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SILAFUNCTIONAL COMPOUNDS IN ORGANIC SYNTHESIS. 29.[1]
OXIDATION OF (ALKENYL)ALKOXYSILANES TO α-HYDROXY KETONES

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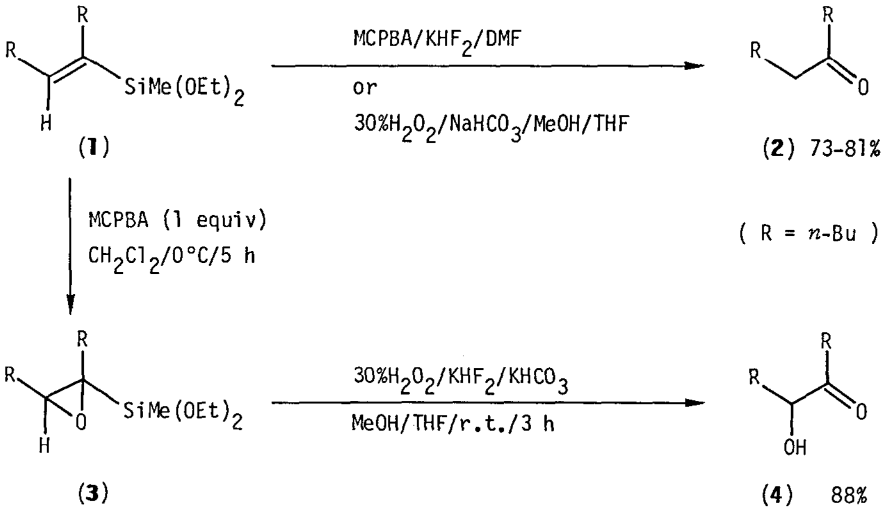
Summary: (Alkenyl)alkoxysilanes are readily transformed into α-hydroxy ketones via epoxidation and the subsequent oxidative cleavage of the carbon-silicon bonds.

Vinylsilanes and their epoxides have now been recognized as useful precursors for carbonyl compounds.[2] Although α,β-epoxysilanes have two oxygen functionalities at the vicinal positions, they are usually transformed into mono-functional carbonyl derivatives via acidolysis.[3] The formation of 1,2-diol derivatives under specific conditions has also been reported recently,[4] but there has been still no methodology for their transformation into difunctional carbonyl derivatives.[5]

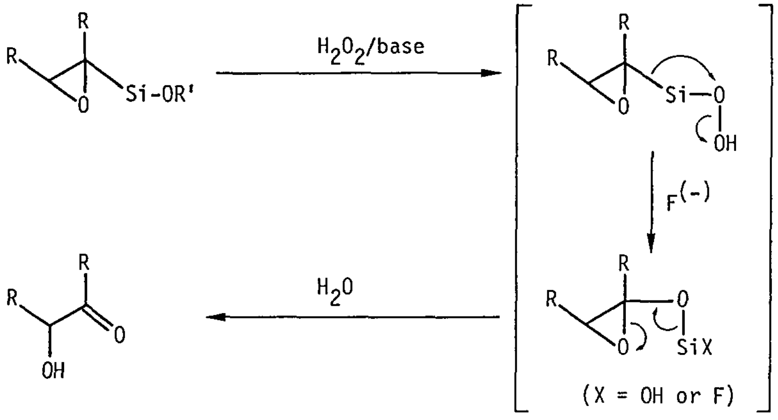
Here, we report that (alkenyl)alkoxysilanes can be converted into α-hydroxy ketones via epoxidation and the subsequent oxidative cleavage of the carbon-silicon bonds therein, thus enabling the effective utility of the two oxygen functional groups already present. Typical transformations are given for the oxidation of 5-decenyldiethoxymethylsilane (**1**) (Scheme 1).



