Oxidation of Olefins and Alcohols by Peroxo-Molybdenum Complex Derived from Tris(cetylpyridinium) 12-Molybdophosphate and Hydrogen Peroxide

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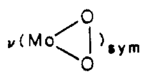
Several peroxo complexes of molybdenum and tungsten have been prepared and used for oxidation of organic substrates such as olefins, sulfides, phosphines, and alcohols.[1] In addition, many Mo-based catalytic systems are known for oxidation of olefins to epoxides or alcohols to carbonyl compounds.[2] Recently, molybdenum- and tungsten-catalyzed oxidations of olefins, alcohols, and diols with dilute hydrogen peroxide under phase-transfer conditions have been studied by Venturello[3] and Bortolini.[4]

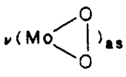
Previously, we have reported that tris(cetylpyridinium) 12-molybdophosphate, $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_{12}O_{40})^{3-}$ (CMP), prepared from 12-molybdophosphoric acid (MPA) and cetylpyridinium chloride (CPC) catalyzes the regioselective epoxidation of allylic alcohols with dilute hydrogen peroxide in chloroform.[5] In the catalytic cycle for this epoxidation, a peroxo-molybdenum species has been suggested as a key intermediate, and the epoxidation pathway shown in Scheme I could be assumed.

We have now found that a peroxo-molybdenum complex (PCMP) can be prepared with ease by treating the CMP with aqueous hydrogen peroxide and can oxidize olefins to epoxides and alcohols to carbonyl compounds in good yields.

The CMP, which is readily available from MPA and 3 equiv of CPC, was treated with 35% hydrogen peroxide to form a pale yellow to white precipitate, PCMP, after centrifugation followed by drying under vacuum at ambient temperature. IR measurement and iodometry of the resulting precipitate showed that a peroxo-molybdenum species, PCMP, is formed. The IR spectrum of the PCMP indicated strong bands at 540 and 590 cm^{-1}, which are respectively assigned to I and II[1c-e] and a shoulder band at 865 cm^{-1} corresponding to III.[6] These absorption bands which are absent in the IR spectrum of the CMP were practically identical with those of the characteristic absorption bands of the peroxo-molybdenum complexes found in the literature.[1c-e] Other absorption bands of the PCMP were similar to those of the CMP consisting of the Keggin structure unit $(PMo_{12}O_{40})^{3-}$.[7] However, it seems that the Keggin structure is no longer held in the PCMP, since the elemental analysis data of the PCMP deviated considerably from the constitution calculated from an idealized compound, CMP·6[O],[8] bonded peroxo oxygen to CMP having the Keggin structure. Unfortunately, the detailed structure of the PCMP is not defined because of the difficulty in obtaining a single crystal suitable for X-ray structure determination.



I



II

ν(O-O)

III

The amount of active oxygen contained in PCMP was estimated to 2.4 mmol per gram of PCMP by iodometry. The PCMP thus obtained was found to act as a favorable oxidizing agent for organic substrates such as olefins, alcohols, and diols.

Scheme I

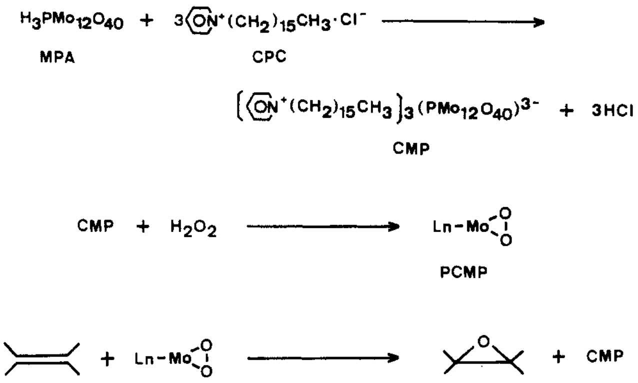


Table I shows the epoxidation of a wide variety of olefins and allylic alcohols by PCMP in chloroform.

