurred in the present reaction. Details are now under investigation.
- 8) In the most cases, oxygenation of cyclic ketones with molecular oxygen was studied to obtain dicarboxylic acids *via* C-C bond cleavage of the carbon skeleton next to the carbonyl group. Oxidation of cyclopentanone or cyclohexanone with molecular oxygen under basic conditions was reported; T. J. Wallace, H. Pobiner, and A. Schriesheim, *J. Org. Chem.*, **30**, 3768 (1965). Oxygenation of 2-methylcyclohexanone into 6-oxoheptanoic acid with molecular oxygen in the presence of ferric chloride was reported; S. Ito, M. Matsumoto, *ibid.*, **48**, 1133 (1983). Oxovanadium(IV) induced oxygenation of cyclic ketones in alcohol was also shown; T. Hirao, M. Mori, and Y. Ohshiro, *Bull. Chem. Soc. Jpn.*, **62**, 2399 (1989).
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