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Hydrogen Peroxide Oxidation Catalyzed by Heteropoly Acids Combined with Cetylpyridinium Chloride: Epoxidation of Olefins and Allylic Alcohols, Ketonization of Alcohols and Diols, and Oxidative Cleavage of 1,2-Diols and Olefins

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A general and versatile oxidation catalyst has been developed by using hydrogen peroxide as the oxidant. Olefins and allylic alcohols were epoxidized with commercially available hydrogen peroxide (30–35% H_2O_2) using a combination of Mo- or W-based heteropoly acids, $H_3PMo_{12}O_{40}$(MPA) or $H_3PW_{12}O_{40}$ (WPA), with an appropriate ammonium salt such as cetylpyridinium chloride (CPC), under two-phase conditions using chloroform as the solvent (Tables I and II). The tris(cetylpyridinium) 12-tungstophosphate (CWP), $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})^{3-}$, prepared independently from WPA and 3 equiv of CPC, catalyzes the efficient ketonization of the secondary hydroxy group of alcohols and diols with H_2O_2 under homogeneous conditions using *tert*-butyl alcohol as the solvent (Table III). Under the same conditions, oxidative cleavage of vic-diols was successfully conducted by the CWP–H_2O_2 system to give carboxylic acids in good yields (Table IV). This catalyst–oxidant system was also efficient for the oxidative cleavage of carbon–carbon double bonds of olefins which provides a new valuable conversion of olefins to carboxylic acids (Table V).

The oxidation of organic substrates with aqueous hydrogen peroxide is very attractive from the viewpoint of industrial technology and synthetic organic chemistry since aqueous hydrogen peroxide is cheap, environmentally clean and easy to handle. For instance, extensive attention has been devoted for a long time to the direct epoxidation of olefins by aqueous hydrogen peroxide.[1] In recent years, it has been reported that olefins can be epoxidized by molybdenum and tungsten derivatives as catalysts with dilute hydrogen peroxide under phase-transfer conditions.[2] Heteropoly acids (HPA) such as 12-molybdophosphoric acid (MPA) or 12-tungstophosphoric acid (WPA) are often used not only for the oxidation of organic substrates but also for many acid-catalyzed reactions, because they possess the dual catalytic functions of oxidizing ability and strong acidity.[3] The use of HPA for the oxidation of olefins with H_2O_2 generally produces trans-glycols because of the subsequent cleavage of the oxirane ring of the resulting epoxides by electrophilic attack of strongly acidic HPA.[4] However, it has been found that MPA combined with cetylpyridinium chloride (CPC) produces, in situ, tris(cetylpyridinium) 12-molybdophosphate (CMP), $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_{12}O_{40})^{3-}$. The reagent catalyzes the epoxidation of allylic alcohols with commercially available aqueous hydrogen peroxide (30–35% H_2O_2) under the two-phase conditions using chloroform as the solvent.[5] Furthermore, CMP, by using *t*-BuOOH as the oxidant, catalyzed also the selective oxidation of the secondary hydroxy groups of alcohols and diols.[6]

On the other hand, oxidative cleavage of 1,2-diols and carbon–carbon double bond of olefins to carboxylic acids is one of the most frequently used transformation in the field of synthetic organic chemistry. For this type of oxidative cleavage of 1,2-diols, oxidation with periodic acids[7] or lead tetraacetate[8] is usually employed. Ozonolysis[9] with oxidative workup and oxidation with chromium(VI),[10] permanganate,[11] and ruthenium[12] reagents are long-standing methods for the oxidative cleavage of olefins. In general, it is difficult to accomplish the oxidative cleavage of olefinic double bonds with usual oxidants such as hydrogen peroxide. More recently, Venturello has explored the oxidative cleavage of 1,2-diols with H_2O_2 in the presence of tungstate in conjunction with phosphate (or arsenate) ions under acidic condition.[13]

In this paper, we describe full details of epoxidation of olefins and ketonization of alcohols with aqueous hydrogen peroxide catalyzed by heteropoly acids. Further, this method has been extended to oxidative cleavage of 1,2-diols and olefins to carboxylic acids.

(A) Epoxidation of Olefins and Allylic Alcohols with Hydrogen Peroxide. To evaluate the potential of heteropoly acids for the epoxidation of olefins, 1-octene (1) was epoxidized to 1,2-epoxyoctane (2) with 35% H_2O_2 by Mo- and W-based heteropoly acids under several reaction conditions (Table I).

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[11] (a) House, H. O. *Modern Synthetic Reactions* 2nd ed.; W. A. Benjamin: New York 1972; p 275. (b) Trahanovsky, W. S., Ed. *Oxidation in Organic Chemistry*; Academic: New York, 1982; Part D, p 147.

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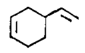
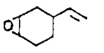
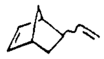
Table I. Epoxidation of Olefins with H_2O_2 Catalyzed by Heteropoly Acids under Various Conditions[a]

run	substrate	catal	additive (equiv)	time, h	conv, %	product[b] (selectivity, %)
1	**1**	H_2MoO_4	CPC (2)	24	trace	**2** (trace)
2	**1**	H_2WO_4	CPC (2)	24	trace	**2** (trace)
3	**1**	WPA	CPC (3)	5	82	**2** (>98)
4[c]	**1**	WPA	CPC (3)	24	37	**2** (89)
5[d]	**1**	WPA	CPC (3)	24	58	**2** (8)[e]
6	**1**	CWP		12	79	**2** (96)
7	**1**	MPA	CPC (3)	24	11	**2** (88)
8	**1**	CMP		24	41	**2** (>98)
9	**1**	SWA[f]	CPC (4)	24	trace	
10	**1**	MWP[g]	CPC (3)	24	24	**2** (98)
11	**1**	PCMP[h]		24	31	**2** (>98)
12	**1**	PCWP[h]		6	75	**2** (92)
13	**1**	WPA	CTMAB (3)[i]	24	80	**2** (95)
14	**1**	WPA	TOMAC (3)[j]	24	77	**2** (98)
15	**1**	WPA	TBAB (3)[k]	24	11	**2** (98)
16	**3**	WPA	CPC (3)	24	96	**4** (>98)
17	 **5**	WPA	CPC (3)	2	96	 (>98) **6**
18	**5**	MPA	CPC (3)	24	66	**6** (92)
19	**5**	CWP		3	97	**6** (>98)
20	**5**	CMP		24	66	**6** (94)
21	 **7**	WPA	CPC (3)	3	90	 (90) **8**

