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SILAFUNCTIONAL COMPOUNDS IN ORGANIC SYNTHESIS. 21.[1]
HYDROGEN PEROXIDE OXIDATION OF ALKENYL(ALKOXY)SILANES

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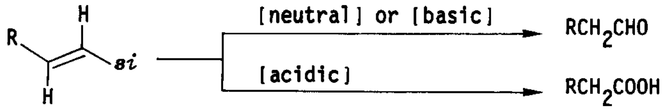
Summary: The carbon-silicon bond in alkenyl(alkoxy)silanes is readily cleaved by hydrogen peroxide to form the corresponding aldehydes, carboxylic acids or ketones, depending upon the nature of the alkenyl group and the reaction conditions.

We have recently reported that the silicon-carbon bond in alkyl(alkoxy)silanes is readily cleaved by hydrogen peroxide to give the corresponding alcohols (eq. 1).[1,2] Three typical reaction conditions have been employed. Throughout this paper, *si* = (alkoxy)silyl group.

$$R\text{-}si \xrightarrow{H_2O_2} R\text{-}OH \qquad (1)$$

[neutral] condition: 30% $H_2O_2/KHF_2/DMF$/r.t.~60°C
[acidic] condition : 30% $H_2O_2/Ac_2O/KHF_2/DMF$/r.t.
[basic] condition : 30% $H_2O_2/KHCO_3/MeOH/THF$/60°C

Described herein is the similar oxidative cleavage of alkenyl(alkoxy)silanes to carbonyl compounds. The reaction courses depend upon the nature of alkenylsilanes and the reaction conditions employed. 1-Alkenylsilanes form the corresponding aldehydes under the neutral or basic condition (eq. 2), while under the acidic condition they are oxidized to carboxylic acids (eq. 3). Internal alkenylsilanes are converted to ketones (eq. 4).



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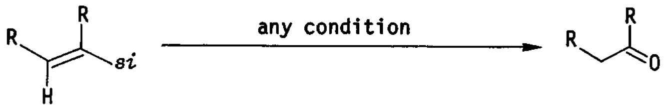
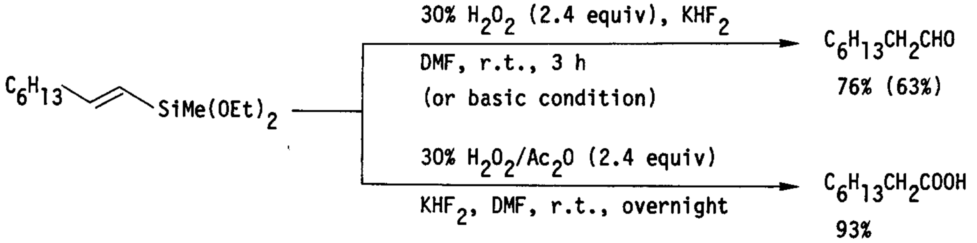


(4)

1-Octenylmethyldiethoxysilane was allowed to react with 30% H_2O_2 under the neutral condition at room temperature or under the basic condition for 3 h to give octanal in 76% or 63% isolated yield, respectively (eq. 5). Under the acidic condition and after a prolonged reaction time, the same alkenylsilane afforded octanoic acid in higher than 90% yield (eq. 6). The $-Si(OEt)_3$ and $-SiMe_2(OEt)$ analogs also gave the acid in 75 ∿ 85% yields.



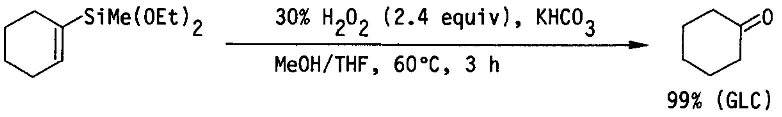
(5)

(6)

In these reactions, the *alkenyl*-silicon bond has been cleaved in preference to the *methyl*-silicon bond. For example, in the aldehyde synthesis (eq. 5), the oxidation occurred at room temperature within a few hours, while under these conditions the cleavage of the alkyl-silicon bond is known to be rather sluggish.[1] The selective cleavage of the alkenyl group may also be confirmed in the carboxylic acid synthesis where only 2 equiv of the oxidant are necessary. Thus, the first equiv of oxidant forms the aldehyde which is then converted to the carboxylic acid by the second;[3] the silicon-methyl bond must have been retained.

