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The Epoxidation of C_5—C_{10} Alkenes with Hydrogen Peroxide Catalyzed by Mo Compounds in Two-phase Solvents

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The epoxidation of terminal alkenes such as 1-heptene, 1-octene, 1-decene, styrene (**1**), α-methylstyrene, and allyl chloride, and inner alkenes such as α-pinene, cyclopentene, cyclohexene (**2**) and cyclooctene was carried out with aqueous 60% hydrogen peroxide in the presence of molybdenum blue (Mob)-bis(tributyltin) oxide (**3**) using a two-phase solvent of chloroform-water at 25 °C. All these olefins gave epoxides in 98 to 48% yields. In the cases of **1** and **2**, the addition of ammonia greatly increased the yields of epoxides; the yield reached 78% and 83%, respectively, after 7 h. Various kinds of amines and organotin compounds were examined as co-catalysts and their effects were discussed.

Recent development of catalysts for the epoxidation of alkenes has revealed several heterogenized reaction systems which enabled the separation of the catalysts or oxidation agents from the reaction products. Among various oxidizing agents, the use of aqueous hydrogen peroxide acquires attention as an easy to handle and clean oxidizing agent which could be reduced to water after oxidation. Also, several metal oxide catalysts such as Mo(VI),[1] V(V),[1] Se(IV),[1] W(VI),[2] Ti(IV),[3] and Pt(II)[4] have been reported for the epoxidation of olefins.

Using hydrogen peroxide as the oxydizing agent, the authors have proposed a Mob-tributyltin chloride on charcoal catalyst for the epoxidation of alkenes[5] and unsaturated fatty acid esters[6] in isopropyl alcohol. However, the activity was poor for terminal alkenes.

Previous authors have found that terminal olefins were easily epoxidized in the presence of ammonium heptamolybdate(VI) and bis(tributyltin) oxide (**3**) in a two-phase system of water-organic solvent such as $CHCl_3$-H_2O or CH_2Cl_2-H_2O under mild conditions.[7] Therefore, in this report, the attention is mainly focused on the epoxidation of terminal alkenes. In addition, the role of amines and organotin compounds in the epoxidation of alkenes is discussed from the standpoint of the activity and the selectivity to epoxides using a chloroform-water solvent.

Experimental

Gas-liquid chromatography(GLC) was carried out on a Hitachi 063 instrument using a column packed with a 2%-Silicone OV-17(3 m) or 20% polyethylene glycol 20M on chromosorb W(4 m) under the programmed oven temperature from 60 to 200 °C (3 °C min^{-1}). High-performance liquid chromatography(HPLC) was run on a Hitachi 633A instrument equipped with an ultraviolet detector (UV at 254 nm) and an M & S pack C-18 column, 4.6 mm×150 mm, with a mobile phase of methanol-water 8:2 (v/v). The flow rate was maintained at 1 ml min^{-1}. The proton magnetic resonance (^{1}H NMR) spectra were determined on a Hitachi R-600 spectrometer at 60 MHz in $CDCl_3$ with tetramethylsilane as an internal standard.

Materials. Molybdenum blue (Mob) was prepared according to the previously reported method.[8] A molybdenum content in Mob of 53% was estimated from colorimetric analysis using the thiocyanate method.

Organotin compounds such as BuSnO, Bu_2SnO and Oct_2SnO from Kyodo Yakuhin Co., Tokyo, aqueous 60% hydrogen peroxide kindly supplied from Tokai Denka Kogyo Co., Tokyo, and other materials obtained were used as received.

General Procedures. The catalyst was prepared in situ by stirring ammonium heptamolybdate(VI) (0.05 mmol) and organotin compound (0.35 mmol) in $CHCl_3$ (5 ml) for 20 min at room temperature. The olefin (14. 6 mmol) was then dissolved in the solution. The reaction started when aqueous 60% hydrogen peroxide (1 ml, 21.9 mmol) was added to the solution. The mixture was shaken slowly at 25 °C, and the progress of the reaction monitored periodically by GLC or HPLC. After the reaction, the $CHCl_3$ layer was separated, washed with a 10% sodium sulfite solution and chromatographed using silica gel (Kiesel gel 60, 230—400 mesh, Merk Co.). Pentane was added to eluate the unreacted olefin and then ether to isolate the epoxide. The oily epoxide thus obtained was identified by comparing the spectral data and the retention time in IR, ^{1}H NMR and GLC with an authentic sample. The purity of the epoxide, determined by GLC or ^{1}H NMR, was >99% in all cases.

