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OXIDATION OF ALCOHOLS WITH OXOPEROXOBIS(N-PHENYLBENZOHYDROXAMATO)MOLYBDENUM(VI)

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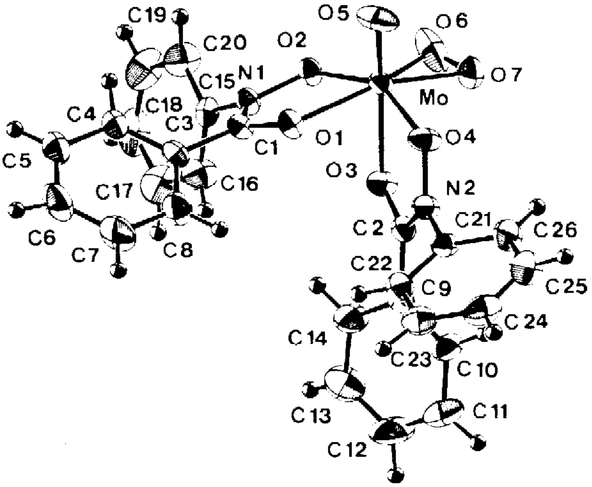
Abstract: The title complex oxidizes primary and secondary alcohols to the corresponding carbonyl compounds. Stereoselective epoxidation of allylic alcohols is also described.

We wish to report here the isolation of a new oxoperoxomolybdenum(VI) compound and the reaction of the complex with simple alcohols and olefinic alcohols.

A mixture of $MoO_2(acac)_2$ (1.61 g, 4.9 mmol) and hydroxamic acid PhCON(Ph)OH (2.10 g, 9.8 mmol) in benzene (100 ml) was stirred for 3 h at 25°C. Filtration of the deposited solid gave $MoO_2(PhCON(Ph)O)_2$ (I) (mp. 178°C (dec), 2.26 g, 83% yield) as white mossy powder.[1] The dioxomolybdenum (I) (2.26 g, 4.1 mmol) was suspended in dichloromethane (15 ml) and treated with excess H_2O_2 (30%, 1.2 ml). A clear orange-yellow solution was obtained after 1 h at 25°C and the stirring was continued for an additional 1 h. Workup (CH_2Cl_2, H_2O) and recrystallization (hexane-CH_2Cl_2) gave orange-yellow crystals II (mp. 150°C (dec), 1.76 g, 76% yield).[2,3]



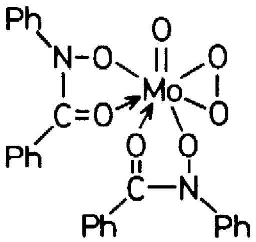
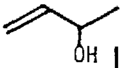
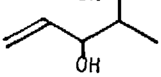
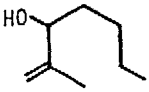
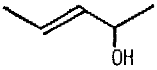
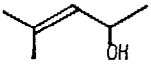
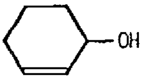
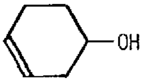
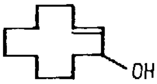


Fig 1. A perspective drawing of the oxoperoxobis(N-phenylbenzohydroxamato)molybdenum(VI) complex with the atom numbering scheme.[5]

Table 1. Epoxidation stereochemistry of olefinic alcohols

	Alcohol	Mo complex II[a] *threo*[d] (*trans*) %	Mo complex II[a] *erythro*[d] (*cis*) %	Mo complex I/^{t}BuOOH[b] *threo* (*trans*) %	Mo complex I/^{t}BuOOH[b] *erythro* (*cis*) %	$Mo(CO)_6$/^{t}BuOOH[c] *threo* (*trans*) %	$Mo(CO)_6$/^{t}BuOOH[c] *erythro* (*cis*) %
1		7	93	35	65	44	56
2		9	91	40	60	35	65
3		6	94	6	94	16	84
4		27	73	71	29	62	38
5		70	30	94	6	95	5
6		<0.5	>99.5	<0.5	>99.5	2	98
7		<0.5	>99.5	<0.5	>99.5	2	98
8		68	32	85	15	77	23

[a] Reactions were done on 0.5 mmol olefin and 0.6 mmol molybdenum complex II in 1,2-dichloroethane (5 ml) at 60-70°C and were carried to >80% completion. [b] Employed 3 mol% molybdenum catalyst I and 1.5 equiv of ^{t}BuOOH in 1,2-dichloroethane at 60-70°C. [c] Cited from ref. 7b and 7d. [d] The resulting mixture of epoxy alcohols, epoxy acetates, or epoxy alcohol trimethylsilyl ethers were analyzed by glpc on 2 m columns packed with 3% silicon OV-17 or 10% PEG 20M.

The complex II was quite reluctant to react with simple olefins,[6] however, allylic alcohols were converted easily to α,β-epoxy alcohols in fair yields (60-70% isolated yields, Table 1).[7] It is worth noting that the stereoselectivities obtained in the reaction with stoichiometric amount of monoperoxo complex are quite different from those in the catalytic epoxidation with ^{t}BuOOH in the presence of 3 mol% molybdenum compound I. The latter gave similar selectivities to those with $Mo(CO)_6$-^{t}BuOOH system.[8]

Table 2. Oxidation of alcohols with the molybdenum complex II[a]

Alcohol	Reaction Time (h)	Product	Yield[b] (%)
$CH_3(CH_2)_5CH(OH)CH_3$	5	$CH_3(CH_2)_5COCH_3$	95
cyclododecanol	4	cyclododecanone	97 90[c]
4-*t*-butylcyclohexanol	6	4-*t*-butylcyclohexanone	83
β-cholestanol	19	β-cholestanone	73[c]
$PhCH_2OH$	7	PhCHO	80
$CH_3(CH_2)_{10}CH_2OH$	13	$CH_3(CH_2)_{10}CHO$	63

[a] Reactions were performed on 0.5 mmol scale at 85°C. [b] Yields were determined by glpc using an internal standard method. [c] Isolated yields.