[a] Substrate (6.5 mmol) was allowed to react with 35% H_2O_2 (9.8 mmol) in the presence of catalyst (0.026 mmol) in $CHCl_3$ (15 mL) at 60 °C. [b] Determine by VPC. [c] Benzene (15 mL) was used as solvent. [d] *t*-BuOH (15 mL) was used as solvent. [e] 1,2-Octanediol was obtained in about 60% selectivity together with heptanoic acid (34%). [f] SWA: $H_4SiW_{12}O_{40}$. [g] MWP: $H_3PMo_6W_6O_{40}$. [h] See Experimental Section for preparation of peroxo complexes PCMP and PCWP. [i] CTMAB: $C_{16}H_{39}N^+(CH_3)_3Br^-$. [j] TOMAC: $CH_3N^+(C_8H_{17})_3Cl^-$. [k] TBAB: $(C_4H_9)_4N^+Br^-$.

The epoxidation of **1** with H_2O_2 was not catalyzed by either molybdate or tungstate ions alone even in the presence of 2 equiv of CPC (runs 1 and 2). The epoxidation of **1** to **2** was successfully carried out under the influence of WPA in the presence of 3 equiv of CPC (abbreviated as the WPA/CPC system) under the two-phase conditions using chloroform as the solvent (run 3). However, the same reaction in benzene led to a considerable decrease of the yield of **2** (run 4). Homogeneous reaction using *tert*-butyl alcohol as the solvent afforded principally cleaved product, 1,2-octanediol, together with a small amount of heptanoic acid (run 5). Tris(cetylpyridinium) 12-tungstphosphate (CWP), $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})^{3-}$, prepared in advance from WPA and 3 equiv of CPC, was slightly less effective than WPA/CPC system (run 6). Mo-based heteropoly acids were found to be less active than the corresponding W-based heteropoly acids (runs 7 and 8). The epoxidation by the alternative heteropoly acids H_4SiWO_{40} and $H_3PMo_6W_6O_{40}$ was also examined under similar conditions as above, but these two were less efficient than WPA (runs 9 and 10). Peroxo complexes PCMP[14] and PCWP,[15] prepared from MPA or WPA, CPC and H_2O_2, respectively, also catalyzed the epoxidation of **1** to **2** in high selectivity (runs 11 and 12). The effect of ammonium salts on the WPA-catalyzed epoxidation of **1** was examined, and it was found that the epoxidation was facilitated by the use of ammonium salts containing at least one long alkyl group in the molecule (runs 13–15).

Cyclooctene (**3**) was also epoxidized satisfactorily by the WPA/CPC system, giving cyclooctene oxide (**4**) in good yield (run 16). The epoxidation of 4-vinyl-1-cyclohexene (**5**), which involves two carbon–carbon double bonds whose reactivities are moderately different, took place regioselectively, but not stereoselectively, to give a stereoisomeric mixture of *cis*- and *trans*-4-vinyl-1,2-epoxycyclohexanes (**6**) (cis/trans = ca. 1/1) in almost quantitative yield (run 17). The epoxidation of 5-vinylbicyclo[2.2.1]hept-2-ene (**7**) could be achieved regio- and stereoselectively, affording *exo*-2,3-epoxy-5-vinylbicyclo[2.2.1]heptane (**8**) (run 21).

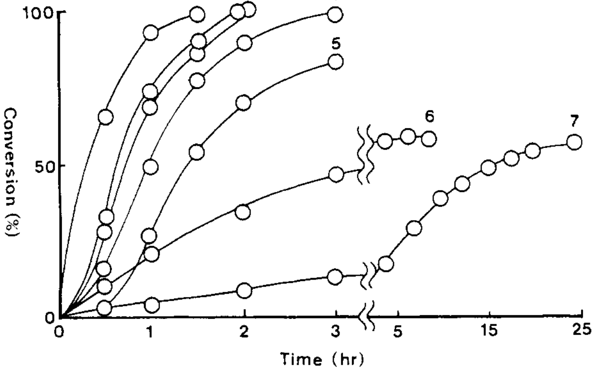


Figure 1. Time-dependence curves for the epoxidation of **5** to **6** by heteropoly acids under several reaction conditions: **5** (6.5 mmol), H_2O_2 (9.8 mmol), catalyst (0.026 mmol), CPC (0.078 mmol), $CHCl_3$ (15 mL) at 60 °C. (1) WPA/CPC; (2) CWP + 1 N H_2SO_4 (10 μL); (3) CWP + 3.8 N HCl (20 μL); (4) CWP, (5) CWP + 10 N H_2SO_4 (10 μL); (6) CMP; (7) MPA/CPC.

The reaction of **5** with H_2O_2 under various reaction conditions shows some significant features of the present heteropoly acid catalyzed epoxidations (Figure 1).

Comparing the three curves observed in tungsten series shows the effect of the acidity on the epoxidation. The initial epoxidation rate by WPA/CPC system was 1.8 times faster than that by CWP catalyst. There is a significant difference in the catalytic system of WPA/CPC and CWP. In the WPA/CPC system which produces CWP with evolution of hydrogen chloride (Scheme I), the reaction medium is slightly acidic, but in the CWP system, the medium is not acidic. The fact that epoxidation proceeded

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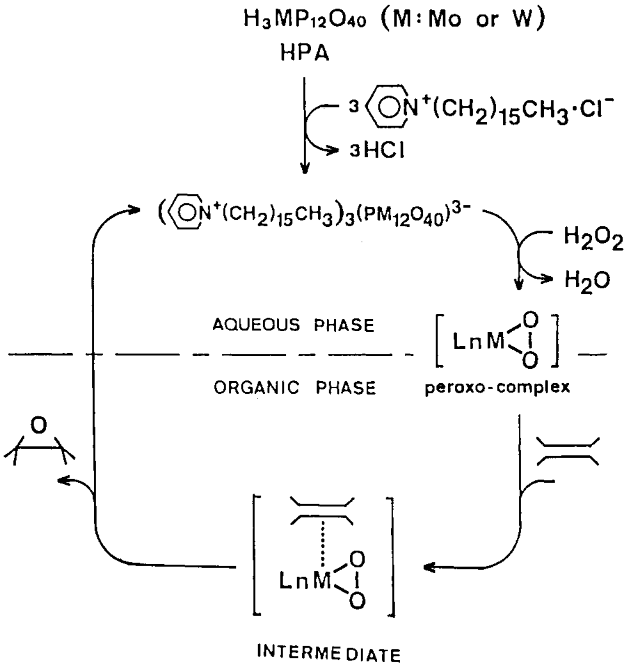
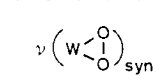
[14] Ishii, Y.; Yamawaki, K.; Yoshida, T.; Ura, T.; Ogawa, M. *J. Org. Chem.* **1987**, *52*, 1868.

