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Highly Efficient Method for Epoxidation of Olefins with Molecular Oxygen and Aldehydes Catalyzed by Nickel(II) Complexes

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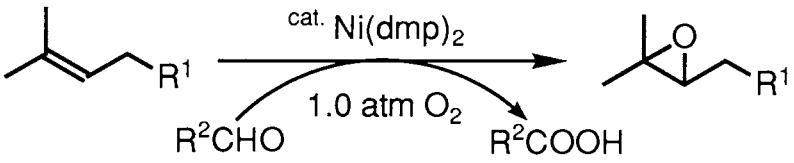
In the presence of a catalytic amount of a bis(1,3-diketonato)nickel(II) complex, trisubstituted and *exo*-terminal olefins or norbornene analogues are smoothly monooxygenated into the corresponding epoxides in high to quantitative yields on treatment with aldehyde under an atmospheric pressure of oxygen at room temperature.

Epoxide is one of the most useful synthetic intermediates for the preparation of oxygen-containing natural products or the production of epoxy resins, *etc.* Much effort has been made to develop the direct epoxidation of olefins by use of molecular oxygen,[1] however, only several catalysts have been reported to be effective for this purpose, for example, iron complex of bleomycin,[2] ruthenium tetramesitylporphyrin,[3] or oxoethoxo(tetra-*p*-tolylporphinato)molybdenum,[4] because of difficulties in controlling the desired epoxidation reactions.

In our previous communication,[5] we reported that reductants, such as primary or secondary alcohols, are essential for the catalytic epoxidation with molecular oxygen catalyzed by bis(1,3-diketonato)nickel(II) complexes.

In this communication, we would like to describe the highly efficient method for epoxidation of olefins catalyzed by nickel(II) complexes with combined use of atmospheric pressure of oxygen (**oxidant**) and an aldehyde (**reductant**) at room temperature.



Scheme 1.

At first, several aldehydes were screened by taking the epoxidation of 2-methyl-2-decene catalyzed by bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II)(Ni(dmp)2)[5] as a model reaction. In the case of employing *n*-butyraldehyde, both conversion of olefin and yield of the epoxide were low (Entry 1 in Table 1), while by the use of aldehydes having secondary or tertiary carbon next to the carbonyl carbon, such as isobutyraldehyde, cyclohexanecarboxaldehyde, or pivalaldehyde, the corresponding epoxides were obtained

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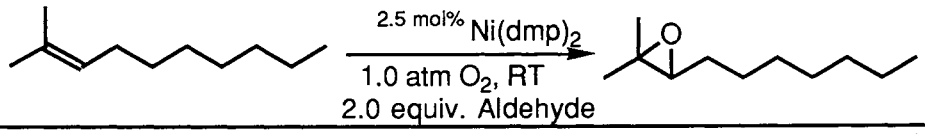
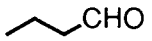
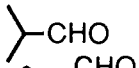
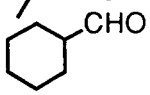
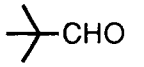
in quantitative yields, respectively (Entries 2-4). After the reaction, the formation of the corresponding carboxylic acids, co-products, was confirmed by GC analysis. It is reasonable to assume that aldehyde behaves as an effective reductant to accept one oxygen atom of molecular oxygen in the present reaction.

Table 1. Epoxidation of 2-Methyl-2-decene by Using Several Aldehydes[a)]

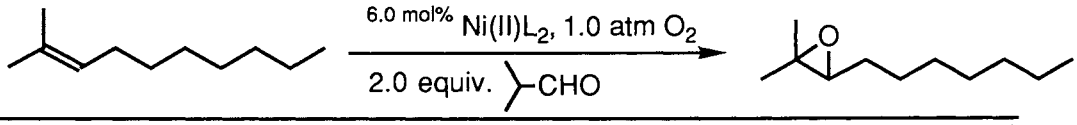


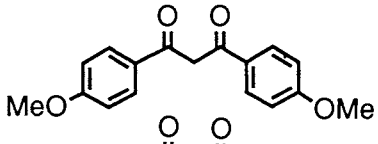
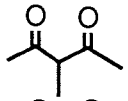
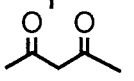
Entry	Aldehyde	Conversion / %[b)]	Yield / %[b)]
1		10	7
2		100	quant.
3		100	quant.
4		100	quant.

a) Reaction conditions; 2-Methyl-2-decene 2.5 mmol in 2.0 ml of 1,2-dichloroethane, 1.0 atm of oxygen for 12 h. b) Determined by GC.

