Epoxidation of Olefins and Allylic Alcohols with Hydrogen Peroxide Catalyzed by Heteropoly Acids in the Presence of Cetylpyridinium Chloride

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The epoxidation of olefins and allylic alcohols with aqueous hydrogen peroxide could be achieved in good yields when catalyzed by heteropoly acids combined with an appropriate ammonium salt under the two-phase condition using chloroform as the solvent. From the results of epoxidation catalyzed by several heteropoly acids, 12-tungstophosphoric acid (WPA) in the presence of cetylpyridinium chloride (CPC) (WPA/CPC system) was found to be the best catalyst (Table 1, Run 3). In the case of terminal olefins such as 1-octene (1), the epoxidation proceeds somewhat slowly to give 1,2-epoxy octane (2) in 82% yield by prolonged reaction (5 hr) (Table 2, Run 1). Dienes, 4-vinyl-1-cyclohexene (3), 5-vinyl-2-norbornene (5), and dicyclopentadiene (7), obtained from Diels-Alder reaction of cyclopentadiene with butadiene, are readily epoxidized in good yields to give their corresponding epoxides, 4, 6 and 8-10, respectively (Table 2, Runs 2-5). The rate of epoxidation depends markedly upon the acidity of the reaction medium, and the epoxidation was found to be facilitated under weak acidic conditions (Figure 1). Allylic alcohols are also epoxidized with ease by the present catalyst-oxidant system to give the corresponding epoxides in good yields (Table 2, Runs 6-8).

1. Introduction

Epoxidation with aqueous hydrogen peroxide is very important from the viewpoint of industrial technology and synthetic organic chemistry, since hydrogen peroxide is cheap, environmentally clean, and also easy to handle. In recent years, it has been reported that olefins can be epoxidized with dilute hydrogen peroxide by molybdenum and tungsten-derivatives as catalysts under phase-transfer conditions.1-3) On the other hand, heteropoly acids (HPA) have frequently been used not only for oxidation of organic substrates but also for many acid-catalyzed reactions owing to their dual characteristics: oxidizing ability and strong acidity.4) Therefore, the use of HPA for oxidation of olefins by hydrogen peroxide usually brings about trans-glycols due to the cleavage of the resulting oxirane ring by subsequent electrophilic attack of HPA itself.

However, HPA in conjunction with an appropriate ammonium salt such as cetylpyridinium chloride (CPC) acts as an efficient epoxidation catalyst of allylic alcohols and olefins in the presence of aqueous hydrogen peroxide.5,6) In a previous paper, we reported that 12-molybdophosphoric acid (MPA) in the presence of CPC and/or tricetylpyridium-12-molybdophosphate (CMP) prepared in advance from the reaction of MPA and CPC underwent epoxidation of allylic alcohols with commercially available aqueous hydrogen peroxide in good yields.5,6) In this epoxidation, a peroxo-molybdenum species (peroxo-CMP) which serves as the actual epoxidizing agent is isolated and prepared independently by treating the CMP with excess hydrogen peroxide. The treatment of olefins with stoichiometric peroxo-CMP thus prepared gives the corresponding epoxides in almost quantitative yields.7) The catalytic cycle for this epoxidation has been outlined in Scheme 1. When 12-tungstophosphoric acid (WPA), an alternative heteropoly acid, in place of MPA was
employed as the catalyst, olefins were epoxidized more efficiently with aqueous hydrogen peroxide under similar conditions. This method, consisting of inexpensive, clean, and nonpolluting aqueous hydrogen peroxide and a nontoxic tungstate catalyst, is particularly convenient for large scale epoxidation. In this paper, we described heteropoly acid-catalyzed epoxidation of olefins, in particular, dienes which are readily available from Diels-Alder reaction of cyclopentadiene with butadiene8), as well as the epoxidation of allylic alcohols with aqueous hydrogen peroxide under the two-phase condition.

2. Experimental

2.1 Materials

Unless otherwise noted, the materials were obtained from commercial suppliers and used without further purification. endo-Dicyclopentadiene (DCP) was prepared by dimerization of cyclopentadiene obtained by destructive distillation of commercially available endo-DCP.

