Tetrahedron Letters,Vol.25,No.39,pp 4417-4420,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

CHEMOSELECTIVE OXIDATION WITH MOLYBDENUM CATALYST—t-BUTYL HYDROPEROXIDE

Yoshiro Masuyama*, Masato Takahashi, and Yasuhiko Kurusu
Department of Chemistry, Sophia University
7-1 Kioicho, Chiyoda-ku, Tokyo 102, Japan

Summary: Benzyltrimethylammonium tetrabromooxomolybdate is an excellent chemoselective catalyst to oxidize secondary alcohols to ketones, primary alcohols to esters, and aldehydes to acids or esters with t-butyl hydroperoxide.

Molybdenum complex—t-butyl hydroperoxide is a significant system for olefin epoxidation.[1] However, use of this system for oxidation of alcohols has been rarely reported.[2] We have been studying the catalytic reactivity of ammonium molybdates (1)[3] for olefin epoxidation.[4] Consequently, we found that benzyltrimethylammonium tetrabromooxomolybdate (BTMA-Mo) (2)[5] did not catalyze olefin epoxidation, but easily decomposed t-butyl hydroperoxide.[4]

$R_4N^+ \ ^-O\text{-}MoBr_4$ 1

$PhCH_2\overset{+}{N}Me_3 \ ^-O\text{-}MoBr_4$ 2

R_4N^+;

1a

$H_3\overset{+}{N}(CH_2)_3\overset{+}{N}H_3$ 1b

We wish to report the advantages of BTMA-Mo (2) for chemoselective oxidation of alcohols and aldehydes with t-butyl hydroperoxide. That is, alcohol oxidation can dominate over olefin epoxidation.[6] Furthermore, a secondary alcohol can be oxidized over a primary one.[7]

A general procedure is as follows. A solution of BTMA-Mo (2) (0.15 mmol), t-BuOOH (5 mmol), and the alcohol (3 mmol) in benzene (3 ml) was stirred at 60°C. After ether extraction and evaporation, the product was purified by distillation or chromatography. The results are summarized in Table.

An equimolar mixture of 1-octanol and 2-octanol under same conditions leads to complete conversion of the secondary alcohol (80% yield of 2-octanone) and to recover the primary alcohol (87%). This selectivity for a secondary over primary alcohol is also easily demonstrated in the intramolecular case (entry 9). Elongation of the reaction time or elevated reaction temperature leads to oxidize 1-octanol to octyl octanoate via hemiacetal intermediate (entry 10, equation 1).

Table. Oxidation of Alcohols[8]

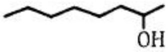
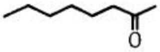
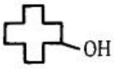
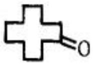
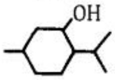
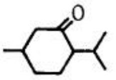
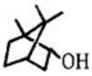
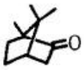
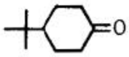
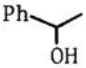
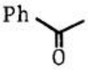
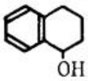
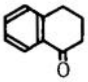
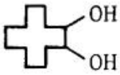
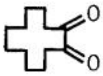
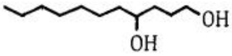
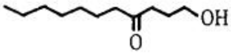
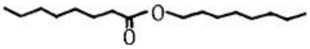
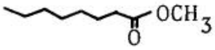
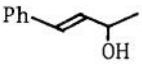
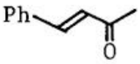
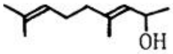
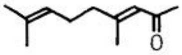
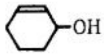
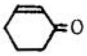
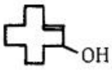
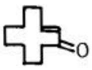
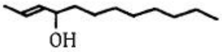
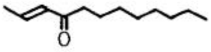
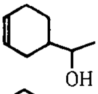
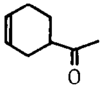
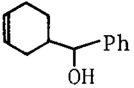
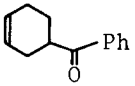
Entry	Alcohol	Time	Product	Yield[a]
1		42 h		80
2		46 h		92
3		12 h		52
4		21 h		~100
5		72 h		87
6		24 h		99
7		24 h		84[b]
8		12 h		50[c]
9		24 h		60[d]
10		72 h		65
11		72 h		94[e]
12		72 h		37[b]
13		20 h		60
14		48 h		48(82)
15		48 h		57
16		72 h		65

Table. Oxidation of Alcohols (contd.)[8]

Entry	Alcohol	Time	Product	Yield[a]
17		24 h		11(97)
18		24 h		18(95)

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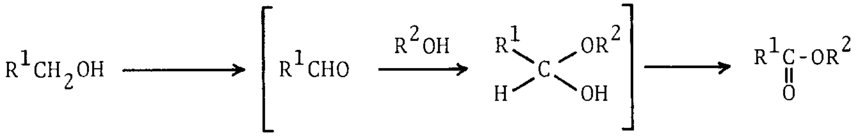
a) All yields are for isolated pure products. Yields in parentheses are based on consumed starting material. No by-product was detected under these conditions. b) Room Temp. c) t-BuOOH 9 mmol, d) in THF, e) in MeOH.

