Direct Epoxidation of Olefins Catalyzed by Nickel(II) Complexes with Molecular Oxygen and Aldehydes

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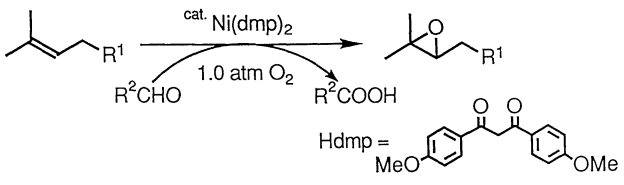
In the presence of a bis(1,3-diketonato)nickel(II) complex, various olefins are directly monooxygenated into the corresponding epoxides on treatment with atmospheric pressure of oxygen or air and aldehydes. Especially, it is noted that bis[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II) behaves as an excellent catalyst in the present epoxidation.

Epoxides are 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 and selective epoxidation of olefins by use of molecular oxygen. However, it is difficult to control the reaction because of over-oxidations or side reactions under conventional severe reaction conditions, such as high pressure of oxygen or high reaction temperature. Then, it is desired to search milder reaction conditions to suppress these reactions for development of an efficient epoxidation method. Only several effective catalysts have been reported for the epoxidation with molecular oxygen under milder reaction conditions, for example, (tetramesitylporphinato)ruthenium(II),[1] or oxoethoxo(tetra-*p*-tolylporphinato)molybdenum(V).[2] We also reported that oxovanadium(IV) complexes[3] and nickel(II) complexes[4] coordinated with 1,3-diketone type ligands behave as fairly good catalysts when treated together with molecular oxygen (Oxidant) and primary or secondary alcohols (Reductant), and it was shown there that reductants are essential for the above catalytic epoxidation. Through our continued studies on the aerobic epoxidation of olefins catalyzed by nickel(II) complexes, it was found that an aldehyde acts as an excellent reductant when used with molecular oxygen at room temperature.[5]

Similar reactions have been reported in the literature. Propylene was monooxygenated into propylene oxide with molecular oxygen in the coexistence of metal complexes and aldehyde, such as acetaldehyde[6] or crotonaldehyde,[7] but the conversion of olefin and the selectivity of epoxide were never reached to satisfactory levels.



Scheme 1.

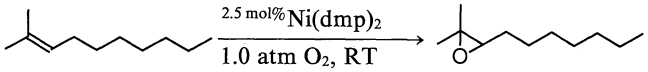
Recently, praseodymium(III) acetate was also shown to be an effective catalyst for the aerobic epoxidation of olefins in the presence of aldehyde.[8] In our previous communication, it was reported that both trisubstituted and *exo*-terminal olefins were smoothly monooxygenated into the corresponding epoxides in high to quantitative yields by combined use of atmospheric pressure of oxygen and aldehydes in the presence of catalytic amount of nickel(II) complexes.[5] However, the epoxidation of 1,2-disubstituted or terminal olefins stopped halfway, and conversions and yields were not reached satisfactory levels, because a part of aldehyde, being employed as a reductant, seemed to be consumed independently of the epoxidation.

Herein, we would like to discuss in detail the highly efficient method for epoxidation of various olefins catalyzed by nickel(II) complexes with molecular oxygen (Oxidant) and aldehydes (Reductant).

Results and Discussion

Epoxidation of Trisubstituted and *exo*-Terminal Olefins. First, several aldehydes, reductants, were screened by taking the epoxidation of 2-methyl-2-decene

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

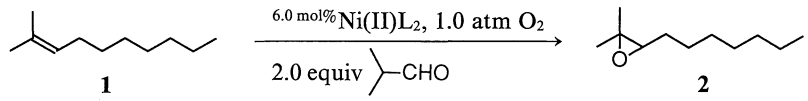


1 **2**

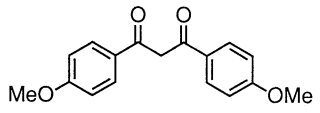
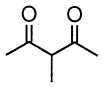
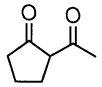
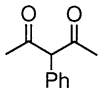
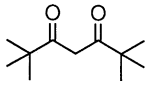
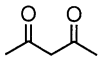
Entry	Aldehyde	Conversion/%[b]	Yield/%[b]
1		10	7
2		100	Quant.
3		100	Quant.
4		100	Quant.

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

Table 2. Effect of Ligand on Epoxidation of 2-Methyl-2-decene (**1**)[a]



1 **2**

Entry	Ligand (LH)		Conversion/%[b]	Yield/%[b]
1		**3b** Hdmp	100	Quant.
2		**4b** Hmac	100	Quant.
3		**5b** Hacp	100	Quant.
4		**6b** Hpac	100	Quant.
5		**7b** Hdpm	100	Quant.
6		**8b** Hacac	100	Quant.
7	Hdmg[c]	**9b**		14
8	H_2salen[d]	**10b**		Trace

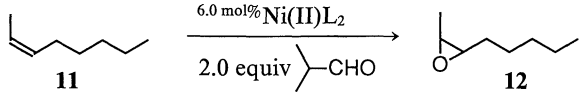
a) Reaction conditions; 2-Methyl-2-decene (**1**) 2.5 mmol in 2.0 ml of 1,2-dichloroethane, 1.0 atm of oxygen for 12 h. b) Determined by GC. c) Dimethylglyoxime. d) *N,N'*-Disalicylideneethylenediamine.

