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Nickel(II) Complex Catalyzed Epoxidation of Olefins with Molecular Oxygen and Primary Alcohol

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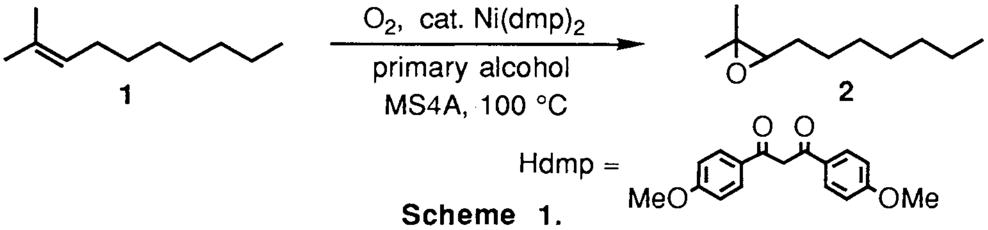
In the presence of a catalytic amount of bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II) (=Ni(dmp)$_2$), various olefins are smoothly monooxygenated into corresponding epoxides in good yields with combined use of molecular oxygen and primary alcohol.

Catalytic epoxidation of olefins with molecular oxygen is one of the challenging topics in organic synthesis and much effort has been made in this field.$^{1)}$ However, no satisfactory results were obtained from the stand point of organic synthesis in terms of efficiency of catalyst or problem of by-products.

In our previous communication,$^{2)}$ a new method for monooxygenation of norbornene analogues with combined use of molecular oxygen (oxidant) and primary or secondary alcohol (reductant) catalyzed by bis(2-alkyl-1,3-diketonato)oxovanadium(IV) was reported. Our continuous study revealed that nickel(II) complexes having electron-donating 1,3-diketone ligands behaved as excellent catalysts for epoxidation of olefins with molecular oxygen, although successful results were obtained in the previous literatures only when iodosobenzene$^{3a)}$ or sodium hypochlorite$^{3b)}$ was used, and not molecular oxygen.

In this communication, we would like to report an efficient method for epoxidation of aliphatic or aromatic olefins with molecular oxygen and primary alcohol catalyzed by nickel(II) complexes.

In the first place, epoxidation of 2-methyl-2-decene (**1**) with molecular oxygen in the presence of a catalytic amount of bis(3-methyl-2,4-pentanedionato)nickel(II) (=Ni(mac)$_2$) or bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II) (=Ni(dmp)$_2$) was tried by heating the stirred mixture in 1,2-dichloroethane (EDC) under an oxygen atmosphere, employing primary or secondary alcohol as a reductant. In the case of using primary alcohol (1-butanol), it was found that epoxide **2** was formed in higher yield compared with the case of



Scheme 1.

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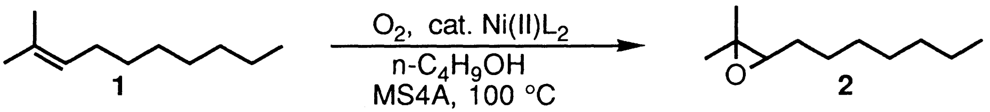
using secondary alcohol (2-propanol) or in the absence of alcohol.

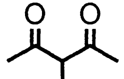
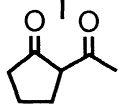
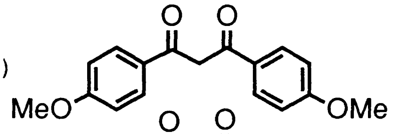
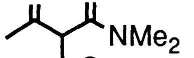
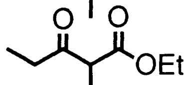
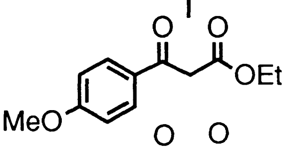
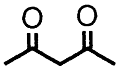
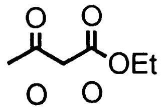
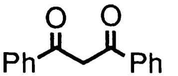
Next, several 1,3-diketone ligands were examined for epoxidation of 2-methyl-2-decene (**1**) with molecular oxygen and 1-butanol, and, as shown in Table 1, nickel(II) complexes having 2-alkyl-1,3-diketones are effective in the present epoxidation (Entries 1 and 2). Then, it was expected that nickel(II) complexes having more electron-donating ligands would behave more effectively as catalysts. Thus, β-diketone having electron-donating substituent or β-ketocarboxylic acid derivatives, for example β-ketoester or β-ketoamide, was employed as a ligand of nickel(II) complex. All these complexes showed good catalytic activities as expected (Entries 3, 5, 6, and 7). Especially, in the case of using bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato] nickel(II)[4] (=Ni(dmp)$_2$), epoxidation proceeded smoothly even under lower oxygen pressure (Entry 4).

