J. Org. Chem. **1993,** *58,* 6421–6425 **6421**

Oxidation of Organic Substrates by Molecular Oxygen/Aldehyde/Heteropolyoxometalate System

Masatoshi Hamamoto, Kouichi Nakayama, Yutaka Nishiyama, and Yasutaka Ishii[*]

Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan

Received April 20, 1993[•]

Heteropolyoxometalate-catalyzed oxidations of organic compounds such as olefins and cyclic ketones with molecular oxygen in the presence of an aldehyde were examined. Olefins were epoxidized with dioxygen in the presence of 2 equiv of 2-methylpropanal under the influence of a catalytic amount of the mixed heteropolyoxometalate NPV_6Mo_6 (**3**) to give the corresponding epoxides in moderate to good yields. This catalytic oxidation method was also applied to the epoxidation of allylic and homoallylic alcohols. In the absence of olefins, the aldehydes were efficiently converted into the corresponding carboxylic acids. In addition, the Baeyer–Villiger oxidation of cyclic ketones was accomplished by using benzaldehyde instead of 2-methylpropanal as the aldehyde.

Although catalytic oxidations of organic compounds can be accomplished with a wide variety of oxidants, a method for direct oxidation with molecular oxygen (dioxygen) under mild conditions has been sought after by chemists. Considerable attention has been devoted to the development of aerobic oxidation catalysts. However, there are only a few reports of practical methods for the oxidation of organic compounds with dioxygen.[1] Recently RuO_2,[2] $Ni(dmp)_2$,[3] $Ni(Salen)_2$,[4] and Fe or Ru[5] have been successfully used as efficient catalysts for the oxidation of various organic compounds with dioxygen in the presence of an aldehyde under mild reaction conditions.

There has been interest in the heteropolyoxometalate-catalyzed direct oxidation of organic substrates with dioxygen. Hill el al. have reported conversions of alkanes to alkenes[6] and alcohols to ketones[7] by means of photochemical dehydrogenation with dioxygen under the influence of polyoxotungstate. In addition, a heteropolyanion, $PV_2Mo_{10}O_{40}{}^{5-}$, and related compounds catalyze various oxidations with molecular oxygen (e.g., oxidative dehydrogenations of dienes,[8] alcohols, and amines;[9] oxidative coupling of phenols;[10] oxidation of sulfides;[11] and oxidative cleavage of ketones[12] and diols[13]).

Previously, heteropolyoxometalates such as $[\pi\text{-}C_6H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})^{3-}$ (CWP) and $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ (PCWP) were found to be excellent catalysts for the H_2O_2 oxidation of alcohols,[14] allylic alcohols,[15] alkenes,[16] alkynes,[17] α,β-unsaturated carbonyl compounds,[18] *vic*-diols,[19] and aliphatic and aromatic amines.[20] During the course of our study on the utilization of heteropolyoxometalates as catalysts for oxidation reactions, we have found a novel heteropolyoxometalate-catalyzed oxidation of organic compounds with molecular oxygen in the presence of an aldehyde. In this paper, we report a new approach to the oxidation of alkenes, aldehydes, and cyclic ketones with dioxygen.

Results and Discussion

1. Use of Heteropolyoxometalates for the Epoxidation of 2-Octene (1). To establish the proper conditions for the formation of epoxides, we examined the effect of aldehydes and heteropolyoxometalates on the epoxidation using the conversion of 2-octene (**1**) to 2,3-epoxyoctane (**2**) as a model reaction (Table I). Several heteropolyoxometalate catalysts[21,22] were prepared according to the literature procedures: $(NH_4)_5H_4PV_6W_6O_{40}\cdot 6H_2O$,[22] $(NH_4)_6HPV_4W_8O_{40}\cdot 9H_2O$,[22] and NPV_6Mo_6 (**3**),[23] etc. The oxidation of **1** with dioxygen (1 atm) in the presence of a catalytic amount of $(NH_4)_5H_4PV_6W_6$-

---

[•] Abstract published in *Advance ACS Abstracts,* October 15, 1993.

[1] See, for example: (a) *Oxidations in Organic Chemistry*; Hudlicky, M., Ed.; ACS Monograph 186: American Chemical Society: Washington, DC, 1990. (b) *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simandi, L. I., Ed.; Elsevier: New York, 1991.

[2] Kaneda, K.; Haruna, S.; Imanaka, S.; Kawamoto, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1467.