(**1**) catalyzed by bis[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II) (Ni(dmp)$_2$, **3a**) as a model reaction. In the case of employing butyraldehyde, both conversion of olefin and yield of the epoxide were low (Entry 1 in Table 1), while the corresponding epoxide **2** was obtained in quantitative yields, respectively (Entries 2—4) when aldehydes having secondary or tertiary carbon next to the carbonyl carbon, such as isobutyraldehyde, cyclohexanecarbaldehyde or pivalaldehyde were employed. The reaction afforded the corresponding carboxylic acids, co-products as confirmed by GC analysis. Therefore, it is reasonable to assume that an aldehyde behaves as an effective reductant to accept one oxygen atom from molecular oxygen in the present epoxidation.

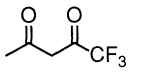
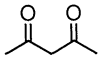
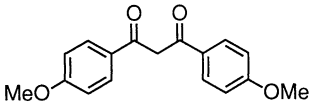
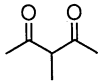
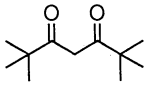
Next, several 1,3-diketone type ligands were examined for the epoxidation of 2-methyl-2-decene (**1**) using isobutyraldehyde under an atmospheric pressure of oxygen (see Table 2). It was found that nickel(II) complexes having 1,3-diketone type ligands behave as excellent catalysts for the present epoxidation of trisubstituted olefins (Entries 1—6, (**A**) **Standard Method**), while Ni(II)(salen) (**9b**)[9] or Ni(II)(dmg)$_2$ (**10b**)[10] is not effectively employed at all (Entries 7 and 8).

Epoxidation of 1,2-Disubstituted Olefins. According to the above procedure (**Method (A)**), the epoxidation of 1,2-disubstituted or terminal olefins was interrupted halfway, and the conversions and the yields were not reached satisfactory levels. Taking the epoxidation of *cis*-2-octene (**11**) as a model reaction, nickel(II) complexes having several 1,3-diketone type ligands were examined. As shown in Table 3, Ni(dmp)$_2$ (**3a**), Ni(mac)$_2$ (**4a**), and Ni(dpm)$_2$ (**7a**) behaved as efficient catalysts for the epoxidation of *cis*-2-octene (**11**) (Entries 2—4). On the contrary, Ni(acac)$_2$ (**8a**), which was an excellent catalyst for the epoxidation of trisubstituted olefin (Entry 6 in Table 2) or Ni(tfa)$_2$ (**13a**) was not effective for the epoxidation of 1,2-disubstituted olefin at all (Entries 1 and 2). Based on the measurements of the oxidation potentials of nickel(II) complexes,[4] it was suggested that Ni(dmp)$_2$ (**3a**, E_{ox} 1.14 V), Ni(mac)$_2$ (**4a**, E_{ox} 0.97 V), and Ni(dpm)$_2$ (**7a**, E_{ox} 1.05 V) would be more readily oxidized with molecular oxygen to form active species of the present epoxidation compared with Ni(acac)$_2$ (**8a**, E_{ox} 1.24 V) or Ni(tfa)$_2$ (**13a**, E_{ox} 1.89 V). Subsequently, the concentration of aldehyde or nickel(II) catalyst in the above reaction was examined in detail to improve yield of the epoxide **12** (see Table 4). In our previous letter,[11] it was reported that Ni(II) complexes, such as Ni(dmp)$_2$ (**3a**), are also employed as excellent

Table 3. Effect of 1,3-Diketone Ligand on Epoxidation of *cis*-2-Octene (**11**)[a]

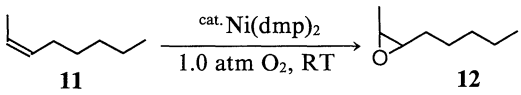


11 **12**

Entry	Ligand (LH)		E_{ox}/V vs. Ag/Ag$^+$[b]	Conversion/%[c]	Yield/%[c]
1		**13b** Htfa	1.89	1	1
2		**8b** Hacac	1.24	5	5
3		**3b** Hdpm	1.14	78	68[d]
4		**4b** Hmac	0.97	78	68[d]
5		**7b** Hdmp	1.05	69	65[d]

a) Reaction conditions; *cis*-2-Octene (**11**) 2.5 mmol, isobutyraldehyde 2.0 equiv, $Ni(dmp)_2$ 6.0 mol%, in 1,2-dichloroethane 2.0 ml, 1.0 atm O_2, RT, 13 h. b) Oxidation potentials (E_{ox}) were measured in CH_3CN solution. c) Determined by GC analysis. d) Mixture of *cis*- and *trans*-epoxides (*cis*:*trans*=28:72).

Table 4. Effect of Concentration on Epoxidation of *cis*-2-Octene (**11**)[a]



11 **12**

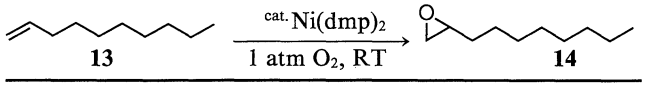
Entry	Aldehyde (equiv)	Catalyst/mol%	Solvent/ml	Conversion/%[b]	Yield/%[b]
1	 (2.0)	6.0	2.0	78	68[c]
2	(3.0)	6.0	2.0	89	77[c]
3	(2.0)	0.3	2.0	88	86[c]
4	(3.0)	0.3	10.0	94	89[c]

a) Reaction conditions; *cis*-2-Octene (**11**) 2.5 mmol in 1,2-dichloroethane, 1.0 atm O_2, RT, 13 h. b) Determined by GC analysis. c) Mixture of *cis*- and *trans*-epoxides.

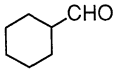
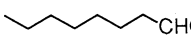
catalysts for the oxidation of aldehydes into the corresponding carboxylic acids in the absence of olefins. Therefore, it is reasonable to assume that a part of aldehyde was consumed to form carboxylic acid independent of epoxidation.

