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Epoxidation of Olefins with Molecular Oxygen and Alcohol Catalyzed by Bis(2-alkyl-1,3-diketonato)oxovanadium(IV)

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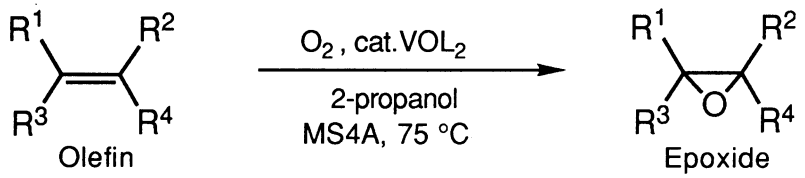
By combined use of molecular oxygen (oxidant) and secondary or primary alcohol (reductant) in the presence of a catalytic amount of bis(2-alkyl-1,3-diketonato)oxovanadium(IV) complexes, norbornene analogues are monooxygenated into the corresponding epoxides in good yields.

Selective monooxygenation of olefins with molecular oxygen forming the corresponding epoxides is one of the current interests in organic synthesis. In order to develop useful monooxygenation reactions, many transition-metal complexes involving cytochrome-P 450,[1a] or Mn,[1b] Fe,[1c] and Ru[1d] porphyrins have been screened, however, practical synthetic methods were not successfully established because of the complicated reaction systems.

In a previous paper,[2a] we have reported "Oxidation-Reduction Hydration" of olefins into the corresponding hydrated compounds using molecular oxygen and secondary alcohol in the presence of a catalytic amount of bis(1,3-diketonato)cobalt(II). Based on the detailed observation on the hydration reaction, it was revealed that one oxygen atom from molecular oxygen and two hydrogen atoms from 2-propanol are simultaneously introduced into olefin to afford the hydrated product wherein secondary alcohol behaves as an effective reductant. Therefore, in the epoxidation with molecular oxygen, it is postulated that secondary alcohol would also behave as a reliable reductant to accomplish a catalytic cycle.

In this communication, we would like to describe a new type of monooxygenation reaction of olefins forming the corresponding epoxides with molecular oxygen (oxidant) and alcohol (reductant) in the presence of a catalytic amount of bis(2-alkyl-1,3-diketonato)oxovanadium(IV).



LH=2-alkyl-1,3-diketone

Scheme 1.

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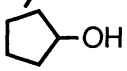
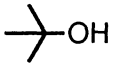
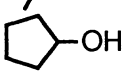
In the first place, the epoxidation of styrene with molecular oxygen and 2-propanol in the presence of a catalytic amount of bis(3-methyl-2,4-pentanedionato)oxovanadium(IV) (=VO(mac)$_2$) was tried with consideration that VO(mac)$_2$ would behave as an efficient catalyst because its oxidation potential is lower than that of VO(acac)$_2$ (see Entries 2 and 3 in Table 2). As expected, formation of styrene oxide was detected (GC analysis) by using VO(mac)$_2$ as a catalyst, while no epoxide was formed when VO(acac)$_2$ was used.

Next, several alcohols (reductant) were examined for epoxidation of styrene or 2-norbornene (**1a**) by using VO(mac)$_2$ as a catalyst (Table1).

Table 1. Effect of Alcohols on Formation of Epoxides[a)]

Olefin $\xrightarrow[\text{alcohol}]{O_2,\ \text{cat.VO(mac)}_2}$ Epoxide

MS4A, 75 °C, 20 h

Entry	Olefin	Alcohol	Conversion /%[b)]	Epoxide	Yield /%[b)]
1	Ph		100	Ph 	21
2			100		19
3		EtOH	100		15
4			82		0
5		none	100		0
6			78[c)]		49[c)]
7	**1a**		41	**3a**	24
8		EtOH	69		35

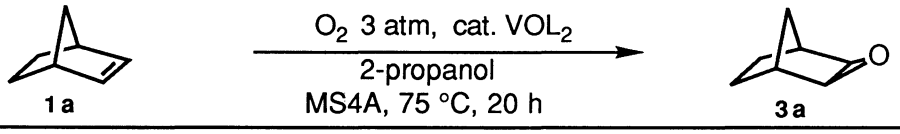
a) Reaction conditions; olefin 10 mmol, alcohol 15 mmol, VO(mac)$_2$ 0.4 mmol (4 mol%), toluene 2.0 ml, Molecular Sieves 4A (MS4A) 1.0 g, 75 °C, 1 atm O_2 (for styrene) or 3 atm O_2 (for 2-norbornene). b) Determined by GC.
c) Without MS4A, conversion of **1a** and yield of epoxide **3a** were decreased into 62% and 33%, respectively.

