Oxidation of Allenes and Alkynes with Hydrogen Peroxide Catalyzed by Cetylpyridinium Peroxotungstophosphate (PCWP)

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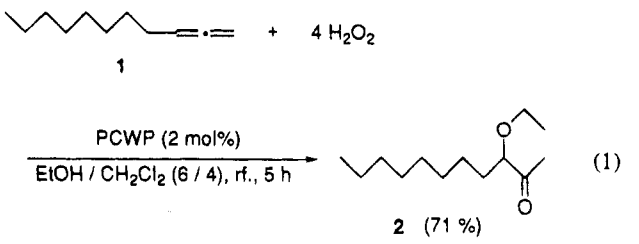
The oxidation of allenes and alkynes with hydrogen peroxide catalyzed by peroxotungstophosphate (PCWP) was examined. A variety of allenes were first converted into the corresponding α-ethoxy ketones upon treatment with 35% H_2O_2 under the influence of PCWP in a mixed solvent consisting of ethanol and dichloromethane. When the reaction was carried out using *tert*-butyl alcohol as a solvent, approximately a 1:1 regioisomeric mixture of α-hydroxy ketones was obtained along with a small amount of α-*tert*-butoxy ketone. Oxidation of internal alkynes such as 4-octyne by the PCWP–H_2O_2 system under phase-transfer conditions using chloroform produced α,β-epoxy ketones in good yields. The same reaction in a mixed solvent of ethanol and chloroform gave α,β-unsaturated ketones rather than α,β-epoxy ketones. Plausible reaction paths are proposed for the oxidation of allenes and alkynes by the PCWP–H_2O_2 system.

Although the oxidation of allenes[1] and alkynes[2] by various stoichiometric oxidizing agents has been studied, there are only a few reports for the catalytic oxidation of allenes[3] and alkynes[4] with the usual oxidants. We have recently shown that heteropolyoxometalates such as $[C_5H_5N(CH_2)_{15}CH_3]_3(PW_{12}O_{40})$ (CWP) and $[C_5H_5N(CH_2)_{15}CH_3]_3\{PO_4[W(O)(O_2)_2]_4\}$ (PCWP) having phase-transfer functions can be applied to the oxidation of a wide variety of organic substrates using hydrogen peroxide as an oxidant (*e.g.*, alkenes to epoxides,[5] carboxylic acids,[5b] and α-hydroxy ketones,[6] alcohols to ketones,[5b,7] *vic*-diols to α-hydroxy ketones[8] and carboxylic acids,[5b] alkynes to α,β-epoxy ketones,[9] amines to oximes and nitrones,[10a] anilines to azoxy-nitroso-, and nitrobenzenes,[10b] and sulfides to sulfoxides and sulfones[11] *etc.*).

In this paper, we wish to report the selective oxidation of allenes to α-alkoxy or α-hydroxy ketones and alkynes to α,β-unsaturated ketones or α,β-epoxy ketones by the PCWP–H_2O_2 system. Furthermore, possible reaction paths for these oxidations will be described in connection with the selectivity of the reaction.

1. Oxidation of Allenes. Although the oxidation of the allene bond with organic peracids produces an allene oxide as a primary product, such oxiranes are generally highly labile[12] and react further to produce complex product mixtures.[1a–d] Crandall *et al.* have studied the stoichiometric oxidation of allenes with a view toward generating a valence tautomerism between an allene oxide and a cyclopropanone.[1a,c,d,12a] However, the oxidation of simple allenes through a catalytic process is still an unsolved subject in oxidation chemistry.

We now find that terminal allenes can be selectively oxidized to α-alkoxy or α-hydroxy ketones by the PCWP–H_2O_2 system in a mixed solvent. The oxidation of 1,2-undecadiene (**1**) with 4 equiv of 35% H_2O_2 in the presence of a catalytic amount of PCWP (2 mol %) in ethanol/dichloromethane (6/4 v/v %) afforded 3-ethoxy-2-undecanone (**2**) with high selectivity (eq 1). Representative



(1)

results of our survey of solvents for the oxidation of **1** by the PCWP-H_2O_2 system are summarized in Table 1. A

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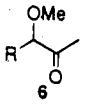
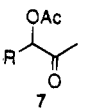
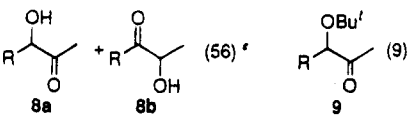
Table 1. Oxidation of 1,2-Undecadiene (1) with H_2O_2 by PCWP in Various Solvents[a]