When 3.0 equivalent of isobutyraldehyde against olefin **11** was employed, both conversion and yield increased up to 89% and 77%, respectively, as expected (Entry 2 in Table 4). It was also found that the use of smaller amount of nickel(II) complex was effective to improve yield of the epoxide **12** (86%, Entry 3). Further, under highly diluted conditions, the corresponding epoxide **12** was obtained in 89% yield as a mixture of *cis*- and *trans*-epoxides. It is reasonable to assume that under highly diluted conditions, oxidation of aldehyde itself into the corresponding acid could be suppressed and then aldehyde would be effectively consumed for the epoxidation to improve both conversion of olefin and

Table 5. Effect of Aldehydes on Epoxidation of 1-Decene (**13**)[a]

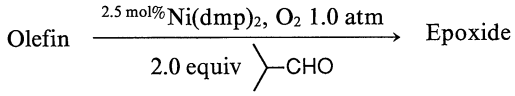


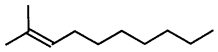
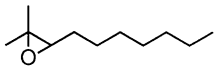
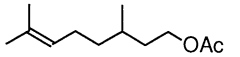
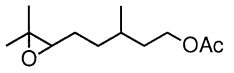
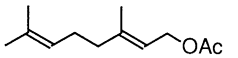
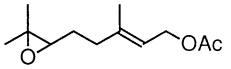
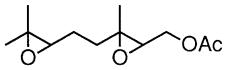
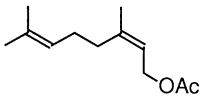
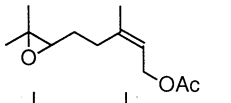
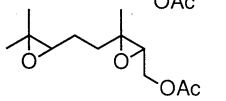
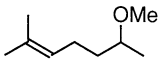
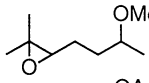
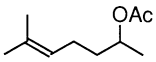
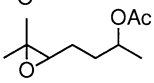
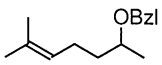
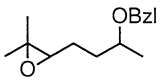
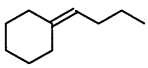
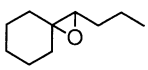
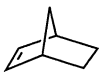
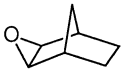
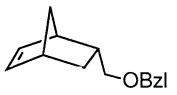
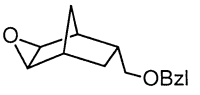
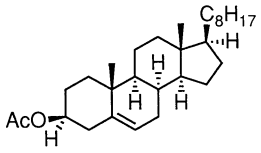
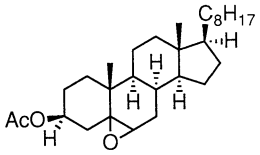
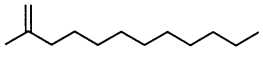
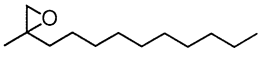
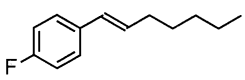
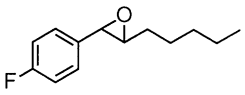
13 **14**

Entry	Aldehyde	Conversion/%	Yield/%
1		61	42
2		41	33
3	CH_3CHO	72	51
4		71	57
5		64	44
6		95	75

a) Reaction conditions; 1-Decene (**13**) 3.0 mmol, aldehyde 6.0 equiv, $Ni(dmp)_2$ **3a** 0.3 mol%, in 1,2-dichloroethane 10.0 ml, 1.0 atm O_2, RT, 24 h.

Table 6. Epoxidation of Various Olefins[a] ((A) **Standard Method**)



Entry[a]	Olefin		Time/h	Epoxide		Yield/%	Note
1		**1**	3		**2**	Quant.[b]	
2[d]			12			Quant.[b]	
3		**15**	3		**16**	95[b]	
4		**17**	13		**18**	68[c]	Total yield 87%
					**19**	19[c]	
5		**20**	43		**21**	61[c]	Total yield 73%
					**22**	12[c]	
6		**23**	3		**24**	95[b]	
7		**25**	6		**26**	Quant.[b]	
8		**27**	13		**28**	95[c]	Bzl = 
9		**29**	3		**30**	89[b]	
10		**31**	3		**32**	80[b]	
11		**33**	3		**34**	Quant.[b]	
12		**35**	13		**36**	84[c]	
13		**37**	5		**38**	84[c]	$\alpha:\beta$ 24:76[e]
14		**39**	13		**40**	93[b]	
15		**41**	43		**42**	85[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. 1.

yield of epoxide (**(B) Dilution Method**).

Epoxidation of Terminal Olefin. Next, when the present procedure (**Method B**) was applied to the epoxidation of terminal olefin, such as 1-decene (**13**), the corresponding epoxide **14** was obtained only in 42% yield (Entry 1 in Table 5). And then, several aldehydes were examined taking the above reaction as a model.

As shown in Table 5, it is interesting to note that normal aliphatic aldehydes were quite effective for the epoxidation of 1-decene (**13**) (Entries 3—6), whereas these aldehydes were less effective for the epoxidation of trisubstituted olefins (Entry 1 in Table 1). Especially, isovaleraldehyde was found to be remarkably effective for the epoxidation of 1-decene (**13**), and 1,2-epoxydecane (**14**) was obtained in 75% yield and 95% conversion (Entry 6, **(C) Isovaleraldehyde Method**).

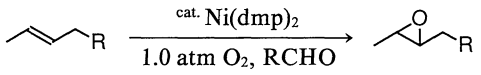
Epoxidation of Various Olefins. The above procedures were successfully applied to the nickel(II)-catalyzed epoxidation of various trisubstituted or *exo*-terminal olefins, norbornene analogues, 1,2-disubstituted and terminal olefins.

