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OXIDATIVE CLEAVAGE OF THE SILICON–CARBON BOND:

DEVELOPMENT, MECHANISM, SCOPE, AND LIMITATIONS

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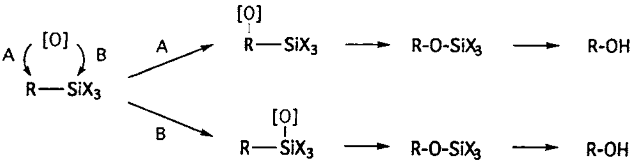
1. INTRODUCTION: HOW TO OXIDATIVELY CLEAVE THE SILICON–CARBON BOND

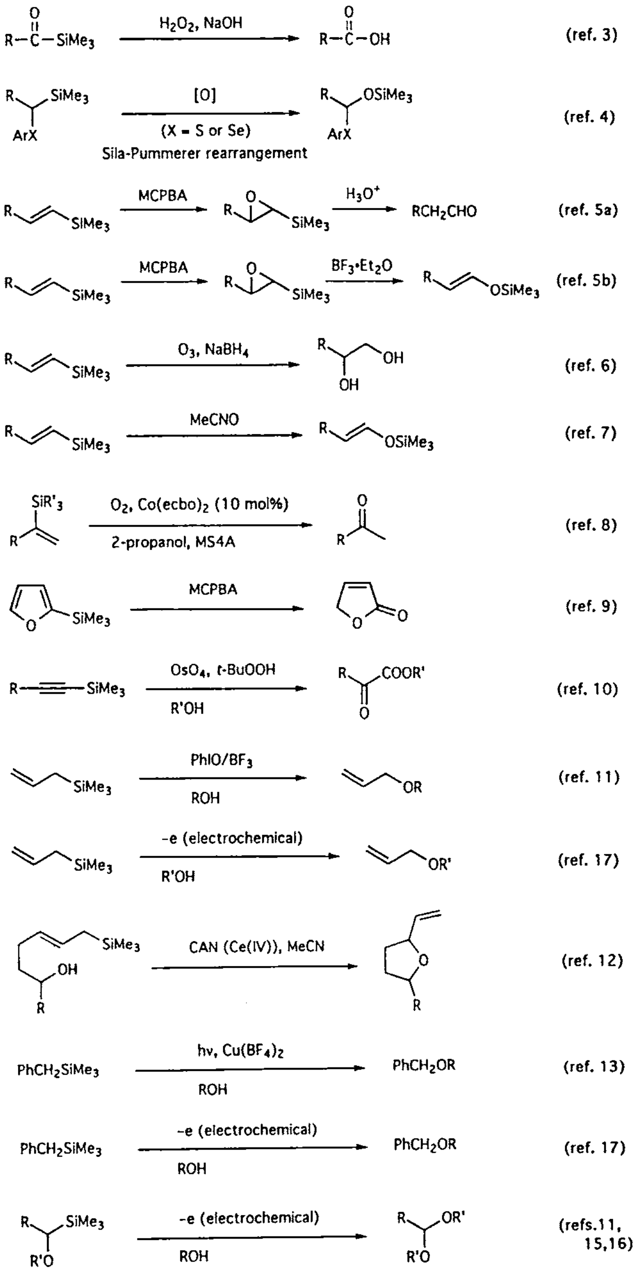
Silicon–carbon bonds are usually stable to oxidative cleavage, as clearly described in a text book as follows: "Silicon–alkyl and, particularly, silicon–aryl bonds are fairly resistant to oxidative cleavage, and appropriately substituted organic groups attached to silicon may be oxidized without cleavage of the silicon–carbon bonds."[1]

In principle, two methodologies may be envisaged for the introduction of an oxygen functionality into an organic group via cleavage of the Si–C bond, as shown in Scheme 1.[2] Thus, the oxidizing agent first interacts either with the organic group (route A) or with the silicon center rather than the organic group (route B). In those cases where the organic group attached to silicon is "activated" towards an oxidizing agent (electrophile), the reagent interacts first with the organic group (route A).

