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Dehomologation of Aldehydes via Oxidative Cleavage of Silyl Enol Ethers with Aqueous Hydrogen Peroxide Catalyzed by Cetylpyridinium Peroxotungstophosphate under Two-Phase Conditions

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Dehomologation of aldehydes has been first successfully achieved via oxidative cleavage of silyl enol ethers, derived from aldehydes and trimethylchlorosilane, using aqueous hydrogen peroxide in the presence of a catalytic amount of peroxotungstophophate (PCWP) under phase-transfer conditions. For instance, the oxidation of 1-[(trimethylsilyl)oxy]-1-octene resulting from octanal and Me_3SiCl with 35% H_2O_2 catalyzed by PCWP in dichloromethane at room temperature afforded the one-carbon shorter aldehyde, heptanal, in 79% yield. A variety of silyl enol ethers were also converted into one-carbon shorter aldehydes in good yields. The oxidation under homogeneous conditions using *tert*-butyl alcohol gave hydrolysis products such as 2-oxooctanol and octanal. It is of interest that [1-(trimethylsilyl)oxy]-1,10-undecadiene involving an enol moiety and a terminal double bond afforded exclusively 9-decenal, in which the enol moiety was selectively oxidized. A plausible reaction path for the oxidative cleavage of silyl enol ethers by the present system has been suggested from the oxidation results of α-[(trimethylsilyl)oxy]styrene.

Introduction

Oxidative cleavage of carbon−carbon double bonds is a fundamental and important transformation in synthetic organic chemistry.[1] Ozonolysis[2] and oxidation by stoichiometric oxidants such as osmiun tetraoxide,[3] ruthenium tetraoxide,[4] and potassium permanganate[5] are frequently used for this purpose. However, because these reagents have the obvious drawbacks of being toxic and expensive, a number of catalytic systems using H_2O_2,[6] NaOCl,[7] $NaIO_4$,[8] and peracetic acid[9] as oxidants have been examined.

Among these oxidants, aqueous hydrogen peroxide, a cheap and environmentally benign oxidant, has attracted much interest in recent years. Tungsten compounds such as polyoxotungstophosphates and tungstic acid are efficient catalysts for the oxidative cleavage of olefinic double bonds to carboxylic acids with aqueous hydrogen peroxide.[6] However, the transformation of alkenes to aldehydes via oxidative cleavage is rarely explored because of the difficulty in controlling the oxidation at the stage of the formation of aldehydes, except for the formation of glutaraldehyde by the oxidative cleavage of cyclohexene with anhydrous hydrogen peroxide using $H_3PMo_{10}W_2O_{40}$ as a catalyst.[10]

The oxidation of silyl enol ethers to α-hydroxyketones has been achieved by using various oxidation systems.[11] In a previous paper, we showed that the silyl enol ether 1-[(trimethylsilyl)oxy]-1-octene (**1**) was first successfully converted into the α-hydroxy ketone 2-oxooctanol (**2**) using aqueous hydrogen peroxide as an oxidant in the presence of a catalytic amount of cetylpyridinium peroxotungstophosphate (PCWP), $[C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4$-

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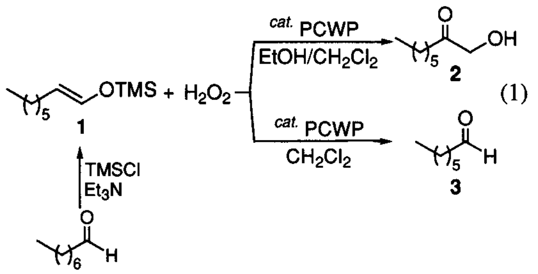
$[W(O)(O_2)_2]_4\}^{3-}$ in a mixed solvent of ethanol and dichloromethane (eq 1).[12] However, under two-phase conditions



using dichloromethane as a solvent, the reaction gave oxidatively cleaved products such as the aldehyde heptanal (**3**). Kaneda et al. have shown that treatment of silyl enol ethers with *tert*-butylhydroperoxide using a molybdenum complex leads to the corresponding carboxylic acids but not to aldehydes.[13] Because silyl enol ethers can be easily prepared by the reaction between the corresponding aldehydes and Me_3SiCl,[14] we are interested in the PCWP-catalyzed dehomologation of aldehydes to one-carbon shorter aldehydes.[15] The synthesis of odd-numbered long-chain aldehydes, which are difficult to obtain by conventional methods, using this methodology seems to be very useful. In this paper, we would like to report further details of the dehomologation of aldehydes via oxidative cleavage of silyl enol ethers with aqueous hydrogen peroxide catalyzed by PCWP under two-phase conditions.