Results and Discussion

1) Epoxidation of Styrene (1) in the Presence of Various Molybdenum Catalysts and Solvents. The epoxidation of **1** has been used frequently as a standard compound for comparing the epoxidation activity of catalysts. We carried out the epoxidation of **1** by using aqueous 60% hydrogen peroxide in the presence of molybdenum oxide and **3** in chloroform at 25 °C. Results are shown in Table 1. No epoxidation occurred on the addition of **3** alone as catalyst; this demonstrated the indispensability of the Mo compounds.

Although the co-presence of bis(acetylacetonato)-dioxomolybdenum(VI) and **3** consumed **1** in a few hours, a poor yield of styrene oxide (**4**) was obtained. When MoO_3, Mob or heteropoly acids such as molyb-

Table 1. Effect of Various Molybdenum Compounds in the Epoxidation of Styrene (**1**) with Aqueous 60% Hydrogen Peroxide and Bis(tributyltin) Oxide (**3**)[a]

Catalyst	Time	Conv.	Yield/%[b]	
	h	%	PhCHO	$PhCH(O)CH_2$
—	6	0	0	0
$MoO_2(acac)_2$	2	92	11	3 (4)
MoO_3	3	49	2	30 (60)
	8	71	8	2 (3)
Mob	1.5	74	4	55 (74)
	5	82	7	32 (39)
$H_3PMo_{12}O_{40}$	2	49	1	44 (89)
	10	68	5	29 (43)
$H_4SiMo_{12}O_{40}$	1.5	60	3	51 (85)
	6	86	7	23 (27)
$(NH_4)_6Mo_7O_{24}$	5	54	1	52 (96)
	10	57	1	54 (95)
Na_2MoO_4	10	1	0	Trace
K_2MoO_4	15	0	0	0

a) **1** (8.7 mmol), H_2O_2 (60%, 21.9 mmol), **2** (0.7 mmol), Mo compound (0.35 mmol) and $CHCl_3$ (10 ml) were used. Mo : Sn (atomic ratio) was 1 : 4, and the reaction was carried out at room temperature. b) Values in parentheses were the selectivities to epoxides.

Table 2. Effect of Various Amines in the Epoxidation of Styrene (**1**) with Aqueous 60% Hydrogen Peroxide[a]

Amine (mmol)	Time	Conv.	Yield/%[b]	
	h	%	PhCHO	$PhCH(O)CH_2$
—	7	85	19	4 (5)
$(NH_4)_6Mo_7O_{24}$	7	67	1	61 (92)
Me_3N (0.35)	7	57	1	53 (93)
Bu_3N (0.4)	7	57	1	55 (96)
$(CH_2CH_2OH)_3N$ (0.4)	7	60	1	58 (96)
Ph_3N (0.35)	7	84	16	3 (4)
Et_2NOH (0.35)	7	80	15	2 (3)
Pyridine (0.46)	7	69	2	52 (76)
$PhNH_2$ (0.42)	7	86	18	4 (5)
CBPB[c] (0.35)	7	20	0	19 (95)
	24	49	1	42 (86)
TOMAC[d] (0.4)	7	21	0	18 (86)
	24	44	1	39 (87)

a) **1** (14.6 mmol), H_2O_2 (60%, 21.9 mmol), Mob (50 mg), **3** (0.35 mmol), and $CHCl_3$ (5 ml) were used. The reaction was carried out at 25 °C. b) Values in parentheses were the selectivity to epoxide. c) Cetyltributylphosphonium bromide. d) Trioctylmethylammonium chloride.

dophosphoric acid and molybdosilicic acid were used with **3**, the epoxidation took place selectively until the conversions approached 50%. After this, the decrease in the selectivity to **4** occurred. The authors found that ammonium heptamolybdate(VI) and **3** gave **4** selectively. However, salts such as sodium and potassium heptamolybdate(VI) gave no products; these salts were weakly soluble to the organic layer.

The kind of solvent also affected the epoxy yield remarkably. The oxidation of **1** in acetonitrile or tert-butyl alcohol in the presence of ammonium heptamolybdate(VI) gave **4** in between 40 to 60% selectivities at 25 °C for 7 h. On the other hand, such hydrophobic solvents as benzene, diethyl ether, dichloromethane, 1,2-dichloroethane and chloroform afforded excellent selectivities (83 to 97%). From these results it was considered that the epoxide **4** once formed in two-phase solvents was protected from hydrolysis or over-oxidation to give a high yield.

2) Effect of Amines on the Epoxidation of 1. In the oxidation of **1** the addition of amines to the molybdenum(VI) oxide affected the selectivity to **4**. The oxidation of **1** in the presence of various amines and Mob is shown in Table 2.