Run	Solvent (mL)	H_2O_2 / equiv	Conv / %	Product (Selectivity / %) [b]
1 [c]	$CHCl_3$ (5)	1.5	58	 (7)  (29)  (5)
				3 4 5
2	EtOH (10)	4	24	**2** (71)
3	EtOH / CH_2Cl_2 (6/4)	4	100	**2** (71)
4	MeOH / CH_2Cl_2 (6/4)	4	50	 (34) **3** (4)
				6
5	MeOH / $CHCl_3$ (6/4)	4	90	**6** (53) **3** (2)
6	AcOH / $CHCl_3$ (6/4)	4	100	 (50) **3** (9)
				7
7 [d]	*t*-BuOH (10)	2	77	 (56) [e] (9) **3** (12)
				8a 8b 9

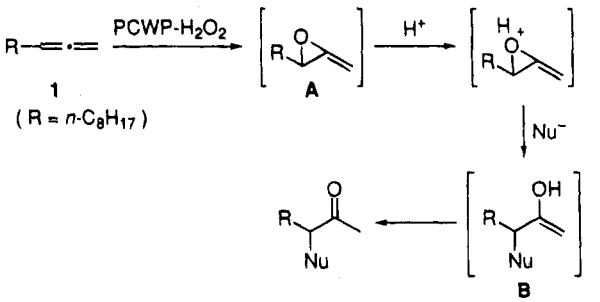
[a] 1 (1 mmol) was oxidized with 35% H_2O_2 by PCWP (0.02 mmol) in a solvent under refluxing for 5–20 h. [b] Based on **1** consumed. (R = *n*-C_8H_{17}). [c] PCWP (0.005 mmol), 60 °C, 1.5 h. [d] PCWP (0.01 mmol), 40 °C, 15 h. [e] Ratio of **8a/8b** is about 1/1.1.

large solvent effect on the selectivity was observed in the oxidation of **1**.

In contrast to the oxidation of alkenes[5] and alkynes[9] where chloroform serves as a good solvent, the oxidation of **1** in chloroform resulted in a complex mixture of various oxidation products (run 1). In a protic solvent like ethanol, **1** was oxidized to **2** in higher selectivity, although the conversion was low (run 2). In order to accomplish the reaction with higher conversion and selectivity, the reaction must be carried out in a mixed solvent of ethanol and dichloromethane (run 3). GC analysis showed that the products consisted of a single component which was subsequently assigned the structure **2**. In a mixed solvent of methanol/chloroform or acetic acid/chloroform, 3-methoxy-2-undecanone (**6**) or 3-acetoxy-2-undecanone (**7**) was formed in 53 or 50% yields, respectively (runs 5 and 6). When the oxidation was conducted in *tert*-butyl alcohol, approximately a 1:1 regioisomeric mixture of α-hydroxy ketones, **8a** and **8b**, was obtained in preference to α-*tert*-butoxy ketone **9** (run 7). The formation of **8** is believed to be due to hydrolysis of **9** as discussed later.

Table 2 shows the oxidation of several allenes in ethanol/dichloromethane by the PCWP–H_2O_2 system. The oxidation of terminal allenes, such as 1,2-nonadiene (**10**) and 3-cyclohexyl-1,2-propadiene (**12**), proceeded regioselectively to form the corresponding α-ethoxy ketones, 3-ethoxy-2-nonanone (**11**), and 1-cyclohexyl-1-ethoxy-2-propanone (**13**), respectively (runs 1 and 2). However, the oxidation of 3-methyl-1,2-nonadiene (**14**) under the same conditions gave 3-ethoxy-3-methyl-2-nonanone (**15**) (20%) and a cleaved product, 2-octanone (**16**) (17%) (run 3). An internal allene such as 6,7-tridecadiene (**17**) was also oxidized to the corresponding α-alkoxy ketone, 5-ethoxy-6-tridecanone (**18**) (50%), together with two cleaved products, hexanoic acid (**19**) (18%) and heptanoic acid (**20**) (21%) (run 4). In the case of an unsymmetrical allene such as 2,3-nonadiene (**21**), the oxidation was difficult to achieve regioselectively, affording a mixture of regioisomers, **22a** and **22b**, in 47% yield (run 5). The oxidation of 1-phenyl-1,2-butadiene (**23**) formed a pair of regioisomers of **24a** and **24b**, but the yields were low (run 6).

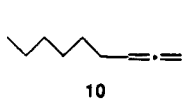
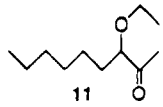
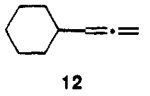
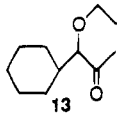
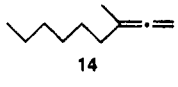
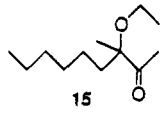
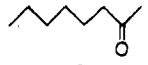
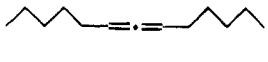
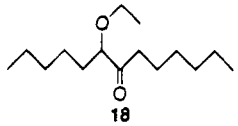
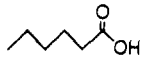
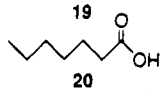
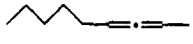
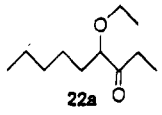
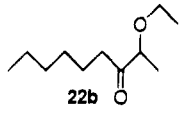
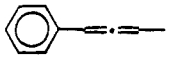
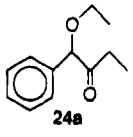
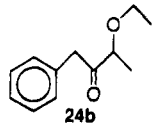
Scheme 1. A Possible Reaction Path for the Oxidation of Allenes by the PCWP–H_2O_2 System