SCHEME 1

As reported previously,[6] the direct oxidative cleavage of the alkenyl-silicon bond in **1** by MCPBA/KHF_2 in DMF, as well as by 30% H_2O_2/$NaHCO_3$, gave 5-decanone (**2**) in high yields. In contrast, treatment of **1** with 1 equiv of MCPBA in CH_2Cl_2 resulted in the formation of the corresponding epoxide (**3**) quantitatively, leaving the carbon-silicon bonds intact. The carbon-silicon bonds in the epoxide were then oxidized by 30% H_2O_2 in the presence of KHF_2 and $KHCO_3$ at room temperature to form 6-hydroxy-5-decanone (**4**) in high yields.

There are two significant features in the present transformation. One is the contrasting behaviors of MCPBA toward **1**: ordinary epoxidation takes place in CH_2Cl_2, while oxidative cleavage of the carbon-silicon bonds is induced in DMF in the presence of KHF_2. The latter unusual behavior may result from the disruption of the intramolecular hydrogen bond in the peracid by polar solvents, which should reduce the epoxidizing ability,[7] but might favor the interaction with the silicon center.[8] The other is the high reactivity of the epoxysilane toward the oxidizing agent, in comparison with the simple alkyl-silicon bond.[9] This feature will be discussed with the aid of a plausible mechanism,[10] shown in Scheme 2, which involves the initial exchange of the alkoxy group on silicon with the oxidizing agent and the subsequent intramolecular migration of the oxiranyl group. In connection with this mechanism, it may be noted here that the carbon-silicon bond in α,β-epoxysilane is readily cleaved by fluoride ion to form an oxiranyl carbanion, as reported by Chan.[11] This carbanionic character of the oxiranyl group is favorable for the migration to the positive oxygen atom in the peroxide intermediate. This may be the main origin of the high reactivity of the epoxysilanes.

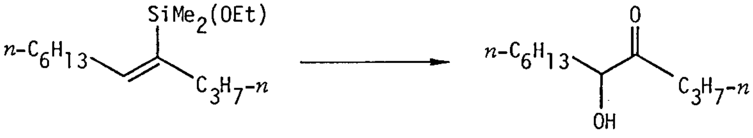


(Two organic groups on silicon are omitted for clarity)

SCHEME 2

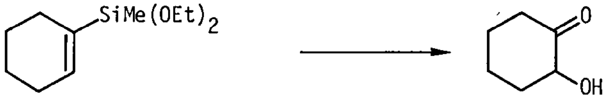
The Chan's report,[11] however, strongly suggested another possibility that the present oxidative cleavage of epoxysilanes might proceed through the initial formation of incipient oxiranyl anionic species, and, if so, epoxy<u>trimethylsilanes</u> instead of the epoxy<u>alkoxysilanes</u> might also undergo the similar oxidation. In order to examine this possibility, we subjected 5,6-epoxy-5-trimethylsilyldecane, Me_3Si analog of **3**, to those oxidation conditions under which **3** was readily oxidized, but only recovered the unchanged epoxysilane. The results demonstrate that the alkoxysilyl group is essential for the present transformation.

Under the standard reaction conditions mentioned above, (Z)-alkenylsilane (equation 1) as well as (E) isomer, terminal alkenylsilane (equation 2),[12] and cyclic alkenylsilanes (equations 3 and 4) were all converted into the corresponding α-hydroxy ketones. No steric hindrance by the cis-substituent is apparent from the smooth reaction shown in equation (1). The results of equations (1) and (2) clearly indicate that the carbonyl group appears on the silicon-bearing olefin carbon atom.[13]

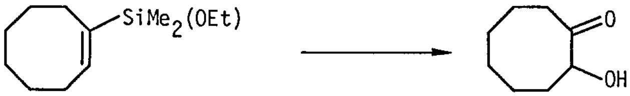


80% (1)

72% (2)

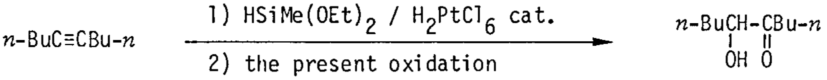


(dimer)[14] 45-75%[14] (3)



74% (4)