Results

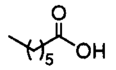
At first, to obtain further information on the oxidation, 1-[(trimethylsilyl)oxy]-1-octene (**1**) was allowed to react with aqueous hydrogen peroxide (35%) in the presence of a catalytic amount of PCWP under selected conditions. Representative results are shown in Table 1. Although excess H_2O_2 (6 equiv) with respect to **1** was employed, the amounts of **3** and heptanoic acid (**4**) were almost the same as those of run 1 except for **2** (run 2). These results suggest that the aldehyde **3** was not further oxidized to carboxylic acid **4** by the PCWP−H_2O_2 system under these conditions. In refluxing temperature (ca. 40 °C), however, a considerable amount of heptanoic acid **4** was formed. Under homogeneous conditions using *tert*-butyl alcohol as a solvent, the oxidative cleavage to **3** was found to take place in competition with the hydrolysis to octanal (**5**) (run 4).

On the basis of these results, a variety of silyl enol ethers, derived from aldehydes and Me_3SiCl, were allowed to react with 35% H_2O_2 in the presence of PCWP in dichloromethane at room temperature (Table 2).

Table 1. Oxidation of 1 by the PCWP−H_2O_2 System Under Selected Conditions[a]

Run	Solvent	H_2O_2 (mmol)	Temp (°C)	Product (Yield/%)			
				2	3	4	5+6
1[b]	CH_2Cl_2	3	25	1	79	<1	<5
2	CH_2Cl_2	6	25	10	77	<1	<5
3	CH_2Cl_2	3	rf	12	48	21	2
4	^{t}BuOH	3	25	31	24	<1	24[c]

[a] **1** (1 mmol) was allowed to react with 35% H_2O_2 in the presence of PCWP (0.02 mmol) in solvent (2.5 mL) for 16 h. [b] Previously reported (ref. 12). [c] Yield of **5**.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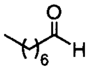
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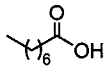
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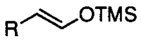
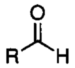
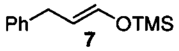
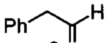
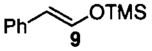
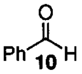
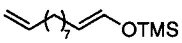
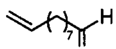
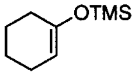
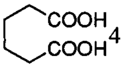
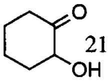
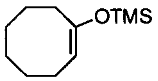
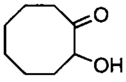
Table 2. Oxidation of Various Silyl Enol Ethers by the PCWP−H_2O_2 System[a]

Run	Substrate	Product	Yield (%)[b]
1	 R = n-C_8H_{17}		72 (63)
2	R = n-$C_{10}H_{21}$		71
3	R = n-$C_{11}H_{23}$		70 (60)
4	 **7**	 **8**	71 (64)
5	 **9**	 **10**	76
6[c]	 **11**	 **12**	58 (52)
7		 48[d] 	21
8			45[e]

[a] Substrate (1 mmol) was allowed to react with 35% H_2O_2 (3 mmol) in the presence of PCWP (0.02 mmol) in CH_2Cl_2 (2.5 mL) at room temperature for 16 h. [b] Yields were estimated by GLC using internal standards technique. Values in parentheses are isolated yields which are obtained by the three-time scale experiments [c] 8,9-Epoxydecenal (<5%) and 9,10-epoxyundecanal (<5%) were formed. [d] Isolated yield (See experimental section). [e] Cyclooctanone (ca.20%) was formed.

Various types of silyl enol ethers were successfully oxidized to one-carbon shorter aldehydes in satisfactory yields (runs 1−5). The odd-numbered aldehydes such as nonanal and undecanal were produced by the oxidation of the even-numbered silyl enol ethers obtained from decanal and dodecanal, respectively (runs 1 and 2). 3-Phenyl-1-[(trimethylsilyl)oxy]-1-propene (**7**) derived from 3-phenylpropionaldehyde was oxidized to phenylacetoaldehyde (**8**) (run 4). In the case of the oxidation of 1-[(trimethylsilyl)oxy]-1,10-undecadiene (**11**) involving enolic and terminal double bonds, the enolic double bond was preferentially oxidized to give 9-decenal (**12**) in 58% yield along with small amounts of 2-oxo-10-undecen-1-ol, 9,10-epoxydecenal, 10,11-epoxyundecanal, and 10-undecenal in <5% yields, respectively; 9,10-epoxy-1-[(trimethylsilyl)oxy]-1-decene formed by the epoxidation of the terminal double bond was not detected. This is

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(12) Yamamoto, H.; Tsuda, M.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1997**, *62*, 7174.

(13) Kaneda, K.; Kii, N.; Jitsukawa, K.; Teranishi, S. *Tetrahedron Lett.* **1981**, *22*, 2595.

