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Epoxidation of α, β-Unsaturated Carboxylic Acids with Hydrogen Peroxide by Heteropoly Acids

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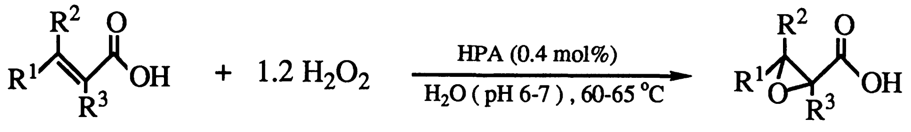
The epoxidation of α, β-unsaturated carboxylic acids with 35%-H_2O_2 was carried out by the use of heteropoly acids (HPA) as catalyst. Among the HPA examined, CWP, prepared from 12-tungstophospholic acid(WPA) and cetylpyridinium chloride(CPC), was found to be the most efficient catalyst. The CWP-H_2O_2 system provides an alternative method to prepare epoxy acids.

α, β-Unsaturated carboxylic acids have been epoxidized with aqueous hydrogen peroxide in the presence of catalytic amount of sodium tungstate as explored by Payne.[1] In recent years, Sharpless et al.[2] have reported that yields of some epoxy acids are substantially improved by a few simple modifications of the Payne procedure.

Recently, we and others have developed that the oxidations of organic substrates with aqueous hydrogen peroxide catalyzed by Keggin type[3,4] and non-Keggin type HPA.[5,6] For instance, tris(cetylpyridinium)12-tungustophosphate (CWP), $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})^{3-}$, which can be easily prepared from WPA and 3 equiv. of CPC,[3c] catalyzes the epoxidation of olefins and allylic alcohols to the corresponding epoxides,[3c] dehydrogenation of alcohols to ketones,[3c] oxidative cleavage of *vic*-diols and olefins to carboxylic acids,[3c] as well as lactonization of α, ω-diols to lactones,[3d] in satisfactory yields.

In continuation of this study, we extend the scope of HPA-catalyzed hyrdrogen peroxide oxidations by carring out the epoxidation of α, β-unsaturated carboxylic acids (Eq. 1).



(1)

In order to examine the potential of HPA catalysts for the epoxidation of α, β-unsaturated carboxylic acids, crotonic acid($\underline{1}$) was chosen as a model substrate and allowed to react under various conditions(Table 1).

A typical reaction was run as follows: $\underline{1}$(10 mmol, 0.86 g) in water(20 ml) was heated to 60-65°C under stirring, and 1 M-KOH was added dropwise until the solid acid was dissolved. The pH of the solution was adjusted to 6-7 by 1 M-KOH and/or 1 M-H_2SO_4. To the solution was added CWP(0.152 g, 0.04 mmol) and then 35%-H_2O_2 (1.2 g, 12 mmol). The pH of the solution was kept between 6 and 7. After stirring the mixture at 60-65 °C for 2 h, the reactant was acidified to pH 1 to 2 by 18 M-H_2SO_4, saturated with ammonium sulfate, and extracted several times with ether. The ether extracts were dried over $MgSO_4$, filtered and evaporated to give almost pure epoxycrotonic acid (2) (1.01 g) whose purity was determined by ^{1}H-NMR. Recrystallization of the crude product from chloroform gave 2 (0.76 g, 75%) as a white precipitate.

Table 1. Epoxidation of Crotonic Acid(1) with 35%-H_2O_2 by HPA under Several Reaction Conditions [a)]

Run	Catalyst	Time/h	pH	Crude product(%) (purity)[b)]
1	CWP	2	6-7	90(>98)(75)[c)]
2[d)]	CWP	12	-	no reaction
3	WPA	2	6-7	85(97)
4	CWP	12	4-5	8(35)
5	CWP	12	8-9	no reaction
6	CMP	12	6-7	49(45)
7	MPA	12	6-7	22(92)

a) 1(10 mmol) was allowed to react with 35%-H_2O_2(12 mmol) in the presence of catalyst(0.4 mol%) in water(20 ml)(pH 6-7) at 60-65 °C.
b) Determined by ^{1}H-NMR. c) Isolated yield. d) Chloroform was used as solvent.

