CHEMISTRY LETTERS, pp. 231-234, 1992.

A Novel Method for Preparation of Glycerol Monoesters from Glycidyl Esters with Molecular Oxygen Catalyzed by Ni(II) Complex

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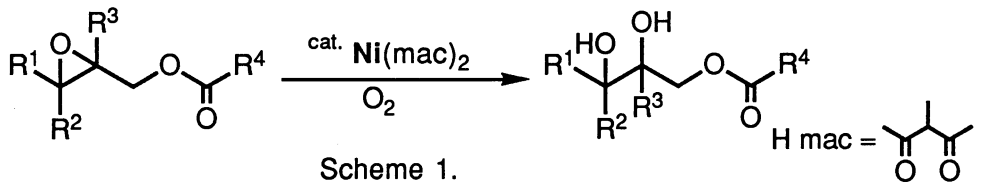
In the presence of a catalytic amount of bis(3-methyl-2,4-pentanedionato)nickel(II) ($Ni(mac)_2$), various glycidyl esters are converted into the corresponding glycerol monoester derivatives with molecular oxygen in good to high yields.

Diols or triols are one of the most important intermediates for the synthesis of various natural products, such as sugars[1, 2] and polyenemacrolide antibiotics.[3] Combination of epoxidation and following ring-opening reactions is the most useful method for preparation of 1,2-diols from olefinic compounds. We have already reported the highly efficient method for epoxidation of various olefins catalyzed by Ni(II) complexes with combined use of atmospheric pressure of oxygen and an aldehyde at room temperature.[4] Transformation of epoxides into 1,2-diols is generally carried out by hydrolytic ring-opening reaction promoted by acids,[5] such as perchloric acid, sulfuric acid, trichloroacetic acid, trifluoroacetic acid, or formic acid, or by bases[2, 5] such as sodium hydroxide or potassium hydroxide. In the case of hydrolysis of glycidyl esters promoted by acids or bases mentioned above, undesired hydrolysis of ester group often takes place to afford free 1,2,3-triols, which are difficult to handle. Thus, in this communication we would like to report a novel method for the preparation of glycerol monoester derivatives by oxidative ring-opening reaction of glycidyl esters with molecular oxygen catalyzed by Ni(II) complex without accompanying the undesirable hydrolysis of ester function.



Scheme 1.

First, the oxidative ring-opening reaction of several epoxides was tried with molecular oxygen catalyzed by Ni(II) complex (see Table 1). Epoxides derived from esters of allyl or homoallyl alcohol were converted into the corresponding 3- or 4-acyloxy-1,2-diol in good yields, respectively (Entries 1 and 2). It was shown that the yield of triol from ester of allyl alcohol was higher than that from ester of homoallyl alcohol, whereas in case of

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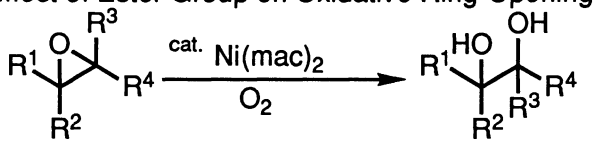
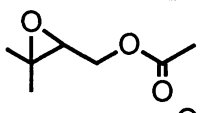
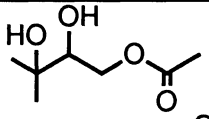
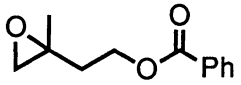
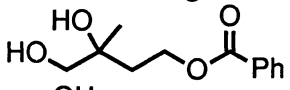
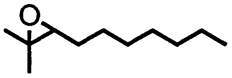
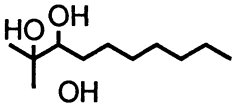
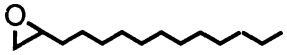
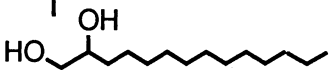
epoxides without any functional group, for example 2,3-epoxy-2-methyldecane (Entry 3) and 1,2-epoxytetradecane (Entry 4), almost all starting epoxides were recovered under the same reaction conditions and no corresponding 1,2-diol was detected at all. It can therefore be pointed out that ester group is necessary for the present oxidative ring-opening reaction.

