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A New Process for Preparing Dialdehydes by Catalytic Oxidation of Cyclic Olefins with Aqueous Hydrogen Peroxide

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Abstract: Dialdehydes were prepared by the reaction between cyclic olefins and aqueous hydrogen peroxide catalyzed by tungstic acid. Glutaraldehyde and adipaldehyde were synthesized by this method with good yield. Several different conditions were tested.

Oxidation of organic substrates with hydrogen peroxide is very attractive and has been long studied. Mugdan and Young [1] reported the hydroxylation of allylic alcohol with hydrogen peroxide catalyzed by various inorganic acids. Payne and Smith [2] studied the reaction between cyclohexene and hydrogen peroxide catalyzed by tunstic acid, in which cyclohexane—1,2—diol was obtained. In recent years, many useful reactions using hydrogen peroxide as oxidant have been developed, such as epoxidation of olefins and allylic alcohols [3,4,5], ketonization of alcohols and diols [5], oxidative cleavage of 1,2—diols [5,6] and olefins [5,7] to carboxylic acids. However, almost no attention has been devoted to the use of hydrogen peroxide for the oxidative cleavage of carbon—carbon double bonds to aldehydes, which is now performed by ozonization of olefins. Venturello and Ricci [6] suggested that aldehydes or semialdehydes were formed but unstable in the reaction medium while 1,2—diols were oxidatively cleaved to carboxylic acids. So there is no efficient method available, which is suitable for synthetic purpose, to obtain aldehydes or ketones by the reaction of olefins and hydrogen peroxide, according to the reaction (eq.(1))

(1)

Recently, Furukawa et al [8] reported that glutaraldehyde was obtained by oxidation of cyclopentene with H_2O_2 catalyzed by heteropoly acids in a non–aqueous medium. Since oxidation with non–aqueous solution of H_2O_2 is not always convenient and practical, we develop in this paper a synthetically useful procedure for the oxidative cleavage of olefins to aldehydes. Aqueous solution of hydrogen peroxide in conjunction with catalytic amount of tungstic acid, under mild condition, gives good selectivity. The method is particularly suitable for the synthesis of dialdehydes from cyclic olefins. Since tungstic acid is an unexpensive catalyst and aqueous hydrogen peroxide is a safe and non–polluting oxidant, a large–scale preparation and industrial manufacture of dialdehydes can be considered.

RESULTS

The catalysts, $WO_3 \cdot nH_2O$ ($n > 3$) was prepared by the method described in ref. 9. Na_2WO_4 was dissolved by hydrogen peroxide at pH 0–1. After bubbling SO_2 gas into the solution, $WO_3 \cdot nH_2O$ precipitated. Workup of the precipitate gave the catalysts . Catalysts thus obtained have better solubility in the reaction medium than that prepared by the conventional methods [14] because $WO_3 \cdot nH_2O$ was prepared at room temperature and not calcinated . Thus, the reaction catalyzed by $WO_3 \cdot nH_2O$ is taken place more easily than that catalyzed by $WO_3 \cdot H_2O$ and the reaction time is made short. But the final yields of products by these two kinds of catalyst are similar.

The reaction was carried out conveniently at given temperature by stirring a solution (alcohols were usually used as solvents) containing olefins, hydrogen peroxide and catalyst. The reaction should better been taken place in homogeneous solution, because $WO_3 \cdot nH_2O$ or $MoO_3 \cdot 2H_2O$ can not dissolve in those solvents which are not water soluble. When cyclopentene was oxidized by this method, gas chromatography analysis showed the formation of cyclopentene oxide at the beginning of the reaction, then it dissappeared progressively at the expense of the oxidative cleavage compounds and the hydrolysis compounds. At the end of the reaction, glutaraldehyde was obtained as the major product, according to the reaction (eq.(2))

 $+ 2H_2O_2 = OHC(CH_2)_3CHO + 2H_2O$ (2)