In the oxidation of these 1-alkenylsilanes, the use of a large excess amount of oxidant and more drastic conditions should be avoided, because the concomitant carbon-carbon double bond cleavage occurs to some extent to give a carboxylic acid with one-carbon loss.[4,5]

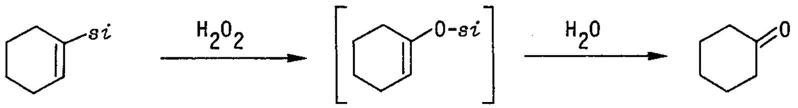
1-Cyclohexenylmethyldiethoxysilane, a typical cyclic vinylsilane, as well as acyclic vinylsilanes (vide infra), is transformed into the corresponding cyclic ketone in high yield (eq. 7). The basic condition is the first choice; the neutral or acidic condition affords only about 50% yield.



(7)

The single-step transformation of cyclic vinylsilanes to ketones should particularly be noted. The present reaction may proceed through direct oxidation[5,6] of the alkenyl-silicon bond to form an enol silyl ether species which is hydrolyzed in the reaction mixture to give the observed ketone, as shown by eq. 8. There has been a well-known standard method for the conversion of vinylsilanes to carbonyl compounds via a sequence of epoxidation and acidolysis, as shown by eq. 9.[7,8] This stepwise method is, however, applicable only to acyclic systems, but not to cyclic ones owing to the stereochemical restrictions, as exemplified by the isolation of a stable diol (eq. 10).[9] The present methodology provides the first clear-cut solution to the problem.

Direct oxidation (present method)



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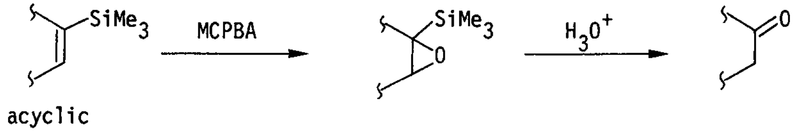
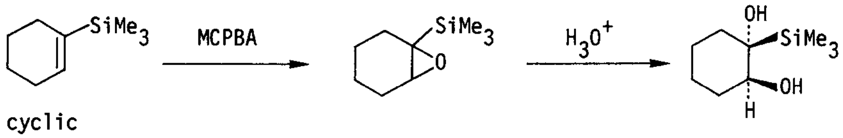
Stepwise oxidation

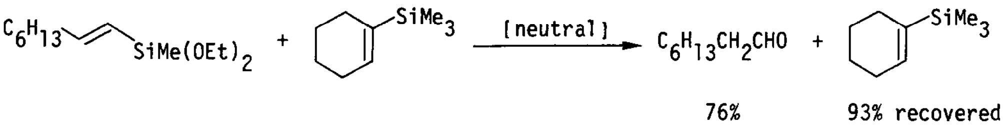


(9)[7]

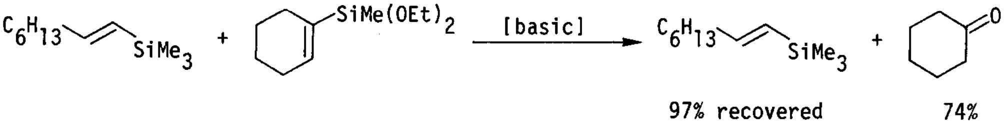


(10)[9]

The present oxidation occurs selectively on an alkenyl-(alkoxy)silyl compound in the presence of an alkenyl-$SiMe_3$ compound, as shown by the following representative results (eqs. 11 and 12).

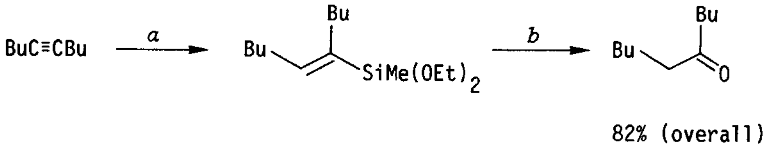


(11)

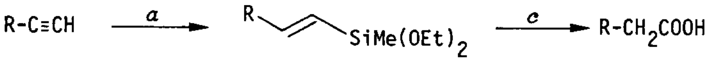


(12)

The present development has opened up a new method for the one-pot transformation of acetylenes to carbonyl compounds via a hydrosilylation-oxidation sequence. Several representative results are given in eqs. 13 and 14.