Crotonic acid 1 was successfully epoxidized with 35%-H_2O_2 under the influence of catalytic amount of W-based HPA in water(pH 6-7) at 60 °C, giving epoxy acid 2 in good yield. Particularly, CWP showed high activity and selectivity for the epoxidation of 1. In contrast to the epoxidation of olefins and allylic alcohols by the present catalyst-oxidant system where the two-phase system using chloroform as solvent was employed,[3c)] the epoxidation of α,β-unsaturated carboxylic acids failed to occur in chloroform (run 2). It was found to be very important that the pH of the medium was kept in the range of 6 to 7 to complete the reaction. Under a weak acidic(pH 4-5) or basic(pH 8-9) medium, the reaction was markedly retarded (runs 4 and 5). Although the epoxidation of olefins and allylic alcohols by WPA in the absence of CPC took place with poor selectivity, 1 was epoxidized in good yield by WPA alone. Mo-based HPA catalysts, tris(cetylpyridinium)12-molybdophosphate (CMP) and 12-molybdophosphoric acid (MPA), were inadequate for the present epoxidation (runs 6 and 7). The CWP seemed to be held the Keggin structure after the reaction, though the IR absorption bands at 1079, 989, 977, 894, 808, and 754 cm^{-1}, which are attributed to the Keggin type HPA,[7] of the recovered CWP became weaker than those of the CWP,[8] without any considerable shifts in their positions.

It is interesting to compare the epoxidation of 1 by the CWP with that by the conventional tungstate catalyst (Table 2).

Table 2. Comparison of Epoxidations of 1 by CWP and Tungstate Catalyst

Method	Catal. (wt%)	pH	Time / h	Crude product (%) (purity)
Payne[a]	$Na_2WO_4 2H_2O$ (38.4)	4-5.5	1	50 (purified)
Sharpless[b]	$Na_2WO_4 2H_2O$ (56.8)	5.8-6.8	3	83.1 (86)
Present	CWP (18.5)	6-7	2	90 (>98)

a) Cited from Ref. 1. b) Cited from Ref. 2.

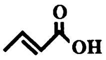
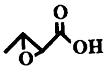
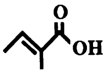
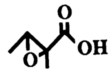
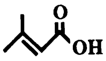
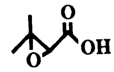
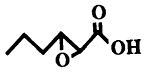
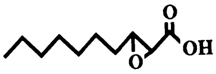
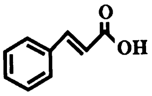
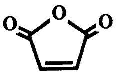
Payne and Sharpless have obtained epoxy acid 2 in 50% yield (isolated) and 83.1% yield (purity 86%) by the use of 0.1 equiv. (38.4 wt%) and 0.15 equiv. (56.8 wt%) of tungstate, respectively. However, the present epoxidation by CWP was accomplished with high conversion (90%) and selectivity (>98%) by the use of 0.04 equiv. (18.5 wt%) of CWP. Therefore, the CWP-H_2O_2 system seems to be a prominent method to synthesize epoxy acids.

The epoxidation of several α,β-unsaturated acids by CWP-H_2O_2 system is shown in Table 3.

2,3-Substituted carboxylic acid, 2-methylcrotonic acid (3), was epoxidized more easily than 1, giving the corresponding epoxy acid 4 in good yield. However, 3-methylcrotonic acid (5) was epoxidized with difficulty to form epoxy acid 6 in somewhat lower selectivity. The epoxidation of 2-hexenoic acid (7) proceeded sluggishly, but epoxy acid (8) was obtained in good yield. However, the same oxidation by WPA led to 8 in lower selectivity than that by CWP. 2-Decenoic acid (9) failed to epoxidize under the conditions employed above. This is believed to be due to the rise of the lipophilicity of carboxylic acid with the lengthening of the carbon chain. When the mixed solvent of ethanol:water (1:1) was employed, epoxide 10 was obtained in about 50% yield. Cinnamic acid (11) and maleic anhydride (12) were not epoxidized by the present catalyst-oxidant system.

In conclusion, W-based HPA, in particular CWP, were found to be an efficient catalyst for the epoxidation of some α,β-unsaturated carboxylic acids. The CWP-H_2O_2 system is of interest as an alternative method to prepare epoxy acids.

Table 3. Epoxidation of α, β-Unsaturated Acids by CWP-H_2O_2 System[a)]

Run	Substrate	Time/h	Conv./%	Product	Selec./%
1	**1** 	2	90	**2** 	>98
2	**3** 	0.7	89	**4** 	97
3	**5** 	4	70	**6** 	83
4	**7** 	8	93(86)[b)]	**8** 	97(60)[b)]
5[c)]	**9** 	8	56	**10** 	80
6	**11** 	24	no reaction		
7	**12** 	24	no reaction		

a) Reactions were carried out by the same method described in Table 1.
b) WPA was used as catalyst. c) H_2O_2:EtOH(1:1) was used as solvent.

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8) The IR specrta of CWP and the recovered CWP, were measured accurately by FT-IR (Perkin Elmer FT-1640, KBr pellet, 4 cm^{-1} resolution) as follows: CWP(recovered CWP): 3019(3019), 2926(2926), 2854(2854), 1633(1634), 1487(1487), 1467(1467), 1215(1215), 1079(1079), (1054), 989(988), 978(977), (951), 896(894), 808(808), 750(754), 680(681), 669(669) cm^{-1}.

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