[3] (a) Yamada, T.; Takai, T.; Rhode, O.; Mukaiyama, T. *Chem. Lett.* **1991**, 1. (b) Yamada, T.; Rhode, O.; Takai, T.; Mukaiyama, T. *Ibid.* **1991**, 5. (c) Yamada, T.; Takahashi, K.; Kato, K.; Takai, T.; Inoki, S.; Mukaiyama, T. *Chem. Lett.* **1991**, 641. (d) Yamada, T.; Takai, T.; Rhode, O.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2109. (e) Takai, T.; Hata, E.; Yamada, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2513. (f) Yamada, T.; Inagawa, K.; Mukaiyama, T. *Chem. Lett.* **1992**, 2109. (g) Yamada, T.; Imanaga, K.; Nagata, T.; Mukaiyama, T. *Chem. Lett.* **1992**, 2231.

[4] Irie, R.; Ito, Y.; Katsuki, T. *Tetrahedron Lett.* **1991**, *32*, 6891.

[5] Murahashi, S.-I.; Oda, Y.; Naota, T. *J. Am. Chem. Soc.* **1992**, *114*, 7913.

[6] Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148.

[7] Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 3528.

[8] Neumann, R.; Lissel, M. *J. Org. Chem.* **1989**, *54*, 4607.

[9] Neumann, R.; Lissel, M. *J. Org. Chem.* **1991**, *56*, 5707.

[10] Lissel, M.; in de Wal; Neumann, R. *Tetrahedron Lett.* **1992**, *33*, 1795.

[11] Kozhevnikov, I. V.; Simagna, V. I.; Varnakova, G. V.; Matveev, K. I. *Kinet. Katal.* **1979**, *20*, 506.

[12] (a) El Ali, B.; Brégeault, J.-M.; Mercier, J.; Martin, J.; Martin, C.; Convert, O. *J. Chem. Soc., Chem. Commun.* **1989**, 825. (b) El Ali, B.; Brégeault, J.-M.; Mercier, J.; Martin, J.; Martin, C. *New J. Chem.* **1989**, *13*, 825.

[13] Brégeault, J.-M.; El Ali, B.; Mercier, J.; Martin, C. *C. R. Acad. Sci. Ser. 2* **1989**, *309*, 459.

[14] Yamawaki, K.; Yoshida, T.; Nishihara, H.; Ishii, Y.; Ogawa, M. *Synth. Commun.* **1986**, *16*, 53.

[15] Matoba, Y.; Inoue, H.; Akagi, J.; Okabayashi, T.; Ishii, Y.; Ogawa, M. *Synth. Commun.* **1984**, *14*, 865.

[16] Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587.

[17] Ishii, Y.; Sakata, Y. *J. Org. Chem.* **1990**, *55*, 5545.

[18] Oguchi, T.; Sakata, Y.; Takeuchi, N.; Kaneda, K.; Ishii, Y.; Ogawa, M. *Chem. Lett.* **1989**, 2053.

[19] Sakata, Y.; Ishii, Y. *J. Org. Chem.* **1991**, *56*, 6233.

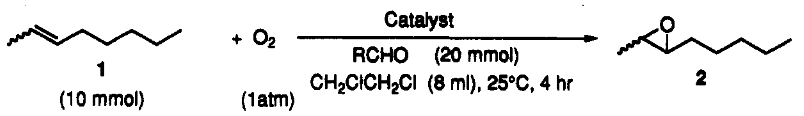
[20] Sakaue, S.; Sakata, Y.; Nishiyama, Y.; Ishii, Y. *Chem. Lett.* **1992**, 289.

[21] Tsigclinos, G. A.; Hallada, C. J. *Inorg. Chem.* **1968**, *7*, 437.

[22] Smith, D. P.; Pope, M. T. *Inorg. Chem.* **1973**, *12*, 331.

[23] Although the NPV_6Mo_6 (**3**) was a reproducible substance, the ^{31}P NMR spectrum indicated numerous signals. This observation suggests that **3** is a complex mixture consisting of many different compositions of V and Mo. Found: H, 2.33; N, 5.20. However, if **3** is assumed to consist of an idealized structure having Keggin unit $(NH_4)_5H_4PV_6Mo_6O_{40}\cdot 6H_2O$, the composition is calculated as follows. Calcd for $H_{36}N_5V_6Mo_6O_{46}P$: H, 2.07; N, 3.99.

Table I. Dioxygen Oxidation of 2-Octene (1) Catalyzed by Heteropolyoxometalates under Several Reaction Conditions



