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Aerobic Epoxidation of Olefins Catalyzed by Cobalt(II) Complex Using Propionaldehyde Diethyl Acetal as a Reductant

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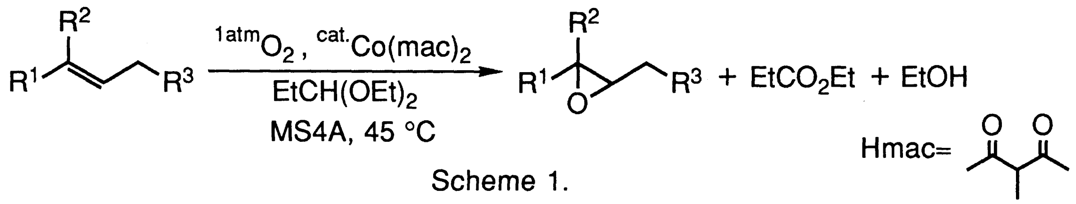
In the presence of bis(3-methyl-2,4-pentanedionato)cobalt(II) complex catalyst, various trisubstituted olefins are smoothly monooxygenated into the corresponding epoxides in high yields under neutral conditions by the combined use of molecular oxygen and propionaldehyde diethyl acetal.

Epoxides are generally prepared from the corresponding olefins by using peroxy compounds, such as *m*-chloroperbenzoic acid (*m*CPBA)[1)] or peracetic acid.[1)] These agents are converted into the corresponding carboxylic acids as co-products during epoxidation of olefins and it has been often pointed out that the resulting epoxide could be destroyed by the influence of the acids. On the other hand, epoxidation with molecular oxygen as an oxidant is very useful and promising synthetic method, and several epoxidation systems of olefins have recently been reported using metal complex catalyst.[2)]

In our previous communications, it was reported that organic reductants, such as aldehydes[3)] or cyclic ketones,[4)] were effective for aerobic epoxidation of olefins catalyzed by transition metal complexes. It was considered that one oxygen atom was introduced to the olefins from molecular oxygen to give the corresponding epoxides, and organic reductants accepted another oxygen atom to provide the corresponding carboxylic acid or α-hydroxy ketone, respectively. Since α-hydroxy ketones were subjected to further oxidation to yield the corresponding 6-oxocarboxylic acid, the reaction mixture was turned into acidic during the epoxidation in both cases.

Here, we would like to report an efficient method for epoxidation of olefins by the combined use of molecular oxygen and propionaldehyde diethyl acetal (**1**) with cobalt(II) complex catalyst. In the epoxidation procedure, the reaction mixture is kept neutral (Scheme 1) because any acidic compounds are not formed.



Scheme 1.

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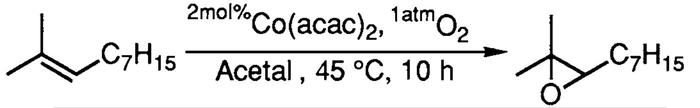
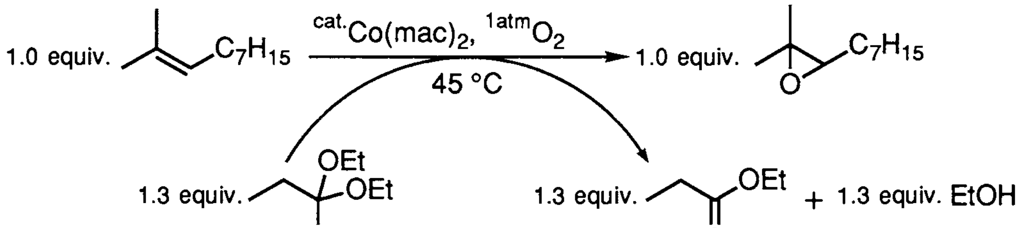
In the first place, several acetals were screened by taking epoxidation of 2-methyl-2-decene with molecular oxygen in the presence of a catalytic amount of bis(2,4-pentanedionato)cobalt(II) (=Co(acac)$_2$) as a model reaction. When the reaction was carried out in the acetal **1**, it was found that aerobic epoxidation of olefin proceeded to give the corresponding epoxide in 48% yield (Entry 1 in Table 1), while isobutyraldehyde diethyl acetal or pivalaldehyde diethyl acetal was not effective to promote the same epoxidation (Entries 2 and 3). Amount of consumed acetal **1** was measured in the epoxidation of 2-methyl-2-decene catalyzed by bis(3-methyl-2,4-pentanedionato)cobalt(II) (=Co(mac)$_2$) (Scheme 2) and when the conversion of olefin was determined as 55%, the epoxide was obtained in 53% yield. In the above reaction, it was found that 1.3 equiv. of acetal to the epoxide was consumed, and that the same molar equivalents of ethyl propionate and ethanol were formed at the same time. The present epoxidation could be illustrated as shown in Scheme 2[5)] indicating that acetal **1** acts as a reductant to accept one oxygen atom from molecular oxygen, and acetal turned into the corresponding ester and alcohol stoichiometrically. Because no further oxidation of the resulting ester and alcohol occurred, the reaction mixture could be kept neutral during the epoxidation.

