Oxidative C–C bond cleavage of *vic*-diols with H_2O_2 catalyzed by heteropolyacids

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Abstract

vic-Diols were oxidized with aqueous hydrogen peroxide in the presence of heteropolyacids to yield carboxylic acids as main products in good yields. Although the oxidation proceeded via α-ketol or α-diketone intermediates, another oxidation path such as direct C–C bond cleavage is suggested in the case of tetra-substituted *vic*-diols as substrates.

Keywords: *vic*-Diol; Hydrogen peroxide; Oxidation; Heteropolyacid; α-Ketol

1. Introduction

Oxidative C–C bond cleavage reactions of *vic*-diols were important from the viewpoint of synthesis of carbonyl compounds and have been used for determination of the molecular structure. Especially the oxidative cleavage of *vic*-diol moieties in sugars has been used for preparing chiral synthones [1]. Oxidants such as chromium trioxide (for example, Ref. [2]), lead tetraacetate [3], and periodic acid [4] are well known as C–C bond cleavage reagents. However, these oxidants contain harmful heavy metals and are therefore restricted for their use. There are a few reports of the oxidative C–C bond cleavage of *vic*-diols using an environmentally clean and inexpensive oxidant like hydrogen peroxide [5–7] or sodium hypochlorite [8–10] with a catalyst.

There are some reports that heteropolyacids are good catalysts for hydrogen peroxide oxidation [11]. Oxidation of *vic*-diols with aqueous hydrogen peroxide has been studied using tungstate ions as catalysts [5,6]. Venturello and Ricci used a mixture of tungstate and phosphate (or arsenate) as a catalyst and obtained carboxylic acids from *vic*-diols [5]. Ishii et al. have reported that quaternary ammonium tungstophosphates were effective as catalyst where active species for this oxidation were peroxotungstophosphates [6]. In both reports, tungstate ions were active for oxidative cleavage while molybdate ions were insufficient as the catalyst.

We have also reported an effective oxidation of phenols to *p*-benzoquinones with a hydrogen peroxide–heteropolyacid system in previous papers [12,13]. Here we report the oxidative cleavage of *vic*-diols using the hydrogen peroxide–heteropolyacid system.

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2. Results and discussion

1,2-Diphenyl-1,2-ethanediol (1 mmol) was treated with 31% aqueous hydrogen peroxide (2 ml) with a heteropolyacid (50 mg) in t-butanol (2 ml) under reflux conditions for 19 h. The oxidation results are listed in Table 1.

When 12-tungstophosphoric acid was used as catalyst, benzoic acid was obtained in a good yield by the C–C bond cleavage of the diol (run 8). The yields were calculated as two moles of the product was formed from one mole of the diols. t-Butyl benzoate as a by-product was formed by esterification of the benzoic acid in the presence of acid. Although it was reported that the catalytic activity of molybdate ions was insufficient for the oxidative C–C bond cleavage with hydrogen peroxide [5,6], 12-molybdophosphoric acid also worked as a good catalyst like as 12-tungstophosphoric acid (run 3). The similar C–C bond cleavage occurred with

other heteropolyacids (runs 9 and 10) or sodium 12-tungstophosphate (run 12). However, without catalyst (run 15) or in the presence of sulfuric acid (run 14), the total yields of benzoic acid and its ester were very low. These results show that the heteropolyacids work better as oxidative catalysts than as acid catalysts. The C–C bond cleavage oxidation specifically proceeded in t-butanol, and in ethanol the yield of benzoic acid was low and the amount of benzoin increased (run 6).

Time course of the oxidation was tested (runs 1–3). In the initial stage of the reaction, conversion of the diol was low and much amount of benzoin was formed. As the reaction proceeded, the yield of benzoin decreased. After 19 h, the reaction was completed and only trace amounts of benzoin were observed. These results show that benzoin was one of the intermediate of this oxidation. Furthermore, benzil was detected in 3% yield in the oxidation with the decreased

Table 1
Oxidation of 1,2-diphenyl-1,2-ethanediol with hydrogen peroxide catalyzed by heteropolyacid [a]

	Conv.		Yield [c] (%)				
run	catalyst [b]	(%)	$PhCO_2H$	$PhCO_2Bu^t$	PhCHO	benzoin	benzil
1	HPM [d]	59	22	tr	4	11	—
2	HPM [e]	95	40	1	8	15	—
3	HPM	100	77	3	—	tr	—
4	HPM [f]	97	47	—	14	12	—
5	HPM [g]	87	34	1	8	17	3
6	HPM [h]	49	5	—	13	9	—
7	HPM [i]	100	80	tr	tr	2	—
8	HPW	100	78	1	tr	—	—
9	HSM	100	79	2	tr	tr	—
10	HSW	80	55	1	10	5	—
11	NaPM	92	34	1	8	15	—
12	NaPW	100	67	1	5	tr	—
13	CPM	100	72	tr	3	—	—
14	H_2SO_4	74	25	—	10	5	—
15	—	66	34	—	—	3	—