[15] Since peroxo complex PCWP was not formed by treating CWP with 35% H_2O_2, it was prepared by treating WPA in 35% H_2O_2 with CPC (see Experimental Section).

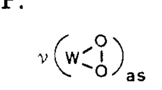
Scheme I. Conceivable Epoxidation Path via Peroxo-Type Intermediate Catalyzed by Heteropoly Acids Combined with Cetylpyridinium Chloride with Hydrogen Peroxide



more rapidly with the WPA/CPC system suggests that the tungsten-catalyzed epoxidation is accelerated under weak acidic media. Indeed, the epoxidation of **5** by CWP catalyst was facilitated by the addition of a very small amount of hydrochloric acid or dilute sulfuric acid to the reaction medium, but the addition of more concentrated sulfuric acid decreased the rate of epoxidation. Contrary to the behavior of tungsten-catalyzed epoxidation where the WPA/CPC system is more effective than CWP, in molybdenum-catalyzed epoxidation, the MPA/CPC system was less efficient than CMP. These results indicate that the epoxidation by the present catalyst–oxidant system depends subtly upon the acidity of the reaction medium. Owing to the complexity of the two-phase reaction medium, it is difficult to predict accurately the effect of acidity of the aqueous phase on epoxidation. In such a system, a peroxo complex of Mo or W which serves the actual epoxidizing agent is formed in the aqueous phase, and it is transferred to the chloroform phase where epoxidation takes place (Scheme I). In fact, the treatment of CMP with H_2O_2 in water gave a peroxomolybdenum complex (PCMP), which involves 1.4–2.4 mmol/g of active oxygen, and PCMP was obtained as a pale yellow to white precipitate moderately soluble in chloroform.[14] However, the same treatment of the corresponding tungsten compound CWP with H_2O_2 gave a white precipitate whose iodometry and IR spectrum showed no presence of peroxo oxygen. When a solution of WPA in aqueous hydrogen peroxide was added to CPC in water, a peroxotungsten complex (PCWP) was found to be formed. This observation indicates that the acidity of the reaction medium influenced not only the rate of the epoxidation but also the formation of peroxo complexes. The IR spectrum of PCWP was quite different from that of CWP, and the characteristic absorption bands at 545 and 570 cm^{-1} were assigned respectively to I and II.[16] The amount of active oxygen contained in PCWP which was estimated to be 1.1–1.5 mmol per gram by iodometry was found to be slightly lower than that of PCMP.



I



II

In the catalytic cycle for this epoxidation, the peroxo species of Mo or W has been predicted as the key intermediate,[17] shown in Scheme I.

It is important to clarify whether the peroxo species predicted in Scheme I was the same as peroxo complex PCMP (or PCWP), prepared from MPA (or WPA), CPC, and H_2O_2, or not. The elemental analyses of the catalysts recovered from the reaction system after the epoxidation of **5** by both CMP and CWP catalysts were in almost agreement with those CMP and CWP, respectively, having Keggin structure.[18] In addition, the IR spectra of the recovered CMP and CWP are in fair agreement with those of the starting CMP and CWP, respectively. These findings indicate that the Keggin structure of CMP and CWP is held after the epoxidation. However, the elemental analysis data of PCMP (or PCWP), prepared independently from MPA (or WPA), CPC, and H_2O_2, deviated considerably from the constitution calculated from an idealized compound, CMP·n[O] (or CWP·n[O]) bonded peroxo oxygen to CMP (or CWP).[19] Furthermore, the IR spectrum of the PCMP recovered after the stoichiometric reaction with olefin **1** which gives epoxide **2** was very analogous to that of the original PCMP except for the broadening of the absorption bands in the range of 545 to 570 cm^{-1}. Therefore, the peroxo complexes, PCMP and PCWP, seem to be alternative compounds having different structures from the peroxo intermediates appeared in the catalytic cycle of the Scheme I. Further characterization of the peroxo complexes, PCMP and PCWP, is currently under way.[20] The PCMP and PCWP thus obtained oxidized not only stoichiometrically olefins to epoxides and secondary alcohols to ketones but also epoxidized catalytically **1** to **2** with H_2O_2 as shown in Table I (runs 11 and 12). Recently, it has been reported that a peroxotungsten complex can be prepared by treating pertungstic acid, derived from H_2WO_4 and H_2O_2, with 4% phosphoric acid in the presence of tetrahexylammonium chloride.[21]

Table II shows the epoxidation of various allylic alcohols with H_2O_2 by Mo- and W-based heteropoly acids.

A variety of allylic alcohols were smoothly epoxidized under ambient temperature (about 25 °C) to give the corresponding epoxy alcohols in good yields. For example, *trans*-2-buten-1-ol (**9**) and 3-methyl-2-buten-3-ol (**11**) were converted satisfactorily to 2,3-epoxy-1-butanol (**10**) and 2,3-epoxy-3-methyl-1-butanol (**12**), respectively, by the CWP catalyst. Unlike the epoxidation of olefins where

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(16) (a) Mimoun, H.; Sajas, L. *Bull. Soc. Chim. Fr.* **1969**, 1481. (b) Le Carpentier, J. M.; Weiss, R. *Acta. Crystallogr., Sect. B* **1972**, *B28*, 1481.

(17) The epoxidation path via such a peroxo species of molybdenum or tungsten has already been pointed out by Mimoun. Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734.

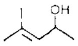
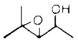
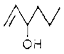
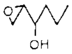
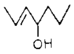
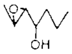
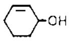
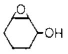
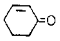
(18) Elemental analyses of the catalysts recovered were as follows. Calcd for $C_{63}H_{114}N_3Mo_{12}O_{40}P$ (CMP): C, 27.65; H, 4.21; N, 1.54. Found: C, 28.70; H, 4.47; N, 1.42. Calcd for $C_{63}H_{114}N_3W_{12}O_{40}P$(CWP): C, 19.96; H, 3.03; N, 1.11. Found: C, 20.96; H, 3.15; N, 1.06.