Next, several 1,3-diketone-type ligands were examined for the epoxidation of 2-methyl-2-decene using isobutyraldehyde as a reductant under an atmospheric pressure of oxygen (see Table 2). It was found that nickel(II) complexes having 1,3-diketone-type ligands behave as excellent catalysts for the present epoxidation of trisubstituted olefins (Entries 1-3), while Ni(II)(salen)[6)] is not effectively employed at all (Entry 4).

Table 2. Several 1,3-Diketone-type Ligands[a)]

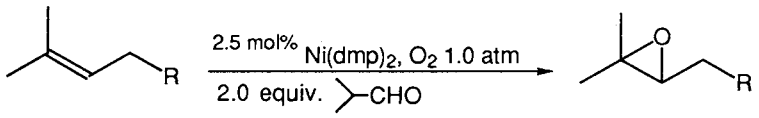


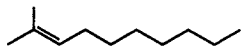
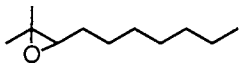
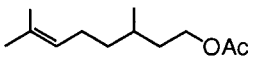
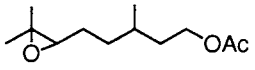
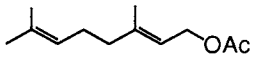
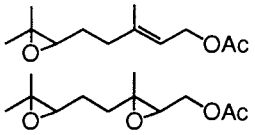
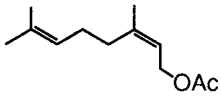
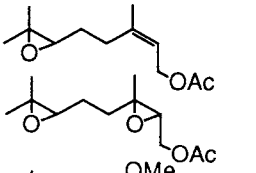
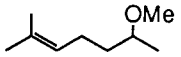
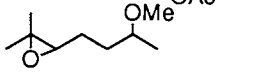
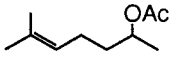
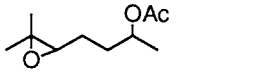
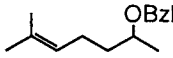
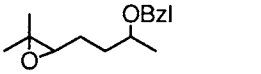
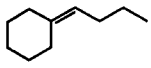
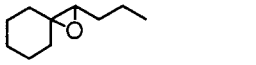
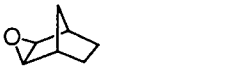
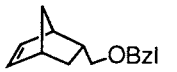
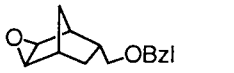
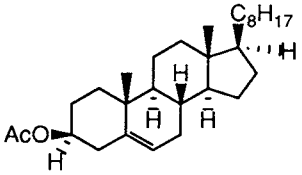
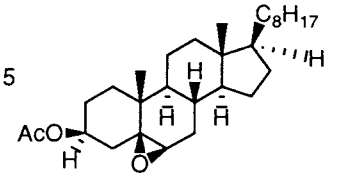
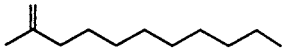
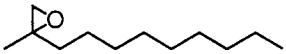
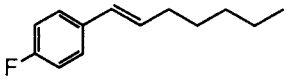
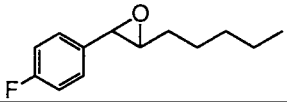
Entry	Ligand (LH)		Conversion / %[b)]	Yield / %[b)]
1		H dmp	100	quant.
2		H mac	100	quant.
3		H acac	100	quant.
4	H_2 salen[c)]			trace

a) Reaction conditions; 2-Methyl-2-decene 2.5 mmol in 2.0 ml of 1,2-dichloroethane,1.0 atm of oxygen for 12 h. b) Determined by GC. c) *N,N*-Disalicylal-ethylenediamine

The present procedure was successfully applied to the epoxidation of various trisubstituted olefins and norbornene analogues, and the corresponding epoxides were obtained under an atmospheric pressure of oxygen at room temperature in high to quantitative yields (Entries 1-13). It should be pointed out here that no over-oxidation at allylic position nor cleavage reaction of carbon-carbon double bonds took place in every case at all. And *exo*-terminal olefin and styrene derivatives were also monooxidized into corresponding epoxides in high yields, respectively (Entries 14 and 15).