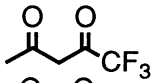
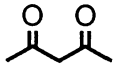
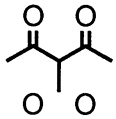
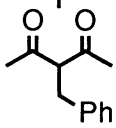
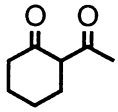
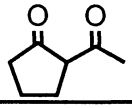
As shown in Table 1, when secondary alcohol, such as 2-propanol or cyclopentanol, or even primary alcohol (ethanol) was used as a reductant, the corresponding epoxides were formed smoothly. Whereas, no epoxide was detected in the case of tertiary alcohol (Entry 4) or in the absence of alcohol (Entry 5) indicating that secondary[2a)] or primary[2b)] alcohol is essential for the above catalytic epoxidation reaction.

In the next place, several 1,3-diketone ligands were examined for the epoxidaton of 2-norbornene (**1a**) with molecular oxygen and 2-propanol. As shown in Table 2, it was found that 1,3-diketone having an electron-withdrawing substituent, such as trifluoroacetylacetone, is not suitable as a ligand in the present epoxidation. On the contrary, 1,3-diketones having an electron-donating substituent at 2-position are quite effective for both conversion and yield. Especially, by using bis(2-acetylcyclopentanonato)oxovanadium(IV) (=VO(acp)$_2$)[3)] as a catalyst, 2-norbornene (**1a**) was oxidized into the corresponding epoxide **3a** in good selectivity (82%).

Actually, these oxovanadium(IV) complexes having 2-alkyl-1,3-diketone ligands indicated lower oxidation potentials than VO(acac)$_2$ (see Table 2). Therefore, it is reasonable to assume that these types of oxovanadium(IV) complexes are easily oxidized by catching up molecular oxygen, and then, resulting spieces would improve both conversion and yield.

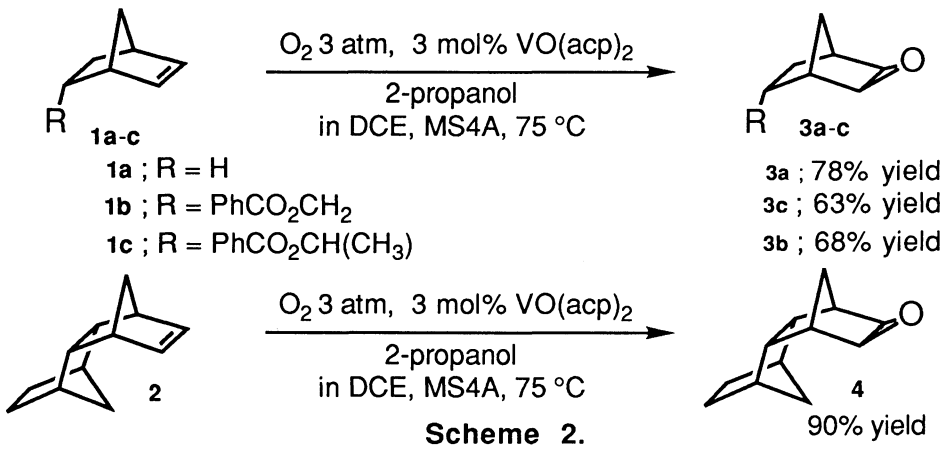
Table 2. Effect of 1,3-diketone Ligands on Selectivity of Epoxide[a)]



Entry	Ligand (LH)	E_{ox} /V vs. Ag/Ag^{+} [b)]	Conversion /%[c)]	Yield /%[c)]	Selectivity /%
1			12	trace	-
2	 (= Hacac)	1.00	31	10	32
3	 (= Hmac)	0.86	78	49	63
4			70	44	63
5			56	40	71
6	 (= Hacp)	0.96	57	47	82

a) Reaction conditions; 2-norbornene (**1a**) 10 mmol, 2-propanol 15 mmol, VOL_2 0.4 mmol (4 mol%), toluene 2.0 ml, MS4A 1.0 g, 75 °C, 3 atm O_2, in a 30 ml microautoclave. b) Oxidation potentials (E_{ox}) were measured in CH_3CN solution as described in reference 4. c) Determined by GC.