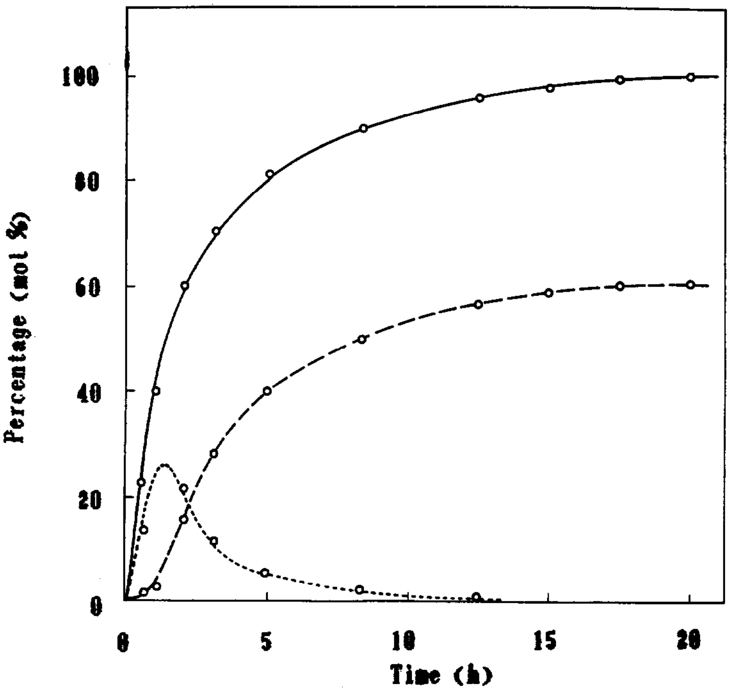


Figure 1 Oxidation of cyclopentene with hydrogen peroxide and $WO_3 \cdot nH_2O$ in t-BuOH at 35℃. Catalyst 1mmol, cyclopentene 56mmol, hydrogen peroxide (30%) 112mmol and t-BuOH 50ml. ——— cyclopentene consumption, - - - - glutaraldehyde formation, ······· cyclopentene oxide formation.

Figure 1 shows a typical plot of cyclopentene consumption, glutaraldehyde and cyclopentene oxide formation vs. time at 35℃, using $WO_3 \cdot nH_2O$ as catalyst and 30% aqueous solution of hydrogen peroxide as oxidant in t–BuOH. A complete conversion of cyclopentene is achieved and the yield of glutaraldehyde is good. The major by–product detected in the reaction is cyclopentane–1,2–diol, the hydrolysis compound of cyclopentene oxide. No oxygen evolution was observed during the reaction. Thus, the decomposition of hydrogen peroxide is negligible. When a stoichiometric amount of hydrogen peroxide required by eq.(2) is used, avoidance of decomposition of hydrogen peroxide is necessary for high yield of glutaraldehyde. This can be seen from Table I. The complete consumption of cyclopentene can not be achieved when H_2O_2: cyclopentene ratio is lower than 2. At ratios lower than 2, precipitation of white tungstic acid was observed and reaction was stopped though there were cyclopentene and hydrogen peroxide unreacted. $MoO_3 \cdot 2H_2O$, which also catalyzed the decomposition of hydrogen peroxide, gave low conversion and selectivity. When the ratio was higher than 3, further oxidation of aldehyde by hydrogen peroxide occured. Thus, a stoichiometric amount of hydrogen peroxide required by eq.(2) is suitable for the preparation of glutaraldehyde.

Table I [a]

H_2O_2: cyclopentene (mol)	cyclopentene consumption (mol%)	glutaraldehyde formation (mol%)
0.6	33.4	18.0
0.9	57.0	27.3
1.2	69.5	34.4
2.0	100	59.8
2.0 [b]	68.3	25.7

a Reaction condition: temp.=35℃, $WO_3 . nH_2O$ 1mmol, cyclopentene 34 mmol, H_2O_2 30% aqueous solution, t-BuOH 25 ml, reaction time = 20 h