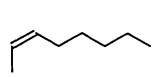
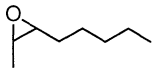
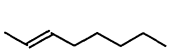
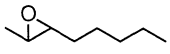
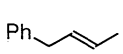
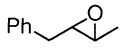
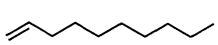
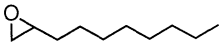
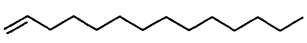
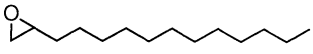
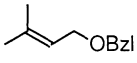
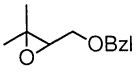
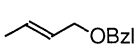
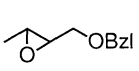
According to the above procedure (**Method (A) Standard Method**), various trisubstituted or *exo*-terminal olefins and norbornene analogues were smoothly monooxygenated into the corresponding epoxides in high to quantitative yields under an atmospheric pressure of oxygen at room temperature as shown in Table 6. It was observed that epoxidation of isolated carbon–carbon double bonds was faster than that of allyl esters (Entries 4 and 5). It should be pointed out here that, in every case, no over-oxidation at allylic position nor cleavage reaction of carbon–carbon double bonds took place to any extent. *exo*-Terminal olefin **39** and styrene derivative **41** were also monooxidized into corresponding epoxides **40** and **42** in high yields, respectively (Entries 14 and 15). In the case of the epoxidation of trisubstituted olefin **1**, the corresponding epoxide **2** was obtained in quantitative yield even under air (Entry 2).

Various 1,2-disubstituted olefins were monooxygenated into the corresponding epoxides in high yields by **Method (B) (Dilution Method)**, and also in the case of terminal olefin by **Method (C) (Isovaleraldehyde Method)**, respectively (see Table 7).

As shown in Table 7, when **Method (B)** was applied to *cis*-olefin (*cis*-2-octene (**11**)) and *trans*-olefin (*trans*-2-octene (**43**)), the corresponding epoxides **12** and **44** were obtained in 97% and 92% yields, respectively, as mixture of *cis*- and *trans*-epoxides (Entries 1 and 2). It is noted

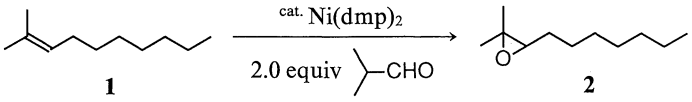
Table 7. Epoxidation of Various Olefins



Entry	Olefin		Time/h	Epoxide		Yield/%	Note
(B) Dilution method							
1		**11**	13		**12**	97[a,c]	*cis*:*trans*=51:49
2		**43**	13		**44**	92[a,c]	*cis*:*trans*=13:87
3		**45**	13		**46**	75[a,c]	
4		**47**	13		**48**	84[a,c]	
(C) Isovaleraldehyde method							
5		**13**	24		**14**	75[b,c]	
6		**49**	47		**50**	89[b,d]	
7		**51**	24		**52**	97[b,d]	Bzl = 
8		**53**	24		**54**	62[b,d]	

a) (B) Dilution method; Reaction conditions; Olefin 2.5 mmol, isobutyraldehyde 3.0 equiv, $Ni(dmp)_2$ **3a** 0.3 mol%, in 1,2-dichloroethane 10.0 ml, 1.0 atm O_2, RT. b) **(C) Isovaleraldehyde method**; Reaction conditions; Olefin 3.0 mmol, isovaleraldehyde 6.0 equiv, $Ni(dmp)_2$ **3a** 0.3 mol%, in 1,2-dichloroethane 10.0 ml, 1.0 atm O_2, RT. c) Determined by GC analysis. d) Isolated yield.

Table 8. Effect of Amount of Ni(II) Complex on the Yield of Epoxide **2**

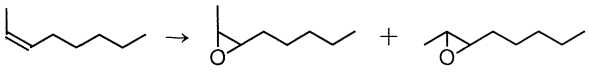


Entry	Amount of catalyst/mol%	Yield/%[b]	Yield based on catalyst/%[b]
1	4.0	100.0	2500
2	0.256	100.0	39000
3	0.0096[a]	98.1	1020000

a) Reaction conditions; 2-Methyl-2-decene (**1**) 10.0 mmol, isobutyraldehyde 20.0 mmol, Ni(dmp)$_2$ **3a** 0.6 mg in 6.0 ml of 1,2-dichloroethane 1.0 atm of oxygen for 12 h. b) Determined by GC.

that cyclohexene (**47**) was also smoothly monooxygenated into 1,2-epoxycyclohexane (**48**) in high yield (Entry 4) accompanied by less than 5% yields of by-product, such as allylic oxidation product, 2-cyclohexen-1-ol or 2-cyclohexen-1-one. With regard to the epoxidation of terminal olefins, isovaleraldehyde was quite effective (**Method C**), and 1-decene (**13**) and 1-tetradecene (**49**) were converted into the corresponding 1,2-epoxyalkanes **14** and **50** in 75% and 89% yields, respectively (Entries 5 and 6).

