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Direct Catalytic Transformation of Olefins into α-Hydroxy Ketones with Hydrogen Peroxide Catalyzed by Peroxotungstophosphate

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Aliphatic olefins were directly converted into α-hydroxy ketones with acidic aqueous hydrogen peroxide in the presence of catalytic amount of peroxotungstophosphate (PCWP) under the biphasic system using chloroform as a solvent. The acidic medium was necessary to open the resulting epoxide to *vic*-diol which was subsequently oxidized to α-hydroxy ketones.

Since α-hydroxy ketones are important intermediates for natural product synthesis, a number of synthetic methods have been developed.1) Acyloin condensation of esters 1a, 1b) and oxidations of oxygen-containing substrates such as silyl enol ethers,1c) *vic*-diols,1d, 5) epoxides,1e) and ketones1f) have generally been used for the preparation of hydroxy ketones. It has been reported that several olefins are converted into α-hydroxy ketones by heterogeneous permanganate oxidation.2) Unfortunately, simple olefins such as 1-decene and 2-octene lead to carboxylic acids without formation of the desired α-hydroxy ketones in this oxidation. In addition, the reaction is not a catalytic process and requires the use of excess oxidant.2) More recently various olefinic compounds were converted into the corresponding α-hydroxy ketones with molecular oxygen and an aldehyde in the presence of OsO_4 and bis(3-methyl-2,4-pentanedionate)nickel(II).3) Previously, we showed that peroxotungstophosphate (PCWP), $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, prepared by treating 12-tungstophosphoric acid (WPA) in aqueous hydrogen peroxide4) with cetylpyridinium chloride (CPC) in water, catalyzes the oxidation of vic-diols to α-hydroxy ketones with 35% H_2O_2 in the biphasic system.5)

In the continuation of this study, our attention has been focused on the direct PCWP-catalyzed conversion of olefins into α-hydroxy ketones with 35% H_2O_2.

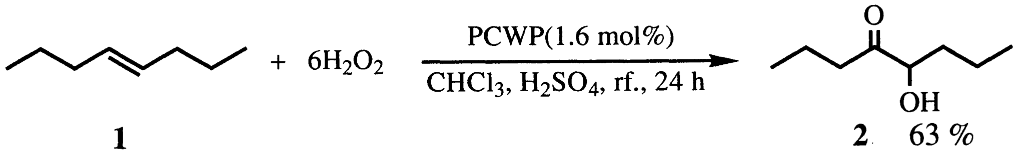
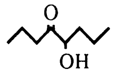
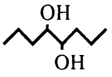
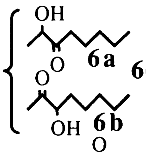
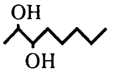
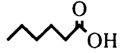
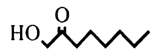
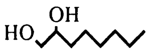
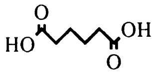
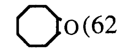


Table 1 shows the representative results for the oxidations with 35% H_2O_2 catalyzed by peroxoheteropoly oxometalates under various reaction conditions.

Table 1. Oxidation of Olefins with 35% H_2O_2 by Peroxoheteropoly Oxometalates under Several Conditions[a)]

Run	Substrates	Cat.	H_2SO_4[b)] / ml	Products (yield / %)[c)]		
1	 **1**	PCWP	-	 **4**(90)		
2	**1**	PCWP	0.2	 **2**(48)	 **3**(13)	**4**(14)
3	**1**	PCWP	1.0	**2**(63)		**4**(11)
4	 **5**	PCWP	1.0	 **6a** **6b** **6**(60)[d)]	 **7**(10)	 **8**(5)
5[e)]	**5**	PCWP	-	 (71)		
6	**5**	PCMP	1.0	**6**(5)	**7**(27)	**8**(22)
7	**5**	CWP	1.0	**6**(7)	**7**(39)	**8**(30)
8	 **9**	PCWP	1.0	 **10**(90)		
9[f)]	**9**	PCWP	1.0	 **11**(40)	 **12**(8)	**10**(9)
10		PCWP	1.0	 (70)[g)]		
11		PCWP	1.0	 (62)		

a) Olefin (3 mmol) was allowed to react with 35% H_2O_2 (18 mmol) in the presence of catalyst (1.6 mol%) in $CHCl_3$ (15 ml) under refluxing for 24 h. b) 1 M H_2SO_4 was added. (1 M=1 mol dm^{-3})

c) Substrates were consumed more than 90% except run 6 (70%). Remainder involves carboxylic acids.

d) **6a**/**6b**=ca. 3/2 e) t-BuOH was used in place of $CHCl_3$. f) $CHCl_3$ (7.5 ml) was used.

g) Isolated as methyl ester.

4-Octene(**1**) afforded only 4,5-epoxyoctane(**4**) by oxidation with 35% H_2O_2 in the presence of PCWP under two-phase conditions using chloroform as a solvent (run 1).