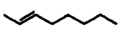
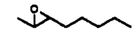
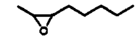
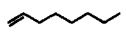
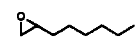
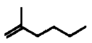
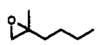
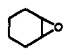
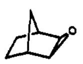
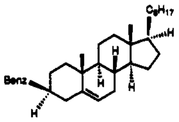
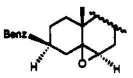
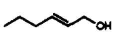
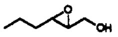
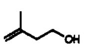
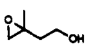
run	catalyst (wt %)	RCHO (equiv)	conv., %[a]	yield (select.), %[a]
1	$(NH_4)_5H_4PV_6W_6O_{40}{\cdot}6H_2O$ (10.0)	$(CH_3)_2CHCHO$ (4) (2)	86	77 (89)
2	NPV_6Mo_6 (3) (7.8)	–	0	–
3	3 (7.8)	C_3H_7CHO (2)	0	–
4	3 (7.8)	4 (2)	75	71 (95)
5	3 (7.8)	4 (1)	14	13 (93)
6	3 (7.8)	$(CH_3)_3CCHO$ (2)	76	72 (95)
7	3 (7.8)	C_6H_5CHO (2)	0	–
8	no catalyst	4 (2)	21	17 (81)
9	$(NH_4)_6HPV_4W_8O_{40}{\cdot}9H_2O$ (11.7)	4 (2)	50	41 (82)
10	$(NH_4)_3[PMo_{12}O_{40}]{\cdot}nH_2O$ (8.4)	4 (2)	37	35 (95)
11	$(NH_4)_3[PW_{12}O_{40}]{\cdot}nH_2O$ (13.1)	4 (2)	39	32 (82)
12	$H_3[PMo_{12}O_{40}]{\cdot}nH_2O$ (8.1)	4 (2)	10	0 (0)
13	$H_3[PW_{12}O_{40}]{\cdot}nH_2O$ (10.1)	4 (2)	10	0 (0)

[a] GLC yields based on the amount of 1.

$O_{40}{\cdot}6H_2O$ and 2 equiv of 2-methylpropanal (4) at room temperature for 4 h gave 2 in 77% yield (run 1). Under the same conditions, the corresponding molybdenum compound (3) gave 2 with higher selectivity than $(NH_4)_5H_4PV_6W_6O_{40}{\cdot}6H_2O$. The reaction was considerably affected by the structure and the amount of the aldehyde used (runs 2–7). With aliphatic aldehydes bearing di- or trialkyl groups on the α-position of the carbonyl carbon, such as 4 or 2,2-dimethylpropanal, 1 was epoxidized to 2 with good selectivity (runs 4 and 6). However, no epoxide was obtained when *n*-butyraldehyde and benzaldehyde were employed (runs 3 and 7). The reaction of 1 in the presence of equimolar 4 resulted in a considerable decrease in the yield of 2 (run 5). In the absence of aldehyde, 1 was recovered unchanged (run 2). The oxidation of 1 with 4 (2 equiv) without catalyst led to 2 with 81% selectivity, but the conversion was low (21%, run 8). Mixed heteropolyoxometalates such as 3, $(NH_4)_5H_4PV_6W_6O_{40}{\cdot}6H_2O$, and $(NH_4)_6HPV_4W_8O_{40}{\cdot}9H_2O$ were found to be more efficient than simple heteropolyoxometalats such as $(NH_4)_3PMo_{12}O_{40}{\cdot}nH_2O$[22] and $(NH_4)_3PW_{12}O_{40}{\cdot}nH_2O$ (runs 1, 4, 10, and 11).[22] In addition, typical heteropoly acids having a Keggin structure such as $H_3PM_{12}O_{40}{\cdot}nH_2O$ (M = Mo or W) were inert in this oxidation reaction (runs 12 and 13).

2. Epoxidation of Various Olefinic Compounds. In order to ascertain the scope of the epoxidation, various olefinic compounds were oxidized with dioxygen in the presence of 3 and 4 (2 equiv) (Table II). When *trans*-2-octene (*trans*-1, *trans/cis* = 99/1) was used as an olefin, the epoxidation took place with excellent stereoselectivity to give *trans*-2,3-epoxyoctane (*trans*-2, *trans/cis* = 99/1) with 89% selectivity (run 1). However, in the case of the epoxidation of *cis*-2-octene (*cis*-1, *trans/cis* = 2/98), an approximately 1:1 mixture of *cis*- and *trans*-2 (*trans/cis* = 44/56) was formed with 90% selectivity (run 2). Similar results have been observed in the $Ni(dmp)_2$-catalyzed epoxidation of olefins with molecular oxygen and an aldehyde.[3d] In contrast to internal olefin 2, terminal olefin 1-octene (5) was converted into epoxide 6 in moderate conversion under these reaction conditions (run 3). However, from terminal olefin 7, bearing an alkyl substituent, the corresponding epoxide (8) was obtained in good yield (run 4). Cyclic olefins such as cyclohexene (9) and norbornene (11) were also epoxidized in substantial yields, but the oxidation of 11 was rather sluggish and required a longer reaction time (runs 5 and 6). Cholesteryl benzoate (13) was converted into the 5,6-β-epoxide, a hindered product, in preference to the α-epoxide (α/β = 40/60) (run 7). It is noteworthy that the oxidation of allylic and homoallylic alcohols such as 1-hydroxy-2-hexene (15) and 1-hydroxy-4-methyl-3-propene (17) provided the corresponding epoxides, 16 and 18, respectively, in 67 and 92% selectivities (runs 8 and 9).

