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# Oxidative Cleavage of Olefins into Carboxylic Acids with Hydrogen Peroxide by Tungstic Acid

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A facile conversion of olefins into carboxylic acids could be achieved by using aqueous hydrogen peroxide (35%-$H_2O_2$) in the presence of catalytic amounts of tungstic acid (5 wt%). The oxidation was markedly influenced by the acidity of the reaction medium, and it was found to proceed favorably under a weak acidic condition (pH 4-5).

Oxidative cleavage of olefins to carboxylic acids is frequently used in synthetic organic chemistry. Ozonolysis with oxidative work-up,1) and oxidation with chromium2) and permanganate3) reagents were long-standing method for this purpose. In more recent years, ruthenium tetraoxide is used stoichiometrically, or catalytically in the presence of an appropriate oxidant such as $NaIO_4$ or NaOCl.4)

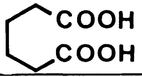
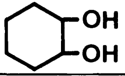
In a previous paper, we showed that tris(cetylpyridinium)12-tungstophosphate [ $\pi$-$C_5H_5N^+(CH_2)_{15}CH_3$ $]_3$ ( $PW_{12}O_{40}$ $)^{3-}$, smoothly undergoes oxidative cleavage of olefins to carboxylic acids with aqueous hydrogen peroxide (35%-$H_2O_2$) in tert-butyl alcohol(t-BuOH).5) A similar oxidative cleavage by heteropoly acids appears in patent work.6) In the course of our study, $H_2WO_4$-$H_2O_2$ system7) was found to be efficient for carbon-carbon bond fission of olefins into carboxylic acids.

This paper describes a facile conversion of olefins into carboxylic acids with aqueous hydrogen peroxide (35%-$H_2O_2$) by tungstic acid.

In order to examine the potential of oxy-metal compounds for the oxidative cleavage of olefins into carboxylic acids, the conversion of cyclohexene to adipic acid was chosen as the model reaction (Table 1).

A typical reaction procedure is as follows: To a solution of $H_2WO_4$ (5 wt%) in t-BuOH (15 ml) was added 4 eqiuv. of 35%-$H_2O_2$ (26 mmol) and cyclohexene (6.5 mmol) under stirring. The reaction mixture was allowed to react under refluxing for 24 h and then subjected to methylesterification in methanol (30 ml) in the presence of *p*-$CH_3C_6H_4SO_3H$ (0.3 g).

Table 1. Oxidative Cleavage of Cyclohexene with 35%-$H_2O_2$ by Oxy-metal Compounds[a)]

| Entry | Catalyst | Solvent | Yield/ % b) | |
|---|---|---|---|---|
| | | |  |  |
| 1 | $H_2WO_4$ | t-BuOH | 62 | 18 |
| 2 | $H_2WO_4$ | $H_2O$ | trace | |
| 3 | $H_2WO_4$ | $CHCl_3$ | trace | |
| 4 | $H_2MoO_4$ | t-BuOH | 12 | 8 |
| 5 | $H_3PMo_{12}O_{40}$ | t-BuOH | 7 | 22 |
| 6 | $H_3PW_{12}O_{40}$ | t-BuOH | 50 | 22 |
| 7 | $Na_2WO_4$ | t-BuOH | trace | |
| 8 | $H_2SeO_4$ | t-BuOH | 23 | 39 |
| 9[c)] | $H_2WO_4$ | t-BuOH | 9 | 40 |
| 10[d)] | $H_2WO_4$ | t-BuOH | 10 | trace |
| 11[e)] | $H_2WO_4$ | t-BuOH | 51 | 5 |
| 12[f)] | $H_2WO_4$ | t-BuOH | 81 | 9 |

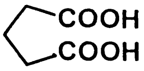
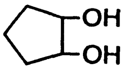
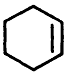
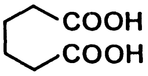
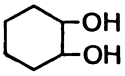
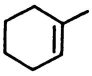
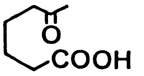
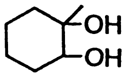
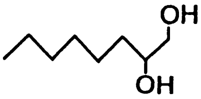
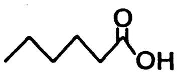
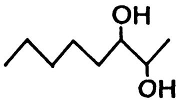
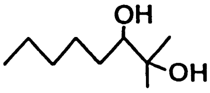
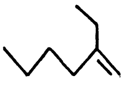
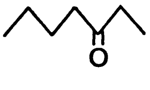
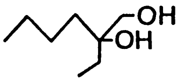
a) Cyclohexene (6.5 mmol) was allowed to react with 35%-$H_2O_2$ (26 mmol) in the presence of catalyst (5 wt%) under refluxing of the solvent (15 ml) for 24 h. b) Adipic acid was isolated as dimethylester. c) The medium was adjusted to pH 2-3 by conc-HCl. d) The medium was adjusted to pH 6-7 by 2 M-KOH. e) Used 20 wt% of $H_2WO_4$. f) Used 20 wt% of $H_2WO_4$. The medium was adjusted to pH 4-5 by 2 M-KOH. ( 1 M = 1 mol $dm^{-3}$ )