In the next place, several primary alcohols, which are considered as a reliable reductant, were screened (see Table 2), and in the cases of higher primary alcohols, such as 1-tetradecanol or 1-octadecanol, both selectivities and yields of epoxides were recognized to increase compared with those of 1-butanol (Entries 3 and 4).

Subsequently, the above procedure of using higher primary alcohol was successfully applied to various olefins (see Table 3). In all cases, olefins are smoothly monooxygenated into corresponding epoxides in good

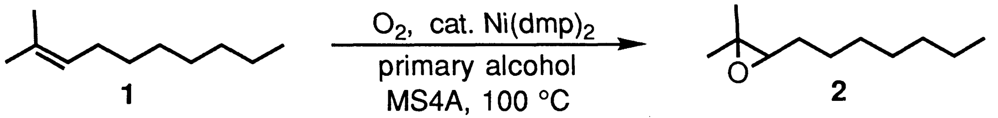
Table 1. Epoxidation of 2-Methyl-2-decene (**1**) Catalyzed by Various Nickel(II) Complexes[a)]



Entry	Ligand (LH)		Time /h	Conversion /%[b)]	Yield /%[b)]
1		(=Hmac)	6	100	67
2		(=Hacp)	8	100	58
3		(=Hdmp)	2	100	59
4[c)]			4[c)]	100	65
5			8	96	60
6			8	100	64
7			9	100	47
8		(=Hacac)	6	77	27
9			6	14	5
10			8	32	12

a) Reaction conditions; olefin **1** 10 mmol, 1-butanol 20 mmol, Ni(II)L_2 0.4 mmol (4.0 mol%), EDC 5.0 ml, Molecular Sieves 4A (MS4A) 1.0 g, 100 °C, 11 atm O_2. b) Determined by GC. c) 4 atm O_2.

Table 2. Effect of Primary Alcohols on Selectivity of Epoxide[a)]



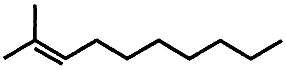
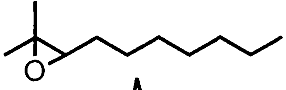
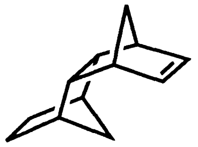
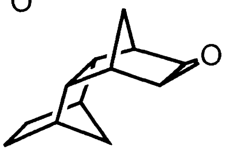
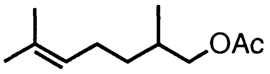
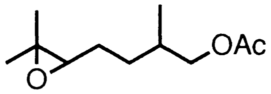
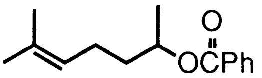
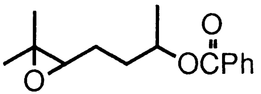
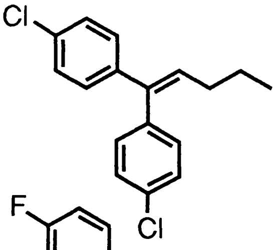
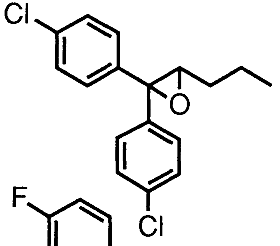
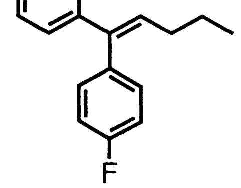
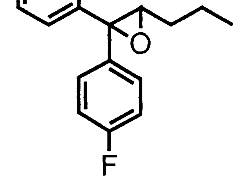
1 **2**

Entry	Alcohol	Conversion /%[b)]	Yield /%[b)]	Selectivity /%
1	$n\text{-}C_4H_9OH$	100	65	65
2	$n\text{-}C_8H_{17}OH$	100	71	71
3	$n\text{-}C_{14}H_{29}OH$	96	70	73
4	$n\text{-}C_{18}H_{37}OH$	92	69	75

a) Reaction conditions; olefin **1** 5.0 mmol, primary alcohol 10 mmol, $Ni(dmp)_2$ 0.2 mmol (4.0 mol%), EDC 3.0 ml MS4A 0.5 g, 100 °C, 4 atm O_2. b) Determined by GC.