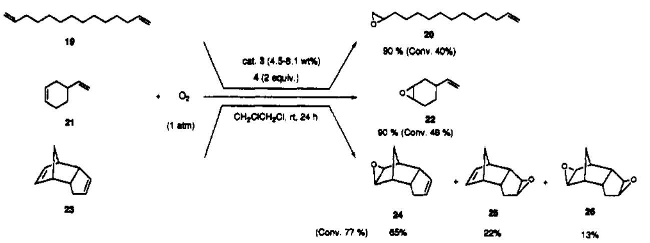
Table II. Epoxidation of Various Olefinic Compounds with Dioxygen and 4 under the influence of 3[a]

run	substrate	product	conv., %	yield (select.) %[b] (*trans/cis*)
1	 1	 2	66	59 (89) (99/1)
2	 1	 2	66	59 (90) (44/56)
3	 5	 6	39	31 (79)
4	 7	 8	100	89 (89)
5	 9	 10	83	78 (94)
6[c]	 11	 12	76	70 (92)
7	 13	 14	82	82 (100) (40/60)[d]
8	 15	 16	96	67 (70)
9	 17	 18	94	92 (98)

[a] Reaction conditions: olefin (10 mmol), 3 (88 mg), 4 (20 mmol), CH_2ClCH_2Cl (8 mL), and O_2 (1 atm) at 25 °C for 4 h. [b] GLC yields based on olefins. [c] 24 h. [d] Ratio of α-isomer to β-isomer.

Some oxidations of dienes were also examinied (Scheme I). When 1,13-tetradecadiene (19) was allowed to react with molecular oxygen in the presence of 3 and 4 under the standard reaction conditions, monoepoxidation oc-

Scheme I



curred selectively to give 1,2-epoxy-11-tetradecene (**20**) in 90% selectivity. The epoxidation of 4-vinyl-1-cyclohexene (**21**), which has two carbon–carbon double bonds whose reactivities are moderately different, took place regioselectively but not stereoselectivity, affording 3,4-epoxy-1-vinylcyclohexene (**22**) with 90% selectivity. In the oxidation of *endo*-dicyclopentadiene (**23**), the norbornene double bond was oxidized in preference to the cyclopentene double bond to form epoxides **24** (65%) and **25** (22%) together with a small amount of diepoxide **26** (13%) in 77% conversion. The regioselectivity in the epoxidation of **23** was estimated by extrapolating the product ratio **24**/**25** to time zero. Table III shows the comparison of the **24**/**25** ratio obtained with the O_2/RCHO/heteropolyoxometalate epoxidation with that obtained with the metal oxide–H_2O_2 system. It is interesting to note that the regioselectivity of the dioxygen epoxidation of **23** was opposite to that of the metal oxide-catalyzed H_2O_2 epoxidation of **23**, where **24** was formed in preference to **25**.[24] The ratio of **24**/**25** obtained with the dioxygen method is rather similar to that reported in the epoxidation of **23** carried out by bubbling in molecular oxygen at 40–60 °C.[25] This fact suggests that the active species generated from the O_2/RCHO/**3** system is different from the oxidant derived from the metal oxide–H_2O_2 system.

3. Conversion of Aldehydes to the Corresponding Carboxylic Acids.

After the oxidation of olefins with the O_2/RCHO/heteropolyoxometalate system, the aldehydes used were recovered as the corresponding carboxylic acids. We then studied the aerobic oxidation of aldehydes in the presence of **3** without olefins (eq 1). The treatment of **4** with dioxygen in the presence of a catalytic amount of **3** afforded 2-methylpropionic acid (**27**) exclusively. Octanal and benzaldehyde were also oxidized to the corresponding carboxylic acids, **28** and **29**, with good selectivities.

$$\mathrm{RCHO} + \mathrm{O_2} \xrightarrow[\mathrm{CH_2ClCH_2Cl,\ rt,\ 1\ h}]{\text{cat. }\mathrm{NPV_6Mo_6}\ (\mathbf{3})} \underset{\mathbf{27\text{-}29}}{\mathrm{RCOOH}} \qquad (1)$$

27: R = $(CH_3)_2CH$ 100 % (Conv. 60 %)

28: R = Ph 96 % (Conv. 78 %)

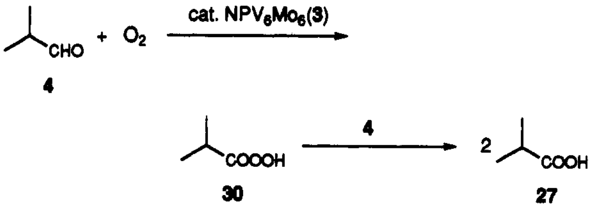
29: R = C_7H_{15} 100 % (Conv. 65 %)