Most of the oxidative transformations reported to date can be categorized as proceeding according to route A, as summarized by the list of reactions shown in Scheme 2. They include the hydrogen peroxide oxidation of acylsilanes to carboxylic acids,[3] the sila-Pummerer rearrangement of α-silyl sulfides via sulfoxides,[4] the oxidation of vinylsilanes to ketones via epoxysilanes,[5] the oxidation of vinylsilanes with ozone[6] or nitrile oxide,[7] the cobalt-catalyzed aerobic oxidation of vinyl-



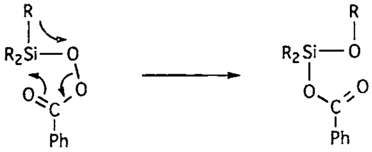
Scheme 1.


R—C(=O)—SiMe3
H2O2, NaOH
R—C(=O)—OH
(ref. 3)
SiMe3
ArX
[O]
(X = S or Se)
Sila-Pummerer rearrangement
OSiMe3
(ref. 4)
MCPBA
H3O+
RCH2CHO
(ref. 5a)
BF3•Et2O
(ref. 5b)
O3, NaBH4
OH
(ref. 6)
MeCNO
(ref. 7)
SiR'3
O2, Co(ecbo)2 (10 mol%)
2-propanol, MS4A
(ref. 8)
(ref. 9)
OsO4, t-BuOOH
R'OH
COOR'
(ref. 10)
PhIO/BF3
ROH
OR
(ref. 11)
-e (electrochemical)
OR'
(ref. 17)
CAN (Ce(IV)), MeCN
(ref. 12)
PhCH2SiMe3
hv, Cu(BF4)2
PhCH2OR
(ref. 13)
(ref. 17)
R'O
(refs.11, 15,16)

Scheme 2.

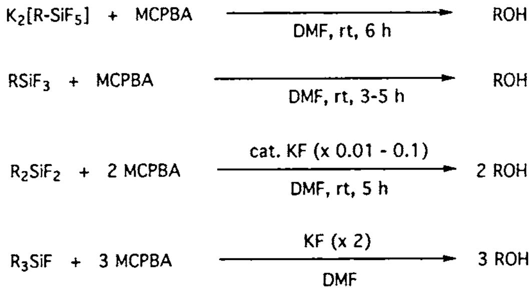
silanes,[8] the MCPBA oxidation of 2-silylfurans to lactones,[9] the oxidation of ethynylsilanes to α-keto esters,[10] the oxidation of allylsilanes with iodosylbenzene,[11] the Ce(IV)-induced oxidation of allylsilanes,[12] the photochemical oxidation of benzylsilanes,[13] and the electrochemical oxidation of α-silyl ethers, sulfides,[14–16] allylsilanes,[17] and benzylsilanes.[17] Thus, the mechanism illustrated by route A may not be applicable to "nonactivated" organic groups such as simple alkyl groups.

In route B, the oxidizing agent coordinates with the silicon center to form a hypercoordinated silicon species in which the silicon–carbon bonds are weakened and therefore readily oxidized. This route may thus be applicable to the Si–C bonds of a wider range without the necessity of activation. A prototype of route B is an intramolecular rearrangement of triorganosilyl perbenzoates to alkoxysilanes, reported by Buncel and Davies in 1958 (eq. 1).[18] Little attention, however, had been paid to the synthetic application of this type of reaction for 20 years.



(1)[18]

In 1978,[19] we reported that the Si–C bond in hexacoordinated organopentafluorosilicate is readily cleaved by MCPBA in polar solvents such as DMF to form the corresponding alcohol (Scheme 3).[20–22] Subsequently, the MCPBA oxidation was found to be applicable to ordinary tetracoordinate organofluorosilanes and alkoxysilanes in the presence of a fluoride ion or polar solvents as a promoter (Scheme 3).[23] The cleavage reaction was found to proceed with complete retention of configuration



$$K_2[R\text{-}SiF_5] + \text{MCPBA} \xrightarrow[\text{DMF, rt, 6 h}]{} \text{ROH}$$

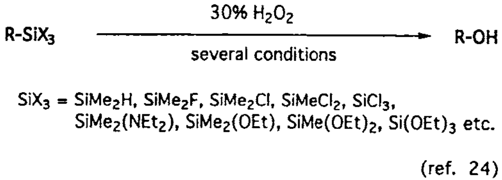
$$RSiF_3 + \text{MCPBA} \xrightarrow[\text{DMF, rt, 3-5 h}]{} \text{ROH}$$

$$R_2SiF_2 + 2\ \text{MCPBA} \xrightarrow[\text{DMF, rt, 5 h}]{\text{cat. KF (x 0.01 - 0.1)}} 2\ \text{ROH}$$

$$R_3SiF + 3\ \text{MCPBA} \xrightarrow[\text{DMF}]{\text{KF (x 2)}} 3\ \text{ROH}$$

(ref. 23)

Scheme 3.