(14) House, H. O.; Czuba, L. L.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(15) Very recently, dehomologation of α-substituted aldehydes to the corresponding ketones via oxidative cleavage of enamine with transition metal oxides such as CrO_3 and $KMnO_4$ has been reported: (a) Harris, C. E.; Lee, L. Y.; Dorr, H.; Sigaram, B. *Tetrahedron Lett.* **1995**, *36*, 2921. (b) Harris, C. E.; Chrisman, W.; Bickford, S. A.; Lee, L. Y.; Torreblanca, A. E.; Sigaram, B. *Tetrahedron Lett.* **1997**, *38*, 981. (c) Sreekumar, R.; Padmakumer, R. *Tetrahedron Lett.* **1997**, *38*, 5143.

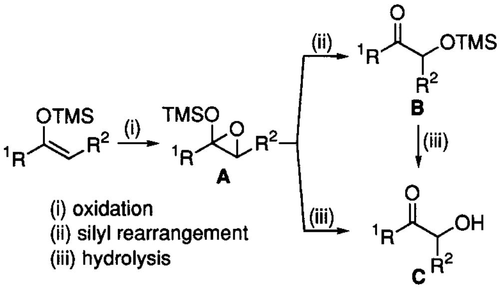
believed to be due to the fact that the electron density of the enolic double bond is higher than that of the terminal bond. In fact, electron densities of C_1, C_2, C_9, and C_{10} were estimated to be +0.059, −0.278, −0.137, and −0.168, respectively, by the PM3 semiempirical method as implemented in the MOPAC 93.[16] Unfortunately, the oxidation of the cyclic silyl enol ether 1-[(trimethylsilyl)oxy]-1-cyclohexene resulted in the formation of adipic acid and 2-hydroxycyclohexanone in 48% and 21% yields, respectively (run 7). Similarly, 1-[(trimethylsilyl)oxy]-1-cyclooctene was oxidized to 2-hydroxyoctanone as a major product (run 8).

Discussions

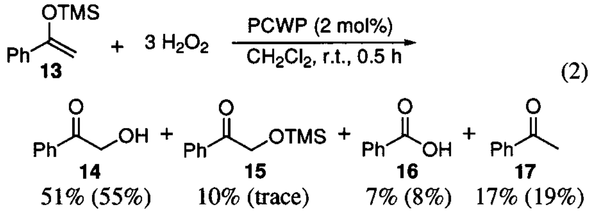
The dehomologation of aldehydes was performed via the oxidative cleavage of silyl enol ethers, synthetic equivalents of aldehydes, upon treatment with the PCWP−H_2O_2 system under two-phase conditions. The successful achievement of this transformation is believed to be due to the fact that the PCWP possesses both powerful oxidizing ability and phase-transfer catalysis.[17] Another important factor is that the reaction could be carried out under the two-phase system using dichloromethane. As a consequence, the hydrolysis of silyl enol ethers to the original aldehydes could be restricted to a considerable extent even in the presence of aqueous hydrogen peroxide. In addition, the reaction proceeded smoothly at room temperature as a result of the higher reactivity toward the peroxo species of enolic double bonds bearing a trimethylsilyloxyl group compared to that of normal olefinic double bonds.

In general, the oxidation of silyl enol ether is thought to proceed via the formation of an α-trimethylsilyloxy epoxide **A**, which then is converted into an α-hydroxy ketone **C** through silyl rearrangement or hydrolysis (Scheme 1).[11,18] It is noteworthy, however, that the present oxidation of silyl enol ethers, having a trimethylsilyloxy group at the terminal position, produced the oxidatively cleaved products, aldehydes, rather than α-hydroxy ketones as major products as shown in Table 2 (runs 1−6).