Preparation of Tricetylpyridinium-12-tungstophosphatate (CWP), [\(\pi\cdot C_5H_5N^+\) \(\text{CH}_2\)\(_{15}\) \(\text{CH}_3\)\(_3\) \(\pi\cdot \text{PW}_{12}\text{O}_{40}\)]

To a solution of CPC (1.87 g, 5.2 mmol) in 70 ml of water, WPA (5.0 g, ca 1.7 mmol) in 10 ml of water was added dropwise at room temperature to form a white precipitate immediately. After stirring continuously for 3—4 hr, the resulting precipitate was filtered and then washed several times with water, dried in vacuo to give CWP in 80—90% yield. Anal. Calcd. for C\(_{63}\)H\(_{114}\)N\(_3\)PW\(_{12}\)O\(_{40}\): C: 19.96, H: 3.03, N: 1.11%. Found: C: 20.27, H: 3.08, N: 1.08%. IR (KBr): 3350, 2900, 2850, 1630, 1480, 1455, 1160, 1070, 970, 885, 820-750, 670, 500 cm\(^{-1}\). CWP was prepared by the same method described above.\(^9\) Anal. Calcd. for C\(_{63}\)H\(_{114}\)N\(_3\)PMO\(_{12}\)O\(_{40}\): C: 27.65, H: 4.21, N: 1.54%. Found: C: 27.57, H: 4.54, N: 1.44%. IR (KBr): 3400, 2900, 2850, 1630, 1480, 1460, 1370, 1160, 1125, 1080, 1050, 980, 950, 840, 770, 720, 680, 645, 570, 545, 520 cm\(^{-1}\).

2.2 Reaction

General Procedure for Epoxidation of Olefins and Allylic Alcohols

To the stirred solution of WPA (75 mg, ca 0.026 mmol), CPC (28 mg, 0.078 mmol) and 35%-H\(_2\)O\(_2\) (960 mg, ca 9.8 mmol) in chloroform (15 ml), olefin (6.5 mmol) was added dropwise, and then the mixture was allowed to react under certain prescribed conditions. After the reaction, partially precipitated catalyst was removed by filtration, and the filtrate was treated with a solution of sodium sulfate to decompose unreacted hydrogen peroxide, then treated with 10%-sodium hydroxide. Epoxides were extracted with chloroform and isolated by distillation under reduced pressure or by chromatography on silica-gel.

Epoxidation of 1-Octene by Peroxo-CWP

To the stirred solution of peroxy-CWP (743 mg) containing about 1 mmol of active oxygen in chloroform (15 ml), 1-octene (112 mg, 1.0 mmol) was added dropwise, and the mixture was allowed to react under refluxing chloroform for 3 hr. After removing the precipitate, the product was subjected to medium-pressure liquid chromatograph.
packed with silica gel (hexane : ethyl acetate = 10 : 1 eluent) to give 1,2-epoxy octane in 86% yield.

2.3 Analysis

The melting point was determined using a Yanagimoto-melting point apparatus and corrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on a JEOL PMX-60 instrument and on a Hitachi R-90H spectrometer in CDCl$_3$ by using Me$_4$Si as the internal standard. GC-MS spectra were obtained with a JMS-QH100 instrument. GC analysis was performed with a Yanagimoto Model G 1800 employing a thermal conductivity detector and a 3 mm × 3 m stainless column packed with PEG-20M 5% or Apiezone Grease-L 10% on Chromosorb W. Yields of products were estimated from the peak areas by using indene, α-methylstyrene, tetralin, and o-xylene as internal standards. Spectral data of the products agreed with those of authentic samples and those available in literature.$^{10-12}$

3. Results and Discussion

In order to evaluate the potential of heteropoly acids as catalysts for epoxidation of olefins, catalytic activities of some heteropoly acids were compared under varying reaction conditions. These results are summarized in Table 1.