Table 9. Stereochemistry in Epoxidation of *cis*-2-Octene (**11**)



11 *cis*-2-Octene — **12** *cis*-Epoxide — **44** *trans*-Epoxide

Entry	Epoxidation conditions	Ratio of epoxide (*cis*:*trans*)[a]
1	1.0 atm O_2, 0.3 mol% Ni(dmp)$_2$ **3a**, 2.0 equiv 	51:49[b]
2	*m*CPBA	98:2
3	*m*CPBA, 0.3 mol% Ni(dmp)$_2$ **3a**	97:3

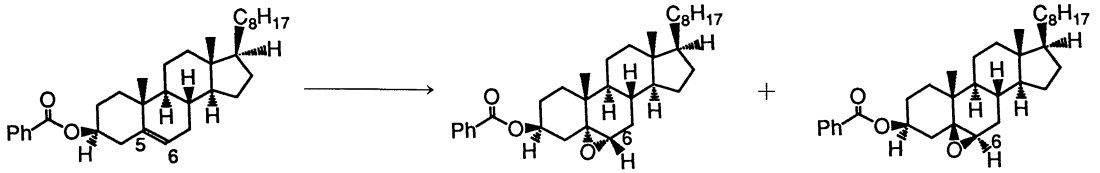
a) Determined by GC analysis. b) During the reaction, isomerization of *cis*-olefin into *trans*-olefin was not observed by GC analysis.

Efficiency of Nickel(II) Complex Catalyst. The efficiency of nickel(II) complexes in the present epoxidation was demonstrated by taking epoxidation of 2-methyl-2-decene (**1**) 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)$_2$ (**3a**) against olefin **1**, respectively (see Table 8), it was found that, even in the case of employing only 0.0096 mol% of Ni(dmp)$_2$, the epoxidation proceeded smoothly and the corresponding epoxide **2** was obtained in 1020000% yield based on Ni(dmp)$_2$ (**3a**) (Entry 3).

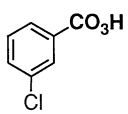
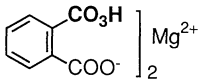
Stereochemistry of the Present Epoxidation.

a) Epoxidation of *cis*-Olefin. According to the

Table 10. Stereoselective Epoxidation of Cholesteryl Benzoate(**55**) Catalyzed by Ni(dmp)$_2$ **3a**



55 — **56** α-Epoxide — **57** β-Epoxide

Entry	Epoxidation reagent	α-Epoxide **56**:β-Epoxide **57**[c]
1[a]	cat. Ni(dmp)$_2$ **3a**, O_2, 	31:69
2[b]	 (*m*CPBA)	71:29
3[b]	 (MMPP)	85:15

Reaction Conditions: a) Cholesteryl Benzoate (**55**) 245 mg (0.5 mmol), isobutyraldehyde (2.0 mmol), catalyst (0.0047 mmol, 0.94 mol%) in 1,2-dichloroethane (5.0 ml), RT, 1.0 atm O_2, 2.0 h. b) Ref. 10. c) Determined by HPLC analysis.

present procedure, *cis*-olefin **11** was converted into a mixture of *cis*- and *trans*-epoxides (**12** and **44**), whereas *cis*-epoxide was formed predominantly when generally known peroxy acid such as *m*-chloroperbenzoic acid (*m*CPBA) was employed (see Table 9).

b) Epoxidation of Cholesterol Derivatives. Stereochemistry of the epoxidation of double bond on 5,6-position in cholesteryl benzoate (**55**) was examined by using $Ni(dmp)_2$ (**3a**) as a catalyst together with molecular oxygen and isobutyraldehyde (see Table 10). It was found that epoxidation catalyzed by nickel(II) complex afforded the *hindered* 5,6β-epoxide **57** as major product (Entry 1). On the contrary, it was reported that by using peroxy acids, such as *m*CPBA or magnesium monoperoxyphthalate hexahydrate (MMPP), cholesteryl benzoate was converted into the corresponding mixture of 5,6α- and 5,6β-epoxides in the ratio of 71:29 or 85:15 indicating that 5,6α-epoxide **56** is formed as a major product, respectively (Entries 2 and 3).[12] It is interesting to point out that the *less hindered* 5,6α-epoxide **56** was obtained as major product in above mentioned peracid epoxidation.[13]

Remarkably opposing stereoselection shown in the above two epoxidations clearly indicates that the active oxidant of the present nickel(II) complex-catalyzed epoxidation is not a simple peroxy carboxylic acid generated from aldehydes by autoxidation manner.

Conclusion

It is concluded that bis(1,3-diketonato)nickel(II) complexes effectively catalyzes the epoxidation of various olefins with an atmospheric pressure of oxygen (Oxidant) and an aldehyde (Reductant) at room temperature to afford the corresponding epoxides in high to quantitative yields. It was shown that $Ni(dmp)_2$ (**3a**) is an effective catalyst, and when $Ni(dmp)_2$ (**3a**) as employed as a catalyst, the epoxide was obtained in more than 1000000% yield based on the catalyst. Further, it is suggested that the active species in the present epoxidation reaction is not a simple carboxylic peracid generated from aldehyde by autoxidation manner. The present procedure thus provides a highly efficient and useful method for the preparation of a variety of epoxides from trisubstituted, 1,2-disubstituted and terminal olefins under mild conditions.

Experimental

General: Melting points were measured on a Mettler FP62 apparatus and uncorrected.

(a) Spectrometers: IR spectra were obtained by using a JASCO Model IR-700 infrared spectrometer on KBr pellets or liquid film on KBr. ^1H NMR spectra were recorded with a JEOL Model FX270 spectrometer using $CDCl_3$ as solvent and with tetramethylsilane as internal standard.

(b) Chromatography: Column chromatography was conducted under silica gel (Daiso gel IR-60). Preparative TLC was carried out on silica gel (E. Merck, 5714). HPLC analysis were performed on a Shimadzu LC-6A chromatograph using a Shimadzu Shimpack-Sil, and the peak area were calculated on a Shimadzu chromatopack CR-4A. GC-analyses were performed on a Shimadzu GC-15A or GC-14A chromatograph using a glass capirally column (Shimadzu CBP-10, 25 m), and the peak areas were obtained with a Shimadzu chromatopack CR-5A.