Scheme 1



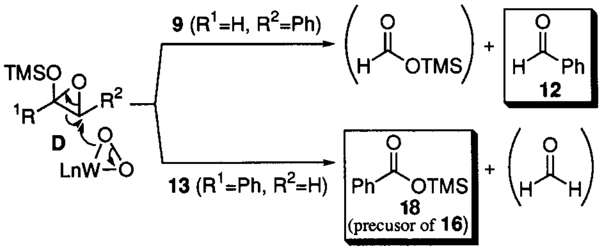
The oxidation of α-[(trimethylsilyl)oxy]styrene (**13**) with 35% H_2O_2 catalyzed by PCWP (2 mol %) at room temperature for 0.5 h afforded 2-hydroxyacetophenone (**14**) (51%), 2-[(trimethylsilyl)oxy]acetophenone (**15**) (10%), and benzoic acid (**16**) (7%) together with acetophenone (**17**) (17%), hydrolysis product of the starting **13**, in >99% conversion (eq 2). It is interesting that **13** bearing an α-silyloxy group gave **14** and **15**, in contrast to the oxidation of **9** bearing a *β*-silyloxy group, for which benzaldehyde **10** was formed as a principal product (Table 2, run 5). The formation of **12** and **16** from α- and *β*- [(trimethylsilyl)oxy]styrenes **9** and **13**, respectively, suggests an alternative oxidation path of the silyl enol ethers (Scheme 2). The formation of **10** from **9** may be rationalized by the further oxidation of α-trimethylsilyloxy epoxide (**D**), which is a primary product generated by the epoxidation of silyl enol ether, to the one-carbon shorter aldehyde (Scheme 2). In the same sense as the formation of **10**, the carbon−carbon bond cleavage of the epoxide **D** derived from **13** leads to the formation of benzoic acid precursor **18**, although the hydrolysis of **D** to α-hydroxyketone **14** is a preferred over the bond cleavage to **18**.



(2)

( ): Parenthese show the reaction for 16 h.

Scheme 2



In conclusion, a variety of silyl enol ethers obtained from aldehydes and Me_3SiCl were first successfully oxidized to one-carbon shorter aldehydes with aqueous hydrogen peroxide in the presence of a catalytic amount of PCWP. The oxidation apparently proceeds via the formation of a trimethylsilyloxy epoxide, which then is converted into an α-trimethylsilyloxy aldehyde whose oxidation results in the one-carbon shorter aldehyde. Because silyl enol ethers are easily prepared from aldehydes and Me_3SiCl, the present reaction provides a novel route for the dehomologation of aldehydes.

Experimental Section

General Procedures. All silyl enol ethers except for **9**, 1-[(trimethylsilyl)oxy]-1-cyclohexene, and **12** were synthesized according to the literature procedures and purified by distillation under reduced pressure.[14] Compounds **9**, 1-[(trimethylsilyl)oxy]-1-cyclohexene, and **12** were commercially available and used without further purification. PCWP was prepared by the method reported previously.[13] GC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-1). ^1H and ^{13}C NMR spectra were measured at 270 or 400 MHz and 67.5 or 100 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. Infrared (IR) spectra were measured using a NaCl plate. GC-MS spectra were obtained at an ionization energy of 70 eV. The product yields were estimated from the peak areas on the basis of the internal standard technique.

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(16) Stewart, J. J. *J. Comput. Chem.* **1989**, *10*, 209.

(17) Sakaguchi, S.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1996**, *61*, 5307 and references therein.

(18) (a) Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 1396. (b) Rubottom, G.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599.

General Procedure for the Oxidation of Silyl Enol Ethers to Aldehydes. To a stirred solution of substrate (1 mmol) and PCWP (40 mg, 2 mol %) in CH_2Cl_2 (0.25 mL) was added 35% H_2O_2 (1 mmol). The reaction mixture was stirred at room temperature for 16 h and extracted with dichloromethane. The extract was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The products were purified by column chromatography on silica gel with hexane/ethyl acetate (10−3/1 v/v). All products except for **3**,[12] **12**, 2-hydroxycylcohexanone,[12] 2-hydroxycyclooctanone,[12] and **15** were commercially available and were identified through the comparison of the isolated products with authentic samples. Compound **15** was identified through the comparison of the isolated products with the compound prepared by the reaction of **14** with TMSCl.

9-Decenal (12): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 9.69 (s, 1 H), 5.77−5.65 (m, 2 H), 4.94−4.83 (m, 2 H), 2.34 (t, $J = 7.3$ Hz, 2 H), 1.97−1.93 (m, 2 H), 1.58−1.53 (m, 2 H), 1.28−1.20 (m, 8 H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 202.8, 139.0, 114.1, 43.8, 33.6, 29.1, 29.0, 28.8, 28.7, 22.0; IR 2928, 1730, 1658, 1253, 1164, 1083, 845, 757.

Oxidation of 1-[(Trimethylsilyl)oxy]-1-Cyclohexene. To a stirred solution of substrate (1 mmol) and PCWP (40 mg, 2 mol %) in CH_2Cl_2 (0.25 mL) was added 35% H_2O_2 (1 mmol). The reaction mixture was stirred at room temperature for 16 h and extracted with dichloromethane. The extract was dried over anhydrous $MgSO_4$. After evaporation of the extract under reduced pressure, a white precipitate was obtained. The precipitate was purified by recrystallization with ethyl acetate to give adipic acid in 48% isolated yield.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for the compounds **3**, **12**, 2-hydroxycylcohexanone, 2-hydroxycyclooctanone, and **15**. This information available free of charge via the Internet at http://pubs.acs.org.

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