From the representative epoxidation results of 1-octene(1) to 1,2-epoxyoctane(2) by oxy-metal compounds, H$_2$MoO$_4$ and H$_2$WO$_4$, and by their corresponding heteropoly acids, H$_3$PMo$_{12}$O$_{40}$ (MPA) and H$_3$PW$_{12}$O$_{40}$ (WPA), it was found that the epoxidation was catalyzed not solely by molybdate or 

![Chart 1](image-url)

Table 1

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Additive$^{(a)}$</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Products Selectivity (%)</th>
</tr>
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<tr>
<td>1</td>
<td>H$_2$MoO$_4$</td>
<td>CPC(2)</td>
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<td>trace</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>H$_2$WO$_4$</td>
<td>CPC(2)</td>
<td>24</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>WPA$^{(c)}$</td>
<td>CPC(3)</td>
<td>5</td>
<td>82</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>WPA$^{(c)}$</td>
<td>CPC(3)</td>
<td>24</td>
<td>50</td>
<td>80$^{(f)}$</td>
</tr>
<tr>
<td>5</td>
<td>CWP</td>
<td>CPC(3)</td>
<td>12</td>
<td>79</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>CWP</td>
<td>H$_2$SO$_4$</td>
<td>10</td>
<td>77</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>CWP</td>
<td>CPC(3)</td>
<td>24</td>
<td>11</td>
<td>98</td>
</tr>
<tr>
<td>8</td>
<td>MPA</td>
<td>CPC(3)</td>
<td>24</td>
<td>11</td>
<td>88</td>
</tr>
</tbody>
</table>

$^{(a)}$ 1-Octene (6.5 mmol) was allowed to react with 35% H$_2$O$_2$ (9.8 mmol) using catalyst (0.026 mmol) in chloroform (15 ml) at 60°C.

$^{(b)}$ Numbers in parentheses showed the molar ratio of additive to catalyst.

$^{(c)}$ t-BuOH (15 ml) was used as solvent.

$^{(d)}$ 1,2-Octane diol was formed as the main product.

$^{(e)}$ 1N-H$_2$SO$_4$ (10 μl) was added to the medium.
tungstate ions (Runs 1 and 2). While the epoxidation of 1 to 2 with aqueous hydrogen peroxide (35%-H₂O₂) was successfully carried out under the influence of 12-tungstophosphoric acid (WPA) in the presence of 3 equivalents of cetylpyridinium chloride (CPC) (abbreviated as WPA/CPC system) under the two-phase condition using chloroform as the solvent (Run 3), 1 was epoxidized to 2 in only 41% yield by the previous method employing 12-molybdophosphoric acid.6) Under homogeneous conditions using tert-butyl alcohol as the solvent, however, 1 yielded a considerable amount of a cleavaged product, 1,2-octanediol (Run 4). The tricetylpyridinium-12-tungstophosphate (CWP), [C₅H₅N(CH₂)₁₅CH₃]₃(PW₁₂O₄₀)³⁻, prepared in advance from the reaction of WPA and CPC, was for epoxidation of 1 (Run 5) somewhat ineffective compared to that of the WPA/CPC system. There is a significant difference in the catalytic systems of WPA/CPC and CWP. In the WPA/CPC system, which produces CWP with evolution of hydrogen chloride (cf. Scheme 1), the reaction medium is slightly acidic because of the resulting hydrogen chloride; but in the CWP system, the medium is not acidic. Comparing the effectiveness of the two catalytic systems, WPA/CPC and CWP, for epoxidation of 1 provides some notable features of catalysis. The fact that epoxidation proceeded more rapidly with the WPA/CPC system suggests that the epoxidation depends subtly upon the acidity of the reaction medium. Indeed, the epoxidation of 1 catalyzed by CWP was facilitated markedly by the addition of a very small amount of 1N-sulfuric acid to the reaction medium (Run 6).

In previous epoxidation of 4-vinyl-1-cyclohexene (3) by molybdenum series, the MPA combined with CPC (MPA/CPC system) was less efficient than the CMP catalyst in contrast to the tungsten series where the WPA/CPC system was more efficient than the CWP catalyst. In the case of molybdenum, the hydrogen chloride generated in the reaction system influenced as an inhibitor for epoxidation of 3.