Octene (**1**) was slightly reluctant to epoxidize, but it was converted to 1,2-epoxyoctane (**2**) in 79% yield when the reaction time was prolonged. Dicyclopentadiene (**3**) reacted with a stoichiometric amount of PCMP giving monoepoxides **4** and **5** along with diepoxide **6** in a ratio of 42:23:23. The assignment of the stereochemistry of these epoxides was established through comparison of ^{13}C NMR data with those of literature values.[9] *endo*-5-Vinylbicyclo[2.2.1]hept-2-ene (**7**) gave only monoepoxide **8**, in which the norbornene double bond was regio- and stereoselectively epoxidized. On the other hand, allylic alcohols, even under mild reaction conditions, were oxidized more easily than olefins by PCMP, giving the corresponding epoxy alcohols in high yields. For example, *trans*-crotyl alcohol (**9**) and 3-methyl-2-buten-1-ol (**11**) were readily epoxidized at room temperature within 0.5-1 h to form epoxy alcohols **10** and **12**, respectively. The ep-

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*Authors to whom correspondence should be addressed.

[1] (a) Mimoun, H In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1982; pp 463-482. (b) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; pp 91-97. (c) Mimoun, H.; Seree de Roch, I.; Sajus, L. *Bull. Soc. Chim. Fr.* **1969**, 1481. (d) Le Carpentier, J. M.; Mitschler, A.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1288. (e) Jacobson, S. E.; Tang, R.; Mares, F. *Inorg. Chem.* **1978**, *17*, 3055. (f) Jacobson, S. E.; Muccigrosso, D. A.; Mares, F. *J. Org. Chem.* **1979**, *44*, 921. (g) Tomioka, H.; Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1980**, *21*, 4843.

[2] (a) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63. (b) Sheldon, R. E.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981; pp 48-70. (c) Chaumette, P.; Mimoun, H. *J. Organomet. Chem.* **1983**, *250*, 291. (d) Torst, B. M.; Masuyama, Y. *Tetrahedron Lett.* **1984**, *25*, 173. (e) Masuyama, Y.; Takahashi, M.; Kurusu, Y. *Tetrahedron Lett.* **1984**, *25*, 4417. (f) Achrem, A. A.; Timoschtschuck, T. A.; Metalitza, D. I. *Tetrahedron* **1974**, *30*, 3165. (g) Frimer, A. A. *J. Chem. Soc., Chem. Commun.* **1977**, 207. (h) Mimoun, H.; Seree de Roch, I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37. (i) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295. (j) Arakawa, H.; Moro-oka; Nozaki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2958.

[3] (a) Venturello, C.; Alneri, E.; Ricci, M. *J. Org. Chem.* **1983**, *48*, 3831. (b) Venturello, C.; Ricci, M. *J. Org. Chem.* **1986**, *51*, 1599.

[4] Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. *J. Org. Chem.* **1985**, *50*, 2688.

[5] Matoba, Y.; Inoue, H.; Akagi, J.; Okabayashi, T.; Ishii, Y. *Synth. Commun.* **1984**, *14*, 865.

[6] Kurusu, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 293.

[7] Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Frank, R. *Spectrochim. Acta, Part A* **1976**, *32A*, 587.

[8] Elemental analysis of the PCMP was as follows. Found: C, 43.66; H, 6.87; N, 2.42. However, if the constitution of the PCMP is assumed to consist of an idealized structure having the Keggin unit, about 2.4 mmol of active oxygen per gram of the PCMP corresponds to CMP·6[O], whose composition was calculated as follows. Calcd for $C_{63}H_{114}N_3Mo_{12}O_{46}P$(CMP·6[O]): C, 26.72; H, 4.06; N, 1.48.

[9] Matoba, Y.; Kagayama, T.; Ishii, Y.; Ogawa, M. *Org. Magn. Reson.* **1981**, *17*, 144.

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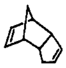
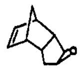
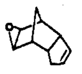
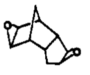
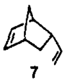
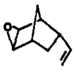
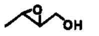
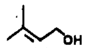
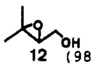
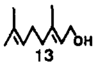
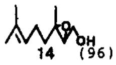
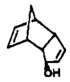
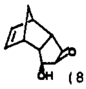
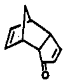
Table I. Oxidation of Olefins and Allylic Alcohols with PCMP^a

run	substrate	temp, °C	time, h	products (yield, %)
1	 1	60	24	 2 (79)
2	 3	60	4	 4 (42)  5 (23)  6 (23)
3	 7	60	5	 8 (76)
4	 9	25	1	 10 (98)
5	 11	25	0.5	 12 (98)
6	 13	25	1	 14 (96)
7^b	13	25	1	14 (90)
8	 15	25	24	 16 (88)  17 (9)

^{a} Substrate (1 mmol) was allowed to react with a stoichiometric amount of PCMP (480 mg), containing about 1 mmol of active oxygen, in $CHCl_3$ (10 cm^3). ^{b} Regenerated PCMP was used.