(c) Cyclic Voltammetry: All cyclic voltammograms were recorded with a BAS Model CV1B-120 in acetonitrile solution containing 0.1 M (M=mol dm^{-3}) tetrabutylammonium perchlorate (TBAP) and 0.001 M nickel(II) complex. The working and auxiliary electrodes were platinum and the reference electrode was Ag/AgCl (Model RE-1B). Tetrabutylammonium perchlorate and acetonitrile (HPLC-grade) were purchased from TCI (Tokyo Kasei Kogyo, Inc) and Kanto Chemical Co. Ltd., respectively.

Preparation of 1,3-Diketones and Bis(1,3-diketonato)nickel-(II) Complexes. Bis(acetylacetonato)nickel(II) (**8a**, $Ni(acac)_2$) and bis(1,1,1-trifluoro-2,4-pentanedinonato)nickel(II) (**13a**, $Ni(tfa)_2$) were purchased from TCI Co., Ltd. Bis(3-methyl-2,4-pentanedionato)nickel(II) (**4a**, $Ni(mac)_2$),[16] bis-(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II) (bis(dipivaloylmethanato)nickel(II), **7a**, $Ni(dpm)_2$),[16] bis(2-acetylcyclopentanonato)nickel(II) (**5a**, $Ni(acp)_2$),[16] and bis(3-phenyl-2,4-pentanedionato)nickel(II) (**6a**, $Ni(pac)_2$)[16] were prepared according to the reported methods, respectively, and the ligands were purchased from TCI Co., Ltd. (**5b** and **7b**), Dojindo laboratories (**6b**), and Aldrich Chemical Company, Inc. (**4b**), respectively.

1,3-Bis(*p*-methoxyphenyl)-1,3-propanedione (3b, Hdmp):[15,17] A refluxing suspension of sodium hydride (0.39 mol) in cyclohexane (400 ml), a solution of *p*-methoxyacetophenone (0.33 mol) and ethyl *p*-methoxybenzoate (0.33 mol) in cyclohexane (200 ml) was added over 1 h, and reflux was continued for another 2 h. After cooling, reaction was quenched with 1.0 mol dm^{-3} aqueous HCl, then crude product was extracted with THF–Et_2O. The organic extract was washed with brine, and dried over anhydrous sodium sulfate, then solvent was removed in vacuo. Recrystallization from hexane–ethyl acetate gave slightly colored needle (58% yield). Mp 131—138 °C; ^1H NMR ($CDCl_3$) δ=3.90 (6H, s), 6.80 (1H, s), 7.00 (4H, m), 7.95 (4H, m); IR(KBr) 2938, 2840, 1687, 1605, 1507, 1429, 1305, 1263, 1230, 1170 cm^{-1}.

Bis[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato] nickel-(II) (3a):[15] A vigorously stirred mixture of Hdmp (0.1 mol) in ether (300 ml), a solution of nickel(II) acetate (0.05 mol) in 10% aqueous ammonia (800 ml) was added in one portion. Precipitated pale green solid was filtered and washed with water. After dried in vacuo for 6 h (110 °C/0.1 mmHg, 1 mmHg= 133.322 Pa), $Ni(dmp)_2$ was yielded as yellow solid. Found: C, 65.45; H, 4.87%. Calcd for $C_{34}H_{30}O_8Ni$: C, 65.31; H, 4.84%.

Bis(3-methyl-2,4-pentanedionato)nickel(II) (4a):[14,16] To the stirred mixture of nickel(II) acetate (0.1 mol) in water (150 ml), 3-methyl-2,4-pentanedione (Hmac, 0.2 mol) in methanol (5 ml) was added. After stirring for 5 min, aqueous sodium acetate (0.2 mol) in water (10 ml) was added over 10 min. Precipitated yellowish green solid was filtered and washed with water. After drying in vacuo for 6 h (90 °C/ 0.1 mmHg), $Ni(mac)_2$ was yielded as purple solid.

Melting Points and IR Spectra of Nickel(II) Complexes. Bis[1,3-bis(*p*-dimethoxyphenyl)-1,3-propanedionato]nickel-(II) (3a, $Ni(dmp)_2$): Yellow solid; mp 279—284 °C; IR (KBr)

2932, 2834, 1604, 1529, 1492, 1431, 1391, 1304, 1256, 1227, 1174 cm^{-1}.

Bis(3-methyl-2,4-pentanedionato)nickel(II) (4a, Ni(mac)$_2$): Purple solid; mp 180 °C (decomp); IR (KBr) 2920, 1599. 1570, 1424, 1388 cm^{-1}.

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II) (bis-(dipivaloylmethanato)nickel(II), 7a, Ni(dpm)$_2$): Purple solid; mp 221—223 °C; IR (KBr) 2956, 1570, 1542, 1502, 1401, 1360 cm^{-1}.

Bis(2-acetylcyclopentanonato)nickel(II) (5a, Ni(acp)$_2$): Light green solid; mp >250 °C (decomp); IR (KBr) 2950, 1602, 1478, 1401, 1272 cm^{-1}.

Bis(3-phenyl-2,4-pentanedionato)nickel(II) (6a, Ni(pac)$_2$): Purple solid; mp 204—207 °C; IR (KBr) 2922, 1583, 1420, 1377, 1301 cm^{-1}.