b $MoO_3 \cdot 2H_2O$ (1 mmol) was used instead of $WO_3 \cdot nH_2O$

Reaction temperature also influences the yield of aldehydes. Figure 2 shows the yields of oxidative compounds from cyclopentene catalyzed by $WO_3 \cdot nH_2O$. At low reaction temperature, glutaraldehyde is the major product with a small amount of 1,2–diol. When the reaction temperature is above 45℃, the yield of aldehydes decreases drastically. Since glutaraldehyde is easy to be oxidized by the residual hydrogen peroxide at high temperature, this decrease may ascribe to the polymerization and further oxidation of the product. The yield of 1,2–diol also increases with the increasing temperature. So a large amount of polymer, carboxylic acids and 1,2–diol are present instead of aldehydes at high temperature and this condition is not favored for the preparation of aldehydes. On the other hand, the rate of reaction becomes very slow below 10℃. In order to keep a reasonable rate, 25—35℃ is a suitable range.

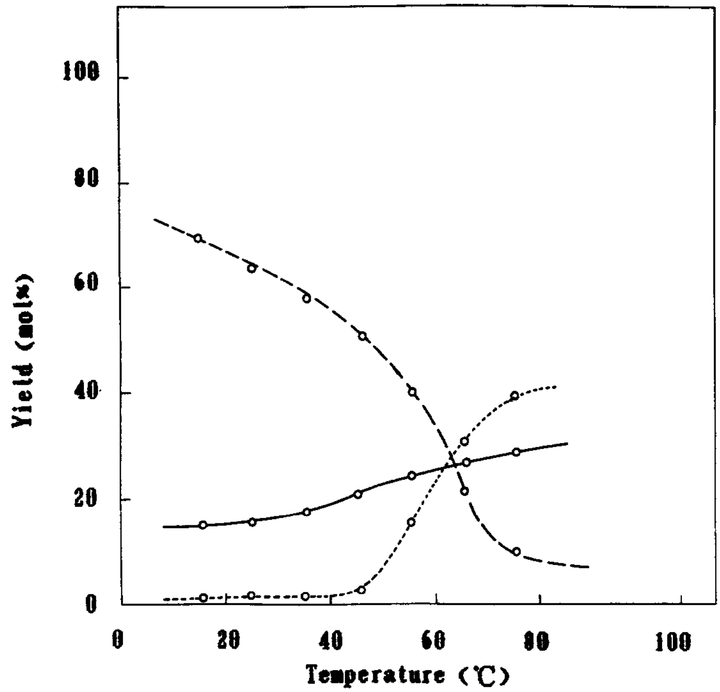


Figure 2 Oxidation of cyclopentene at various temperature. Reaction condition is as same as that in Figure 1. ----- glutaraldehyde, ——— 1, 2-cyclopentanediol, ······· glutaric acid.

The nature of solvents has great effect on the oxidation. Table II shows the results obtained from the oxidation of cyclopentene by 30% aqueous hydrogen peroxide in various solvents. High yield of glutaraldehyde is obtained in t–BuOH solvent with the lowest yield of hydroxylation compound of epoxide. When methanol is used as solvent, the major product is the hydroxylation compound: 2–methoxyl–1–cyclopentanol. The amount of the hydroxylation compounds decreases in the order: $-CH_3 > -C_2H_5 > -CH(CH_3)_2 > -C(CH_3)_3$, in accord with the increasingly steric effect of the R–group. The presence of water in the medium also has effect on the reaction. Figure 3 shows the results when cyclopentene was oxidized in t–BuOH with different