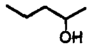
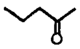
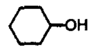
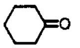
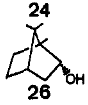
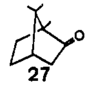
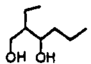
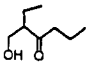
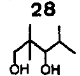
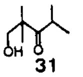
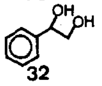
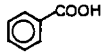
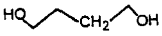
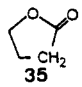
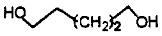
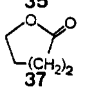
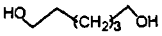
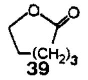
oxidation of geraniol (**13**) occurred regioselectively at the allylic double bond to give epoxy geraniol (**14**) in almost quantitative yield. For 4α-hydroxy-*endo*-tricyclo-[5.2.1.0^{2,6}]deca-3,8-diene (**15**) containing a reactive norbornene double bond, the allylic double bond was preferentially epoxidized to give epoxy alcohol **16**, but a small amount of dehydrogenated product, enone **17**, was also produced.

In a previous work, we concluded that the CMP–*tert*-butyl hydroperoxide (*t*-BuOOH) system catalyzes the oxidation of secondary alcohols to ketones.[10] It is noteworthy that hydrogen peroxide was inadequate as an oxidant for the above oxidations but that the PCMP prepared from hydrogen peroxide and CMP served as a convenient oxidant of alcohols to carbonyl compounds.

Table II shows the oxidation of a variety of alcohols and diols by PCMP in benzene.

Treatment of 2-octanol (**20**) and 2-pentanol (**22**) with a stoichiometric amount of PCMP resulted in the corresponding ketones **21** and **23**, respectively. However, the oxidation of the primary alcohol, 1-octanol (**18**), under the same conditions proceeded with difficulty to give octanal **19** in moderate yield. Cyclic alcohols, cyclohexanol (**24**) and borneol (**26**), were also converted to cyclohexanone (**25**) and camphor (**27**), respectively, in good yields. In the oxidation of diols containing primary and secondary hydroxy functions in their molecules, secondary hydroxy groups were oxidized chemoselectively by PCMP. The stoichiometric reaction of 2-ethyl-1,3-hexanediol (**28**) with PCMP afforded 76% 2-ethyl-3-hexanon-1-ol (**29**). Similarly, 2,2,4-trimethyl-1,3-pentanediol (**30**) gave 1-hydroxy-2,2,4-trimethyl-3-pentanone (**31**) in 92% yield. Similar chemoselectivities have been observed for oxidations of diols by $VO(acac)_2$–*t*-BuOOH,[11] $Ti(Oi\text{-}Pr)_4$–*t*-BuOOH,[12] and $Mo(CO)_6$–*t*-BuOOH[13] systems.

Table II. Oxidation of Alcohols and Diols with PCMP^a

run	substrate	time, h	products (yield, %)
1	 18	5	 19 (49)
2	 20	2	 21 (99)
3	 22	2	 23 (85)
4	 24	2	 25 (78)
5	 26	2	 27 (94)
6	 28	5	 29 (76)
7	 30	2	 31 (92)
8	 32	2	 33 (46)
9^b	 34	2	 35 (66)
10^b	 36	2	 37 (77)
11^b	 38	2	 39 (54)

^{a} Substrate (1 mmol) was allowed to react with a stoichiometric amount of PCMP (480 mg), containing about 1 mmol of active oxygen, in benzene (10 cm^3) at 80 °C. ^{b} PCMP (0.36 mmol).

1,2-Diol was cleaved by this reagent; e.g., phenylethylene glycol (**32**) gave benzoic acid (**33**) in 46% yield. Meanwhile, α,ω-diols were allowed to react with 2 equiv of PCMP in refluxing benzene to form the corresponding lactones,

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(10) Yamawaki, K.; Yoshida, T.; Nishihara, H.; Ishii, Y.; Ogawa, M. *Synth. Commun.* **1986**, *16*, 537.

(11) Kaneda, K.; Kawanisi, Y.; Jitsukawa, K.; Teranishi, S. *Tetrahedron Lett.* **1983**, *24*, 5009.