Table 1. Epoxidation of 2-Methyl-2-decene in Several Acetals[a)]



Entry	Acetal	Conversion /%[b)]	Yield /%[b)]
1	EtCH(OEt)$_2$	52	48
2	^{i}PrCH(OEt)$_2$	36	25
3	^{t}BuCH(OEt)$_2$	25	18

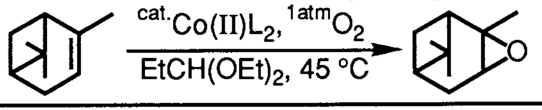
a) Reaction conditions; 2-methyl-2-decene 3.2 mmol, propionaldehyde diehtyl acetal 5 ml, Co(acac)$_2$ 0.065 mmol (2 mol%). b) Determined by GC.

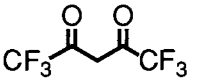
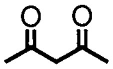
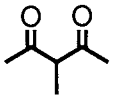


Scheme 2.

Next, various cobalt(II) complexes were examined for the epoxidation of α-pinene with molecular oxygen in the presence of a catalytic amount of cobalt(II) complex in acetal **1** as a solvent. In the case of employing bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)cobalt(II) complex (=Co(hfa)$_2$), both conversion of olefin and yield of epoxide were low (Entry 1 in Table 2). While, when Co(acac)$_2$ or Co(mac)$_2$ was used as a catalyst, the corresponding epoxides were obtained in 35-41% yields, respectively (Entries 2 and 4). The above distinction between Co(hfa)$_2$ and Co(mac)$_2$ can be explained as follows: Cobalt(II) complexes coordinated by 1,3-diketone ligands with electron-donating groups, such as Co(mac)$_2$, were reported to indicate lower oxidation potentials compared with Co(hfa)$_2$ which has electron-withdrawing group on the ligand.[6)] Therefore, it is reasonable to presume that Co(mac)$_2$ is quite easily oxidized into the active cobalt(III) complex by capturing molecular oxygen to convert olefin into the epoxide in good yield. In the case of employing Co(mac)$_2$ as a catalyst, the above

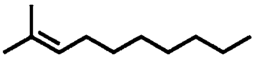
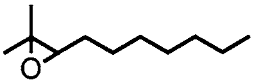
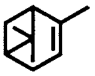
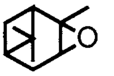
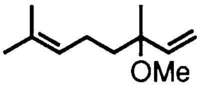
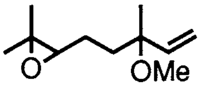
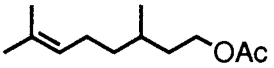
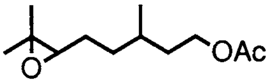
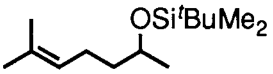
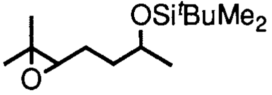
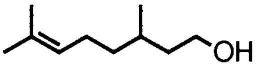
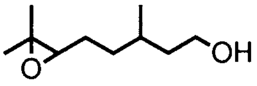
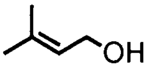
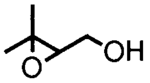
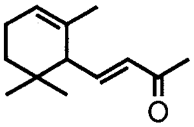
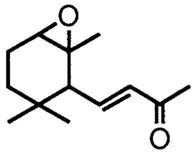
Table 2. Epoxidation of α-Pinene Catalyzed by Co(II) Complexa)



Entry	Ligand(LH)		Conv. /%b)	Yield /% b)	Additive
1		(Hhfa)	19	14	—
2		(Hacac)	48	35	—
3		(Hacac)	84	80	MS4Ac)
4		(Hmac)	45	41	—
5		(Hmac)	96	93	MS4Ac)

a) Reaction conditions; α-pinene 3.2 mmol, propionaldehyde diethyl acetal 20 ml, Co(II)L_2 0.065 mmol (2 mol%), 10 h. b) Determined by GC. c) MS4A 500 mg.