Table 3. Epoxidation of Various Olefins Catalyzed by $Ni(dmp)_2$[a)]

$$\text{Olefin} \xrightarrow[\text{primary alcohol, MS4A, 100 °C}]{O_2\text{, cat. } Ni(dmp)_2} \text{Epoxide}$$

Entry	Olefin	Alcohol	Time /h	Epoxide	Yield /%
1[b)]		$n\text{-}C_{18}H_{37}OH$	8		78[c)]
2		$n\text{-}C_{11}H_{23}OH$	6		80[c)]
3[d)]		$n\text{-}C_{14}H_{29}OH$	4		72[c)]
4		$n\text{-}C_8H_{17}OH$	5		67[e)]
5		$n\text{-}C_{14}H_{29}OH$	8		86[e)]
6		$n\text{-}C_{14}H_{29}OH$	4		81[e)]

a) Reaction conditions; olefin 5.0 mmol, primary alcohol 10 mmol, $Ni(dmp)_2$ 0.2 mmol (4.0 mol%), 1,3,5-trimethylbenzene 3.0 ml, MS4A 0.5 g, 100 °C, 4 atm. b) 1-Octadecanol 15 mmol was used. c) Determined by GC. d) 3-Pentanone (3.0 ml) was used as a solvent. e) Isolated yield.

to high yields. Further, olefins bearing ester groups were converted into corresponding epoxides without destroying these functional groups (Entries 3 and 4). In particular, aromatic olefins substituted with electron-withdrawing groups were epoxidized in high yields (Entries 5 and 6).

Typical procedure is described for the epoxidation of 1,1-bis(*p*-chlorophenyl)-1-butene (Entry 5 in Table 3); a mixture of olefin (5.0 mmol), Ni(dmp)$_2$ (0.20 mmol, 4.0 mol%), 1-tetradecanol (10 mmol) and Molecular Sieves 4A (0.50 g) in 1,3,5-trimethylbenzene (3.0 ml) was stirred at 100 °C in a microautoclave (30 ml) under 4 atm of oxygen for 8 h. Then solvent was removed under reduced pressure, and residue was purified by silica-gel column chromatography (hexane / ethyl acetate) to yield the corresponding epoxide **10** as a colorless oil (86% yield).

It is noted that, in the presence of a catalytic amount of Ni(dmp)$_2$, various olefins are monooxygenated with molecular oxygen and primary alcohol into corresponding epoxides in good to high yields.

Further investigation on the epoxidation of olefins catalyzed by nickel(II) complexes is now under way.

References

1) J. -C. Marchon and R. Ramasseul, *Synthesis*, **1989**, 389; S. Ito, K. Inoue, and M. Matsumoto, *J. Am. Chem. Soc.*, **104**, 6450 (1982). References are cited therein.

2) T. Takai, T. Yamada, and T. Mukaiyama, *Chem. Lett.*, Submitting.

3) a) J. D. Koola and J. K. Kochi, *Inorg. Chem.*, **26**, 908 (1987); J. F. Kinnerly, J. S. Albert, and C. J. Burrows, *J. Am. Chem. Soc.*, **110**, 6124 (1988); b) H. Yoon and C. J. Burrows, *ibid.*, **110**, 4087 (1988).

4) Preparation of a ligand, 1,3-di(*p*-methoxyphenyl)-1,3-propanedione (=Hdmp), is described as follows; to 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 2 h. After cooling, reaction mixture was quenched with 1 mol/l aqueous HCl, then crude product was extracted with THF / ether. 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. Preparation of nickel(II) complex, Ni(dmp)$_2$, is described as follows; to 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), Ni(dmp)$_2$ was yielded as yellow solid. Mp 279-284 °C.

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