(19) Elemental analyses of PCMP and PCWP were as follows. Found for PCMP: C, 43.66; H, 6.87; N, 2.42. Found for PCWP: C, 36.18; H, 5.48; N, 1.94. If the constitutions of the PCMP and PCWP are assumed to consist to idealized structure having the Keggin unit, about 2.4 and 1.5 mmol of active oxygen per gram of PCMP and PCWP correspond to CMP·6[O] and CWP·[O], respectively, whose compositions were calculated as follows. Calcd for $C_{63}H_{114}N_3Mo_{12}O_{46}P$ (CMP·6[O]): C, 26.72; H, 4.06; N, 1.48. Calcd for $C_{63}H_{114}N_3W_{12}O_{45}P$ (CWP·5[O]): C, 19.55; H, 2.96; N, 1.09.

(20) Despite attempts to obtain the single crystal of PCMP or PCWP for X-ray analysis, these crystals have not yet been isolated.

(21) Venturello, C.; Aloisio, R. D.; Bart, J. C.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107.

Table II. Epoxidation of Allylic Alcohols with H_2O_2 Catalyzed by Heteropoly Acids[a]

run	substrate	catal	time, h	conv, %	product, (selectivity, %)
1	**9**	CWP	15	98	**10** (>98)
2	**9**	WPA/CPC	15	98	**10** (>98)
3	**9**	CMP	15	74	**10** (>98)
4	**9**	MPA/CPC	15	72	**10** (>98)
5	**11**	CMP	24	82	**12** (98)
6	**11**	CWP	24	98	**12** (>98)
7	 **13**	CMP	24	91	 (98) **14**
8	**13**	CWP	24	98	**14** (85)
9	 **15**	CMP	12	98	 (94) (98:2)[c] **16**
10	**15**	CWP	15	90	**16** (85) (94:6)[c]
11[b]	 **17**	CMP	24	64	 (85) (55:45)[c] **18**
12	 **19**	CMP	24	90	 (>98) (65:35)[c] **20**
13[b]	 **21**	CMP	24	52	 (63) **22**  (37) **23**
14	**21**	CWP	6	69	**22** (10) **23** (87)

[a] Substrate (6.5 mmol) was allowed to react with 35% H_2O_2 (9.8 mmol) in the presence of catalyst (0.026 mmol) in $CHCl_3$ (15 mL) at room temperature. [b] At 60 °C. [c] threo:erythro ratio.

CWP was less efficient than WPA/CPC, the activity of CWP was comparable to that of WPA/CPC (run 2). In the epoxidation of allylic alcohols, W-based heteropoly acids were more active than the corresponding Mo ones (runs 1–6). The epoxidation of geraniol (**13**) proceeded chemoselectively to give epoxygeraniol **14** in which the allylic double bond was epoxidized. The epoxidation of 4-methyl-3-penten-2-ol (**15**) proceeded with high stereoselectivity to form *threo*-3,4-epoxy-4-methyl-2-pentanol (**16**). Similar high stereoselectivity for **15** has been reported in the epoxidation with organic peracid or V, Mo,[22] and Al[23] catalysts with *t*-BuOOH. It has recently been described that tungstate-catalyzed epoxidation of **15** with H_2O_2 under buffer condition gives **16** in 90% threo selectivity.[24] The epoxidation of 1-hexen-3-ol (**17**) occured with some difficulty, giving a diastereomeric mixture of threo and erythro isomers **18** in a ratio of 55:45. 2-Hepten-4-ol (**19**) was epoxidized in good yield to form a diastereoisomer of 2,3-epoxy-4-heptanol (**20**) (threo:erythro = 65:35). 2-Cyclohexen-1-ol (**21**) was converted to 2,3-epoxy-1-cyclohexanol (**22**) and 2-cyclohexen-1-one (**23**) in a ratio of 63:37 by CMP, but by CWP the dehydrogenation occurred in preference to the epoxidation to give **23**.

(B) Ketonization of Alcohols and Diols with Hydrogen Peroxide. Table III shows the ketonization of a variety of alcohols and diols with H_2O_2 under the influence of heteropoly acids combined with CPC. The oxidation of 2-octanol (**24**) to 2-octanone (**25**) by heteropoly acids under several conditions indicates the catalytic feature of heteropoly acids for the ketonization of alcohols with H_2O_2.

In contrast to epoxidation in the two-phase condition, the ketonization of **24** to **25** was successfully carried out under homogeneous conditions using *tert*-butyl alcohol as the solvent. It is interesting to note that H_2O_2 was more efficient than *t*-BuOOH for the W-catalyzed ketonization (run 3), despite the fact that *t*-BuOOH was much more effective than H_2O_2 in the Mo-catalyzed ketonization[6] (runs 5 and 7). Benzene was used as the solvent when *t*-BuOOH was employed as the oxidant. The failure of ketonization of alcohols with H_2O_2 by CMP is believed to be due to the difficulty of regenerating the peroxo species in the reaction system, probably because of the coordination of alcohols to the CMP. In fact, in the absence of alcohol, CMP reacted readily with H_2O_2 to form a peroxo complex, PCMP, and treatment of alcohol **24** with stoichiometric amount of PCMP afforded ketone **25** in almost theoretical yield.[14] The ketonization of **24** by the WPA/CPC system, which generates CWP in situ with hydrogen chloride, was markedly retarded compared to that of CWP (run 8), although the epoxidation of olefins was facilitated under weakly acidic conditions. Therefore, the addition of sulfuric acid to the CWP-catalyzed oxidation of **24** resulted in a considerable decrease in the yield of 25 (run 9). The oxidation of primary alcohols such as 1-octanol (**26**) hardly took place with the present catalyst–oxidant system, affording octanal (**27**) in poor yield (run 10). Cyclic alcohols, cyclohexanol (**28**), L-menthol (**30**), and borneol (**32**), were oxidized with H_2O_2 to form cyclohexanone (**29**), L-menthone (**31**), and camphor (**33**), respectively. It is noteworthy that L-menthol (**30**) was oxidized in good yield by CWP, although **32** was oxidized with difficulty by the CMP-*t*-BuOOH system (run 13). In the oxidation of diols possessing both the primary and secondary hydroxy groups, the secondary hydroxyl group was oxidized chemoselectively, giving the hydroxyl ketones in good yields. For instance, 2-ethyl-1,3-hexanediol (**34**) and 2,2,4-tri-

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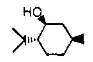
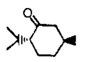
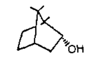
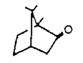
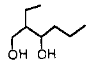
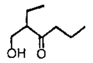
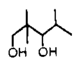
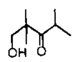
(22) (a) Tanaka, S.; Yamamoto, H.; Nozaki, H.; Sharpless, K. B.; Michaelson, R. C.; Cutting, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 5254. (b) Rossiter, B. E.; Verhoeven, T. R.; Sharpless, K. B. *Tetrahedron Lett.* **1979**, *20*, 4733.