Table 3. Epoxidation of Various Olefins Catalyzed by Co(mac)$_2$a)

Entry	Olefin	Time /h	Epoxide	Conv. /%c)	Yield /%
1b)		12		99	97c)
2		20		96	93c)
3		20		100	quant.c)
4		20		100	86c)
5		14		100	91c)
6b)		10		100	82d)
7b)		10		100	85d)
8		21		93	71c)

a) Reaction conditions; olefin 3.2 mmol, propionaldehyde diehtyl acetal 20 ml, Co(mac)$_2$ 0.065 mmol (2 mol%), MS4A 500 mg. b) Propionaldehyde diethyl acetal 5 ml. c) Determined by GC. d) Isolated yield.

epoxidation reaction stopped halfway. Then, several additives were examined to improve the yield of epoxide, and when Molecular Sieves 4A (MS4A) was used together,7) yield of α-pinene oxide increased up to 93% (Entry 5).

The above procedure of combined use of acetal **1** and molecular oxygen catalyzed by Co(mac)$_2$ was successfully applied to various olefins as shown in Table 3. Trisubstituted olefins were smoothly monooxygenated into the corresponding epoxides in high yields (Entries 1 and 2). 3-Methoxy-3,7-dimethyl-1,6-octadiene was also chemoselectively oxygenated into the corresponding mono-epoxide in quantitative yield (Entry 3). Olefins having ester or silyloxy group were converted into the corresponding epoxides in good to high yields without accompanying undesirable decomposition of these functional groups (Entries 4 and 5). Epoxidation of olefinic alcohols proceeded smoothly to afford the corresponding epoxides in good yields (Entries 6 and 7), and α-ionone was also converted into the corresponding epoxide in good yield (Entry 8). Other olefins with different substitution patterns were also epoxidized by this procedure, though the chemical yields were diminished to some extent.8)

A typical procedure for epoxidation of citronellol (Entry 6 in Table 3) is described as follows; citronellol (512 mg, 3.2 mmol), Co(mac)$_2$ (19 mg, 0.065 mmol, 2.0 mol%) and Molecular Sieves 4A (500 mg) in propionaldehyde diethyl acetal (20.0 ml) was stirred at 45 °C under an atmospheric pressure of oxygen. After kept stirring for 10 h, solvent was removed under reduced pressure. The residue was purified by column chromatography on silica-gel (Hexane/AcOEt=1/1) to afford the corresponding epoxide (465 mg, 82% yield).

It is noted that, by using acetal derived from propionaldehyde, aerobic epoxidation of olefins proceeds smoothly to afford the corresponding epoxides in good to high yields in the presence of Co(mac)$_2$ catalyst. Since the acetal is converted into the neutral compounds, ester and alcohol, the present epoxidation proceeds under neutral conditions to enable the preparation of acid sensitive epoxides.

Further investigation on the present epoxidation of olefins is now under way.

References

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2) Y. Matsuda, H. Koshima, K. Nakamura, and Y. Murakami, *Chem. Lett.*, **1988**, 625; J.-C. Marchon and R. Ramasseul, *Synthesis*, **1989**, 389; Y. Kaku, M. Otsuka, and M. Ohno, *Chem. Lett.*, **1989**, 611.

3) T. Yamada, T. Takai, O. Rhode, and T. Mukaiyama, *Chem. Lett.*, **1991**, 1; *Bull. Chem. Soc. Jpn.*, **64**, 2109 (1991).

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5) Acetals of aldehydes are converted into the corresponding esters by the action of ozone or peroxy acid, respectively; P. Deslongchamps and C. Morean, *Can. J. Chem.*, **49**, 2465 (1977); D. L. Heywood and B. Phillips, *J. Org. Chem.*, **52**, 1699 (1987); P. A. Grieco, T. Oguri, and T. Yokoyama, *Tetrahedron Lett.*, **1978**, 419.

6) K. Kato, T. Yamada, T. Takai, S. Inoki, and S. Isayama, *Bull. Chem. Soc. Jpn.*, **63**, 179 (1990).

7) By the addition of MS4A, the remarkable acceralation of reaction rate was observed, however, detail for the effect of MS4A is under investigation.

8) According to the present procedure, 2-methyl-1-decene (*exo*-terminal olefin) and cyclooctene (1,2-disubstituted olefin) were converted into the corresponding epoxides in 54% and 58% yields, respectively.

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