Then, the reaction was applied to several esters of 2,3-epoxy-3-methylbutanol (see Table 2). In cases of alkyl substituents as R in esters, such as acetate, heptanoate, and pivarate, and in case of benzoate (R=Ph), epoxides were smoothly converted to the corresponding glycerol monoester derivatives in high yields (Entries 1,

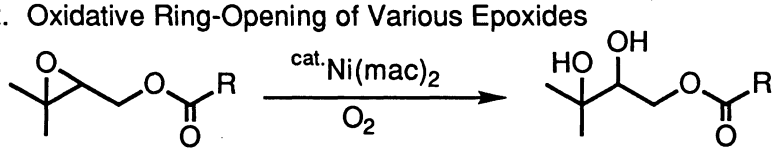
Table 1. Effect of Ester Group on Oxidative Ring-Opening



Entry [a]	Epoxide	Diol	Yield /%[c]
1			72
2[b]			56
3			0
4			0

a) Reaction conditions; epoxide 2.5 mmol, $Ni(mac)_2$ 0.075 mmol (3 mol%), 2,4-dimethyl-3-pentanone 0.5 ml, *trans*-2-octenal 1.5 mmol (0.6 equiv.), MS4A 250 mg in 1,2-dichloroethane 1.5 ml, 6 atm O_2, 100 °C, 2 h. b) Reaction time 4 h. c) Determined by GC analysis.

Table 2. Oxidative Ring-Opening of Various Epoxides



Entry [a]	R	Reaction time /h	Yield /%	Note[d]
1	CH_3-	4	84[b]	92: 8
2	$CH_3(CH_2)_6$-	6	82[c]	90:10
3	$(CH_3)_3C$-	6	85[c]	85:15
4		8	90[b]	85:15

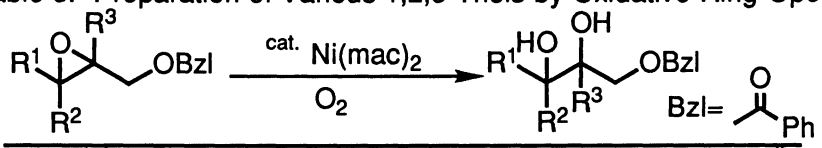
a) Reaction conditions; epoxide 2.5 mmol, $Ni(mac)_2$ 0.075 mmol (3 mol%), 2,4-dimethyl-3-pentanone 0.5 ml, *trans*-2-octenal 1.5 mmol (0.6 equiv.), MS4A 250 mg in 1,2-dichloroethane 1.5 ml, 6 atm O_2, 100 °C. b) Determined by GC analysis. c) Isolated yield. d) Ratio of 3-acyloxy-1,2-diol to 2-acyloxy-1,3-diol determined by ^1H NMR.

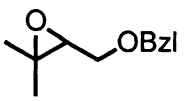
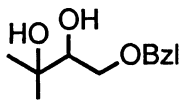
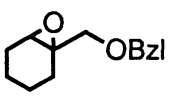
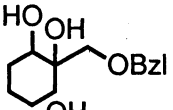
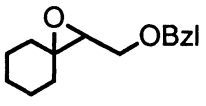
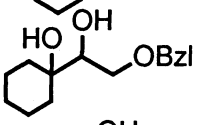
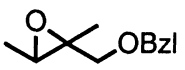
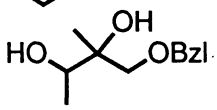
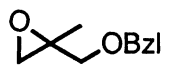
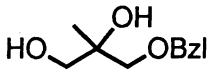
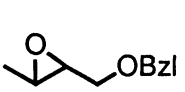
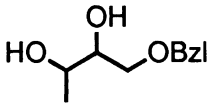
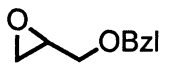
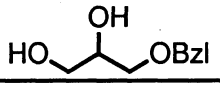
3-Acyloxy-1,2-diol 2-Acyloxy-1,3-diol

2, 3, and 4). It is noted that the present procedure could be applied to the preparation of glycerol derivatives from various kinds of esters of 2,3-epoxy-3-methylbutanol.[6] In every case, 2-acyloxy-1,3-diols were obtained as minor products due to the acyl rearrangement of 3-acyloxy-1,2-diols. The yields in Table 2 show the total yields of 1,2-diols and 1,3-diols and the ratios are shown in the column of Note.