(23) (a) Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1980**, *21*, 1657. (b) Takai, K.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3791.

(24) Part D: Delpech, B.; Lett, P. *Tetrahedron Lett.* **1986**, *27*, 711.

Table III. Oxidation of Alcohols and Diols with H_2O_2 Catalyzed by Heteropoly Acids[a]

run	substrate	catal	solv	conv, %	product (selectivity, %)
1	**24**	CWP	*t*-BuOH	90	**25** (>98)
2	**24**	CWP	$CHCl_3$	17	**25** (>98)
3[c]	**24**	CWP	*t*-BuOH	12	**25** (>98)
4[c]	**24**	CWP	Ph-H	35	**25** (>98)
5	**24**	CMP	*t*-BuOH	31	**25** (>98)
6[c]	**24**	CMP	*t*-BuOH	30	**25** (>98)
7[c]	**24**	CMP	Ph-H	71	**25** (>98)
8	**24**	WPA/CPC	*t*-BuOH	23	**25** (90)
9	**24**	CWP + H_2SO_4	*t*-BuOH	25	**25** (>98)
10	**26**	CWP	*t*-BuOH	22	**27** (73)
11	**28**	CWP	*t*-BuOH	>98	**29** (>98)
12	 **30**	CWP	*t*-BuOH	94	 (>98) **31**
13[c]	**30**	CMP	PhH	20	**31** (>98)
14	 **32**	CWP	*t*-BuOH	>98	 (>98) **33**
15[d]	 **34**	CWP	*t*-BuOH	>98	 (>98) **35**
16[c,e]	**34**	CMP	PhH	>98	**35** (>98)
17[d]	 **36**	CWP	*t*-BuOH	>98	 (>98) **37**
18[c]	**36**	CMP	PhH	>98	**37** (>98)
19	**38**	CWP	*t*-BuOH	>98	**39** (>98)
20	**40**	CWP	*t*-BuOH	>98	**41** (>98)

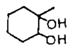
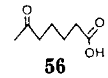
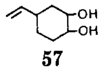
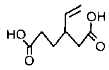
[a] Substrate (2 mmol) was allowed to react with 35% H_2O_2 (6 mmol) in the presence of catalyst (0.04 mmol) in solvent (15 mL) at refluxing temperature for 24 h. [b] Determined by VPC. [c] *t*-BuOOH (6 mmol) was used instead of H_2O_2. [d] 7 h. [e] 17 h.

methyl-1,3-pentanediol (**36**) were converted to the corresponding hydroxy ketones **35** and **37**, respectively. Similar chemoselectivities have appeared in the oxidation of diols by several catalyst–oxidant system.[2,25]

On the other hand, treatment of α,ω-diols, 1,4-butanediol (**38**) and 1,5-pentanediol (**40**) with H_2O_2 and CWP gave lactones, γ-butyrolactone (**39**) and δ-valerolactone (**41**), respectively, in 97% and 95% yields, although several methods are available for the selective lactonization.[26]

(C) Oxidative Cleavage of *vic*-Diols and Olefins with Hydrogen Peroxide. The oxidation of 1,2-butanediol (**42**) was examined to evaluate the potential of heteropoly acid for oxidative cleavage of *vic*-diols with H_2O_2 to carboxylic acids. The oxidative cleavage of **42** by CWP was successfully conducted by using 3 equiv of H_2O_2 with refluxingg *t*-BuOH (Table IV). The WPA/CPC system was less effective than CWP in this oxidation. Mo-based heteropoly acids were insufficient as the catalyst for oxidative cleavage of 1,2-diols. 1-Phenyl-1,2-ethanediol (**44**) and 1,2-octanediol (**46**) were converted to benzoic acid (**45**), and heptanoic acid (**47**), respectively, in fair yields. The oxidation of 2,3-butanediol (**48**) and 2,3-octanediol (**50**) involving secondary-secondary hydroxy groups easily occurred compared with that of **42** and **46** involving primary–secondary hydroxy groups to yield acetic acid (**49**) and hexanoic acid (**51**), respectively, in good yields. However, 2-ethyl-1,2-hexanediol (**52**) bearing the tertiary hydroxy group was not oxidized, and the starting diol was recovered in almost quantitative yield. Cyclic diol, 1,2-cyclohexanediol (**53**) (about 1:1 mixture of cis and trans), was also cleaved oxidatively to adipic acid (**54**), which on subsequent esterification in methanol afforded its methyl ester in good yield (88%). 1-Methyl-1,2-cyclohexanediol (**55**) was cleaved in excellent yield to give the keto acid 6-oxaheptanoic acid (**56**). The oxidation of 4-vinyl-1,2-cyclohexanediol (**57**) gave 3-vinyladipic acid (**58**) in 55% yield.

Table IV. Oxidative Cleavage of 1,2-Diols to Carboxylic Acids with H_2O_2 Catalyzed Heteropoly Acids[a]

run	substrate	catal	product	yield, %[b]
1	**42**	CWP	**43**	86
2	**42**	WPA/CPC	**43**	60
3	**42**	WPA	**43**	22
4[c]	**42**	CMP	**43**	41
5	**44**	CWP	**45**	55
6	**46**	CWP	**47**	52
7	**48**	CWP	**49**	140
8	**50**	CWP	**51**	80
9	**52**	CWP		
10	**53**	CWP	**54**	88[d]
11	 **55**	CWP	 **56**	95
12	 **57**	CWP	 **58**	55

[a] Substrate (10 mmol) was allowed to react with 35% H_2O_2 (30 mmol) in the presence of catalyst (0.2 mmol) at refluxing temperature of *t*-BuOH (20 mL) for 24 h. [b] Isolated yield. [c] The reaction was carried out by using of *t*-BuOOH (30 mL) in place of H_2O_2 at refluxing temperature of benzene (20 mL). [d] Isolated as methyl ester.