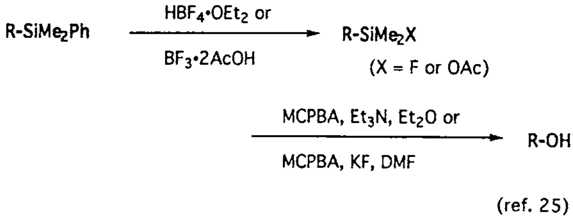


$$\text{R-SiX}_3 \xrightarrow[\text{several conditions}]{30\%\ \text{H}_2\text{O}_2} \text{R-OH}$$

SiX_3 = $SiMe_2H$, $SiMe_2F$, $SiMe_2Cl$, $SiMeCl_2$, $SiCl_3$, $SiMe_2(NEt_2)$, $SiMe_2(OEt)$, $SiMe(OEt)_2$, $Si(OEt)_3$ etc.

(ref. 24)

Scheme 4.



$$\text{R-SiMe}_2\text{Ph} \xrightarrow[\text{BF}_3\cdot 2\text{AcOH}]{\text{HBF}_4\cdot\text{OEt}_2\ \text{or}} \underset{(\text{X} = \text{F or OAc})}{\text{R-SiMe}_2\text{X}} \xrightarrow[\text{MCPBA, KF, DMF}]{\text{MCPBA, Et}_3\text{N, Et}_2\text{O or}} \text{R-OH}$$

(ref. 25)

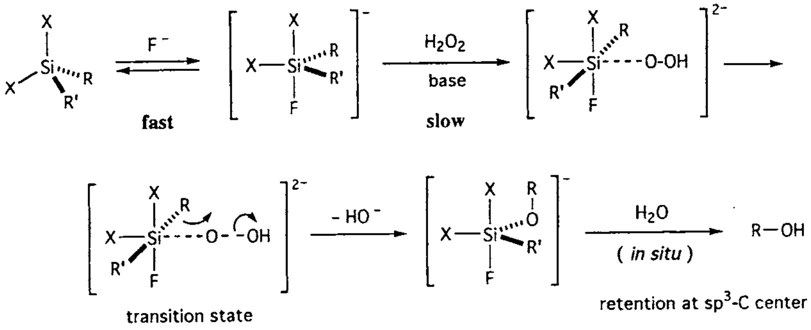
Scheme 5.

at the *sp*^{3} carbon center.[23] In 1983, we eventually found that the Si–C bonds in certain functionalized silicon compounds such as alkoxysilanes can also be cleaved by hydrogen peroxide (Scheme 4).[24] In 1984, Fleming reported that the R–Si bond in R–$SiMe_2Ph$ systems can be cleaved oxidatively in two steps (Scheme 5).[25] Since those reports, the oxidative cleavage reactions of organosilanes have been recognized to be a practically useful standard method for the synthesis of alcohols.[26–28]

This review is concerned with the oxidative cleavage of the Si–C bond of the type illustrated by route B (Scheme 1), focusing on the mechanistic aspects, and the scope and limitations of the transformation, together with brief summary of the synthetic applications. The literature coverage has been attempted to be complete through the middle of 1995, with some material from the literature of 1996. Just after completion of this review, two review articles reported by the Fleming group have appeared.[29,30]

2. MECHANISM OF THE HYDROGEN PEROXIDE OXIDATION: THE ESSENTIAL ROLE OF A HETEROATOM ON SILICON

The oxidative cleavage of the silicon–carbon bond requires the presence of at least one heteroatom on silicon, as will be discussed later in detail. This is a most important feature in connection with the mechanism. While a variety of functionalized silyl groups and a variety of reaction conditions have been proposed for the oxidative cleavage reactions, the



(ref. 31)

Scheme 6.

role of the heteroatom in the cleavage step is common and necessary in all cases where hydrogen peroxide or peracids are used as oxidants. It is thus informative to discuss the mechanism proposed for the hydrogen peroxide oxidation of diorganodifluorosilanes in the presence of fluoride ion as a promoter since this has been the only serious mechanistic study so far reported.[31]

The proposed mechanism involves formation of a pentacoordinate silicon species as the initial key intermediate and a hexacoordinate silicon species in the transition state, as shown in Scheme 6. This mechanism is based on the following observations.