To gain further insight into the mechanism of the conversion of aldehyde into carboxylic acid, the oxidation of **4** under the standard conditions was monitored by ^1H NMR. The signal at δ 2.44 due to the methine proton [$(CH_3)_2CHCHO$] observed at the initial stage of the reaction disappeared, and signals at 2.60 and 2.72 appeared. The signal at δ 2.60 intensified as time elapsed, but the peak at δ 2.72 eventually disappeared. From the comparison of these spectra with that of 2-methylpropionic acid (**27**), the signal at δ 2.60 was assigned to the methine proton of **27**. Hence, it seems reasonable to state that the signal at 2.72 ppm is the methine proton of the perisobutyric acid (**30**) derived from **4**. These observations suggest that **4** is oxidized with dioxygen by **3** to produce peracid **30**, which is subsequently reduced by **4** to form **27** (from **4** and **30**) (eq 2).

Table III. **Regioselectivities in the Epoxidation of 23**

oxidation method	3/O₂/aldehyde	Ox-1[a]	Ox-2[b]	H_2O_2 SeO₂	H_2O_2 H_2MoO_4[c]	H_2O_2 H_2WO_2[c]
24/25 ratio	3.0	7.0	1.3	0.34	0.33	0.31

[a] Oxidation with molecular oxygen at 40–60 °C. These values cited from ref 25. [b] Oxidation with organic peracid at 0 °C. These values cited from ref 25. [c] Oxidation with hydrogen peroxide at 40 °C.



(2)

4. Baeyer–Villiger Oxidation of Cyclic Ketones.

The Baeyer–Villiger oxidation is an important and frequently used reaction.[26] In general, the oxidation has been achieved with a percarboxylic acid such as peracetic acid or *m*-CPBA, or hydrogen peroxide combined with metal oxide catalysts such as SeO_2.[27,28] Because it appeared that a peracid was generated from the O_2/RCHO/heteropolyoxometalate system, we expected that ketones would undergo a Baeyer–Villiger reaction when subjected to these reaction conditions. Thus, we first examined the Baeyer–Villiger oxidation of cyclohexanone (**31**) with **4** as an aldehyde under the usual reaction conditions. However, ε-caprolactone (**32**) was formed in poor yield (run 1 in Table IV). When benzaldehyde was employed in place of **4** as an aldehyde, the oxidation proceeded smoothly to form **32** in satisfactory yield (run 2). In order to ascertain the scope of the present method, the Baeyer–Villiger oxidations of various ketones were carried out under the same reaction conditions (Table IV). 4-Methylcyclohexanone (**33**) was converted into the corresponding ε-caprolactone (**34**) with 87% selectivity (run 3). Unsymmetrical cyclic ketone 2-methylcyclohexanone (**35**) rearranged regioselectively to give 6-methyl-ε-caprolactone (**36**) with 78% selectivity (run 4). In the case of cyclopentanone (**39**), δ-valerolactone (**38**) was obtained with high selectivity, though the conversion was moderate (run

---

[24] Ishii, Y.; Matoba, Y.; Ito, H.; Muguruma, A.; Oda, K.; Ogawa, M. *J. Jpn. Petrol. Inst.* **1978**, *21*, 410.

[25] Sato, T.; Murayama, E. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1207.

[26] For reviews on the Baeyer–Villiger reaction, see: (a) J. March *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons, Inc.: New York, 1985; pp 990–991. (b) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: New York, 1972; pp 321–329.

[27] Syper, L. *Synthesis* **1989**, 167 and references cited therein.

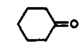
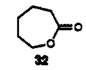
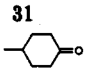
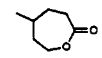
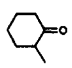
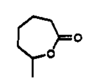
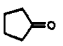
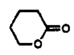
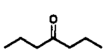
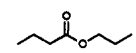
[28] Recently it was reported that bis(trimethylsilyl) peroxide,[29] magnesium monoperoxyphthalate,[30] sodium percarbonate/trifluoroacetic acid,[31] and a $Ni(dmp)_2$–O_2–RCHO system[3c] can be used for the Baeyer–Villiger reaction of ketones.

[29] (a) Suzuki, M.; Takeda, H.; Noyori, R. *J. Org. Chem.* **1982**, *47*, 902. (b) Matsubara, S.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2029.

[30] Brougham, P.; Cooper, M. S.; Cummerson, D. A.; Heaney, H.; Thompson, N. *Synthesis* **1987**, 1015.

[31] Olah, G. A.; Wang, Q.; Trivedi, N. J.; Prakash, G. K. S. *Synthesis* **1991**, 739.