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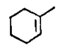
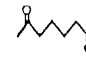
(25) (a) Yamawaki, K.; Yoshida, T.; Suda, T.; Ishii, Y.; Ogawa, M. *Synthesis* **1986**, 59. (b) Yamawaki, K.; Ishii, Y.; Ogawa, M. *Chem. Express* **1986**, *1*, 95. (c) Kaneda, K.; Kawanishi, Y.; Jitsukawa, K.; Teranishi, S. *Tetrahedron Lett.* **1983**, *24*, 5009. (d) Tomioka, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 539. (e) Jung, M. E.; Spelts, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7882.

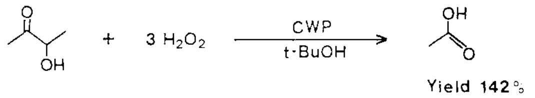
(26) (a) Ishii, Y.; Suzuki, K.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *J. Org. Chem.* **1986**, *51*, 2822. (b) Miyazawa, T.; Endo, T. *J. Org. Chem.* **1985**, *50*, 3930. (c) Murahashi, S.; Itoh, K.; Naota, T.; Maeda, Y. *Tetrahedron Lett.* **1981**, *22*, 5327. (d) Kageyama, T.; Kawahara, K.; Ueno, Y.; Okawara, M. *Chem. Lett.* **1983**, 1097.

Table V. Oxidative Cleavage of Olefins to Carboxylic Acids with H_2O_2 Catalyzed by CWP[a]

run	substrate	product	yield, %[b]
1	**1**	**47**	45
2	**60**	**51**	72
3	**61**	**62**	66[c]
4	**63**	**54**	70[c]
5	 **64**	 56	90

[a] Substrate (10 mmol) was allowed to react with 35% H_2O_2 (40 mmol) in the presence of CWP (0.2 mmol) at refluxing temperature of *t*-BuOH (20 mL) for 24 h. [b] Isolated yield. [c] Isolated as methyl ester.

Venturello[27] has recently reported that 1,2-diols are converted to carboxylic acids with H_2O_2 in the presence of tungstate and phosphate (or arsenate) ions under acidic conditions. The oxidative cleavage of 1,2-diols is believed to involve the formation of α-ketol, followed by C–C bond fission of the α-ketol.[27] The fact that the secondary hydroxy group of diols was readily oxidized by CWP (Table II, runs 15–17) indicates that the present oxidative cleavage of 1,2-diols proceeds via α-hydroxy ketone similar to the sequence reported by Venturello. Indeed, the treatment of 3-hydroxy-2-butanone (**59**) with H_2O_2 under the influence of CWP afforded acetic acid (eq 1).



Yield 142% (1)

Since the oxidation of olefin **1** with H_2O_2 by CWP under the homogeneous condition gave glycol and small amounts of carboxylic acid as shown in Table I (run 4), it is expected that the treatment of olefins with excess H_2O_2 under the influence of CWP results in the formation of carboxylic acids. Thus, the oxidation of terminal alkene **1** with 4 equiv of 35% H_2O_2 in *t*-BuOH under the influence of catalytic amount ($^1/_{50}$ equiv) of CWP gave heptanoic acid **47** in 45% yield (Table V). This oxidative procedure works particularly well for internal alkenes. 2-Octene (**60**) was oxidized with cleavage of the carbon–carbon double bond to hexanoic acid **51** (72%). The oxidation of cycloalkenes, cyclopentene (**61**) and cyclohexene (**63**), followed by esterification with methanol, gave dimethyl esters of glutaric acid (**62**) and **54**, respectively. The CWP catalyzed oxidation of 1-methyl-1-cyclohexene (**64**) with H_2O_2 yielded keto acid **56** in good yield (90%).

From the synthetic and industrial points of view, it is worth noting that the hydrogen peroxide oxidation catalyzed by heteropoly acids combined with CPC has been successfully extended for the oxidative cleavage of the carbon–carbon double bond of olefins to carboxylic acids.

Experimental Section

Melting point were determined on a Yanagimoto capillary melting point apparatus and are uncorrected. GLC analyses were performed on a Yanagimoto G1800 employing a thermal conductivity detector using a 3 mm × 3 m column (5% silicone OV-7 on Chromasorb W) or a Shimazu 12A gas chromatograph with a flame ionization detector using a 25-m HR-101 capillary column. GC/MS analysis was obtained by using a silicon OV-7 (3 m) column in a JEOL JMS-QH 100 instrument. Infrared (IR) spectra were measured with a Jasco Model A-202 spectrometer. ^1H and ^{13}C NMR were measured with a JEOL PMX-60 and a Hitachi R-90H spectrometers in $CDCl_3$ using Me_4Si as the internal standard, respectively. The yields of products estimated from the peak areas depended on an internal standard technique.

Preparation of Tris(cetylpyridinium) 12-Molybdophosphate $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_{12}O_{40})^{3-}$(CMP) and Tris(cetylpyridinium) 12-Tungstophosphate $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})^{3-}$(CWP). CMP was prepared by the same procedure reported previously.[5] CWP was prepared in the similar manner as CMP. To a solution of CPC (1.87 g, 5.2 mmol) in 70 mL of water was added dropwise WPA (5.0 g, ca. 1.7 mmol) in 10 mL of water with stirring at ambient temperature to form a white precipitate immediately. After being stirred continuously for 3–4 h, the resulting mixture was filtered, then washed several times with distilled water, and dried in vacuo to give CWP in 80–90% yield.

Anal. Calcd for $C_{63}H_{114}N_3PW_{12}O_{40}$: 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}.

Preparation of Peroxo Complexes PCMP and PCWP. PCMP was prepared by treating of CMP with H_2O_2,[14] but PCWP could not be prepared by the same method as PCMP. To a solution of CPC (1.1 g, 3.1 mmol) in 35% H_2O_2 (40 mL) was added WPA (3.0 g, ca. 1.0 mmol) in 35% H_2O_2 (10 mL), and the mixture was stirred at 40 °C for 4–5 h. The suspended mixture was cooled to room temperature until a white precipitate was produced. After centrifugation, the precipitate was washed repeatedly with water and dried in vacuo to give a 40–50% yield by weight of the peroxo complex, PCWP, based on the starting mass of WPA and CPC. The active oxygen found by iodometry of PCWP was estimated to be 1.1–1.5 mmol per gram of PCMP.

