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Regioselectivity in Epoxidation of Dienes on $PW_{11}CoO_{39}^{5-}$ by Molecular Oxygen in the Presence of Aldehyde

Noritaka MIZUNO,* Masaki TATEISHI, To-oru HIROSE, and Masakazu IWAMOTO
Catalysis Research Center, Hokkaido University, Sapporo 060

The regioselectivity comparable to those on moderately hindered Mn(TTMPP)Cl with NaOCl was found for the epoxidation of (*R*)-(+)-limonene, 4-vinyl-1-cyclohexene, and 1-methyl-1,4-cyclohexadiene on mono-cobalt-substituted Keggin-type heteropolytungstate by molecular oxygen in the presence of aldehydes.

More electron-rich double bond is selectively attacked when dienes are epoxidized. Efforts to use bulky catalysts for regioselective epoxidation of more accessible, but less nucleophilic double bonds have had only limited success.[1,2] Therefore, the regioselectivities on bulky heteropolyanions are interesting for the wide application to the organic synthesis. On the other hand, Keggin-type heteropoly compounds are useful catalysts for the liquid-phase epoxidation of alkenes with hydrogen peroxide, iodosylbenzene, or *tert*-butyl hydroperoxide.[3] We have also reported that cobalt-substituted Keggin-type heteropolytungstate ($PW_{11}CoO_{39}^{5-}$, denoted by PW_{11}-Co) was the most active for the epoxidation of cyclohexene by molecular oxygen in the presence of aldehyde among PW_{11}-M (M = Co, Cu, Fe, Ni, Mn).[4] However, little is known of the effect of Keggin-type heteropolyanions on the selectivities as macro- and oxo-ligands. In this communication we wish to report the regioselectivity in the epoxidation of (*R*)-(+)-limonene (Fig. 1), 4-vinyl-1-cyclohexene, and 1-methyl-1,4-cyclohexadiene on a mono-cobalt-substituted heteropolytungstate.

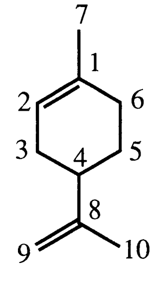

Fig. 1. (*R*)-(+)-Limonene.

The tetra-*n*-butylammonium salt of PW_{11}-Co was prepared as reported previously.[4] Co(TPP) (TPP, 5, 10, 15, 20-tetraphenylporphyrin) and $CoCl_2 \cdot 6H_2O$ were commercially obtained. A reaction was performed as follows: The catalyst (0.25 μmol) was introduced in a sealable glass vial (40 cm^3) containing a magnetic stir bar and 3 cm^3 of the appropriate solvent. The 250 μmol of the substrate ((*R*)-(+)-limonene, 4-vinyl-1-cyclohexene, or 1-methyl-1,4-cyclohexadiene) and aldehyde (100 - 1000 μmol) were added to the solution, and the vial was sealed. Then 1 atm O_2 was introduced to the system. The reaction vessel was placed at 303 K and vigorously stirred. The reaction solution was analyzed by NMR together with gas chromatography.

The regioselectivities of (*R*)-(+)-limonene are shown in Table 1. The 8,9-epoxide / 1,2-epoxide ratio was 0.48 in the epoxidation on PW_{11}-Co by O_2 in the presence of trimethylacetaldehyde in dichloromethane (Entry 1). It is noted that the value of 0.48 was higher than and comparable to those reported for Mn(TPP)(OAc) (8,9-epoxide / 1,2-epoxide ratio = 0.22[3d]) and moderately hindered Mn(TTMPP)(OAc) (TTMPP, 5,10,15,20-tetrakis(2,4,6-trimethoxyphenyl)porphyrin) (0.48, Entry 6), respectively, with NaOCl. The reaction little proceeded on PW_{11}-Mn under similar conditions to that of Entry 2. The regioselectivity to 8,9-epoxide on PW_{11}-

Table 1. Epoxidation of (*R*)-(+)-Limonene

Entry	Catalyst	Solvent	Oxidant	Total epoxide yield[a] / %	Epoxide ratio (8,9-/1,2-oxide)
1	PW_{11}-Co[b,c]	Dichloromethane	O_2	7	0.48
2	PW_{11}-Co[b,d]	Acetonitrile	O_2	4	0.23
3	Co(TPP)[b,e]	Dichloromethane	O_2	8	0.16
4	$CoCl_2$[b,f]	Acetonitrile	O_2	10	0.10
5	PW_{11}-Co[b,g]	Acetonitrile	PhIO	6	0.13
6	Mn(TTMPP)(OAc)[h]	Dichloromethane	NaOCl	4-6	0.48

a)Sum of the amounts of limonene 1,2- and 8,9-oxide formed / amount of limonene introduced. b)(*R*)-(+)-Limonene, 250 μmol; catalyst, 0.25 μmol; solvent, 3 cm^3; 303 K. The reaction condition was controlled to keep the conversion less than 8% for the inhibition of the double epoxidation. The detailed evaluation of the activities were reported in Ref. 4. Limonene 1, 2-oxide was found as a mixture of cis and trans isomers and limonene 8,9-oxide was a mixture of two diastereomers as has been reported by Mansuy et al.[1c)] c)Trimethylacetaldehyde, 100 μmol; 6 h. d)Isobutyraldehyde, 1000 μmol; 1 h. e)Trimethylacetaldehyde, 250 μmol; 0.5 h. f)Trimethylacetaldehyde, 250 μmol; 6 h. g)PhIO, 25 μmol; N_2, 1 atm; 2 h. h)300 K. Cited from Ref. 1c.

Co was the highest among Co-containing catalysts tested: The 8,9-epoxide / 1,2-epoxide ratios of Co(TPP) and $CoCl_2$ were 0.16 and 0.10, respectively, lower than that of PW_{11}-Co (Entries 1 - 4). In addition, the regioselectivity to 8,9-epoxide in the present system was higher than those of *m*-chloroperbenzoic acid (8,9-epoxide / 1,2-epoxide ratio = 0.08[1c)]) and PhIO (0.13, Entry 5). The latter system has been reported to be effective for the epoxidation of alkenes.[3c)] PW_{11}-Co showed similar regioselectivities to those of Mn(TTMPP)(OAc) in the epoxidation of 4-vinyl-1-cyclohexene[5a)] and 1-methyl-1,4-cyclohexadiene;[5b)] the ratios of the less hindered epoxide / total epoxide yield were 0.06 and 0.69, respectively, and close to the values, 0.05 and 0.70, respectively, found with Mn(TTMPP)(OAc).[1c)] Thus, $PW_{11}O_{39}{}^{7-}$ polyanion shows a comparable steric effect to the moderately hindered TTMPP ligand.

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5) a)4-Vinyl-1-cyclohexene, 250 μmol; PW_{11}-Co, 0.25 μmol; isobutyraldehyde, 250 μmol; acetonitrile; 303 K; 1 h; total epoxide yield, 11%. b)1-Methyl-1,4-cyclohexadiene, 50 μmol; PW_{11}-Co, 2.5 μmol; isobutyraldehyde, 1000 μmol; acetonitrile; 323 K; 15 min; total epoxide yield, 4%.

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