Owing to the complexity of the reaction medium of the present epoxidation method that adopted the two-phase system, it is difficult to predict accurately the effect of acidity of the aqueous phase on epoxidation. However, we can make several assumptions which seem to agree with the experimental data. In such a system, a molybdenum or a tungsten-peroxo complex, which serves as the actual epoxidizing agent, is formed in the aqueous phase, and it is transferred to the chloroform phase where the epoxidation takes place (Scheme 1). In fact, the treatment of CMP with hydrogen peroxide in water gave a peroxo-molybdenum complex, which involves 1.4–2.4 mmol/g of active oxygen13), and the peroxo-complex obtained as a pale yellow precipitate, dissolved readily in chloroform.7) On the other hand, the corresponding tungsten compound (CWP) was treated with hydrogen peroxide under similar conditions to give a white precipitate whose iodometry and IR spectrum, however, showed no presence of peroxy-oxygen. However, WPA in the presence of 3 equivalents of CPC was treated in excess hydrogen peroxide to yield a peroxo-tungsten complex (peroxo-CWP) whose IR spectrum indicated the characteristic absorption bands at 545 and 570 cm⁻¹ which were assigned respectively to I and II.14),15)

Recently, it has been reported that peroxo-tungsten complex is prepared by treating 40% H₃PO₄ and pertungstic acid (prepared by dissolving H₂WO₄ in 30% H₂O₂) in the presence of tetrahexylammonium chloride.16) The treatment of 1 with the stoichiometric amount of peroxo-CWP thus prepared in chloroform formed epoxide 2 in good yield (Eq. 1)

From these results, it is probable that acidity of the aqueous phase affects the rate of formation of peroxo-complexes and their reactivities and stabilities in the reaction medium.

Figure 1 shows typical time-dependent curves for the molybdenum and tungsten-catalyzed epoxidation of 3 to 4.

Epoxidation of 3 by molybdenum catalysts stopped at about 65% olefin-consumption before
reaching completion; but 3 was converted by the corresponding tungsten catalysts of 4 in good yields in a short time. A comparison of the three curves observed in the tungsten series provides the effect of acidity on the epoxidation. The rate of epoxidation by WPA/CPC system was about 1.8 times faster than that by CWP catalyst. The addition of hydrochloric acid\textsuperscript{17) to the CWP-catalyzed epoxidation resulted in an increase in the epoxidation rate as was expected. A similar result was obtained by the addition of 1N-sulfuric acid, but the addition of more concentrated sulfuric acid (10N-H\textsubscript{2}SO\textsubscript{4}) decreased the rate of epoxidation. These findings suggest that the epoxidizing ability of heteropoly tungstic acid be superior to that of the corresponding molybdenum compound and that the rate of the epoxidation be strongly influenced by the acidity of the reaction medium.

Table 2 shows epoxidations of a variety of olefins with aqueous hydrogen peroxide catalyzed by the WPA/CPC system in chloroform.

Although terminal olefins such as 1-octene 1 are usually reluctant to oxidation, 1 was smoothly epoxidized with aqueous hydrogen peroxide by the WPA/CPC system to epoxide 2 in 86% yield. Epoxidation of dienes, such as 3 and 5-vinyl-2-norbornene (5), which involves two carbon-carbon double bonds whose reactivities are moderately different with each other could be achieved regioselectively. Diene 3 was epoxidized within 2 hr to form a stereoisomeric mixture of cis- and trans-3,4-epoxy-1-vinylcyclohexanes (4) (cis/trans = ca 1/1) in almost quantitative yield. Epoxidation of 5 took place regio- and stereo-selectively to give 2,3-epoxy-5-vinylnorbornane (6) as the sole product (Run 3). Dicyclopentadiene (7), having two reactive double bonds in the molecule, was readily epoxidized even at room temperature; but monoepoxides, 8 and 9, and diepoxide 10 were formed in a ratio of 60 : 22 : 18 (Run 4). The composition of these epoxides was dependent upon reaction conditions, especially, on temperature and on quantities of hydrogen peroxide. For instance, epoxidation at 60°C increased the yield of diepoxide 10 (Run 5).

Allylic alcohols were also epoxidized with ease by aqueous hydrogen peroxide at room temperature. 3-Methyl-2-buten-1-ol (11) and a simple terpenoid alcohol, geraniol (13), were epoxidized in good yields to give respectively (Runs 6 and 7), 2,3-epoxy-3-methylbutanol (12) and epoxy geraniol (14) in which the allylic double bond was epoxidized chemoselectively. Epoxidation of 1,2-hydroxydicyclopentadiene (15) occurred exclusively at the allylic position to produce epoxide (16) along with a small amount of dehydrogenation product, enone (17). The directing and promoting effects of the hydroxy group of dicyclopentadiene derivatives on epoxidation have been discussed in a previous paper.\textsuperscript{18) In conclusion, 12-tungstophosphoric acid (WPA) with aqueous hydrogen peroxide is a versatile epoxidation catalyst of olefins by controlling its acidity, by combining it with an appropriate ammonium salt such as cetylpyridinium chloride (CPC). This direct epoxidation method of olefins involving by commercially available aqueous hydrogen peroxide is very attractive from the viewpoint of both
oxidation chemistry and industrial technology.