In the absence of amines, the yield of **4** was poor (Table 1). However, the addition of ammonia improved the selectivity for **4** from 4% for bis(acetylacetonato)dioxomolybdenum(VI) to 96% for ammonium heptamolybdate(VI). The addition of aliphatic amines and pyridine gave similar results. On the other hand, the addition of triphenylamine and aniline did not improve the yield. Interestingly, the addition of a phase-transfer catalyst (PTC) such as trioctylmethylammonium chloride improved the selectivity for **4**. These results suggest that our catalyst system worked as a kind of PTC. In a typical example, the effect of the concentration of tributylamine on the epoxidation of **1** is shown in Fig. 1. The yield of epoxide was increased with increasing the amount of tributylamine until one equivalent to molybdenum(VI) ions. On the other hand, the addition of an excess amount of tributylamine decreased the yields of **4**. Therefore it was supposed that the presence of amines worked either for the stabilization of the catalyst or for the suppression of the decomposition of **4** once formed.

To confirm this, we carried out the oxidation of **4** in the presence or absence of tributylamine under the

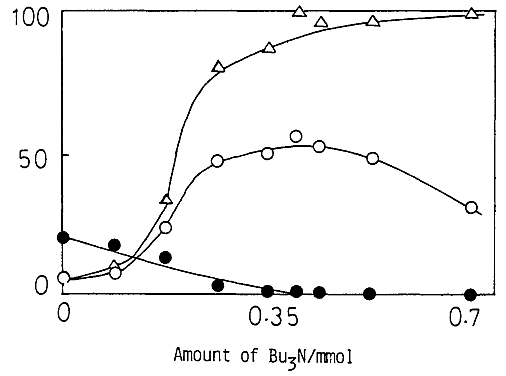

Fig. 1. Effect of Bu_3N addition on the selectivity to styrene oxide in the epoxidation of styrene (**1**): △; selectivity to styrene oxide, ○; yield of styrene oxide, ●; yield of benzaldehyde. **1** (14.6 mmol), H_2O_2 (60%, 21.9 mmol), $(Bu_3Sn)_2O$ (0.35 mmol), Mob (50 mg), Bu_3N, and $CHCl_3$ (5 ml) were used. The reaction was carried out at 25 °C for 7 h.

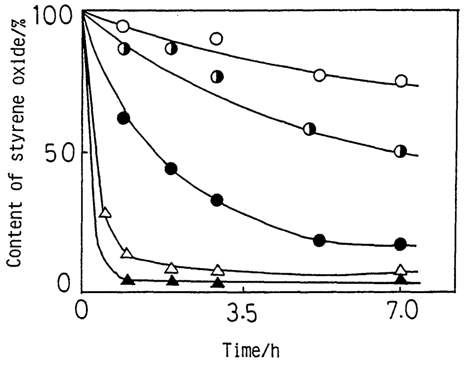

Fig. 2. Effect of Bu_3N addition on the activity in the oxidation of styrene: ○, 0.7 mmol; ◑, 0.42 mmol; ●, 0.35 mmol; △, 0.175 mmol; ▲, none. **4** (14.6 mmol), H_2O_2 (60%, 21.9 mmol), Mob (50 mg), **3** (0.35 mmol), Bu_3N, and $CHCl_3$ (5 ml) were used. The reaction was carried out at 25 °C.

Table 3. Effect of Various Organotin Compounds in the Epoxidation of Styrene (**1**) with Aqueous 60% Hydrogen Peroxide[a]

Organotin compound	Time	Conv.	Yield/%[b]	
	h	%	PhCHO	PhCH(O)CH_2
—	7	15	0	0
Me_3SnCl	7	3	0	0
BuSnO	7	20	Trace	3 (15)
Bu_2SnO	7	80	1	75 (94)
$Bu_2Sn(AcO)_2$	7	64	13	5 (8)
Bu_2SnCl_2	7	15	3	1 (7)
Bu_3SnCl	7	14	1	Trace
$(Bu_3Sn)_2O$	7	67	1	61 (91)
$(Bu_3SnO)_2MoO_2$[c]	7	70	3	60 (86)
Bu_4Sn	7	34	5	2 (6)
Oct_2SnO	7	82	Trace	78 (95)
Ph_3SnOH	7	24	3	4 (17)

a) **1** (14.6 mmol), H_2O_2 (21.9 mmol), $(NH_4)_6Mo_7O_{24}$ (0.05 mmol), and $CHCl_3$ (5 ml) were used. Mo : Sn (atomic ratio) was 1 : 2, and the reaction was carried out at 25 °C. b) Values in parentheses were the selectivities to styrene oxides. c) $(Bu_3SnO)_2MoO_2$ (0.35 mmol) and Me_3N (30%, 0.35 mmol) were used.

same conditions as was employed for the epoxidation of **1**. The results are shown in Fig. 2. In the absence of tributylamine, the oxidation of **4** to benzaldehyde and benzoic acid occurred during an hour. Increase in the amount of tributylamine decreased the rate of the decomposition of **4**; the addition of two equivalents of tributylamine to molybdenum(VI) ions suppressed the decomposition of **4** considerably.