IR (KBr) 3350, 2900, 2850, 1700, 1630, 1480, 1460, 1370, 1160, 1125, 1080, 1050, 980, 950, 840, 770, 720, 680, 645, 570, 545, 520 cm^{-1}.

General Procedure for Epoxidation of Olefins and Allylic Alcohols. To the stirred solution of heteropoly acid (ca. 0.026 mmol), CPC (28 mg, 0.078 mmol) and 35% H_2O_2 (960 mg, 9.8 mmol) in chloroform (15 mL) was added the olefin (or allylic alcohol) (6.5 mmol), and the mixture was allowed to react under refluxing temperature (or room temperature for allylic alcohols). After the partially precipitated catalyst was separated by filtration, the filtrate was treated with a solution of 10% sodium hydrogen sulfite to decompose unreacted H_2O_2 and then with 10% sodium hydroxide. The product was extracted with chloroform. Pure product was obtained by distillation or silica gel column chromatography (hexane/ethyl acetate, 10/1–2, eluent). Spectral data of each product were compared with those of authentic samples and the literature values.[22,23,28]

General Procedure for Ketonization of Alcohols and Diols. To the stirred solution of CWP (152 mg, 0.040 mmol), 35% H_2O_2 (583 mg, ca. 6.0 mmol) in *t*-BuOH (15 mL) was added alcohol or diol (2 mmol), and the mixture was allowed to reflux for 24 h. After the reaction, the mixture was treated with a 10% sodium hydrogen sulfite solution to decompose the unreacted H_2O_2 and then with 10% sodium hydroxide. The product was extracted with ethyl acetate. Pure product was obtained by chromatography on silica gel (hexane/ethyl acetate, 10–20/1, eluent). Spectral data of each product were compared with those of authentic samples and the literature values.[25a,28] The same procedure was employed for the lactonization of α,ω-diols.

General Procedure for Oxidative Cleavage of *vic*-Diols and Olefins. To the stirred solution of CWP (760 mg, 0.2 mmol), 35% H_2O_2 (2.91 g, 30 mmol, for *vic*-diols or 3.88 g, 40 mmol, for olefins) in *t*-BuOH (20 mL) was added vic-diol or olefin (10 mmol), and the mixture was allowed to reflux for 24 h. After the reaction, the mixture was treated with a 10% sodium hydrogen sulfite to decompose the unreacted H_2O_2. The product was extracted with diethyl ether. Pure product was obtained by chromatography on silica gel (hexane/diethyl ether, 1–10/1, eluent). Spectral data of each product were compared with those of authentic samples and the literature values.[28]

6: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 142.9 (d), 142.8 (d), 112.7 (t), 112.7 (t), 52.5 (d), 52.0 (d), 51.2 (d), 51.0 (d), 36.8 (d), 33.5 (d), 30.9 (t), 30.0 (t), 26.5 (t), 25.1 (t), 24.2 (t), 23.2 (t); ^1H NMR ($Me_4Si/CDCl_3$) δ 5.93–5.26 (m, 1 H), 5.05–4.62 (m, 2 H), 3.20–2.90

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(27) Venturello, C.; Ricci, M. *J. Org. Chem.* **1986**, *51*, 1599.

(28) (a) Simoms, W. W.; Zanger, M. *The Sadtler Guide to NMR Spectra*; Sadtler Research Laboratories: Philadelphia, 1972. (b) Pouchert, C. J.; Campbell, J. R. *The Aldrich Library of NMR Spectra*; Aldrich Chemical Company: Milwaukee, Wisconsin, 1974.

(m, 2 H), 2.80–0.73 (m, 7 H); IR (NaCl) 3080, 2720, 1640, 1260, 990, 850, 810 cm^{-1}.

8: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 139.4 (d), 114.8 (t), 51.2 (d), 49.5 (d), 44.6 (d), 42.0 (d), 37.5 (d), 30.8 (t), 27.4 (t); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 5.80 (m, 1 H), 5.00 (m, 2 H), 3.15 (m, 2 H), 2.30 (m, 3 H), 1.95–0.64 (m, 4 H); IR (NaCl) 2950, 1640, 1440, 1275, 905, 850 cm^{-1}.

15: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 133.2 (s), 129.6 (d), 64.6 (d), 25.7 (q), 23.7 (q), 18.0 (q); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 5.26–4.92 (m, 1 H), 4.70–4.18 (q, 1 H), 2.22 (s, 1 H), 1.66 (s, 6 H), 1.18 (d, 3 H); IR (NaCl) 3400, 3000, 2950, 1650, 1450, 1380, 1070, 950, 870 cm^{-1}.

16: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 68.5 (d), 66.9 (d), 59.2 (s), 24.9 (q), 19.2 (q), 19.1 (q); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 3.54 (m, 2 H), 2.66 (d, 1 H), 1.30 (s, 6 H), 1.19 (d, 3 H); IR (NaCl) 3400, 2960, 1460, 1380, 1110, 1070, 1040, 880, 820 cm^{-1}.

18: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 71.5 (d), 68.4 (d), 55.6 (d), 54.6 (d), 45.1 (t), 43.6 (t), 36.4 (t), 35.7 (t), 18.6 (t), 14.1 (q); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 3.90–3.20 (m, 1 H), 3.13–2.60 (m, 3 H), 2.30 (s, 1 H), 1.70–1.23 (m, 4 H), 1.23–0.75 (m, 3 H); IR (NaCl) 3430, 2950, 1470, 1380, 920, 860 cm^{-1}.

19: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 134.4 (d), 126.3 (d), 72.7 (d), 39.5 (t), 18.7 (t), 17.6 (q), 14.0 (q); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 5.66–5.33 (m, 2 H), 3.27 (s, 2 H), 1.67 (d, 3 H), 1.60–1.23 (m, 4 H), 1.10–0.80 (m, 3 H); IR (NaCl) 3430, 2970, 1630, 1450, 1380, 970, 950 cm^{-1}.

20: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 71.2 (d), 68.6 (d), 62.9 (d), 62.0 (d), 52.9 (d), 51.2 (d), 36.4 (t), 35.7 (t), 18.6 (t), 17.2 (q), 14.1 (q); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 4.00–3.55 (m, 1 H), 3.55–3.10 (m, 1 H), 3.10–2.76 (m, 1 H), 2.76–2.50 (m, 1 H), 1.73–1.44 (m, 4 H), 1.28 (d, 3 H), 1.10–0.70 (m, 3 H); IR (NaCl) 3450, 2950, 1470, 1390, 880, 760 cm^{-1}.