In combination with hydrosilylation, acetylenes can be converted into α-hydroxy ketones efficiently, as shown in equation (5). This represents virtually the first straightforward method for such transformation with a high selectivity.[15] Other synthetic applications of the present transformation are now under investigation.



$$n\text{-BuC}\equiv\text{CBu-}n \xrightarrow[\text{2) the present oxidation}]{\text{1) HSiMe(OEt)}_2\text{ / H}_2\text{PtCl}_6\text{ cat.}} n\text{-Bu}\underset{\text{OH}}{\text{CH}}\text{-}\underset{\text{O}}{\overset{}{\text{C}}}\text{Bu-}n \qquad (5)$$

(**4**) overall 81%

A typical experimental procedure is as follows. To a solution of 1 (818 mg; 3.0 mmol) in dichloromethane (10 ml) was added MCPBA (80% purity; 647 mg; 3.0 mmol) at 0°C with stirring. After 5 h-stirring at 0°C, the mixture was diluted with hexane (10 ml) and filtered with suction, the filter cake being washed with cold hexane. The solvents in the combined filtrate were evaporated under reduced pressure at 45°C. To the remaining oil, essentially pure epoxide (3),[16] were added successively KHF_2 (469 mg; 6.0 mmol), $KHCO_3$ (900 mg; 9.0 mmol), MeOH (12 ml), THF (12 ml) and 30% H_2O_2 (0.72 ml; ca. 7 mmol). The mixture was stirred at room temperature for 3 h. The resulting white mixture was poured into an aqueous solution of $NaHSO_3$ (750 mg in 70 ml) at 0°C and extracted with ether five times. The ether layer was washed with a saturated $NaHCO_3$ solution and water and then dried over Na_2SO_4. After evaporation of the solvent the remaining oil was subjected to preparative TLC (Silica Gel; hexane/ethyl acetate 3/1; Rf 0.66) to give **4** (453 mg; 88% yield).[17,18]

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(11) T. H. Chan, P. W. K. Lau and M. P. Li, Tetrahedron Lett., 2667 (1976).

(12) The oxidation of 1-silyl-1-alkenes such as $RCH{=}CHSiMe(OEt)_2$ to α-hydroxy aldehydes has not been satisfactorily achieved yet.

(13) Both monoalkoxy- and dialkoxy-silyl derivatives were employed without difficulty, while trialkoxysilyl derivatives encountered rather sluggish epoxidation. For the dependency of the reactivity of the alkoxysilanes on the number and the nature of the alkoxy groups, see our previous paper: K. Tamao, N. Ishida, T. Tanaka and M. Kumada, Organometallics, **2**, 1694 (1983).

(14) 2-Hydroxycyclohexanone readily dimerizes to a solid 1,4-dioxane derivative which exhibits no infrared carbonyl absortions and has a low solubility in common organic solvents. The yield of purified product was around 50%. Cf., P. B. Bartlett and G. F. Woods, J. Am. Chem. Soc., **62**, 2933 (1940) and The Aldrich Library of Infrared Spectra, Second Ed., 1975, 231A.

(15) Cf., L. I. Simandi in "The Chemistry of Triple-Bonded Functional Groups", S. Patai and Z. Rappoport (Ed.), Part 1, John-Wiley, New York, 1983, pp. 513-570.

(16) Epoxysilane **3** seemed to be thermally unstable. ^1H NMR (CCl_4, 100 MHz) δ (ppm): 0.10 (s, 3H), 0.8-1.1 (m, 6H), 1.20 (t, J = 7 Hz, 6H), 1.1-1.7 (m, 12H), 2.70-2.90 (m, 1H), 3.74 (q, J = 7 Hz, 4H). High resolution mass: Found 288.2137; Calcd for $C_{15}H_{32}O_3Si$ 288.2121.

(17) The oxidative cleavage of **3** was also achieved by MCPBA (1 equiv) and KF (2 equiv) in DMF at room temperature overnight, but the yield of **4** was somewhat lower (75%).

(18) We thank Shin-etsu Chemical Industrial Co., Ltd. for a gift of organosilicon starting materials.

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