AN EFFICIENT OXIDATIVE CLEAVAGE OF CARBON-SILICON BONDS
# BY A DIOXYGEN/HYDROQUINONE SYSTEM[1]

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Summary: Carbon-silicon bonds in alkylalkoxysilanes readily undergo cleavage by dioxygen in the presence of hydroquinone derivatives to give the corresponding alcohols in good yields. The real oxidant is dry hydrogen peroxide generated in situ. The oxidation proceeds with complete retention of configuration at an sp^3 carbon center.

Since organosilicon compounds are generally quite stable to oxidants, oxidative cleavage of carbon-silicon bonds is one of the challenging topics in silicon chemistry.[2] We and some other groups have reported the oxidative cleavage of certain carbon-silicon bonds by various oxidants such as peroxy acids,[3] hydrogen peroxide,[4] and amine oxide;[5] these oxidations are finding a variety of synthetic uses.[6]

Oxidative cleavage of carbon-silicon bonds by dioxygen, however, had been unknown until recently we reported a new oxidation by dioxygen, catalyzed by a flavin-dihydronicotinamide redox system.[7] In this paper we now report an efficient oxidative cleavage of carbon-silicon bonds by a dioxygen-hydroquinone system which generates dry hydrogen peroxide in situ under mild conditions.[8] As shown in eq. 1, a 1-octylalkoxysilane is readily converted into 1-octanol in a high yield.

$$\text{(1)}$$
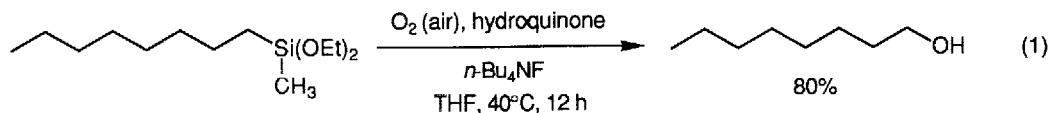
A typical experimental procedure is as follows.   A mixture of 1-octylmethyldiethoxysilane (1 mmol), hydroquinone (2 mmol), tetra-*n*-butylammonium fluoride (TBAF, 1 mmol; 1 M THF solution) and dry THF (10 ml) was stirred at 40°C for 10-20 h under air in a flask equipped with a CaCl$_2$ drying tube. The reaction mixture was filtered and the filter cake was washed with ether. The combined filtrate was evaporated and brown

tarry residue was subjected to column chromatography (silica gel, hexane/ethyl acetate 5:1) to give pure 1-octanol in 80% isolated yield.

The initial rate of the present oxidation is enhanced with an increase in dioxygen pressure. Thus, in the oxidation of 1-$C_8H_{17}SiMe(OEt)_2$ as a model substrate in THF at 40°C the yield of 1-octanol was observed as follows: under 1 atm of dioxygen (balloon) ; 39% (1 h), 62% (2 h), 74% (3 h), and under air; 14% (1 h), 21% (2 h), 28% (3 h). Yields of 1-octanol reached 85-90% after 12 h in both cases, irrespective of the concentration of dioxygen in solution.

The rate of the oxidation depends on the nature of hydroquinone derivatives (Fig. 1). Fig. 1 shows some interesting features. (1) The efficiency increases in the order of hydroquinone < 2-methylhydroquinone < 2,3-dimethylhydroquinone. The order is consonant with the reactivity order of hydroquinones in autoxidation, reported by James and his co-workers.[8] (2) No induction period was ovserved in the formation of 1-octanol in all cases. (3) In the case of 2,3-dimethylhydroquinone-dioxygen system, the rate of formation of 1-octanol is comparable with that of the oxidative cleavage by 90% hydrogen peroxide[9] and faster than that of the usual oxidation by 30% hydrogen peroxide.[9] These results demonstrate that dry hydrogen peroxide generated in situ from the dioxygen-hydroquinone system cleaves carbon-silicon bonds smoothly, the rate of the oxidation being determined by the rate of generation of hydrogen peroxide.
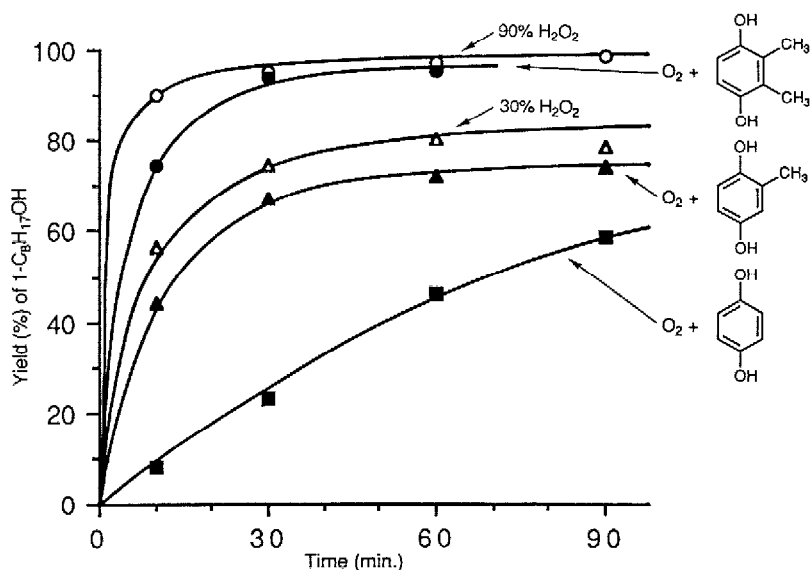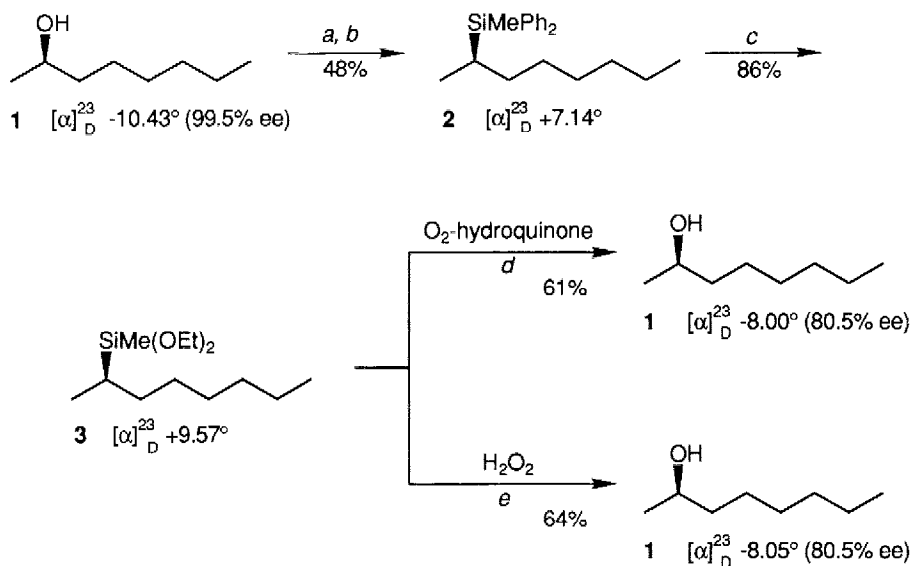