The carbon-carbon double bond of cyclohexene was successfully cleaved with 4 equiv. of $H_2O_2$ under the influence of catalytic amounts of $H_2WO_4$ in t-BuOH (Entry 1). The reaction did not take place in water or under two-phase condition using chloroform as the solvent (Entries 2 and 3). The corresponding Mo-catalyst, $H_2MoO_4$, and heteropoly acids, $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$, were found to be less efficient than $H_2WO_4$ (Entries 4-6). Sodium tungstate showed no activity for the present oxidation. Selenic acid, $H_2SeO_4$, resulted in the preferential formation of diol rather than cleaved product. The reaction was influenced by the pH of the medium. In the reaction using 5 wt% of $H_2WO_4$, the solution remains pH 4 to 5, and the oxidative cleavage smoothly proceeded. The medium became more acidic (pH 2-3) when 20 wt% of $H_2WO_4$ was used and the yield of adipic acid was lowered to 51% contrary to the expectation (Entry 11). By adjusting the medium to pH 4-5 with 2 M-KOH, adipic acid was obtained in 81% yield (Entry 12).

Table 2 shows the oxidative cleavage of several olefins by the $H_2WO_4$-$H_2O_2$ system.

In a similar manner as oxidation of cyclohexene, cyclopentene was also cleaved to glutaric acid in moderate yield (Entry 2). 1-Methyl-1-cyclohexene gave keto carboxylic acid in good yield (Entry 3). In the case of aliphatic olefins, such as 1-octene and 2-octene, the reaction took place with somewhat difficulty to form heptanoic acid and hexanoic acid, respectively (Entries 4 and 5). Tri-substituted olefin, 2-methyl-2-octene, was also subjected to oxidative cleavage to give hexanoic acid in good yield (Enrty 6). The oxidation of an alternative trisubstituted olefin, such as 2-ethyl-1-hexene, lacking the internal vinylic hydrogen in their molecule resulted in small amounts of the corresponding *vic*-diol and 3-heptanone, probably given by further oxidation of the resulting *vic*-diol, without formation of carboxylic acid (Entry 7).

Table 2. The Oxidative Cleavage of Several Olefins with 35%-$H_2O_2$ by $H_2WO_4$ a)

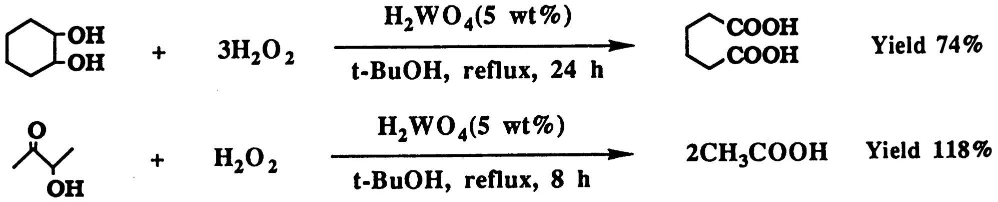
| Entry | Olefin | Product | | | |
|---|---|---|---|---|---|
| | | Yield/ % b) | | | |
| 1 |  |  | (48)c) |  | (12) |
| 2 |  |  | (62)c) |  | (18) |
| 3 |  |  | (72)d) |  | (7) |
| 4 |  |  | (33) |  | (16) |
| 5 |  |  | (54) |  | (2) |
| 6 |  |  | (60) |  | (14) |
| 7 |  |  | (11) |  | (32) |

a) Olefin (6.5 mmol) was allowed to react with 35%-$H_2O_2$ (26 mmol) in the presence of $H_2WO_4$ (5 wt%) under refluxing of t-BuOH (15 ml) for 24 h

b) Isolated yield. c) Isolated as dimethylester.

d) Isolated as monomethylester.

The present oxidative cleavage of olefins is believed to involve the formation of 1,2-diol which on subsequent dehydrogenation gives α-ketol, followed by C-C bond fission of the α-ketol.5,8) Actually, the treatment of 1,2-cyclohexanediol with 35%-$H_2O_2$ by $H_2WO_4$ gave adipic acid in good yield. Further, the oxidation of 3-hydroxy-2-butanone with 35%-$H_2O_2$ in the presence of $H_2WO_4$ afforded acetic acid in good yield.



The direct oxidative cleavage of olefins to carboxylic acids by the present catalyst-oxidant system is attractive from the viewpoint of both the oxidation chemistry and the industrial technolgy.

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