References

9) If the peroxo-CWP is constituted from its idealized form, \([\pi-C_5H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})_3\cdot[nO](CWP\cdot n[O]),\) the content of active oxygen (1.1–1.5 mmol per gram of peroxo-CWP) corresponds approximately to CWP \cdot 4–5[O]. However, since a detailed structure of peroxo-CWP is not ascertain, the active oxygen content per mole can not estimate accurately.
13) The content of active oxygen per gram of peroxo-CMP was dependent on the preparing conditions, especially, amounts of hydrogen peroxide and reaction temperature.
17) A 20 µl of 3.8N-HCl was added. The amount of hydrochloric acid added to the reaction system was estimated from the quantity of WPA and CPC employed as the catalyst.
要 旨
塩化セルビリジニウム存在下ヘテロポリ酸触媒による
オレフィンおよびアルリアルール類の過酸化水素水によるエポキシ化

岡林 卓治, 山脇 一公, 西原 英樹, 山田 浩司, 渋 利和, 石井 康敬, 小川 雅弥
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12-タングストリン酸, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (WPA) は塩化セルビリジニウム, $\sigma$-$\text{C}_2\text{H}_5\text{N}^+$ ($\text{CH}_3$)$_2$-$\text{CH}_2$-$\text{Cl}^-$ (CPC) のような適当な4級アンモニウム塩の存在下で12-タングストリン酸トリセルビリジニウム, $\left[\sigma$-$\text{C}_2\text{H}_5\text{N}^+$ ($\text{CH}_3$)$_2$-$\text{CH}_2$-$\text{Cl}^-\right]_3$($\text{PW}_{12}\text{O}_{40}$)$^{3-}$ (CWP) を形成し、クロホルムを溶媒とする二相系条件のもとでオレフィンやアルリアルール類を過酸化水素水で良好にエポキシ化することがわかった。

$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ や $\text{H}_3\text{PW}_{12}\text{O}_{40}$ に相当するオキシ金属化合物, $\text{H}_3\text{MoO}_4$ や $\text{H}_2\text{WO}_4$ による1-オクタン (1) のエポキシ化反応の結果から, 本エポキシ化反応がモリブデン酸タングステンイオンのみでは触媒作用がないことがわかった (Table 1, Runs 1 ～2)。12-モリブデン酸, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (MPA) と WPA 触媒による1のエポキシ化反応結果から, WPA 触媒のエポキシ化活性が MPA のそれに比べ著しく高いことが明らかとなった (Table 1, Runs 3, 7)。本ヘテロポリ酸系触媒によるエポキシ化反応は反応媒体の酸性度を強く依存し, WPA/CPC 系では弱い酸性条件のもとでエポキシ化は良好に進行するのに対し, MPA/CPC 系では中性に近い条件でエポキシ化反応が促進されることがわかった (Fig. 1)。

シクロペンタジェンとフェニルエンの Diels-Alder 反応から生成する付加体 (3, 5, 7) の利用を目的として、これらジエン類のエポキシ化反応を試みたところ、いずれも好収率でエポキシ化され、相当するエポキシド (4, 6, 8～10) が得られた。アルリアルール類 (11, 13, 15) の過酸化水素によるエポキシ化反応は本触媒系で容易な条件のもとで進行し、アルリアルールの二重結合が位置選択的にエポキシ化されたエポキシアルール (11, 12, 14, 16) が良い収率で得られた (Table 2, Runs 6～8)。

以上のよう、WPA/CPC 系によるオレフィン類のエポキシ化反応が、安価でしかもクリーンな過酸化水素水を酸化剤として、好収率、好選択的に促進されることから、合成にも工業的見地からも興味ある触媒系であることが明らかとなった。

Keywords
Epoxidation, Heteropoly acid, Hydrogen peroxide, Phase transfer catalyst, Tricetylpyridinium salt, 12-Tungstophosphoric acid

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