Subsequently, the present procudure for epoxidation by use of molecular oxygen, 2-propanol and a catalytic amount of $VO(acp)_2$ was successfully applied to the epoxidation of several norbornene analogues. As shown in Scheme 2, it was found that 1,2-dichloroethane (DCE) was more appropriate solvent than toluene, and all these compounds were smoothly oxidized in DCE solvent into the corresponding *exo*-epoxides in good yields. Further, olefins having ester groups were epoxidized without decomposition of these functional groups under the present reaction conditions (**3b** and **3c**). It is also noted that tetracyclododecene **2** gave the corresponding *exo*-epoxide **4** in 90% yield.



Scheme 2.

A typical procedure is described for the epoxidation of 1-(bicyclo[2.2.1]hept-5-en-2-yl)ethyl benzoate (**1c**); a mixture of ester **1c** (10 mmol), $VO(acp)_2$ (0.4 mmol, 4 mol%), 2-propanol (15 mmol) and Molecular Sieves 4A (1.0 g) in 1,2-dichloroethane (2.0 ml) was stirred at 75 °C in a microautoclave (30 ml) under 3 atm of oxygen for 40 h. Then solvent was removed under reduced pressure, and residue was purified by silica gel column chromatography (hexane/ethy acetate) to yield the corresponding epoxide **3c** as a colorless oil (68% yield).

It is noted that, in the presence of a catalytic amount of bis(2-alkyl-1,3-diketonato)oxovanadium(IV), especially $VO(acp)_2$, norbornene analogues are monooxygenated by combined use of molecular oxygen and 2-propanol to afford the corresponding epoxides in good yields.

References

1) a) F. P. Guengrich and T. L. Macdonald, *Acc. Chem. Res.*, **17**, 9 (1984); b) I. Tabushi and M. Kodera, *J. Am. Chem. Soc.*, **108**, 1101 (1986); D. Mansuy, M. Fontecve, and J. -F. Bartoli, *J. Chem. Soc., Chem. Commun.*, **1981**, 874; c) D. H. Chin, G. N. La Mar, and A. L. Balch, *J. Am. Chem. Soc.*, **102**, 1446 and 4344 (1980); d) J. T. Groves and R. Quinn, *ibid.*, **107**, 5790 (1985).

2) a) K. Kato, T. Yamada, T. Takai, S. Inoki, and S. Isayama, *Bull. Chem. Soc. Jpn.*, **63**, 179 (1990); b) Primary alcohol (ethanol) was used as a reductant. D. E. Hamilton, R. S. Drago, and A. Zombeck, *J. Am. Chem. Soc.*, **109**, 374 (1987).

3) $VO(acp)_2$ was prepared as follows; to the stirred mixture of 2-acetylcyclopentanone (0.2 mol) in MeOH-H_2O (1/1, 200 ml), $V(IV)OSO_4$ (0.1 mol) in water (50 ml) was added. After stirring for 5 min, aqueous solution of K_2CO_3 (0.1 mol, 50 ml) was added over 1 h. Precipitated yellow solid was filtered and washed with water. After drying, crude product was purified by Soxhlet extraction with Et_2O, then by vacuum sublimation (170 °C / 0.1 mmHg) to afford emerald green needle. Mp 220-221 °C; Found C, 53.17; H, 5.63; V, 16.24%; Calcd for $C_{14}H_{18}O_5V$; C, 53.01; H, 5.72; V, 16.06%. All other V(IV)O complexes were prepared in a similar manner.

4) The oxidation potentials (E_{ox}) were measured in CH_3CN solution containing 0.1 mol/l tetrabutylammonium perchlorate and 0.001 mol/l V(IV)O complex in the cell equipped with a reference electrode (Ag/AgCl), a working electrode (Pt) and an auxiliary electrode (Pt).

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