A possible reaction path is shown in Scheme 1. It is reasonable to assume that allene oxide is formed in the first step of the present oxidation, because allene oxide is actually isolated by the oxidation of di-*tert*-butylallene with *m*-CPBA or peracetic acid.[12] In the case of terminal allenes such as **1**, the oxidation occurs regioselectively at the more reactive internal allene bond to form an allene oxide (**A**). The latter undergoes subsequent nucleophilic attack by alcohol or acetic acid producing α-alkoxy or α-acetoxy ketone, respectively, presumably via the corresponding enol (**B**).

Owing to the complexity of the reaction medium, it is rather difficult to confirm exactly the formation of **8a** and **8b** in the oxidation of **1** in *t*-BuOH. However, it seems likely that the major part of **8a** and **8b** was indeed formed through α-*tert*-butoxy ketone **9**. Because **8a** and **8b** were

Table 2. Oxidation of Several Allenes to α-Ethoxy Ketones by the PCWP-H_2O_2 System in EtOH/CH_2Cl_2 (6/4)[a]

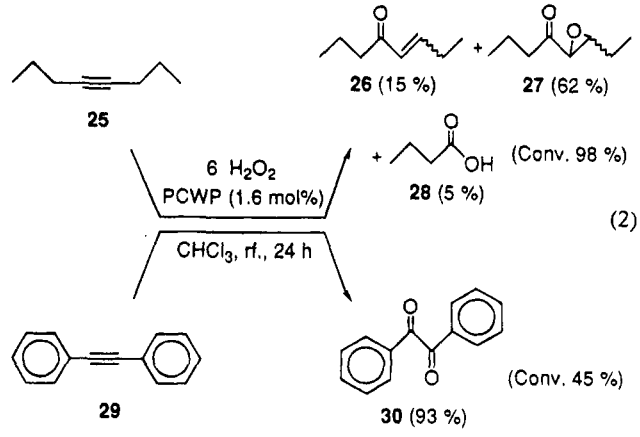
Run	Allene	Product (yield / %) [b]			
1	 10	 11	(66)		
2	 12	 13	(48)		
3	 14	 15	(20)	 16	(17)
4	 17	 18	(50)	 19  20	(18) (21)
5	 21	 22a	(20)	 22b	(27)
6	 23	 24a	(8)	 24b	(22)

[a] Substrate (2 mmol) was allowed to react with 35% H_2O_2 (8 mmol) in the presence of PCWP (0.04 mmol) in EtOH (12 mL) and CH_2Cl_2 (8 mL) at 80 °C for 5 h. [b] The conversion of allenes were more than 90% in each oxidation.

obtained by allowing **9** to react in an acidic medium (a 1:1 mixture of *t*-BuOH and 1 M H_2SO_4). By contrast, **2** was quite stable under these reaction conditions. Although the direct attack of water on the allene oxide intermediate **A** to lead to **8a** and **8b** is possible, the hydrolysis path is highly probable because no α-hydroxy ketone **8** is produced as the major product in the reaction using protic solvents other than *t*-BuOH.

Thus, the first catalytic oxidation of allenes with hydrogen peroxide has been conducted using PCWP as the catalyst. This method provides a direct preparative method for α-alkoxy ketones which are difficult to prepare by conventional methods.

2. Oxidation of Alkynes. Alkynes are stoichiometrically oxidized by various oxidizing agents such as organic peracids,[2a-c] $Th(NO_3)_2$,[2d] OsO_4,[2e] permanganates,[2f,i] RuO_4,[2g] peroxymonophosphoric acid,[2h] peroxomolybdenum complex,[2j] and dioxirane.[2k,l] However, very few investigations of the catalytic oxidation of alkynes have been reported.[4] Tomaselli *et al.* have reported that terminal alkynes are converted into α-oxo aldehydes by hydrogen peroxide oxidation in the presence of $[C_5H_5N(CH_2)_{15}CH_3]_3(PM_{12}O_{40})$ (M = Mo or W) and $Hg(OAc)_2$.[4b,c] In a previous communication,[9] we showed that internal alkynes such as 4-octyne (**25**) can be oxidized with hydrogen peroxide in the presence of PCWP under two-phase conditions, giving α,β-epoxy ketones (**27**) along with α,β-unsaturated ketones (**26**). Diphenylacetylene (**29**) was also converted into benzil (**30**) with high selectivity under the same reaction conditions (eq 2). Herein, we describe the full details of the reaction path in the PCWP-catalyzed oxidation of alkynes with hydrogen peroxide to form α,β-epoxy and α,β-unsaturated ketones.