The oxidation of 1-octanol in methanol provides methyl octanoate (entry 11, equation 1).

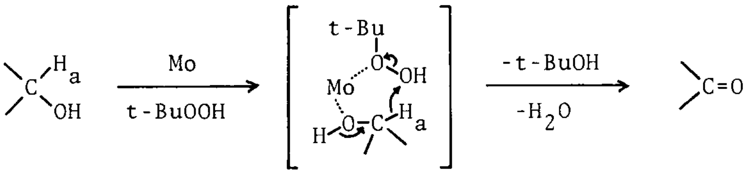


(1)

Investigation of aldehyde oxidation establishes quantitatively to convert octanal into octanoic acid in benzene and octanal into methyl octanoate in methanol at 60°C for 24 h. 1,2,3,6-Tetrahydrobenzaldehyde is also oxidized at 60°C in benzene to give 1,2,3,6-tetrahydrobenzoic acid (36%) without observing olefin epoxidation.

BTMA-Mo (2) does not catalyze the epoxidation of cyclohexene and 2-octene under same conditions contrary to the catalytic activity of 1a and 1b for olefin epoxidation.[4] So, the oxidation of olefinic alcohols chemoselectively gives olefinic ketones (entry 12-18).

This oxidation may depend on the abstraction of hydride H_a^- by t-BuOOH (stability of carbenium ion), because of 1) high reactivity of secondary over primary alcohols (entry 9) and the formation of ester from primary alcohol (no isolation of aldehyde) (entry 10) and 2) no effect of radical scavengers (e.g., 2,6-di-t-butyl-4-methylphenol) (equation 2).[9]



(2)

References and Notes

1. H. Mimoun, "The Chemistry of Peroxides," in "The Chemistry of Functional Groups," S. Patai, ed. John Wiley & Sons, New York, 1982, pp 463-482; H. Mimoun, Pure Appl. Chem., 53, 2389 (1981); R. A. Sheldon, J. K. Kochi, "Metal Catalyzed Oxidations of Organic Compounds," Academic Press, New York, 1981, pp 48-97; K. B. Sharpless, T. R. Verhoeven, Aldrichimica Acta, 12, 63 (1979).
2. Similar oxidation of alcohols with molybdenum peroxide: S. E. Jacobson, D. A. Muccigrosso, and F. Mares, J. Org. Chem., 44, 921 (1979); H. Tomioka, K. Takai, K. Oshima, and H. Nozaki, Tetrahedron Lett., 21, 4843 (1980); B. M. Trost and Y. Masuyama, ibid., 25, 173 (1984).
3. For preparation: J. F. Allen and H. M. Newmann, Inorg. Chem., 3, 1612 (1964).
4. Y. Masuyama and Y. Kurusu, unpublished results.

Catalyst	Yield(%)[a]		
	Decompn. of t-BuOOH (1h)	Epoxidn. of  (1h)	Oxidn. of 2-octanol (24h)
2	85	~0	80
1a	37	66	78
1b	10	78	77

a) Yields are determined by glpc using an internal standard method.

Decomposition of t-BuOOH with ammonium molybdate ($R_4\overset{+}{N}\ \bar{O}\text{-}MoBr_4$) seems to be inversely proportional to epoxidation of cyclohexene and independent of oxidation of 2-octanol.

5. See ref. 3 for the preparation: Treatment of MoO_3 (10g, 0.07mol) with 47% HBr (50ml) at 70°C followed by addition of the solution of $PhCH_2\overset{+}{N}Me_3Cl^-$ (13g, 0.07 mol) in 47% HBr (50ml) give 2 (14.3g, 35% after recrystallization from 47% HBr). Found: Mo, 15.8; Br, 54.6%. Calcd for $C_{10}H_{16}Br_4MoNO$: Mo, 16.49; Br, 54.94%.
6. B. M. Trost and Y. Masuyama, Tetrahedron Lett., 25, 173 (1984).
7. J. Wicha and A. Zarecki, Tetrahedron Lett., 3059 (1974); M. A. Neirabeyeh, J. C. Ziegler, and B. Gross, Synthesis, 811 (1976); Y. Ueno and M. Okawara, Tetrahedron Lett., 4597 (1976); M. E. Jung and L. M. Speltz, J. Am. Chem. Soc., 98, 7882 (1976); M. E. Jung and R. W. Brown, Tetrahedron Lett., 2771 (1978); G. H. Posner, R. B. Perfetti, and A. W. Runquist, ibid., 3499 (1978); H. Tomioka, K. Oshima, and H. Nozaki, ibid., 23, 539 (1982); B. M. Trost and Y. Masuyama, ibid., 25, 173 (1984).
8. All products obtained here were identified by comparison of the physical properties with those of the authentic samples.
9. For Mechanism of hydride abstraction: S. E. Jacobson, D. A. Muccigrosso, and F. Mares, J. Org. Chem., 44, 921 (1979).

(Received in Japan 4 June 1984)