The present procedure was successfully applied to various glycidyl esters (see Table 3). In case of trisubstituted epoxides except 2,3-epoxy-2-methylbutyl benzoate, the oxidative ring-opening reactions were carried out under 6 atm of oxygen and the corresponding glycerol derivatives were obtained in high yields, respectively (Entries 1, 2, and 3). Benzoate of 2,3-epoxy-2-methylbutanol was converted under 8 atm of oxygen to the corresponding 1,2,3-triol in good yield (Entry 4). Other epoxides were also oxidized under 8 atm of oxygen, and the reaction of 2,3-epoxy-2-methylpropyl benzoate proceeded smoothly to afford only 1,2-diol derivative in high yield without accompanying acyl rearrangement (Entry 5). Glycerol derivatives could also be prepared from 1,2-disubstituted and monosubstituted epoxides in good yields, respectively (Entries 6 and 7).

Table 3. Preparation of Various 1,2,3-Triols by Oxidative Ring-Opening



Entry[a]	Epoxide	Diol	Yield /% (Ratio[d])
1[b]			90[e](85:15)
2[b]			82[f](64:36)
3[b]			80[f](77:23)
4[c]			75[f](60:40)
5[c]			84[f](100:0)
6[c]			74[f](58:42)
7[c]			65[f](89:11)

a) Reaction conditions; epoxide 2.5 mmol, $Ni(mac)_2$ 0.075 mmol (3 mol%), 2,4-dimethyl-3-pentanone 0.5 ml, *trans*-2-octenal 1.5 mmol (0.6 equiv.), MS4A 250 mg in 1,2-dichloroethane 1.5 ml, 100 °C, 8 h. b) 6 atm O_2. c) 8 atm O_2. d) Ratios of 1,2-diol to 1,3-diol determined by ^1H NMR. e) Determined by GC analysis. f) Isolated yield.

A typical procedure is described for the preparation of 2,3-dihydroxy-2-methylpropyl benzoate (Entry 5 in Table 3): The solution of 2,3-epoxy-2-methylpropyl benzoate (2.5 mmol), $Ni(mac)_2$ (0.075 mmol, 3 mol%), *trans*-2-octenal (1.5 mmol), 2,4-dimethyl-3-pentanone (0.5 ml), and Molecular Sieves 4A (250 mg) in 1,2-dichloroethane (1.5 ml) was stirred at 100 °C in a microautoclave (30 ml) under 8 atm of oxygen for 8 h. After the reaction, solvent was removed under reduced pressure, and the residue was purified by preparative silica-gel thin layer chromatography (hexane/ethyl acetate) to yield the corresponding 1,2-diol[7] (84% yield).

It is noted that various glycerol ester derivatives are prepared from glycidyl esters in good to high yields with molecular oxygen catalyzed by bis(3-methyl-2,4-pentanedionato)nickel(II) ($Ni(mac)_2$) without accompanying any undesirable hydrolysis of ester function.

References

1) T. Mukaiyama, I. Shiina, and S. Kobayashi, *Chem. Lett.*, **1990**, 2201, and references are cited therein.

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3) S. Masamune, G. S. Bates, and J. W. Corcoran, *Angew. Chem., Int. Ed. Engl.*, **16**, 585 (1977); T. Nakata, T. Suenaga, and T. Oishi, *Tetrahedron Lett.*, **30**, 6525 (1989); T, Nakata, T. Suenaga, K. Nakashima, and T. Oishi, *ibid.*, **30**, 6529 (1989).

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

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6) Chiral 2,3-epoxy-3-methylbutyl benzoate (76% e.e.) was converted into 2,3-dihydroxy-2-methylbutyl benzoate (30% e.e.). The starting chiral epoxide was prepared with Sharpless' method (Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune, and K. B. Sharpless, *J. Am. Chem. Soc.*, **109**, 5765 (1987)).

7) ^1H NMR ($CDCl_3$) δ=1.27 (3H, s), 3.51 (1H, d, J=11.5 Hz), 3.62 (1H, d, J=11.5 Hz), 3.72 (2H, br s), 4.25 (1H, d, J=11.2 Hz), 4.35 (1H, d, J=11.2 Hz), 7.41 (2H, m), 7.54 (1H, m), 8.02 (2H, m); IR (KBr) 3440, 3366, 1690 cm^{-1}.

(Received November 8, 1991)