[a] Diol: 1 mmol, H_2O_2 (31%): 2 ml, catalyst: 50 mg, t-BuOH: 2 ml, reflux, 19 h.
[b] HPM:$H_3PMo_{12}O_{40} \cdot nH_2O$, HPW: $H_3PW_{12}O_{40} \cdot nH_2O$, HSM: $H_4SiMo_{12}O_{40} \cdot nH_2O$, HSW: $H_4SiW_{12}O_{40} \cdot nH_2O$, NaPM: $Na_3PMo_{12}O_{40} \cdot nH_2O$, NaPW:$Na_3PW_{12}O_{40} \cdot nH_2O$, CPM: $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_{12}O_{40})^{3-}$.
[c] GC yields except for benzoic acid (isolated).
[d] Reflux for 3 h.
[e] Reflux for 12 h.
[f] 0.5 ml of H_2O_2 (31%) was used.
[g] 1 ml of H_2O_2 (31%) was used, and reflux for 7.5 h.
[h] EtOH (2 ml) was used instead of t-BuOH.
[i] 8.0 mmol of t-BuOOH was used instead of H_2O_2.

Table 2
Oxidation of vic-diols [$R^1R^2C(OH)C(OH)R^3R^4$] with hydrogen peroxide catalyzed by 12-molybdophosphoric acid [a]

Run	R^1	R^2	R^3	R^4	Products (yield [b]/%)
16	Ph	H	H	H	$PhCO_2H$ (57), PhCHO (1)
17	Ph	Me	Ph	H	$PhCO_2H$ (52), PhCHO (7), PhCOMe (69)
18	Ph	Me	Ph	Me	PhCOMe (91)
19	H	–(CH$_2$)$_4$–		H	adipic acid (50) as dimethyl ester [c]

[a] Diol: 1 mmol, H_2O_2 (31%): 2 ml, $H_3PMo_{12}O_{40} \cdot nH_2O$: 50 mg, t-BuOH: 2 ml, reflux, 19 h.
[b] Isolated yields except for benzaldehyde and acetophenone (GC yield).
[c] Esterification was carried out with $BF_3 \cdot CH_3OH$ after the reaction.

amount (1 ml) of hydrogen peroxide for 7.5 h (run 5). Such α-diketone formation from vic-diols was reported in the oxidation with the peroxotungstophosphate under biphasic conditions [14]. When the isolated products, that is, benzoin, benzil, and benzaldehyde, were oxidized with hydrogen peroxide in the presence of 12-molybdophosphoric acid, benzoic acid was formed in 56, 71, and 65% yields, respectively. It is thus likely that these compounds were intermediates of the oxidation.

The other vic-diols were oxidized with hydrogen peroxide in the presence of 12-molybdophosphoric acid (Table 2). The C–C bond cleavage occurred on the diol moieties, and carbonyl compounds, carboxylic acids and/or ketones, were obtained in high yields. The oxidation proceeded for an aliphatic diol like 1,2-cyclohexanediol (run 19) as well as phenyl substituted vic-diols. It is noteworthy that the bond cleavage also occurred on tetra-substituted vic-diol oxidation. It was reported that vic-diols were oxidized to carboxylic acids by way of α-ketols and aldehydes [5,6]. However, in the case of oxidation of 2,3-diphenyl-2,3-butanediol which never forms the corresponding α-ketol, the C–C bond cleavage did occur to produce acetophenone in good yield (run 18). This result suggests that the C–C bond cleavage directly occurred from diol moieties of the tetra-substituted vic-diols. Therefore, it is likely that the

way of the C–C bond cleavage depends on kinds of substituents on the vic-diols.

From the fact that the oxidation proceeded only in t-butanol, it can be considered that t-butyl hydroperoxide which formed from t-butanol and hydrogen peroxide was the first active species for the oxidation. The C–C bond cleavage actually occurred with t-butyl hydroperoxide as oxidant in the presence of 12-molybdophosphoric acid (Table 1, run 7). It was also reported by Yamawaki et al. that t-butyl hydroperoxide oxidized phenyl-1,2-ethanediol to benzoic acid in the presence of quaternary ammonium 12-molybdophosphoric acid [15]. Although t-butyl hydroperoxide can be formed from t-butanol and hydrogen peroxide in the presence of strong acid [16], the C–C bond cleavage did not accelerate in the presence of sulfuric acid (Table 1, run 14). These results, therefore, suggest that the second active species for the C–C bond cleavage existed, which was formed from the heteropolyacids and t-butyl hydroperoxide. It is likely that peroxo complexes of heteropolyacids are formed and then cleave the C–C bonds in vic-diols in the present oxidation.

3. Experimental

3.1. Oxidation of vic-diols

To the mixture of a vic-diol (1 mmol) and a heteropolyacid (50 mg) in t-butanol (2.0 ml), 31% aqueous hydrogen peroxide (2.0 ml, ca. 20 mmol) was added dropwise. The reaction mixture was refluxed under stirring for 19 h. After cooling the mixture to room temperature, aqueous sodium hydroxide solution were added. Reaction products were extracted with dichloromethane. Organic layer was dried over magnesium sulfate and the products were analyzed with gas chromatography over a Hicap-CBP1 column (Shimadzu) with a flame ionization detector using diphenyl as an internal standard. Aqueous layer was made acidic with di-

luted hydrochloric acid and the products were extracted with dichloromethane. The dichloromethane layer was dried over magnesium sulfate and the solvent was evaporated to give the corresponding carboxylic acid.

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