Table IV Baeyer–Villiger Reaction of Various Ketones with Dioxygen and Benzaldehyde by the Influence of 3

run	ketone	ester	conv., %[b]	yield (select.), %[b]
1[c]	 31	 32	18	16 (87)
2	31	32	84	72 (86)
3	 33	 34	76	66 (87)
4	 35	 36	65	51 (78)
5	 37	 38	48	41 (85)
6	 39	 40	3	trace

[a] Reaction conditions: ketone (5 mmol), benzaldehyde (15 mmol), 3 (44 mg), CH_2ClCH_2Cl (10 mL), O_2 (1 atm) at 25 °C for 20 h. [b] GC yields based on ketones. [c] 4 was used instead of benzaldehyde.

5). However, aliphatic ketone 4-heptanone (**39**) did not rearrange, and the benzoic acid and **39** used were recovered in almost quantitative yields (run 6). We propose that the difficulty with the Baeyer–Villiger oxidation of aliphatic ketones is that the perbenzoic acid, generated from oxygen and benzaldehyde in the presence of **3**, oxidizes benzaldehyde itself rather than the ketone to form benzoic acid in preference to the Baeyer–Villiger product.

5. Oxidation of Thianthrene 5-Oxide. Recently, thianthrene 5-oxide (**41**) has been used as a mechanistic probe to determine whether the oxidant in an oxygen transfer rection was electrophilic or nucleophilic in character.[32] Thus, 41 was oxidized with the O_2/RCHO/heteropolyoxometalate system. The treatment of 41 with dioxygen under the standard conditions gave a mixture of thianthrene 5,10-dioxide (**42**) (61%) and thianthrene 5,5-dioxide (**43**) (32%) with 44% conversion (Scheme II).

It is difficult to determine whether the oxidant generated by the O_2/RCHO/heteropolyoxometalate system is an electrophilic or a nucleophilic species. However, the fact that the epoxidation of **1** did not take place in the presence of a radical scavenger such as 1,4-dihydroquinone under the standard conditions suggests the intervention of a radical pathway.

Recently, in the epoxidation of olefins by dioxygen with Ni(II) complexes as catalysts under Mukaiyama's conditions, the intervention of radical species was suggested.[33,34]

Although the reaction mechanism in this oxidation is not clear, we believe that **3** catalyzes not only the generation of percarboxylic acid from the aldehyde and dioxygen but also the epoxidation of olefins and the Baeyer–Villiger reaction of cyclic ketones.

In conclusion, the O_2/RCHO/heteropolyoxometalate system is a convenient method for the oxidation of olefinic compounds and the Baeyer–Villiger reaction of cyclic ketones as well as the conversion of aldehydes into the corresponding carboxylic acids under mild conditions.

Experimental Section

^1H and ^{13}C NMR spectra were obtained at 60, 90, or 400 MHz with tetramethylsilane as an internal standard. Analytical GLC was performed on PEG-HF and Silicone SE-30 equipped with a flame ionization detector. Analytical HPLC was performed on a Shimadzu CLC-ODO column. Aldehydes were purchased from commercial sources and purified by distillation. 1,2-Dichloroethane, alkenes, and ketones were purchased from commercial sources and used without further treatment. Thianthrene 5-oxide (**41**)[32] was prepared by the literature method.

Preparation of Catalysts. $(NH_4)_5H_4PV_6W_6O_{40}\cdot 6H_2O$,[22] $(NH_4)_6HPV_4W_8O_{40}\cdot 9H_2O$,[22] $(NH_4)_3[PMo_{12}O_{40}]\cdot nH_2O$,[21] $H_3[PMo_{12}O_{40}]\cdot nH_2O$,[21] and $(NH_4)_3[PW_{12}O_{40}]\cdot nH_2O$[21] were prepared by literature procedures. NPV_6Mo_6 (**3**) was prepared by a modification of the Pope method[22] using $Na_2MoO_4\cdot 2H_2O$ in place of $Na_2WO_4\cdot 2H_2O$. To a solution of $NaVO_3$ (7.32 g, 60 mmol) in water (38 mL) was added $Na_2MoO_4\cdot 2H_2O$ (8.22 g, 34 mmol) in water (12 mL). To the resulting solution, 85% H_3PO_4 (7.6 g, 60 mmol) in water (10 mL) was added dropwise, and the mixture was stirred for 1 h at 95 °C. After the reaction mixture was cooled to 0 °C, a sufficient amount of aqueous saturated ammonium chloride solution was added to the solution to give a brown precipitate (ca. 8.2 g). The resulting precipitate was recrystallized twice from water to form clean brown crystals of NPV_6Mo_6 (**3**): ^{31}P NMR (D_2O) δ −2.24, −2.23, −2.48, −2.57, −2.66, −2.72, −2.79, −2.85, −3.01, −3.05, −3.12, −3.40, −3.53 (^{31}P NMR shifts were referenced to external 85% H_3PO_4). IR spectrum (KBr): 3570, 3125, 1637, 1400, 984, 954, 840, 742 cm^{-1}. Found: H, 2.33; N, 5.20. If catalyst **3** is assumed to consist of idealized structure $(NH_4)_5H_4PV_6Mo_6O_{40}\cdot 6H_2O$, the composition is calculated as follows. Calcd for $H_{36}N_5V_6Mo_6O_{46}P$: H, 2.07; N, 3.99.