(12) Yamawaki, K.; Ishii, Y.; Ogawa, M. *Chem. Express* **1986**, *1*, 95.

(13) Yamawaki, K.; Yoshida, T.; Suda, T.; Ishii, Y.; Ogawa, M. *Synthesis* **1986**, 59.

although several methods are available for the selective lactonization.[14,15] 1,4-Butanediol (**34**) was converted to γ-butyrolactone (**35**) in 66% yield. Six- and seven-membered lactones, **37** and **39**, were obtained by treatment of 1,5-pentanediol (**36**) and 1,6-hexanediol (**38**) with 2 equiv of PCMP, respectively.

A precipitate was gradually formed during the course of the oxidation, and most of the oxidant consumed could be precipitated from the reaction mixture by concentration or by dilution with hexane. A precipitate recovered was subjected to oxidation with hydrogen peroxide to generate PCMP in about 70% yield based on the starting PCMP. The active oxygen contained in the PCMP regenerated was almost the same as that in the original PCMP. Thus, treatment of **13** with the regenerated PCMP gave epoxy alcohol **14** in 90% yield (Table I, run 7).

In summary, the PCMP which can be easily prepared from CMP and hydrogen peroxide was found to be effective for the oxidation of olefins to epoxides and secondary alcohols to ketones as well as α,ω-diols to lactones.

Experimental Section

Melting points were determined with a Yanagimoto capillary melting point apparatus. All melting points are uncorrected. Infrared (IR) spectra were measured with a Jasco Model A-202 spectrometer. ^{1}H and ^{13}C NMR were measured with JEOL PMX-60 and a Hitachi R-90H spectrometers in $CDCl_3$ by using Me_4Si as the internal standard, respectively. GLC analysis was carried out with a Yanagimoto G1800 apparatus employing a thermal conductivity detector. The yields of products were estimated from the peak areas by using an internal standard technique.

Preparation of Tris(cetylpyridinium) 12-Molybdophosphate $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_{12}O_{40})^{3-}$ (CMP). To a solution of cetylpyridinium chloride, $\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3Cl^-$ (3.0 g, 8.4 mmol), in distilled water (70 cm^3) was added dropwise 12-molybdophosphoric acid, $H_3PMoO_{40}\cdot nH_2O$ (5.1 g, ca. 2.8 mmol), in distilled water (10 cm^3) to form immediately a yellow precipitate (CMP). After stirring was continued for 2 h, the resulting precipitate was filtered off, washed several times with distilled water, and dried in vacuo to give CMP in 90–95% yield: IR (KBr) 3400, 2900, 2850, 1630, 1480, 1460, 1060, 950, 870, 790 cm^{-1}. Anal. Calcd for $C_{63}H_{114}N_3Mo_{12}O_{40}P$: C, 27.65; H, 4.21; N, 1.54. Found: C, 27.57; H, 4.54; N, 1.44.

Preparation of PCMP. To aqueous 35% hydrogen peroxide (50 cm^3) was added CMP (5 g, 1.8 mmol), and the mixture was stirred at 40–45 °C for 48 h. The suspended solution was cooled to room temperature to give a fine pale yellow to white precipitate. After centrifuging, the precipitate was washed repeatedly with distilled water and dried in vacuo to give PCMP in 70–75% yield by weight based on the starting CMP. The active oxygen contained in PCMP was estimated to be 2.3–2.5 mmol per gram of PCMP by iodometry: IR (KBr) 3400, 2900, 2850, 1630, 1480, 1460, 1165, 1070, 990, 865, 590, 540 cm^{-1}; ^{13}C NMR ($Me_4Si/CDCl_3$) δ 145.5, 144.2, 128.6, 62.6, 31.6, 29.8, 29.4, 29.2, 26.3, 22.7, 14.1.

General Procedure for Epoxidation of Olefins and Allylic Alcohols. To a stirred solution of PCMP (480 mg) containing about 1 mmol of active oxygen in chloroform (10 cm^3) were added dropwise olefins (1.0 mmol) at room temperature. After removal of the precipitate by centrifugation and filtration, the products were isolated by MPLC (on silica gel hexane:ethyl acetate = 5:1 eluent). The spectral data of the products agreed with those of authentic samples and literature values.[16,17]

Spectral Data for 4:[16] ^{13}C NMR ($Me_4Si/CDCl_3$) δ 134.8 (d), 134.7 (d), 61.7 (d), 60.6 (d), 51.9 (t), 50.9 (d), 46.4 (d), 44.6 (d), 43.9 (d), 31.0 (t); ^{1}H NMR ($Me_4Si/CDCl_3$) δ 6.15 (d, 2 H), 3.17 (t, 1 H), 3.00 (d, 1 H), 2.82 (m, 2 H), 2.55 (m, 1 H), 1.85 (q, 1 H), 1.55 (m, 2 H), 1.30 (d, 1 H), 1.22 (t, 1 H); IR (NaCl) 3045, 2980, 2900, 1460, 840, 760 cm^{-1}.