In order to ascertain the features of alkyne oxidations by the PCWP–H_2O_2 system, **25** was chosen as a model substrate and allowed to react under various conditions. The oxidation of **25** with 35% H_2O_2 (6 equiv) by PCWP (1.6 mol %) at 60 °C for 24 h under the two-phase conditions using chloroform as a solvent led to 5-octen-4-one (**26**) (*E*-isomer), 3,4-epoxy-5-octanone (**27**) (*E*/*Z* = 17/83), and a cleaved product, butanoic acid (**28**), in 15, 62, and 5% yields, respectively (eq 2). To obtain information on the product distribution in the oxidation of **25**, the time-dependence of the products was followed by measurement of GC at appropriate time intervals (Figure 1).

The GC analysis of the reaction product showed that α,β-unsaturated ketones, *Z*-**26** and *E*-**26**, are formed as main products at an early stage of the oxidation. Furthermore, Figure 1 illustrates that α,β-epoxy ketones, *Z*-**27** and *E*-**27**, are formed by successive oxidation of the corresponding ketones, *Z*-**26** and *E*-**26**, and that the

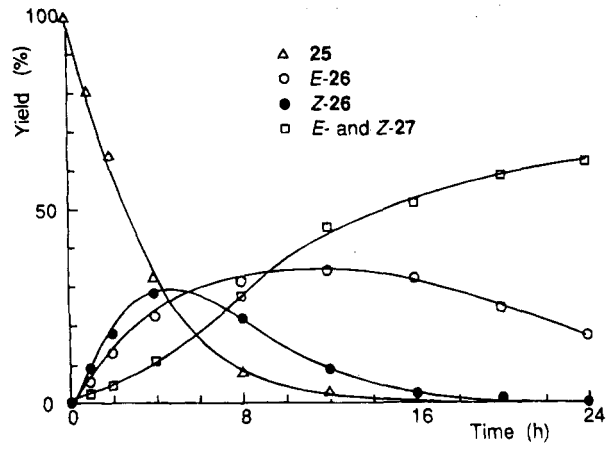
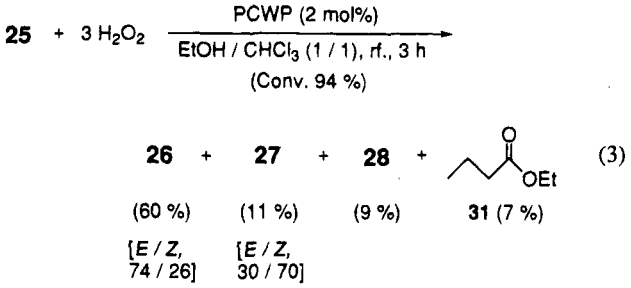
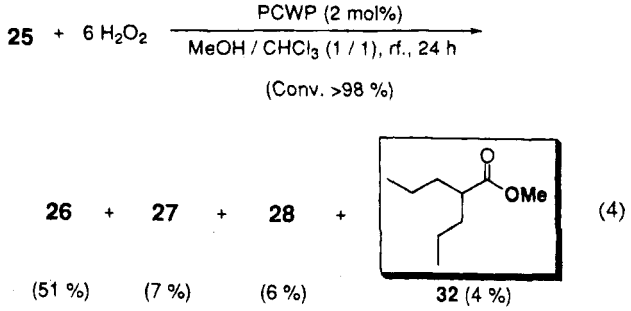


Figure 1. Time-dependence curves for the oxidation of 4-octyne (**25**) by the PCWP–H_2O_2 System.

epoxidation of *Z*-**26** occurs more rapidly than that of *E*-**26**. Indeed, the individual oxidation of *Z*-**26** and *E*-**26** by the PCWP–H_2O_2 system under the same conditions showed that *E*-**26** is rather more unreactive than *Z*-**26**.

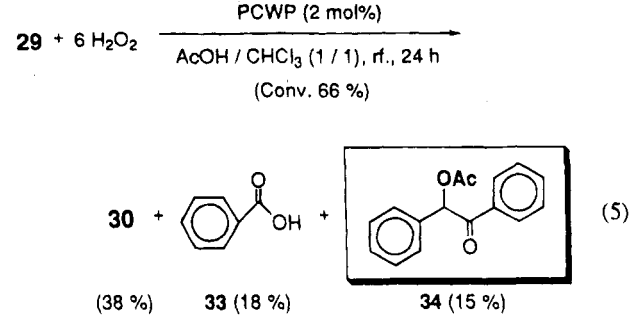
Fortunately, it was found that α,β-unsaturated ketone **26** was obtained with higher selectivity when the oxidation was carried out in a mixed solvent consisting of ethanol and chloroform (eq 3). In a mixed solvent of methanol/chloroform (1/1 v/v %), **25** gave **26**, **27**, **28** and a new product, methyl 2-propylpentanoate (**32**), which was not observed in the oxidation of **25** using chloroform as the solvent (eq 4).





