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Effect of Amines on the Epoxidation of Alkenes with H_2O_2 in the Presence of Molybdenum(VI) Oxide-Bis(tributyltin) Oxide Catalysts

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The epoxidation of alkenes with H_2O_2 was carried out in the presence of molybdenum oxide(VI)-$(Bu_3Sn)_2O$ in $CHCl_3$ at 25 °C. In the oxidation of cyclohexene, styrene, and α-pinene, the addition of amines was indispensable and the yields of oxides reached 87 to 57%.

In recent years, the catalytic epoxidation of alkenes has been studied extensively by using aqueous H_2O_2, an easy handle and clean oxidizing agent, in the presence of various metal oxides such as Mo(VI), W(VI), V(V), Se(IV),[1] Ti(IV),[2] and Pt(II).[3] However, drastic reaction conditions(reflux of the solvents) frequently decreased the yield. We found a highly active molybdenum oxide(VI)-$(Bu_3Sn)_2O$ catalyst system which oxidized various alkenes at room temperature and increased the selectivity to epoxides by the addition of amines.

The catalyst was prepared in situ by stirring olefins, molybdenum blue(MoB),[4] and $(Bu_3Sn)_2O$ in $CHCl_3$ for 20 min at room temperature. The reaction was started by the addition of aqueous H_2O_2(60%) at 25 °C under slow shaking. During the course of reaction, H_2O_2 and $CHCl_3$ made two layers between the solutions.

Results are shown in Table 1. In the oxidation of styrene, the MoB-$(Bu_3Sn)_2O$ catalyst gave poor selectivity to styrene oxide. However, the addition of trimethylamine(TMA) of an equimolecular weight to $(Bu_3Sn)_2O$ greatly improved the selectivity to styrene oxide. TMA was also indispensable for the oxidation of cyclohexene and α-pinene. The addition of various amines such as ammonia used as a form of ammonium molybdate(VI), CH_3NH_2, $(CH_3)_2NH$, $C_2H_5NH_2$, and $(C_4H_9)_3N$ in place of TMA gave similar results. On the other hand, the addition of triphenylamine or aniline was less effective. These amines worked for the stabilization of the epoxides once formed since styrene oxide was decomposed swiftly under the lack of TMA. Interestingly, our catalyst system oxidized alkenes in the absence of phase transfer catalyst(PTC); the presence of trioctylmethylammonium chloride(TOMAC) or cetyltributylphosphonium bromide(CBPB) decreased the yield. Therefore, it was suggested that molybdenyl bis(tributyltin) oxide, $(Bu_3SnO)_2MoO_2$, an adduct formed from MoB and $(Bu_3Sn)_2O$ worked itself as a kind of PTC. This is to our knowledge the first example of such an active molybdenum catalyst for the epoxidation of alkenes with H_2O_2. Further studies of the application to other olefins are in progress in our laboratory.

Table 1. Effect of Ammonia and Trimethylamine on the Epoxidation of Various Olefins with H_2O_2 in the Presence of Molybdenum Oxide(VI)-$(Bu_3Sn)_2O$ at 25 °C

Entry	Olefin	Olefin/H_2O_2 (molar ratio)	Catalyst	TMA	Time/h	Conv./%	Yield/% [a)]
1	Styrene	2	MoB-$(Bu_3Sn)_2O$	none	7	87	10
2		2	MoB	Me_3N	7	4	0
3		2	$(Bu_3Sn)_2O$	Me_3N	7	8	0
4		2	MoB-$(Bu_3Sn)_2O$	Me_3N	7	90	77 (72)[b)]
5		2	$(NH_4)_6Mo_7O_{24}$-$(Bu_3Sn)_2O$	none	7	92	75
6		2	$(Bu_3SnO)_2MoO_2$[c)]	Me_3N	7	91	69
7		0.67	MoB-$(Bu_3Sn)_2O$	Me_3N	7	57	53
8	Cyclopentene	0.4	$(NH_4)_6Mo_7O_{24}$-$(Bu_3Sn)_2O$	none	5	100	98
9		0.4	MoB-$(Bu_3Sn)_2O$	none	1	100	84
10	Cyclohexene	0.4	MoB-$(Bu_3Sn)_2O$	Me_3N	7	95	87
11		0.4	MoB-$(Bu_3Sn)_2O$	none	7	100	0
12	α-Pinene	0.4	$(NH_4)_6Mo_7O_{24}$-$(Bu_3Sn)_2O$	none	3	59	57
13		0.4	MoB-$(Bu_3Sn)_2O$	none	1	72	0

Aq. H_2O_2(Tokai Denka Kogyo Co., 60%, 21.9 mmol), MoB(50 mg, Mo 53.4%), $(Bu_3Sn)_2O$(0.35 mmol), aq. TMA(30%, 0.35 mmol), and $CHCl_3$(5 ml) were used.
a) Yields to epoxides obtained by GLC analyses. b) Isolated yield. c) Prepared from $MoO_2(acac)_2$ and $(Bu_3Sn)_2O$. Yields of entries 1 to 6 were based on H_2O_2 and those of entries 7 to 13 were based on olefins.

References

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