1. The reactivity of organosilanes is highly dependent upon the number of functional groups on silicon. The reactivity of a series of phenylfluorosilanes, $PhSiMe_{3-n}F_n$, has been found to fall in the order $n = 2 \gg 1 > 3 \gg 0$ (no reaction).
2. Addition of an extra equivalent of fluoride ion greatly accelerates the oxidation of $PhMeSiF_2$ by H_2O_2 in THF. Thus, while in the absence of a fluoride ion no oxidation occurs at all, in the presence of one to two equivalents of fluoride ion as KF/18-crown-6 the oxidation proceeds smoothly even at 10 °C to form phenol in high yields; the reaction being nearly complete in 1 h.
3. In the presence of fluoride ion, diorganodifluorosilanes are quantitatively converted into pentacoordinate fluorosilicates: the formation constant of $[PhMeSiF_3]^- n\text{-}Bu_4N^+$ in a mixture of $PhMeSiF_2$ and $n\text{-}Bu_4NF$ in THF has been estimated to be 1.8×10^3 mol L^{-1} at 18 °C.[32]

4. Isolated pentacoordinate silicates such as $[PhMeSiF_3]^-$,K^+18-crown-6 are readily oxidized by H_2O_2 without added fluoride ion. All the above results (1)–(4) indicate that pentacoordiante silicates are key early intermediates in the oxidative cleavage reaction.
5. A kinetic study on the reaction between $[R_2SiF_3]^-$ and H_2O_2 has shown that the oxidation rate is roughly first order with respect to the concentration of each component, $-d[[R_2SiF_3]^-] / dt = k_2[[R_2SiF_3]^-][H_2O_2]$, having $k_2 = 0.15$ mol L^{-1} s^{-1} at –26 °C. The results indicate that the rate-determining step involves the interaction of hydrogen peroxide with the intermediate pentacoordinate silicate species.
6. Electronic effects of the H_2O_2 oxidation have been determined by intramolecular competition reactions of pentacoordinate silicates. Hammett plots between the product ratios, XC_6H_4OH / C_6H_5OH, and the σ_p constants afford small positive ρ values: $\rho = +0.5$. Thus, electron withdrawing groups accelerate the oxidative cleavage reaction. In the transition state, the organic group should bear a negative charge, but the rather small ρ values support a concerted nature for the reaction.

All the results (1)–(6) are consistent with the proposed mechanism as shown in Scheme 6. In the hexacoordinate transition state, the silicon–carbon bonds are weakened so that an R group readily migrates from silicon to the adjacent oxygen atom. This intramolecular migration mechanism accounts for the complete retention of configuration of the sp^3 carbon center as the migrating terminus. A recent report has described a four-centered mechanism involving a simultaneous attack of the two oxygen ends of the peroxide oxidant on the silicon center and the carbon center in the pentacoordinate silicon intermediate.[31a]

The essential role of the functional groups is thus ascribed to the enhancement of the Lewis acidity of the silicon center for the favorable formation of the penta- and hexacoordinated silicon species.

3. SILYL GROUPS AND OXIDATION CONDITIONS

A variety of conditions have been examined to cleave the silicon–carbon bond. Typical oxidation conditions for heteroatom-substituted silicon–carbon bonds are summarized in Table 1. Table 2 summarizes conditions

Table 1. Typical Oxidation Conditions for Heteroatom-Substituted Silicon–Carbon Bonds

$$R{-}SiR'_{3-n}X_n \xrightarrow[]{\text{oxidation condition}} R{-}OH$$

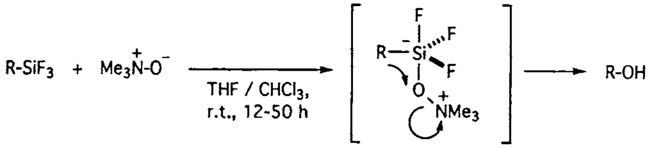
$n = 1 \sim 3$
$X = H, F, Cl, Br, OR'', NR''_2$