Diphenylacetylene **29** was difficult to oxidize in a solvent containing methanol or ethanol, probably because of its low reactivity. Thus, **29** was oxidized in acetic acid/chloroform (1/1 v/v %) to form **30** (38%), benzoic acid (**33**) (18%), 1,2-diphenyl-2-acetoxyethan-1-one (**34**) (15%), and a small amount of benzophenone (1%) (eq 5).

Recently, the Curci[2k] and Murray[21] groups have reported the oxidation of alkynes by dioxiranes, and they propose that the reactions proceed via oxirenes which can equilibrate to oxocarbenes as intermediates. Similar postulates have been made in the oxidation of alkynes by peracids.[2a–c] In contrast to these reports where the oxirenes are postulated as the primary products, it has



been reported that the oxidation of **29** with *tert*-butyl hydroperoxide by an oxodiperoxomolybdenum complex proceeds via molybdenum–oxacarbene complexes.[13] In addition, in the same oxidation by oxo(salen)chromium-(V) triflate, the intermediate is most likely a metallaoxetene and/or a related species, such as a metallocarbene.[14] None of the products of these oxidations had the Wolff rearrangement product structure as might be formed via the intermediacy of oxocarbenes.

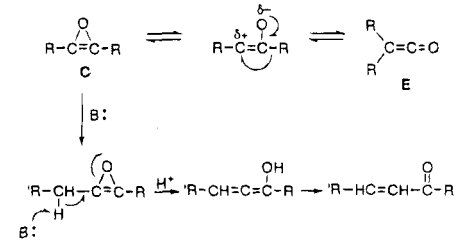
In the present oxidation of alkynes by the PCWP–H_2O_2 system, it is probable that the reaction proceeds via an oxirene and/or an oxocarbene[15,16] to yield α,β-unsaturated ketones **26**, α,β-epoxy ketones **27**, 1,2-diones **30**, and α-acetoxy ketones **34**, etc.

A plausible reaction path is shown in Scheme 2.[17]

The first step of the oxidation involves the electrophilic attack on the alkyne with the peroxo species derived from PCWP and H_2O_2 to form an oxirene (**C**), which can readily isomerize to an α-ketocarbene (**D**). The subsequent 1,2-hydrogen shift from **D** results in the formation of α,β-unsaturated ketone **26**. When chloroform is used as the solvent, the resulting **26** is further oxidized to α,β-epoxy ketone **27**. However, in the mixed solvent of methanol and chloroform, the reaction stopped at the stage of **26**, because the catalytic activity of PCWP is considerably depressed by the coordination of methanol to the catalyst. In addition, the formation of methyl ester **32** seems to be due to the addition of methanol to a ketene (**E**)[18] arising from the Wolff rearrangement of **D**.

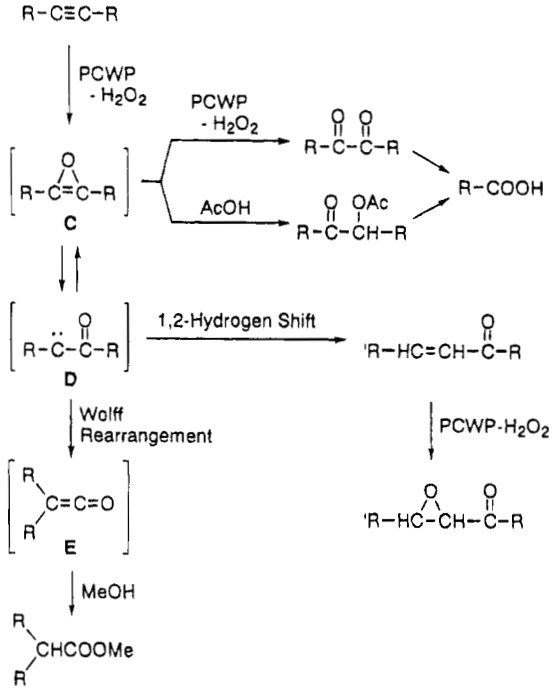
It appears that the dicarbonyl compound is formed when the further oxidation of **C** occurs in preference to the rearrangement into ketene **E** or a 1,2-hydrogen shift to afford α,β-unsaturated ketone.

(13) Matlin, S. A.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2851.
(14) Rither, B.; SriHari, S.; Hunter, S.; Masnovi, J. *J. Am. Chem. Soc.* **1993**, *115*, 3918.
(15) (a) Tanigaki, K.; Ebbesen, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 5883. (b) Bechmann, C.; N'Guessan, T. Y.; Debû, F.; Monnier, M.; Pourcin, J.; Aycard, J. P.; Bodot, H. *Ibid.* **1990**, *112*, 7488.
(16) Lewars, E. G. *Chem. Rev.* **1983**, *83*, 519.
(17) The following path on the oxidation of **25**, in which α-keto carbene (**D**) is not formed as an intermediate, has been suggested by a reviewer.