A series of primary and secondary alcohols were easily oxidized to the corresponding carbonyl compounds in fair to good yields.[9] The results are summarized in Table 2. The experimental procedure is illustrated for the preparation of cyclododecanone. A solution of the complex II (0.34 g, 0.6 mmol) and cyclododecanol (92 mg, 0.5 mmol) in 1,2-dichloroethane (5 ml) was heated to reflux for 4 h. Ethereal extracts of the reaction mixture were washed with brine, dried, and concentrated. Purification by silica gel column chromatography gave cyclododecanone (82 mg, 90% yield).

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References and Notes

1. F. Triforo, P. Forzatti, S. Preiti, and I. Pasquon, *J. Less-Common Met.*, 36, 319 (1974).
2. Similar monooxomolybdenum(VI) complex has been reported. S. E. Jacobson, R. Tang, and F. Mares, *Inorg. Chem.*, 17, 3055 (1978).
3. Assignment of the complex II structure was based on the following observations. Dioxo compound I showed two very strong infrared absorptions at 906 and 935 cm^{-1} indicative of *cis* orientation of the oxo groups,[4] while the oxoperoxomolybdenum(VI) showed only one oxo absorption at 950 cm^{-1}. Found: C, 54.71; H, 3.42; N, 4.87%. Calcd for $C_{26}H_{20}N_2O_7Mo$: C, 54.94; H, 3.55; N, 4.93%.
4. E. I. Stiefel, "The Coordination and Bioinorganic Chemistry of Molybdenum," in "Progress in Inorganic Chemistry," ed by S. J. Lippard, An Interscience Publication, John Willy &

Sons, Inc., New York (1977), vol. 22, pp. 1-223.

5. Structure of the complex II was established by X-ray diffractometry, with an orange-yellow crystal of dimensions 0.32x0.28x0.24 mm, grown from hexane-CH_2Cl_2 (10:1). Crystallographic data are: $C_{26}H_{20}N_2O_7Mo$, M. W. = 568.39, monoclinic, C2/c, Z = 8, a = 25.345(4), b = 8.813(1), c = 22.887(3) Å, β = 102.30(1)°, U = 4994.8(10) $Å^3$, D_x = 1.512 gcm^{-3}, μ(Mo Kα) = 5.69 cm^{-1}. 4430 independent reflexions with $|Fo| \geq 3\sigma(|Fo|)$, collected on a Rigaku AFC-5 diffractometer with monochromatized Mo Kα radiation (0.7107 Å), were used in the structure analysis. The structure was solved by the heavy-atom method and anisotropically refined by block-diagonal least-squares technique (R = 0.038 and R_w = 0.045). Figure 1 shows a perspective-view of the complex. The Mo atom is surrounded by four O atoms (O(1)-O(4)) of hydroxamic acid ligands as well as by three O atoms of oxo and peroxo groups (O(5)-O(7)). The crystal contains ca. 30% of inverted structure having oxo and peroxo groups interchanged in Figure 1. The inverted disposition is coincident with the depicted one by rotating itself on the pseudo two-fold axis which contains Mo atom and midpoint of O(1) and O(3). This type of crystallographical positional disorder should account for the shorter O-O distance of the peroxo group than the normal value of 1.44 Å. Selected bond distances (Å) and angles (°) with their e.s.d.'s are as follows.

Mo---O(5)	1.733(2)	O(6)-Mo-O(7)	38.30(16)
Mo---O(6)	1.830(3)	O(1)-Mo-O(2)	74.44(8)
Mo---O(7)	1.864(4)	O(3)-Mo-O(4)	73.83(9)
O(6)-O(7)	1.212(5)	Mo-O(1)-C(1)	115.89(18)
Mo---O(1)	2.131(2)	Mo-O(3)-C(2)	116.21(19)
Mo---O(2)	2.002(2)	Mo-O(2)-N(1)	116.35(16)
Mo---O(3)	2.157(2)	Mo-O(4)-N(2)	116.31(19)
Mo---O(4)	2.031(2)		

6. Molybdenum diperoxo compound such as Mimoun's reagent is known to epoxidize olefins. (a) H. Mimoun, I. Seree de Roch, and L. Sajus, *Tetrahedron*, 26, 37 (1970); (b) K. B. Sharpless, J. M. Townsend, and D. R. Williams, *J. Am. Chem. Soc.*, 94, 295 (1972).

7. Transition metal catalyzed stereoselective epoxidation of olefinic alcohols has been studied extensively. (a) K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.*, 95, 6136 (1973); (b) T. Itoh, K. Jitsukawa, K. Kaneda, and S. Teranishi, *ibid.*, 101, 159 (1979); (c) E. D. Mihelich, *Tetrahedron Lett.*, 1979, 4729; (d) B. E. Rossiter, T. R. Verhoeven, and K. B. Sharpless, *ibid.*, 1979, 4733.

8. Sheldon has reported that the rate of the molybdenum-catalyzed epoxidation with ^tBuOOH is independent of the structure of the molybdenum compounds initially added as catalyst. R. A. Sheldon, *Recl. Trav. Chim. Pays-Bas*, 92, 253, 367 (1973).

9. Oxidation of secondary alcohols by molybdenum diperoxo complexes has been reported. S. E. Jacobson, D. A. Muccigrosso, and P. Mares, *J. Org. Chem.*, 44, 921 (1979).

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