46: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 72.4 (d), 66.7 (t), 33.1 (t), 31.8 (t), 29.4 (t), 25.6 (t), 22.6 (t), 14.0 (q); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 4.33 (s, 2 H), 3.80–3.23 (m, 3 H), 1.63–1.06 (m, 10 H), 1.06–0.53 (t, 3 H); IR (NaCl) 3400, 2930, 1470, 1070 cm^{-1}.

50: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 74.8 (d), 70.3 (d), 31.8 (t), 31.7 (t), 25.7 (t), 22.5 (t), 16.3 (q), 13.9 (q); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 3.93–3.36 (m, 4 H), 1.80–1.23 (m, 8 H), 1.23–0.66 (m, 6 H); IR (NaCl) 3400, 2930, 1460, 1060 cm^{-1}.

52: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 75.1 (s), 67.6 (t), 34.8 (t), 28.0 (t), 25.5 (t), 23.3 (t), 14.0 (q), 7.8 (q); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 3.36 (s, 4 H), 1.73–1.06 (m, 8 H), 1.06–0.66 (m, 6 H); IR (NaCl) 3350, 2930, 1460, 1140, 1040 cm^{-1}.

54 (methyl ester): ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 173.5 (s), 51.4 (q), 33.7 (t), 24.4 (t); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 3.76 (s, 6 H), 2.66–2.20 (m, 4 H), 1.90–1.50 ((m, 4 H); IR (NaCl) 2960, 1740, 1440, 1200 cm^{-1}.

55: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 74.8 (d), 71.6 (s), 36.9 (t), 30.3 (t), 26.5 (q), 23.2 (t), 21.6 (t); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 3.46–3.20 (t, 1 H), 2.85 (s, 2 H), 1.76–1.30 (m, 8 H), 1.21 (s, 3 H); IR (NaCl) 3400, 2940, 1450, 1370, 750 cm^{-1}.

56: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 209.3 (s), 178.5 (s), 43.1 (t), 33.7 (t), 29.8 (q), 24.1 (t), 23.1 (t); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 10.10 (s, 1 H), 2.64–2.24 (m, 4 H), 2.16 (s, 3 H), 1.76–1.50 (m, 4 H); IR (NaCl) 3400–2900, 2960, 1720, 1410, 1370 cm^{-1}.

57: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 141.3 (t), 114.1 (d), 74.9 (d), 71.3 (d), 36.3 (d), 36.3 (t), 28.3 (t), 27.8 (t); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 6.10–5.50 (q, 1 H), 5.16–4.95 (m, 1 H), 4.95–4.75 (m, 1 H), 4.24 (s, 2 H), 3.77–3.10 (m, 2 H), 2.70–1.75 (m, 7 H); IR (NaCl) 3400, 2910, 1640, 1450, 1220, 1060 cm^{-1}.

58: ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 178.5 (s), 177.2 (s), 139.3 (t), 116.5 (d), 39.6 (d), 39.6 (t), 31.6 (t), 28.9 (t); ^{1}H NMR (Me$_4$Si/CDCl$_3$) δ 8.22 (s, 2 H), 5.80–5.40 (m, 1 H), 5.20–4.92 (m, 2 H), 2.64–2.15 (m, 4 H), 1.95–1.40 (m, 3 H); IR (NaCl) 3400–2900, 2950, 1710, 1650, 1420, 930 cm^{-1}.

62 (methyl ester): ^{13}C NMR (Me$_4$Si/CDCl$_3$) δ 173.3 (s), 51.6 (q), 33.1 (t), 20.2 (t); ^{1}H NMR (me$_4$Si/CDCl$_3$) δ 3.76 (s, 6 H), 2.66–2.26 (t, 4 H), 2.26–1.80 (m, 2 H); IR (NaCl) 2960, 1740, 1440, 1200 cm^{-1}.

Rates of H/D Exchange of 9-Fluorenyl Sulfoxides: Evidence for an Irreversible E1cB Mechanism for Base-Induced Sulfine Formation from Methyl Diarylmethanesulfinates[1]

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A previous study[2] had shown that the base-catalyzed, sulfine-forming eliminations of methyl 9-fluorenesulfinate (**4**) and other methyl diarylmethanesulfinates take place by either an E1cB-irreversible or an E2 mechanism, rather than the E1cB-reversible mechanism that had been expected. In the present work the rates (k_{exch}) of DABCO (diazabicyclooctane)-catalyzed H/D exchange of the 9-H in a series of 9-fluorenyl sulfoxides (**3**) have been determined at 25 °C in CD$_3$OD. From a plot of log k_{exch} vs σ^* for R in **3** the anticipated rate for the DABCO-catalyzed formation of the 9-fluorenyl carbanion from **4** (eq 3, R = OCH$_3$) can be estimated. Comparison of this rate with the actual rate (k_{elim}) of the DABCO-catalyzed, sulfine-forming elimination of **4** (eq 5) indicates that the elimination does *not* take place by an E2 mechanism in which there is a significant degree of cleavage of the S(O)–OCH$_3$ bond in the rate-determining transition state. The results are, however, entirely consistent with an E1cB-irreversible mechanism for the elimination.

A recent study[2] has shown that methyl diarylmethanesulfinates (**1**) undergo base-catalyzed elimination (eq 1)

$$\underset{\mathbf{1}}{\text{ArAr}'\text{CHS(O)OCH}_3} \xrightarrow[\text{MeOH}]{\text{base}} \underset{\mathbf{2}}{\text{ArAr}'\text{C}{=}\text{S}{=}\text{O}} + \text{CH}_3\text{OH} \qquad (1)$$

in methanol to form the corresponding sulfine (**2**) in quantitative yield. The absence of detectable H/D exchange of the C*H*S(O) proton in MeOD prior to reaction and the kinetic isotope effects for both the methoxide-induced (k_H/k_D = 6.1) and amine-induced (k_H/k_D = 3.8 for quinuclidine) eliminations of methyl 9-fluorenesulfinate-*9-d* demonstrated that eq 1 proceeds by either an (E1cB)$_{\text{irrev}}$ or an E2 mechanism, rather than the (E1cB)$_{\text{rev}}$ mechanism that might have been anticipated based on the behavior of related sulfene-forming eliminations of arylmethanesulfonates.[3]

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