General Procedure for the Epoxidation of Alkenes. A 1,2-dichloroethane (8 mL) solution of alkene (10 mmol), 2-methylpropanal (**4**) (20 mmol), and NPV_6Mo_6 (**3**) (88 mg) was fitted with a balloon filled with about 3 L of oxygen. The mixture was stirred at 25 °C for 4 h. After the reaction, the reaction mixture was extracted with CH_2Cl_2 (20 mL × 5). The combined extracts were washed with aqueous $NaHCO_3$ (50 mL × 2). The organic layer was dried over $MgSO_4$ and analyzed by GLC with an internal standard. Removal of the solvent under reduced pressure afforded a clear liquid, which was purified by column chromatography on silica gel giving the corresponding epoxide. Epoxides **2**,[3f] **6**,[3e] **10**, **14**,[3f,35] **16**,[3e] **22**,[16] **24**,[24] **25**,[24] and **26**[24] were idenfified by comparison of their ^1H and ^{13}C NMR with those of authentic samples or with literature values.

8: ^1H NMR ($CDCl_3$) δ 2.61 (d, J = 5.1 Hz, 1H), 2.60 (d, J = 5.1 Hz, 1H), 1.61–1.56 (m, 1H), 1.51–1.45 (m, 1H), 1.31 (s, 3H), 1.39–1.27 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 57.1, 54.0, 36.5, 27.4, 22.8, 20.9, 14.0.

12: ^1H NMR ($CDCl_3$) δ 3.06 (bs, 2H), 2.45 (bs, 2H), 1.65 (bs, 0.5H), 1.51–1.45 (m, 1.5H), 1.35–1.28 (m, 1H), 1.27–1.18 (m, 2H), 0.70 (d, J = 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 51.3, 36.6, 26.2, 25.1.

18: ^1H NMR ($CDCl_3$) δ 3.55 (t, J = 5.3 Hz, 2H), 3.45 (bs, 1H), 2.63 (d, J = 5.5 Hz, 1H), 2.47 (d, J = 5.5 Hz, 1H), 1.88 (t, J = 7.0 Hz, 2H), 1.33 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 59.2, 56.5, 53.3, 38.1, 21.9.

20: ^1H NMR ($CDCl_3$) δ 5.84–5.77 (m, 1H), 4.96 (dd, J = 17.2 and 0.5 Hz, 1H), 4.92 (dd, J = 11.0 and 0.5 Hz, 1H), 2.93–2.87 (m, 1H), 2.74 (dd, J = 5.2 and 4.8 Hz, 1H), 2.46 (dd, J = 5.2 and 2.7 Hz, 1H), 1.53–1.27 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 139.2, 114.1, 52.4, 47.1, 33.8, 32.5, 29.6, 29.52, 29.51, 29.4, 29.4, 29.2, 29.0, 26.0.

24: ^1H NMR ($CDCl_3$) δ 5.68–5.63 (m, 1H), 5.61–5.55 (m, 1H), 3.23–3.13 (m, 2H), 2.92 (d, J = 2.6 Hz, 1H), 2.71–2.63 (m, 1H), 2.55–2.52 (m, 1H), 2.51–2.47 (m, 1H), 2.30–2.18 (m, 2H), 1.38 (d, J = 9.5 Hz, 1H), 0.84 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 132.0, 129.4, 53.3, 50.9, 49.1, 41.8, 39.8, 38.5, 31.4, 29.0.

25: ^1H NMR ($CDCl_3$) 6.11 (dd, J = 6.0 and 2.6 Hz, 2H), 3.33 (t, J = 2.6 Hz, 1H), 3.18 (d, J = 2.6 Hz, 1H), 2.81–2.85 (m, 2H), 2.51–2.58 (m, 1H), 1.91 (dd, J = 15.0 and 9.1 Hz, 1H), 1.56 (s, 2H), 1.39–1.37 (m, 1H), 1.35–1.33 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 135.0, 132.8, 61.9, 60.8, 52.0, 51.0, 45.4, 44.6, 43.9, 31.1.