Epoxidation of 1,5-Dimethyl-4-hexenyl Benzoate (27) (Method (A), Standard Method, see Entry 8 in Table 6). A mixture of olefin (3.0 mmol), Ni(dmp)$_2$ (40.0 mg, 0.064 mmol, 2.1 mol%) an isobutyraldehyde (6.25 mmol) in 1,2-dichloroethane(2.0 ml)[3,4] 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).

Epoxidation of *trans*-4-Phenyl-2-butene (45) (Method (B), Dilution Method, see Entry 3 in Table 7). A mixture of olefin (2.0 mmol), Ni(dmp)$_2$ (4.0 mg, 0.006 mmol, 0.3 mol%) and isobutyraldehyde (6.0 mmol) in 1,2-dichloroethane (10.0 ml)[3,4] was stirred at room temperature under an atmospheric pressure of oxygen overnight. After the reaction, organic layer was washed with sat. $NaHCO_3$ and brine. Purification with TLC on silica gel to afford the corresponding epoxide (223 mg, 75% yield).

Epoxidation of 1-Tetradecene (49) (Method (C), Isovaleraldehyde Method, see Entry 6 in Table 7). A mixture of olefin (10.0 mmol), Ni(dmp)$_2$ (12.0 mg, 0.019 mmol, 0.19 mol%) and isovaleraldehyde (60.0 mmol) in 1,2-dichloroethane (30 ml)[3,4] was stirred at room temperature under an atmospheric pressure of oxygen for 47 h. After the reaction, organic layer was washed with sat.$NaHCO_3$ (4 times) and brine. Purification with silica-gel column chromatography afforded the corresponding epoxide (1.89 g, 89.2% yield).

^{1}H NMR and IR Spectra of the Epoxides (in Table 6 and Table 7). **1,2-Epoxydecane (14), *exo*-2,3-Epoxybicyclo[2.2.1]-heptane (34), 1,2-Epoxycyclohexane (48).** ^{1}H NMR spectra, IR spectra, and retention time in GC analysis agreed with those of the authentic sample.

2,3-Epoxy-2-methyldecane (2); ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.92 Hz), 1.26 (3H, s), 1.28 (10H, m), 1.31 (3H, s), 1.50 (2H, m), 2.71 (1H, t, J=6.27 Hz); IR(neat) 2925, 2850, 1465 cm^{-1}.

***cis*-2,3-Epoxyoctane (12);** ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, t, J=7.09 Hz), 1.27 (3H, d, J=5.28 Hz), 1.35—1.45 (4H, m), 1.48—1.55 (4H, m), 2.90 (1H, m), 3.06 (1H, m); IR(neat) 2958, 2928, 2856, 1466, 1381 cm^{-1}.

6,7-Epoxy-3,7-dimethyloctyl Acetate (16); ^{1}H NMR ($CDCl_3$) δ=0.94 (3H, d, J=6.27 Hz), 1.27 (3H, s), 1.31 (3H, s), 1.40—1.60 (7H, m), 2.05 (3H, s), 2.70 (1H, t, J=6.06 Hz), 4.11 (2H, m); IR(neat) 2960, 2924, 2872, 1741, 1461, 1379, 1367, 1241 cm^{-1}.

***trans*-6,7-Epoxy-3,7-dimethyl-2-octenyl Acetate (18);** ^{1}H NMR ($CDCl_3$) δ=1.26 (3H, s), 1.31 (3H, s), 1.60—1.80 (5H, m), 2.05 (3H, s), 2.10—2.30 (2H, m), 2.70 (1H, t, J=6.26 Hz), 4.59 (2H, d, J=7.25 Hz), 5.40 (1H, m); IR(neat) 2960, 2926, 1740, 1454, 1380, 1234 cm^{-1}.

2,3:6,7-Diepoxy-3,7-dimethyloctyl Acetate (19); ^{1}H NMR ($CDCl_3$) δ=1.30 (6H, m), 1.50—1.80 (7H, m), 2.10 (3H, s), 2.70 (1H, m), 3.05 (1H, m), 4.05 (1H, m), 4.30 (1H, m); IR(neat) 2970, 2929, 1743, 1455, 1380, 1232 cm^{-1}.

***cis*-6,7-Epoxy-3,7-dimethyl-2-octenyl Acetate (21);** ^{1}H NMR ($CDCl_3$) δ=1.27 (3H, s), 1.31 (3H, s), 1.63 (2H, dt, J_1=7.75 Hz, J_2=6.27 Hz), 1.78 (3H, s), 2.05 (3H, s), 2.26 (2H, t, J=7.75 Hz), 2.71 (1H, t, J=6.27 Hz), 4.58 (2H, d, J=6.60 Hz), 5.41 (1H, t, J=6.60 Hz); IR(neat) 2964, 2930, 1739, 1670, 1453, 1379, 1234 cm^{-1}.

2,3:6,7-Diepoxy-3,7-dimethyloctyl Acetate (22); ^{1}H NMR ($CDCl_3$) δ=1.28 (3H, s), 1.32 (3H, s), 1.35 (3H, s), 1.60—1.80 (4H, m), 2.72 (1H, m), 3.00 (1H, m), 4.09 (1H, m), 4.35 (1H, m); IR(neat) 2970, 2931, 1744, 1454, 1378, 1234 cm^{-1}.

2,3-Epoxy-6-methoxy-2-methylheptane (24); Bp 84—85 °C (20 mmHg); ^{1}H NMR ($CDCl_3$) δ=1.15 (3H, d, J=6.26 Hz), 1.27 (3H, s), 1.31 (3H, s), 1.45—1.80 (4H, m), 2.75 (1H, m), 3.25—3.40 (1H, m), 3.30 (3H, s); IR(neat) 2968, 1462, 1377, 1090 cm^{-1}.