Spectral Data for 5:[9] ^{13}C NMR ($Me_4Si/CDCl_3$) δ 132.0 (d), 129.4 (d), 53.3 (d), 50.9 (d), 49.1 (d), 41.8 (d), 39.8 (d), 38.5 (d), 31.4 (t), 29.0 (t); ^{1}H NMR ($Me_4Si/CDCl_3$) δ 5.65 (m, 2 H), 3.04 (d, 2 H), 2.76 (d, 2 H), 2.47 (m, 2 H), 2.27 (m, 2 H), 1.40 (d, 1 H), 0.78 (d, 1 H); IR (NaCl) 3150, 2960, 1720, 1450, 1370, 1220, 850, 708 cm^{-1}.

Spectral Data for 6:[17] ^{13}C NMR ($Me_4Si/CDCl_3$) δ 61.6 (d), 58.5 (d), 48.8 (d), 48.6 (d), 48.4 (d), 44.6 (d), 39.9 (d), 39.1 (d), 29.6 (t), 26.9 (t); ^{1}H NMR ($Me_4Si/CDCl_3$) δ 3.60–3.30 (m, 2 H), 3.18 (t, 2 H), 2.80–2.33 (m, 4 H), 1.97–1.60 (t, 2 H), 1.60–1.16 (t, 1 H), 0.92 (t, 1 H); IR (NaCl) 2950, 1450, 1390, 1220, 850 cm^{-1}.

General Procedure for Oxidation of Alcohols and Diols. To a stirred solution of PCMP (480 mg) in benzene (20 cm^3) were added dropwise alcohols or diols (1.0 mmol), and then the mixture was stirred under reflux for 2–6 h. The isolation and identification of products were carried out in a manner similar to that described above.

Spectral Data for 29: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 214.7 (s), 62.6 (t), 55.4 (d), 44.9 (t), 21.4 (t), 16.8 (t), 13.7 (q), 11.7 (q); ^{1}H NMR ($Me_4Si/CDCl_3$) δ 3.66 (d, 2 H), 3.54 (s, 1 H), 2.82–2.20 (m, 1 H), 2.43 (t, 2 H), 1.70–1.16 (m, 4 H), 0.89 (t, 3 H), 0.86 (t, 3 H); IR (NaCl) 3450, 2925, 1700, 1455, 1370, 1030 cm^{-1}.

Spectral Data for 31: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 221.2 (s), 69.3 (t), 49.6 (s), 34.5 (d), 21.1 (q), 19.8 (q); ^{1}H NMR ($Me_4Si/CDCl_3$) δ 3.50 (s, 2 H), 3.26–2.82 (m, 1 H), 2.58 (s, 1 H), 1.17 (s, 6 H), 1.05 (d, 6 H); IR (NaCl) 3450, 2950, 1685, 1460, 1370, 1020 cm^{-1}.

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Use of Difference NOE Experiments To Assign the Geometry of Trimethylsilyl Enol Ethers

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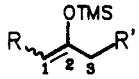
During the course of our investigations on 14-membered ring keto lactones, we synthesized a number of trimethylsilyl (Me_3Si) enol ether derivatives of the ketone carbonyl. The most widely used method for assigning the geometry of trimethylsilyl enol ethers is ^{13}C NMR spectroscopy. Heathcock et al. have demonstrated that the allylic carbon 3 (see **A**) of an *E* trimethylsilyl enol ether resonates 5–6 ppm upfield from the *Z* isomer.[1]



A

However, this method suffers from two shortcomings: First, both isomers must be available to assign the geometry with confidence.[2] Second, in highly functionalized molecules, it can be challenging to identify the allylic carbon of interest. Furthermore, Friedrich et al. have prepared both trimethylsilyl enol ethers of cyclodecanone and their ^{13}C NMR spectra appear to violate Heathcock's generalization.[3]

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