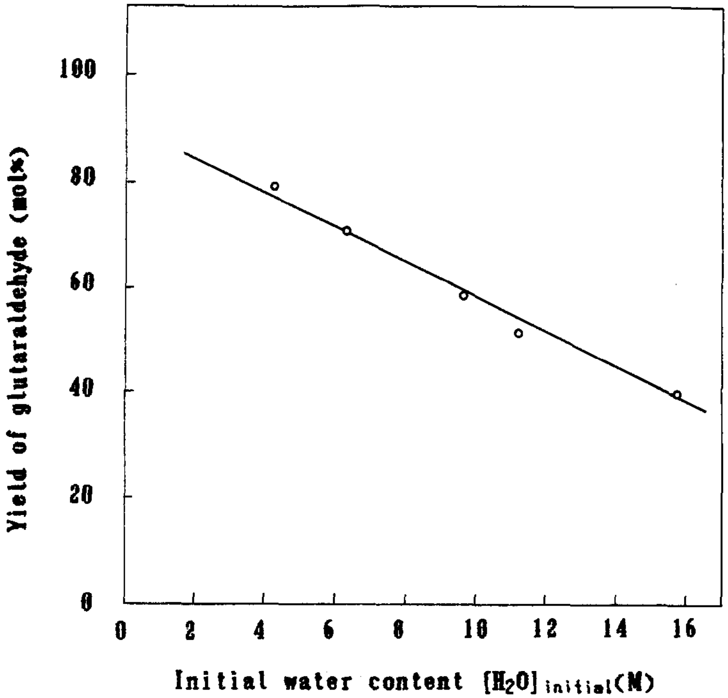


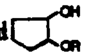
Figure 3 Water effect on oxidation of cyclopentene with H_2O_2 catalyzed by $WO_3 \cdot nH_2O$ in t-BuOH. Reaction condition: temp.=35 ℃, $WO_3 \cdot nH_2O$ 0.6 mmol, cyclopentene 34 mmol, H_2O_2 68 mmol, t-BuOH was added to keep the volume of the reaction mixture equal (31 ml), reaction time 35 h.

Table III Oxidation of cyclopentene [a]

solvent	yield (mol%)	
	glutaraldehyde	1, 2- diol
THF	47.1	19.0
dioxane	51.4	21.8
dimethoxyethane	54.1	29.5
1, 4-butyrolactone	31.3	37.5
acetonitrile	44.4	12.6

[a] Reaction condition: temp.=35℃, $WO_3 . nH_2O$ 0.6mmol, cyclopentene 34 mmol, H_2O_2(30%) 68 mmol, solvent 25 ml, reaction time = 20 h

Table II Oxidation of cyclopentene with H_2O_2 catalyzed by $WO_3 \cdot nH_2O$ in various solvents [a]

solvent	yield (mol%)		
	glutaraldehyde	1,2-diol	hydroxylation compound 
methanol[b]	12.1	22.1	60.0 (R=$-CH_3$)
methanol[c]	12.8	13.7	68.9
ethanol[b]	38.5	26.4	25.6 (R=$-C_2H_5$)
ethanol[c]	47.4	18.7	34.6
2-propanol[b]	57.4	19.6	7.4 (R=$-CH(CH_3)_2$)
2-propanol[c]	68.4	16.2	10.2
tert-butanol[b]	64.1	18.4	2.2 (R=$-C(CH_3)_3$)
tert-butanol[c]	79.9	11.6	2.7

a Reaction condition: temp.=35℃, $WO_3 . nH_2O$ 0.6mmol, cyclopentene 34 mmol, H_2O_2 68 mmol, solvent 25 ml, reaction time = 20 h

b 30% H_2O_2 was used, $[H_2O]_{initial}$ = 8.8M

c 50% H_2O_2 was used, $[H_2O]_{initial}$ = 4.2M

water content. In Table II it also gives the results of oxidation with 50% aqueous hydrogen peroxide in various solvents. These results seem that hydrogen peroxide solution can not be used at any dilution when high yield of aldehyde is desired. The oxidation is best carried out in t–BuOH solvent. Some other water soluble solvents, which have no trend to give hydroxylation compounds, were tested and the results are shown in Table III. The yield of glutaraldehyde is not satisfactory in those solvents. Greater trend of hydrolysis of epoxide is observed than that in alcohol solvents. The nature of oxidation in these solvents are not clear.

The reactivity of several different olefins towards hydrogen peroxide catalyzed by $WO_3 \cdot nH_2O$ is illustrated in Table IV. Terminal olefins have low reactivity than that of cyclic olefins. But in all cases the carbon–carbon double bond is cleaved and the aldehydes are produced in good yield or high selectivity.