(18) In fact, the GC-MS analyses show the formation of dipropyl ketene in the oxidation of **25**, but it cannot be isolated: MS (70 eV) *m/z* 126 (6), 84 (100), 55 (32), 42 (35), 41 (37), 39 (31).

Scheme 2. A Possible Reaction Path for the Oxidation of Alkynes by the PCWP–H_2O_2 System



Although we are unable to explain clearly the failure to observe alkyl dicarbonyl compound in the oxidation of **25**, in contrast **29**, it seems reasonable to assume that the conversion of **25** to **26** is much faster than to dicarbonyl compound or that the oxidation of the resulting alkyl dione to carboxylic acid **28** occurs faster than it is formed. In fact, the oxidative cleavage of alkyl dione took place under the influence of hydrogen peroxide. The formation of **34** can be explained by the nucleophilic attack of acetic acid on the oxirene **C**.

In summary, we have shown that the oxidation of allenes and alkynes with hydrogen peroxide is catalyzed by peroxotungstophosphate (PCWP). The selective oxidation of allenes to α-ethoxy ketone was satisfactorily carried out by the use of the mixed solvent ethanol/dichloromethane. On the other hand, the oxidation of alkyne **25** in chloroform leads to α,β-epoxy ketone **27** in good yield, while in ethanol/chloroform α,β-unsaturated ketone **26** is obtained with high selectivity. The formation of α-alkoxy ketones from allenes and α,β-unsaturated ketone **26** or dione **30** from alkynes can be explained by postulating an allene oxide and an oxirene, respectively, as intermediates.

As a result of the present study, we are now able to oxidize various types of carbon–carbon multiple bonds (such as alkenes, alkynes, allenes, allylic alcohols, and α,β-unsaturated carbonyl compounds) with aqueous hydrogen peroxide in a biphasic system by a process employing PCWP as a catalyst. PCWP has two attributes of special interest here: its high oxidizing ability and its suitability as a phase transfer catalyst.

Experimental Section

Materials. Allenes **1**, **10**, **12**, **14**, **17**, **21**, and **23**, were synthesized by literature procedures[19] and purified by distillation under reduced pressure or by column chromatography on silica gel (hexane). 4-Octyne (**25**) and diphenylacetylene (**29**) were commercially available and were used without further purification. PCWP was prepared by the method reported previously.[9] GC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-1). ^{1}H- and ^{13}C-NMR were measured at 400 and 100 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. Infrared (IR) spectra were measured using NaCl pellets. GC-MS spectra were obtained at an ionization energy of 70 eV. The yields of products were estimated from the peak areas based on the internal standard technique.

General Procedure for Oxidation of Alkenes. To a stirred solution of PCWP (0.083 g, 2 mol %), 35% H_2O_2 (8 mmol), and 0.05 M H_2SO_4 (0.06 g) in EtOH (12 mL) and CH_2Cl_2 (8 mL) was added allene (2 mmol), and the reaction mixture was stirred at 80 °C for 5 h. The resulting solution was treated with aqueous $NaHSO_3$ to decompose the unreacted H_2O_2 and was extracted with ether. The extract was dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The products were purified by column chromatography on silica gel (hexane/ethyl acetate (5/1)).

n-Nonanal (**3**), 1-decene (**4**), 1,2-epoxydecane (**5**), 2-octanone (**16**), *n*-hexanoic acid (**19**), and *n*-heptanoic acid (**20**) were identified through comparison of isolated products with authentic samples.

3-Ethoxy-2-undecanone (2): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.61 (dd, J = 5.5 Hz and 7.7 Hz, 1H), 3.54–3.48 (m, 1H), 3.48–3.39 (m, 1H), 2.16 (s, 3H), 1.67–1.53 (m, 2H), 1.45–1.20 (m, 12H), 1.23 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 212.4, 85.9, 66.0, 32.2, 31.8, 29.4, 29.4, 29.2, 25.2, 25.0, 22.6, 15.3, 14.1; MS (70 eV) *m/z* 171 (63), 83 (62), 69 (97), 55 (38), 43 (100).

3-Methoxy-2-undecanone (6): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.55 (dd, J = 5.9 Hz and 7.0 Hz, 1H), 3.36 (s, 3H), 2.16 (s, 3H), 1.67–1.56 (m, 2H), 1.47–1.23 (m, 12H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C-NMR δ ($CDCl_3$, 100 MHz) δ 211.7, 87.5, 58.1, 31.9, 31.8, 29.4, 29.3, 29.2, 25.1, 25.0, 22.6, 14.1; MS (70 eV) *m/z* 157 (100), 83 (63), 69 (97), 55 (28), 43 (94).