4,5-Epoxy-1,5-dimethylhexyl Acetate (26); ^{1}H NMR ($CDCl_3$) δ=1.25 (9H, s), 1.45—1.85 (4H, m), 2.00 (3H, s), 2.70 (1H, m), 4.90 (1H, m); IR(neat) 2974, 1737, 1376, 1243 cm^{-1}.

4,5-Epoxy-1,5-dimethylhexyl Benzoate (28); ^{1}H NMR ($CDCl_3$) δ=1.20—1.40 (9H, m), 1.55—2.00 (4H, m), 2.75 (1H, m), 5.20 (1H, m), 7.40—7.60 (3H, m), 8.05 (2H, m); IR(neat) 2974, 1716, 1276, 1111, 714 cm^{-1}.

2-Propyl-1-oxaspiro[2.5]octane (30); Bp 82 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ=0.95 (3H, m), 1.40—1.80 (14H, m), 2.70 (1H, t, J=5.94 Hz); IR(neat) 2930, 1449, 913 cm^{-1}.

1-Methyl-1,2-epoxycyclohexane (32); ^{1}H NMR ($CDCl_3$) δ=1.30—1.40 (2H, m), 1.60—1.70 (2H, m), 1.80—2.00 (4H, m), 2.95 (1H, s); IR(neat) 2982, 2936, 2858, 1555, 1538 cm^{-1}.

5,6-Epoxybicyclo[2.2.1]hept-2-ylmethyl Benzoate (36); ^{1}H NMR ($CDCl_3$) δ=0.90 (2H, m), 1.40 (2H, m), 1.80 (1H, m), 2.26 (1H, m), 3.25 (2H, m), 4.30 (2H, m), 7.45 (2H, m), 7.55 (1H, m), 8.05 (2H, m); IR(neat) 3030, 2964, 2870, 1719, 1602, 1452, 1314, 1276, 1113 cm^{-1}.

5,6-Epoxycholesteryl Acetate (38); ^{1}H NMR ($CDCl_3$) δ=0.60 (3H, m), 0.80—1.60 (6H, m), 1.80—2.20 (34H, m), 2.00 (3H, s), 2.90 (0.24H, d, J=2.90 Hz), 3.10 (0.76H, d, J=2.00 Hz), 4.70—5.00 (1H, m); IR(KBr) 2950, 1734, 1470, 1368, 1247, 1041 cm^{-1}.

1,2-Epoxy-2-methylundecane (40); ^{1}H NMR ($CDCl_3$) δ= 0.88 (3H, t, J=6.80 Hz), 1.27 (3H, s), 1.29 (14H, m), 1.50 (2H, t, J=10.9 Hz), 2.57 (1H, d, J=10.9 Hz); IR(neat) 2924, 2852, 1465 cm^{-1}.

1,2-Epoxy-1-(*p*-fluorophenyl)heptane (42); ^{1}H NMR ($CDCl_3$) δ=0.80 (3H, s), 1.10—1.60 (8H, m), 2.90 (0.15H, m), 3.15 (0.85H, m), 3.60 (0.15H, d, J=1.98 Hz), 4.05 (0.85H, d, J=3.95 Hz), 7.05 (2H, m), 7.25 (2H, m); IR(neat) 2928, 1511, 1222, 837 cm^{-1}.

***trans*-2,3-Epoxyoctane (44);** ^{1}H NMR ($CDCl_3$) δ=0.89 (3H, t, J=6.93 Hz), 1.29 (3H, d, J=5.27 Hz), 1.33 (4H, br), 1.45—1.52 (4H, m), 2.62 (1H, m), 2.75 (1H, m); IR(neat) 2960, 2930, 2854, 1464, 1378 cm^{-1}.

2,3-Epoxy-1-phenylbutane (46); ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, d, J=5.30 Hz), 2.70—2.90 (4H, m), 7.20—7.40 (5H, m); IR(neat) 2980, 1495, 1453, 1381, 737, 699 cm^{-1}.

2,3-Epoxy-3-methylbutyl Benzoate (52); ^{1}H NMR ($CDCl_3$) δ=1.40 (6H, s), 3.15 (1H, m), 4.30 (1H, m), 4.60 (1H, m), 7.40—7.60 (3H, m), 8.05 (2H, m); IR(neat) 2964, 1721, 1272, 1114, 712 cm^{-1}.

2,3-Epoxybutyl Benzoate (54); ^{1}H NMR ($CDCl_3$) δ=1.36 (3H, d, J=5.94 Hz), 3.00 (2H, m), 4.20 (1H, dd, J_1=5.94 Hz, J_2=12.2 Hz), 4.60 (1H, dd, J_1=3.30 Hz, J_2=12.2 Hz); IR(neat) 1722, 1273, 712 cm^{-1}.

5,6-Epoxycholesteryl Benzoate (Mixture of 56 and 57); ^{1}H NMR ($CDCl_3$) δ=0.60 (3H, m), 0.80—1.60 (6H, m), 1.80—2.20 (34H, m), 2.90 (0.31H, d, J=2.90 Hz), 3.10 (0.69H, d, J=2.00 Hz), 4.70—5.00 (1H, m), 7.20—7.40 (5H, m); IR(KBr) 2950, 1734, 1470, 1368, 1247, 1041 cm^{-1}.

Measurement of Cyclic Voltammetry. The acetonitrile solution containing 0.1 M TBAP and 0.001 M nickel(II) complex was degassed by bubbling of argon for 15 min and the measurements were performed at the scan rate of 200 mV s^{-1}. The range of measurement was between −2.0 V and +2.0 V.

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