Table IV Reactivity of olefins [a]

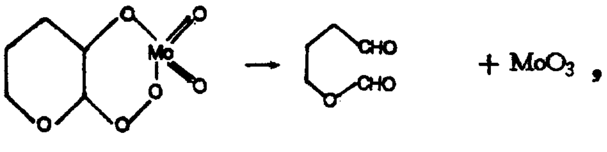
olefin	product (yield %)	conversion %
cyclopentene	glutaraldehyde (79.9) cyclopentane-1,2-diol (11.6)	100
cyclohexene	adipaldehyde (47.3) cyclohexane-1,2-diol (34.9)	90
1-heptene	hexanal (29.8) 1,2-heptanediol (4.1)	39.4
styrene	benzaldehyde (14.8) formaldehyde (n.d.)[b]	55.4
allylic alcohol	glycolaldehyde (n.d.)[b] formaldehyde (34.2)	53.3

a Reaction condition: temp.=35℃, $WO_3 \cdot nH_2O$ 0.6mmol, olefin 34 mmol, H_2O_2(50%) 68 mmol, t-BuOH 25 ml, reaction time = 20 h

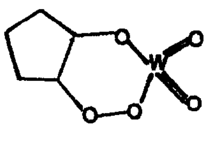
b The product was detected without quantitative analysis.

DISCUSSION

These results indicated that the aldehydes are prduced via the corresponding epoxides. Carbonyl compounds from oxidative cleavage of epoxides by peroxides has been observed by Mimoun [10] and Frimer [11]. Frimer [11], when using $MoO_5 \cdot$ HMPA to oxidize 3,4—dihydro—2H—pyran, suggested that the corresponding cleavage product, 4—formyloxy—butanal 2, was formed through the intermediate 1



1 2



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Oxidation of cyclopentene to glutaraldehyde may be occured through a similar intermediate 3 produced by the reaction between cyclopentene oxide and per—tungstic acid. A control experiment showed that cyclopentene oxide (or cyclohexene oxide) could conveniently be transfered to glutaraldehyde (or adipaldehyde) under the same condition under which cycloolefin was oxidized. The results are listed in Table V:

Table V Oxidation of epoxides [a]

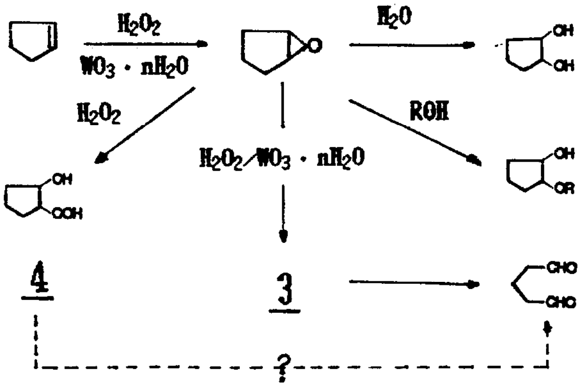
epoxide	catalyst	product (yield%)	conversion (%)
cyclopentene oxide[b]	$WO_3 \cdot nH_2O$	glutaraldehyde (54.7) cyclopentane-1, 2-diol (11.0)	100
cyclohexene oxide	$WO_3 \cdot nH_2O$	adipaldehyde (40.4) cyclohexane-1, 2-diol (29.4)	100
	$MoO_3 \cdot 2H_2O$	adipaldehyde (19.0) cyclohexane-1, 2-diol (34.6)	100
	H_2SO_4	adipaldehyde (12.2) cyclohexane-1, 2-diol (57.9)	90
	none	adipaldehyde (7.7) cyclohexane-1, 2-diol (7.9)	77

a. Reaction condition: temp. =35 ℃, epoxide 9.9 mmol, H_2O_2 (50%) 10.5 mmol, catalst 0.2 mmol, t-BuOH 10 ml, reaction time 35 h.

b. 30% aqueous H_2O_2 was used instead of 50% aqueous H_2O_2.