3) Effect of Various Kinds of Organotin Compounds. In the epoxidation of alkenes the presence of both molybdenum(VI) oxide and organotin compounds was essential. Therefore, the effect of organotin compounds on the epoxidation of **1** was examined. The results are shown in Table 3. No epoxidation activity was observed in ammonium heptamolybdate(VI) itself. The addition of such alkyltin oxides as dibutyltin oxide, bis(tributyltin) oxide, and dioctyltin oxide gave **4** in good yields at 25 °C for 7 h. On the other hand, such alkyltin chlorides as trimethyltin chloride, dibutyltin chloride, and tributyltin chloride gave **4** in poor yields. In these cases, the molybdenum species were almost completely transferred to the aqueous solution. Tetrabutyltin and triphenyltin hydroxide were inactive for epoxidation. These organotin compounds could not form an adduct with the molybdenum species.

4) Epoxidation of Various Alkenes. The selectivity to the epoxides was affected by the amount of amine and the kind of alkene. Several alkenes were epoxid-

Table 4. Effect of Ammonia or Trimethylamine in the Epoxidation of Various Olefins with Aqueous 60% Hydrogen Peroxide in the Presence of Molybdenum Oxide-$(Bu_3Sn)_2O$ (**3**)[a]

Olefin	Molybdenum	Amine	Time	Conv.	Yield[b]
			h	%	%
α-Pinene	$(NH_4)_6Mo_7O_{24}$	—	3	59	57[f]
	Mob	—	1	72	0[f]
Cyclopentene	$(NH_4)_6Mo_7O_{24}$	—	5	100	98[f]
	Mob	—	1	100	84[f]
Cyclohexene	Mob	Me_3N	7	95	87[f]
	Mob	—	7	100	0[f]
α-Methylstyrene[c]	Mob	—	7	84	70
1-Heptene[c]	Mob	—	7	86	80
1-Octene	Mob	—	7	85	80[e]
	Mob	—	3	95	88
	$(Bu_3SnO)_2MoO_2$[c]	—	3	93	84
	Mob	Me_3N	24	70	66
Cyclooctene[c]	Mob	—	1.25	100	98
1-Decene[c]	Mob	—	7	81	74
Allyl chloride	Mob[d]	—	10	52	48

a) Olefin (8.7 mmol), and aq H_2O_2 (60%, 21.9 mmol), Mob (50 mg), **3** (0.35 mmol), aq TMA (30%, 0.35 mmol), and $CHCl_3$ (5 ml) were used. b) Yields to epoxides were calculated based on olefin conversions. c) Olefin (14.6 mmol) was used. d) Prepared from $MoO_2(acac)_2$ and $(Bu_3Sn)_2O$. e) Oct_2SnO was used. f) Ref. 9.

ized in the presence of a catalyst composed of ammonium heptamolybdate(VI) and **3** (or dibutyltin oxide) (Table 4). Also, **2**, α-pinene, and cyclopentene were epoxidized in chloroform in good yields. In contrast, a higher yield (88%) of 1-octene oxide was obtained in the absence of amines. Furthermore, the addition of amine (Me_3N) suppressed the oxidation of 1-octene. Similar tendencies were observed in the epoxidation of 1-heptene, 1-decene, cyclooctene, α-methylstyrene and allyl chloride. These results suggest that the above mentioned epoxides were stable enough for the oxidation conditions employed even under the lack of amines. In fact, in separate experiments the decomposition rate of 1-octene oxide was 25% and that of cyclooctene oxide was negligible after 5 h at 25 °C. On the other hand, **4** was decomposed completely under the same conditions.

The active species for the epoxidation in the presence of an Mob-**3** catalyst in isopropyl alcohol have been proposed to be an adduct obtained from molybdenum(VI) oxide and **3**.[9] In our two-phase system, a white powdery adduct of molybdenum(VI) oxide and **3**, $(Bu_3SnO)_2MoO_2$, also showed a similar activity to the Mob-**3** catalyst in chloroform. Therefore, this adduct was considered to be an active species for the epoxidation in a two-phase system.

In conclusion, molybdenum(VI) oxide in chloroform is highly active epoxidation catalyst for olefins which works under mild reaction temperature (25 °C). In the epoxidation of **1**, **2**, cyclopentene, and α-pinene, over-oxidation could be prevented by the addition of amines to molybdenum oxides to give the epoxides in good yields.

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