However, when the aqueous phase was acidified to pH 1 with 1M H_2SO_4 (0.2 ml), 5-hydroxy-4-octanone (**2**) was produced in 48% yield along with a smoll amount of 4,5-octanediol (**3**) and the epoxide **4** (run 2). By adding 1.0 ml of 1M H_2SO_4 to the reaction system, the yield of **2** was improved to be 63% (run 3). The oxidation of unsymmetrical internal olefins produced a pair of regioisomers. For example, *trans*-2-octene (**5**) formed a 3:2 mixture of 2-hydroxy-3-octanone (**6a**) and 3-hydroxy-2-octanone (**6b**) together with 2,3-octanediol (**7**) and 2,3-epoxyoctane (**8**) (run 4). Although terminal olefins such as 1-octene (**9**) afforded 1,2-epoxyoctane (**10**) under the same reaction condition as above, 1-hydroxy-2-octanone (**11**) was obtained in 40% yield when chloroform was reduced by one-half. In this oxidation, no regioisomer, 2-hydroxyoctanal was formed. Cyclohexene was cleaved to adipic acid, though reactions were carried out under various conditions (*e.g.*, time, temperature, quantity of solvent, oxidant or catalyst, and so on). On the contrary, cyclooctene yielded exclusively 1,2-epoxycyclooctane with no cleavage product. This difference may be attributed to the stability of the resulting epoxides.

The potential of the corresponding molybdenum peroxocomplex, PCMP, prepared by using 12-molybdophosphoric acid (MPA) in place of WPA,[6] was examined, but the PCMP was found to be less active than the PCWP to form **6** in moderate yield (run 6). Tris(cetylpyridinium)-12-tungstophosphate (CWP), $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3PW_{12}O_{40}{}^{3-}$, showing high activity for the epoxidation of olefins,[7] was insufficient for this purpose (run 7).

In order to obtain the information on the reaction path, the oxidation of **1** by the PCWP-H_2O_2 system was pursued by taking the GC at regular time intervals (Fig. 1).

From the time-dependence curve of reaction products, **1** was found to be rapidly epoxidized to **4** in the early stage of the reaction. The resulting **4** was gradually cleaved to the diol **3** which, on the subsequent dehydrogenation, gave the α-hydroxy ketone **2**. This observation suggests that the ring opening of **4** to **3** is the most important step in the present reaction. Therefore, the adoption of the acidic biphasic system is essential to achive the present reaction, because the ring opening of the epoxide does not take place under non-acidic biphasic system (shown in Table 1, run 1).

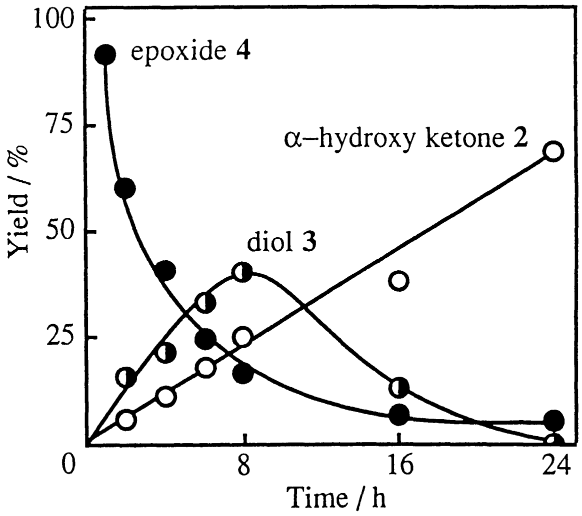
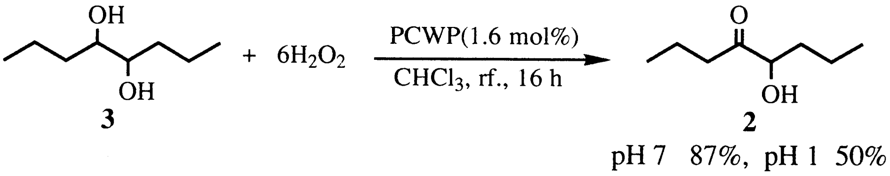


Fig. 1. Time-dependence curves for the oxidation of 4-octene (**1**) by the PCWP-H_2O_2 system.

However, under the homogeneous condition using t-butyl alcohol as the solvent, olefins were cleaved to carboxylic acids (run 5).

In contrast to the present reaction where the acidic biphasic system must be adopted to convert olefins into α-hydroxy ketones, the oxidation of *vic*-diols to α-hydroxy ketones by the same catalyst-oxidant system progressed smoothly under the non-acidic biphasic condition.5) For example, **3** was oxidized to α-hydroxy ketone **2** in 87% yield by the PCWP-H_2O_2, while under the acidic biphasic condition the yield of **2** was lowered to 50% due to the formation of carboxylic acid by over-oxidation.5) Consequently, in the present reaction, the acidic medium is necessary to open the oxirane ring to *vic*-diol.



In conclusion, it is worth noting that acyclic olefins were directly converted into α-hydroxy ketones, since it is very difficult to achieve this type of oxidation by the conventional method.

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