3-Acetoxy-2-undecanone (7):[20] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.98 (dd, J = 4.8 Hz and 8.4 Hz, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 1.80–1.70 (m, 2H), 1.43–1.21 (m, 12H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 205.4, 170.6, 78.7, 31.8, 30.2, 29.3, 29.2, 29.1, 26.1, 25.1, 22.6, 20.7, 14.1.

3-Hydroxy-2-undecanone (8a) + 2-Hydroxy-3-undecanone (8b). Compounds **8a** and **8b** could not be isolated and were obtained in ratio of 1/1.1 (**8a**/**8b**) as shown by ^{1}H-NMR: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.19–4.16 (m, 1H), 4.14–4.11 (m, 1H), 3.52 (d, J = 4.4 Hz, 1H), 3.40 (d, J = 4.8 Hz, 1H), 2.44–2.36 (m, 2H), 2.13 (s, 3H), 1.61–1.49 (m, 2H), 1.31 (d, J = 7.0 Hz, 3H), 1.40–1.10 (m, 24H), 0.81 (t, J = 7.3 Hz, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 212.7, 210.0, 76.9, 72.8, 37.8, 33.8, 32.1, 32.0, 29.7, 29.7, 29.5, 29.5, 29.5, 29.3, 25.4, 25.0, 23.9, 22.9, 22.9, 20.1, 14.3, 14.3.

3-*tert*-Butoxy-2-undecanone (9). Compound **9** could not be purified completely: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.76 (dd, 1H), 2.16 (s, 3H), 1.56–1.22 (m, 14H), 1.17 (s, 9H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 214.2, 78.8, 74.6, 33.6–22.6, 14.1; MS (70 eV) *m/z* 199 (9), 141 (7), 83 (4), 69 (8), 57 (100), 43 (37).

3-Ethoxy-2-nonane (11): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.61 (dd, J = 5.5 Hz and 7.7 Hz, 1H), 3.54–3.47 (m, 1H), 3.47–3.41 (m, 1H), 2.16 (s, 3H), 1.67–1.53 (m, 2H), 1.44–1.22 (m, 8H), 1.23 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 212.3, 85.9, 65.9, 32.1, 31.6, 29.0, 25.1, 24.9, 22.5, 15.2, 14.0.

1-Cyclohexyl-1-ethoxy-2-propanone (13): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.54–3.46 (m, 1H), 3.42–3.34 (m, 1H), 3.31 (d, J = 7.0 Hz, 1H), 2.14 (s, 3H), 1.84–1.46 (m, 6H), 1.22 (t, J = 7.0 Hz, 3H), 1.29–1.05 (m, 5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 212.6, 90.7, 66.5, 40.4, 28.8, 28.6, 26.2, 25.9, 25.8, 25.7, 15.2.

3-Ethoxy-3-methyl-2-nonanone (15): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.42–3.35 (m, 1H), 3.29–3.22 (m, 1H), 2.18 (s,

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3H), 1.70–1.55 (m, 2H), 1.35–1.15 (m, 8H), 1.24 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 213.8, 84.2, 59.1, 36.6, 31.6, 29.6, 24.7, 23.2, 22.5, 19.5, 15.8, 14.0.

6-Ethoxy-7-tridecanone (18): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.63 (dd, J = 5.5 Hz and 7.7 Hz, 1H), 3.53–3.45 (m, 1H), 3.45–3.37 (m, 1H), 2.50 (dt, J = 3.3 Hz and 7.3 Hz, 2H), 1.64–1.52 (m, 4H), 1.48–1.21 (m, 12H), 1.23 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 214.1, 85.8, 66.0, 37.3, 32.3, 31.6, 31.6, 29.0, 25.0, 23.1, 22.5, 22.4, 15.3, 14.0, 14.0; MS (70 eV) *m/z* 129 (100), 113 (4), 83 (83), 55 (48), 43 (26).

4-Ethoxy-3-nonanone (22a): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.66 (dd, J = 5.5 Hz and 7.3 Hz, 1H), 3.52–3.40 (m, 2H), 2.54 (q, J = 7.3 Hz, 2H), 1.67–1.53 (m, 2H), 1.46–1.29 (m, 6H), 1.23 (t, J = 7.0 Hz, 3H), 1.05 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 214.5, 85.7, 66.0, 32.4, 31.6, 30.5, 25.0, 22.4, 15.3, 13.9, 7.2.

2-Ethoxy-3-nonanone (22b): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.81 (q, J = 7.0 Hz, 1H), 3.51–3.44 (m, 2H), 2.60–2.45 (m, 2H), 1.61–1.53 (m, 2H), 1.37–1.22 (m, 6H), 1.28 (d, J = 7.0 Hz, 3H), 1.24 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 213.7, 81.2, 65.4, 37.0, 31.6, 28.9, 23.2, 22.5, 17.6, 15.3, 14.0.