The epoxides were oxidized to the corresponding dialdehydes when $WO_3 \cdot nH_2O$ was used as catalyst. So it is reasonable to describe the feature of the oxidation reaction as Scheme 1

Scheme 1



It should be noted that the epoxide can also react with hydrogen peroxide to give 2—hydroxyl—hydroalkylperoxide, such as 4. Some workers pointed out [2] that this kind of peroxide could be transfered to dialdehydes if heat was introduced. Adipaldehyde was detected when the corresponding peroxide was heated at 160–180℃ [12]. It was also declared in some patents [13] that glutaraldehyde was prepared by heat treatment of 4 at high temperature. But it is doubtful that at the reaction temperature below 50℃, intermediate 4 thus formed will transfer to glutaraldehyde without any catalyst. So glutaraldehyde from the intermediate 3 seems more reasonable under the present condition.

The method mentioned above appears to be useful to prepare aldehydes by oxidative cleavage of olefins with hydrogen peroxide. It has some advantages compared with the ozonization method. With high selectivity of aldehyde at quite complete conversion of olefins, it is very suitable for the preparation of dialdehydes from cyclic olefins.

EXPERIMENTAL SECTION

Materials Reagent–grade solvents were used without further purification. Olefins such as cyclopentene (Fluka), 1–heptene (Merck), cyclohexene were distilled before use; other olefinic compounds and 30% or 50% aqueous solution of hydrogen peroxide were used without further purification. The following materials were prepared as authentic samples according to the methods described in literature: cyclopentene oxide and cyclopentane–1,2–diol [15a)], cyclohexene oxide [15b)], cyclohexane–1,2––diol [15c)] and adipaldehyde [15d)]. Other authentic samples of the oxidative products were purchased or prepared according to the authentic methods.

Preparation of Catalysts $WO_3 \cdot nH_2O$ ($n \geq 3$) was prepared by a new method describled in ref.9. $Na_2WO_4 \cdot 2H_2O$ was dissolved in water and 30% aquoous H_2O_2 was added ($W{:}H_2O_2 = 2{:}1$ (mol)). The solution was adjusted to pH 0–1 by dilute HCl and SO_2 gas was bubbled into the system. Hydrogen peroxide was destroyed and a yellow precipitate was obtained. It was easy to wash the precipitate with dilute HCl, water and ethanol. Dried in the air at room temperature, a yellow powder was obtained as $WO_3 \cdot nH_2O$ ($n \geq 3$), Na content $\leq$ 50 ppm. Other catalysts such as $MoO_3 \cdot 2H_2O$ and $WO_3 \cdot H_2O$ were prepared according to the methods outlined in ref. 14.

Oxidation Procedure (choosing oxidation of cyclopentene as an instance) In a 500–ml glass flask $WO_3 \cdot nH_2O$ was dissolved by 30% aqueous solution of hydrogen peroxide at room temperature. Then the solvent and cyclopentene were added. The flask was equipped with a condenser and a magnetic stirrer. The reaction mixture was stirred at the reaction temperature for 20 h. Then the solvent was distilled under reduced pressure and some water was added to the residue to prevent polymerization. The residual peroxide was destroyed by stirring the solution at 60℃ with 0.5% Pd/active carbon. The catalyst and Pd—C were filtered out and the crude product was concentrated to an adequate concentration, the yield of glutaraldehyde was 55—60% by titration analysis. Frational distillation of the crude product through a suitable column under reduced pressure gave pure glutaraldehyde, yield 48—50%.

Analysis The reaction was followed by gas chromatography; the products with high boiling point were detected on a flame—ion model GC using a 2—m column of SE—30 10%+PEG—20M 7% on white Chromosorb 101 and other products were detected on a thermo—conduct model GC using a 4—m column of PEG—20M 10% on white Chromosorb 102. Titration[16] was done when pure products were obtained. Identification of products was achieved by GLC—MS coupling and comparison of the mass spectra with those of authentic samples.

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