(13)[1]



(14)

R = $n\text{-}C_6H_{13}$- 68%, $t\text{-}C_4H_9$- 73%,[10] Ph- 61%[11]

[a] $HSiMe(OEt)_2$ (1.2 equiv), H_2PtCl_6 cat., r.t., 0.5 h

[b] 30% H_2O_2 (12 equiv), KHF_2 (2 equiv), DMF, 60°C, 4 h

[c] 30% H_2O_2/Ac_2O (2.4 equiv), KHF_2 (2 equiv), DMF, r.t., 20 h

While many advantages mentioned in the previous paper[1] should apply to the present reaction also, the regioselectivity becomes a big problem in the acetylene series. The ketone synthesis may be applied only to symmetrical internal acetylenes, since unsymmetrical acetylenes suffer from a low regioselective hydrosilylation.[12] The H_2PtCl_6 catalyzed hydrosilylation of terminal acetylenes with $HSiMe(OEt)_2$ attaches the silyl group to the terminal carbon atom predominantly or exclusively; e.g., the terminal to internal ratios are 80/20, 100/0, and 65/35 for $C_6H_{13}C{\equiv}CH$, t-$BuC{\equiv}CH$, and $PhC{\equiv}CH$, respectively. The regioselectivity is dependent upon the nature of the hydrosilane, as exemplified by the improved ratio 75/25 for $PhC{\equiv}CH$ attained with $HSi(OEt)_3$. Although the direct oxidation of the isomeric mixture of hydrosilylation products should afford a mixture of carboxylic acid and ketone, the desired carboxylic acid can easily be isolated by the standard alkaline extraction work-up; the overall yields are in the range of acceptable 60-70%.[13] While the acetylene-to-carboxylic acid transformation has already been achieved by hydroboration of silylacetylenes and the subsequent oxidation,[14] the present method provides a more convenient alternative.[15]

REFERENCES AND NOTES

(1) For part 20 see: K. Tamao, N. Ishida, T. Tanaka, and M. Kumada, *Organometallics*, in press.

(2) K. Tamao, N. Ishida, and M. Kumada, *J. Org. Chem.*, **48**, 2120 (1983).

(3) Octanal was the main product within several hours of the reaction.

(4) For example, $C_6H_{13}CH{=}CHSi(OEt)_3$ gave a 23/77 mixture of $C_6H_{13}COOH$ and $C_6H_{13}CH_2COOH$ in a 76% total yield by the oxidation with 6 equiv of 30% H_2O_2 at 60°C for 4 h.

(5) Cf., K. Tamao, M. Akita, and M. Kumada, *J. Organomet. Chem.*, **254**, 13 (1983).

(6) Cf., K. Tamao, T. Kakui, M. Akita, T. Iwahara, R. Kanatani, J. Yoshida, and M. Kumada, *Tetrahedron*, 39, 983 (1983).

(7) G. Stork and E. Colvin, *J. Am. Chem. Soc.*, **93**, 2080 (1971).

(8) E. W. Colvin, "Silicon in Organic Synthesis", Butterworths, London, 1981, pp. 83-96.

(9) P. F. Hudrlik, J. P. Arcoleo, R. H. Schwartz, R. N. Misra, and R. J. Rona, *Tetrahedron Lett.*, 591 (1977).

(10) Eight equiv of 30% H_2O_2/Ac_2O were used.

(11) $HSi(OEt)_3$ was used in stead of $HSiMe(OEt)_2$.

(12) Functional group mediated regioselective hydrosilylation of unsymmetrical acetylenes is currently under investigation in our laboratories.

(13) A typical procedure is as follows. To a mixture of 1-octyne (322 mg; 3.01 mmol) and $HSiMe(OEt)_2$ (490 mg; 3.66 mmol) were added a few drops of a solution of $H_2PtCl_6{\cdot}6H_2O$ in *i*-PrOH (0.1 mol/l) at room temperature. The hydrosilylation proceeded exothermically and completed within 0.5 h. To the mixture were added successively KHF_2 (570 mg; 7.31 mmol), DMF (10 ml), and Ac_2O (0.88 ml; ∿8.8 mmol), and then 30% H_2O_2 (0.88 ml; ∿8.8 mmol) dropwise at room temperature with stirring. An exothermic reaction occurred. After stirring at room temperature overnight, the usual work-up, alkaline extraction, acidification, ether extraction, drying over Na_2SO_4, and bulb-to-bulb distillation, gave 297 mg (68% overall yield) of octanoic acid.

(14) G. Zweifel, and S. J. Backlund, *J. Am. Chem. Soc.*, **99**, 3184 (1977).

(15) We thank Sin-etsu Chemical Industrial Co., Ltd., for support of this work and for a gift of hydrosilanes.

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