1-Ethoxy-1-phenyl-2-butanone (24a): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.41–7.29 (m, 5H), 4.78 (s, 1H), 3.54–3.47 (m, 2H), 2.62–2.52 (m, 1H), 2.52–2.44 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 209.8, 136.7, 128.7, 128.3, 126.8, 87.4, 65.1, 30.4, 15.2, 7.3.

3-Ethoxy-1-phenyl-2-butanone (24b): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.34–7.20 (m, 5H), 3.88 (q, J = 7.0 Hz, 1H), 3.85 (s, 2H), 3.49–3.39 (m, 2H), 1.31 (d, J = 7.0 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 210.4, 133.9, 129.6, 128.5, 126.8, 80.7, 65.5, 44.1, 17.4, 15.3.

Hydrolysis of α-*tert*-Butoxy Ketone 9 to α-Hydroxy Ketone 8 under Acidic Conditions. Compound **9** was isolated by column chromatography on neutral aluminum oxide with hexane/ethyl acetate (5/1) eluent from the oxidation products of allene **1** in *t*-BuOH. A stirred solution of **9** *t*-BuOH/1 M H_2SO_4 (1/1 wt %) was allowed to react under refluxing for 24 h. The reactant was extracted with ether. GC and GC-MS analyses showed the formation of **8a** and **8b** in >98 % selectivity.

General Procedure for Oxidation of Alkynes. To a stirred solution of PCWP (0.083 g, 2 mol %), 25% H_2O_2 (6 mmol) and 0.05 M H_2SO_4 (0.06 g) in $CHCl_3$ (2.5 mL) and EtOH (2.5 mL) was added the alkyne (2 mmol), and the reaction mixture was stirred at 80 °C for 5 h. The workup was performed by the same method as described above, and the products were purified by column chromatography on silica gel (hexane/ethyl acetate (10/1)).

Butanoic acid (**28**), benzil (**30**), and benzoic acid (**33**) were identified through comparison of isolated products with authentic samples. Ethyl butanoate (**31**) and methyl 2-propylpentanoate (**32**) were identified through comparison of their spectral data with those obtained by esterification between the corresponding acids and alcohols in the presence of sulfuric acid in refluxing dichloromethane. 1,2-Diphenyl-1-acetoxyethan-2-one (**34**) was assigned by comparing with the literature value.[21]

(*E*)-5-Octen-4-one (*E*-26):[9] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 6.88 (dt, J = 6.4 Hz and 15.8 Hz, 1H), 6.10 (d, J = 15.8 Hz, 1H), 2.53 (t, J = 7.3 Hz, 2H), 2.25 (dq, J = 6.4 Hz and 7.3 Hz, 2H), 1.64 (tq, J = 7.3 Hz and 7.3 Hz, 2H), 1.08 (t, J = 7.7 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 200.9, 148.5, 129.4, 41.9, 25.5, 17.7, 13.8, 12.2.

(*Z*)-5-Octen-4-one (*Z*-26):[22] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 6.11 (d, J = 11.4 Hz, 1H), 6.04 (dt, J = 7.0 Hz and 11.4 Hz, 1H), 2.62 (dq, J = 7.0 Hz and 7.3 Hz, 2H), 2.43 (t, J = 7.3 Hz, 2H), 1.63 (tt, J = 7.3 Hz and 7.3 Hz, 2H), 1.04 (t, J = 7.7 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 201.9, 150.0, 126.2, 46.2, 22.9, 17.5, 13.8, 13.7.

(*E*)-3,4-Epoxy-5-octanone (*E*-27): ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.23 (d, J = 2.2 Hz, 1H), 3.04 (dt, J = 2.2 Hz and 5.5 Hz, 1H), 2.47–2.39 (m, 1H), 2.31–2.21 (m, 1H), 1.73–1.56 (m, 4H), 1.03 (t, J = 7.7 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 208.3, 59.6, 59.5, 39.3, 25.2, 16.9, 14.0, 9.9.

(*Z*)-3,4-Epoxy-5-octanone (*Z*-27):[9] ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.61 (d, J = 4.8 Hz, 1H), 3.18 (dt, J = 1.8 Hz and 4.8 Hz, 1H), 2.52 (t, J = 7.3 Hz, 2H), 1.66 (dq, J = 1.8 Hz and 7.3 Hz, 2H), 1.63–1.52 (m, 1H), 1.51–1.42 (m, 1H), 1.03 (t, J = 7.7 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 206.2, 59.7, 58.7, 43.0, 20.9, 16.7, 13.7, 10.4.

Oxidation of α,β-Unsaturated Ketones 26 to α,β-Epoxy Ketones 27. To a stirred solution of PCWP (0.076 g, 1.6 mol %) and 35% H_2O_2 (12 mmol) in $CHCl_3$ (5 mL) was added **26** (2 mmol), and the reaction mixture was stirred at 60 °C. The time-dependence curves for the oxidation products was followed by utilizing the GC at appropriate time intervals.

Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra of all compounds (38 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.

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