Table.3 Epoxidation of Various Olefins[a)]

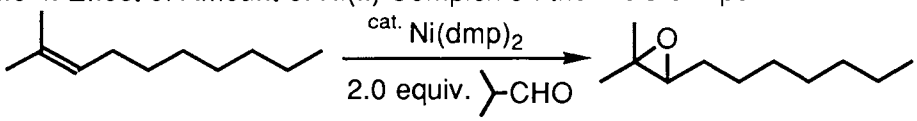


Entry[a)]	Olefin	Time/h	Epoxide	Yield/%	Note
1		3		quant.[b)]	
2[d)]		12		quant.[b)]	
3		3		94.5[b)]	
4		13		67.9[c)] 19.1[c)]	total yield 87.0%
5		43		61.2[c)] 12.4[c)]	total yield 73.6%
6		3		95.3[b)]	
7		6		quant.[b)]	
8		13		95.0[c)]	Bzl = 
9		3		89.1[b)]	
10		3		79.7[b)]	
11		3		quant.[b)]	
12		13		83.8[c)]	
13		5		84.4[c)]	α:β 24:76[e)]
14		13		93.4[b)]	
15		43		84.9[b)]	

a) Reaction conditions; Olefin 2.5 mmol in 1,2-dichloroethane. b) Determined by GC analysis. c) Isolated yield.
d) Under an atmospheric pressure of air. e) Diastereomer ratio was determined by NMR, see Ref. 3.

Furthermore, the effect of amount of nickel(II) complex on yield of epoxide was examined by taking epoxidation of 2-methyl-2-decene as a model reaction. Through three experiments carried out in the presence of 4.0 mol%, 0.256 mol%, and 0.0096 mol% of $Ni(dmp)_2$ against olefin, respectively (see Table 4), it was found that, even in the case of employing only 0.0096 mol% of $Ni(dpm)_2$, the epoxidation proceeded smoothly and the corresponding epoxide was obtained in 1020000% yield based on $Ni(dmp)_2$(Entry 3).

Table 4. Effect of Amount of Ni(II) Complex on the Yield of Epoxide



Entry	Amount of catalyst / mol%	Yield / %[b]	Yield based on catalyst / %[b]
1	4.0	100.0	2,500
2	0.256	100.0	39,000
3	0.0096[a]	98.1	1,020,000

a) Reaction conditions; 2-Methyl-2-decene 10.0 mmol, isobutyraldehyde 20.0 mmol, $Ni(dmp)_2$ 0.6 mg in 6.0 ml of 1,2-dichloroethane 1.0 atm of oxygen for 12 h. b) Determined by GC.

A typical procedure is described for the epoxidation of 1,5-dimethyl-4-hexenyl benzoate (see Entry 8 in Table 3): A mixture of olefin (3.0 mmol), $Ni(dmp)_2$ (40.0 mg, 0.064 mmol, 2.1 mol%) and isobutyraldehyde (6.25 mmol) in 1,2-dichloroethane(2.0 ml) was stirred at room temperature under an atmospheric pressure of oxygen overnight. The crude product was purified by column chromatography on silica gel (hexane-ethyl acetate) to afford the corresponding epoxide[7](713.0 mg, 95% yield).

It is noted that, in the presence of bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II) ($Ni(dmp)_2$), trisubstituted or *exo*-terminal olefins are smoothly monooxygenated into the corresponding epoxides in high to quantitative yields by combined use of atmospheric pressure of oxygen and an aldehyde, as a reductant.

References

1) T.Takai, T. Yamada, and T. Mukaiyama, *Chem. Lett.*, **1990**, 1657. References are cited therein.
2) Y. Kaku, M. Otsuka, and M. Ohno, *Chem. Lett.*, **1989**, 611.
3) J.-C. Marchon and R. Ramasseul, *Synthesis*, **1989**, 389.
4) Y. Matsuda, H. Koshima, K. Nakamura, and Y. Murakami, *Chem. Lett.*, **1988**, 625.
5) T. Mukiyama, T. Takai, T. Yamada, and O. Rhode, *Chem. Lett.*, **1990**, 1661.
6) H. Yoon and C. J. Burrows, *J. Am. Chem. Soc.*, **110**, 4087(1988).
7) ^1H NMR($CDCl_3$) δ=1.26(6H, m), 1.37(3H, d, J=6.3 Hz), 1.55-2.00(4H, m), 2.75(1H,m), 5.10-5.30(1H, m), 7.35-7.60(3H, m),8.05(2H, m); IR(neat) 2974, 1716, 1276, 1111, 714 cm^{-1}.

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