26: ^1H NMR ($CDCl_3$) δ 3.54 (d, J = 2.2 Hz, 1H), 3.41 (d, J = 2.2 Hz, 1H), 3.23 (d, J = 3.7 Hz, 1H), 2.69–2.65 (m, 1H), 2.63–2.56

---

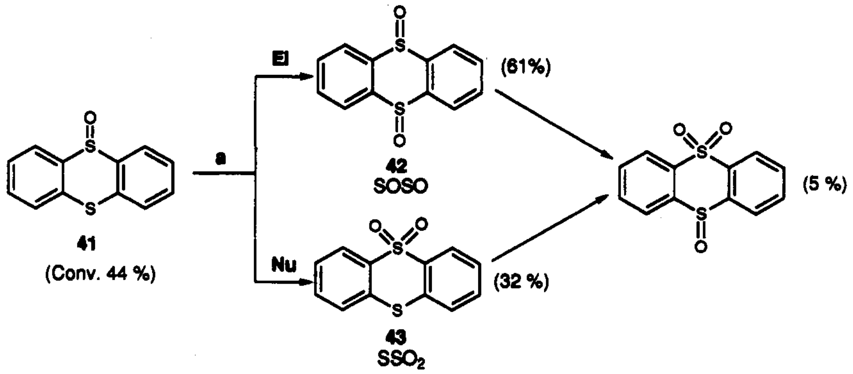
[32] (a) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202. (b) Ballistreri, F. P.; Tomaselli, G. A.; Toscuno, R. M.; Conte, V.; Furia, F. D. *Ibid.* **1991**, *113*, 6209.

[33] Oda, T.; Irie, R.; Katsuki, T.; Okawa, H. *Synlett.* **1992**, 641.

[34] Lazlo, P.; Levart, M. *Tetrahedron Lett.* **1993**, *34*, 1127.

[35] Marchon, J.-C.; Ramassenl, R. *Synthesis* **1989**, 389.

Scheme II. Oxidation of Thianthrene 5-Oxide[a]



[a] Reaction conditions: 41 (1 mmol), 4 (2 mmol), 3 (9 mg), CH_2ClCH_2Cl (30 mL), O_2 (1 atm), at 25 °C for 2 h.

(m, 1H), 2.51–2.45 (m, 1H), 2.17 (m, 3H), 1.45 (d, $J = 9.9$ Hz, 1H), 0.85 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 61.8, 58.7, 49.0, 48.8, 48.4, 44.6, 39.9, 39.2, 29.6, 26.9.

General Procedure for the Oxidation of Aldehydes. A 1,2-dichloroethane (8 mL) solution of aldehyde (5 mmol) and NPV_6Mo_6 (**3**) (88 mg) was fitted with a balloon containing about 3 L of oxygen. The mixture was stirred at 25 °C for 20 h. The same workup described for the epoxidation of alkenes was carried out, and the resulting extracts were analyzed by GLC and purified by column chromatography on silica gel. Carboxylic acids were identified by comparison of their ^1H and ^{13}C NMR spectra and GLC retention times with those of authentic samples.

General Procedure for the Baeyer–Villiger Oxidation of Ketones. A 1,2-dichloroethane (10 mL) solution of ketone (5 mmol), benzaldehyde (15 mmol), and NPV_6Mo_6 (**3**) (44 mg) was fitted with a balloon filled with about 3 L of oxygen. The mixture was stirred at 25 °C for 20 h. After the reaction, the reaction mixture was extracted with CH_2Cl_2 (50 mL × 5). The combined extracts were washed with aqueous $NaHCO_3$ (50 mL × 2). The organic layer was dried over $MgSO_4$ and analyzed by GLC with an internal standard. Removal of the solvent under reduced pressure afforded a clear liquid, which was purified by column chromatography on silica gel giving the corresponding ester. Products (**32**, **34**, **36**,[3c] and **38**) were identified by comparison of their ^1H and ^{13}C NMR with those of authentic samples or with literature values.

Oxidation of Thianthrene 5-Oxide. A 1,2-dichloroethane (30 mL) solution of thianthrene 5-oxide (1 mmol), 2 methylpropanal (**4**) (2 mmol), and **3** (9 mg) was fitted with a balloon filled with about 3 L of oxygen. The mixture was stirred at 25 °C for 2 h. The same workup described for the epoxidation of alkenes was carried out and the resulting extracts were analyzed by HPLC and purified by column chromatography on silica gel. All products were identified by comparison of their ^1H and ^{13}C NMR and HPLC retention time data with those of authentic samples.

Acknowledgment. We thank Prof. W. Adam for providing the samples of **41**, **42**, **43**, and thianthrene 5,5,10-trioxide.

Supplementary Material Available: NMR spectra data of **2**, **6**, **10**, **16**, **22**, **27–29**, **32**, **34**, **36**, **38**, **42**, and **43** and copies of spectra of **8**, **12**, **14**, **18**, **20**, **22**, and **24–26** (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.