Figure 1.   Yield-time plots for oxidation of 1-$C_8H_{17}SiMe(OEt)_2$ by dioxygen in the presence of 2,3-dimethylhydroquinone (●), 2-methylhydroquinone (▲), and hydroquinone(■), and by 90% H_2O_2 (○) and 30% H_2O_2 (▵).

In order to elucidate the stereochemistry at an sp^3 carbon center during the conversion of alkylsilane to alcohol, we investigated the oxidation of (R)-2-octylmethyldiethoxysilane (3), as shown in Scheme 1. Thus, the oxidation of 3 by the present dioxygen-hydroquinone system gave (R)-2-octanol (1) in 61% yield, $[\alpha]^{23}$D = -8.00°(c 0.93, CHCl₃), 80.5% ee.[10] Similarly the reaction of 3 with 30% hydrogen peroxide also gave (R)-2-octanol (1) in 64% yield, $[\alpha]^{23}$D = -8.05° (c 1.31, CHCl₃), 80.5% ee.[10] The stereochemical outcomes disclosed that the dioxygen-hydroquinone oxidation as well as the hydrogen peroxide oxidation[4] proceeds with complete retention of configuration.[11] The stereochemical aspect clearly demonstrates that the present oxidation involves no alkyl radical species which might be assumed by traditional autoxidation, but proceeds with hydrogen peroxide as real oxidant.

The present dioxygen (air) oxidation of carbon-silicon bonds, which occurs smoothly under mild conditions by means of readily available hydroquinone and TBAF as additives, may find uses in synthetic reactions.

Scheme 1

OH

1   $[\alpha]^{23}_D$ -10.43° (99.5% ee)

$\xrightarrow[48\%]{a,\,b}$

SiMePh₂

2   $[\alpha]^{23}_D$ +7.14°

$\xrightarrow[86\%]{c}$

SiMe(OEt)₂

3   $[\alpha]^{23}_D$ +9.57°

O₂-hydroquinone
d
61%

OH

1   $[\alpha]^{23}_D$ -8.00° (80.5% ee)

H₂O₂
e
64%

OH

1   $[\alpha]^{23}_D$ -8.05° (80.5% ee)

[a] Ph₂PCl (inversion).   [b] Ph₂MeSiLi, THF (inversion).
[c] (1) Dry HCl, AlCl₃ (cat.), C₆H₆; (2) EtOH, NH₃, Et₂O.
[d] O₂(1 atm), hydroquinone, n-Bu₄NF, THF, 40°C, 10 h.
[e] 30% H₂O₂, KF, KHCO₃, THF, MeOH, room temp., 9 h.

References and Notes

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9. Experimental procedure by 30% or 90% H_2O_2 as oxidants: $1-C_8H_{17}SiMe(OEt)_2$ (1 mmol), H_2O_2 (2 mmol), TBAF (1 mmol), dry THF (10 ml; making a 0.1 M solution), 40°C.

10. Enantiomeric purity of **1** was determined by HPLC analysis of its 3,5-dinitrophenyl-carbamate (ArNCO/pyridine/toluene) with a chiral stationary phase column (Sumipax OA-4100, hexane/dichloroethane/ethanol = 100/20/1).

11. About 20% drop in the optical purity of 2-octanol during the overall transformation should be ascribed to the first two steps, chlorination (inversion)[12] and subsequent silylation by $PhMe_2SiLi$ (inversion).[13]

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