Condition[a]	*Abbreviation*	*Refs.*
H_2O_2, $KHCO_3$, KF, THF, MeOH, r.t. to 40 °C	[standard]	33–37
H_2O_2, $KHCO_3$, THF, MeOH, 40–50 °C	[basic]	24,38
H_2O_2, 15% KOH, THF, MeOH, r.t.	[KOH]	34,39
H_2O_2, KHF_2, THF, MeOH, r.t. to 60 °C	[neutral]	24,38
H_2O_2, KHF_2, Ac_2O, DMF, r.t.	[acidic]	24,38,40
O_2, hydroquinone, TBAF, THF, 40 °C	[O_2/HQ]	41
t-BuOOH, CsOH, TBAF, r.t.	[*t*-BuOOH]	42
MCPBA, DMF, r.t.	[MCPBA]	23,43
MCPBA, KF, DMF, r.t.	[MCPBA/KF]	23

Note: [a] H_2O_2 means 30% H_2O_2, usually used in an amount of ca. 1.2 equivalent per one Si–C bond. TBAF = tetrabutylammonium fluoride. MCPBA = *m*-chloroperbenzoic acid. Small variations have also been used: other weak bases such as K_2CO_3 and $NaHCO_3$, and other fluoride ion sources such as TBAF may be used.

for the two-step oxidative transformation of siloxy-, aryl-, allyl-, and silyl-substituted silicon–carbon bonds.

Some other conditions involve an MCPBA/phosphate system for oxidation of organo(alkoxy)silanes under somewhat drastic conditions[72] and trimethylamine oxide for oxidation of organo(alkoxy)silanes[73] and organotrifluorosilanes[74] in the presence and in the absence of fluoride ions, respectively. The last reaction has been proposed to proceed through a pentacoordinate silicon species (Scheme 7).[74]



(ref. 74)

Scheme 7.

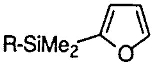
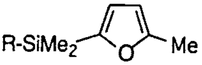
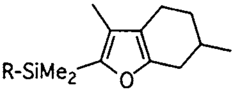
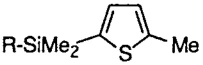
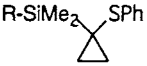
Table 2. Typical Oxidation Conditions for Two-Step Cleavage of Siloxy, Aryl-, Allyl-, and Silyl-Substituted Silicon–Carbon Bonds

$$\text{R-SiR}'_2\text{R}'' \xrightarrow[\text{functionalization}]{\text{1st step}} \text{R-SiR}'_2\text{X} \xrightarrow[\text{oxidation}]{\text{2nd step}} \text{R-OH}$$

$$\text{X} = \text{F, OH, etc.}$$

Silyl Group	*Conditions*		
Entry	*1st step*	*2nd step*[a]	*Refs.*
R–$SiMe_2OSiMe_2R'$			
1	CF_3CO_2H, KHF_2, 50 °C, 3 h	[basic]	38
2	(1) H_2O_2, $KHCO_3$, THF, MeOH (2) KF, reflux (one pot)		44
R–$SiMe_2Ph$			
3	Br_2 (or KBr), AcOOH, AcOH NaOAc (one pot)		28,45
4	$Hg(OAc)_2$, AcOOH, AcOH (one pot)		28,45
5	0.2 $Hg(OAc)_2$, 0.1 $Pd(OAc)_2$ AcOOH, AcOH (one pot)		28,45
6	$Hg(OCOCF_3)_2$, CF_3COOH, AcOH	AcOOH	46
7	$HBF_4{\cdot}OEt_2$ or $BF_3{\cdot}2AcOH$	MCPBA, Et_3N, Et_2O [MCPBA, KF] [standard]	25,28
8	CF_3COOH, (KHF_2), (MeOH)	[standard]	38,47
9	(1) ICl, (2) *i*-PrOH, Et_3N	[standard]	47
10	(1) Li, NH_3, THF, EtOH, –78 °C (2) TBAF, THF	[basic]	48
11	NaH (or TBAF), THF	[standard]	49,50
12	*t*-BuOK, DMSO	[standard]	47,51
R–$SiMe_2Tol$ (Tol = *p*-tolyl)			
13	KBr, AcOOH, AcOH NaOAc (one pot)		52,53
R–$SiPh_3$			
14	$Hg(OAc)_2$, AcOOH, AcOH (one pot)		54
15	TBAF (×4.4), THF, reflux	[basic, KF]	55
R–$SiMe_2(CH_2CH{=}CH_2)$			
16	CF_3CO_2H, KHF_2, $CHCl_3$, 50 °C	[basic]	38,56
17	(1) Br_2 (2) HF·pyridine	[standard]	57

Table 2. (Continued)

Silyl Group	*Conditions*		
Entry	*1st step*	*2nd step*^{a}	*Refs.*
$R{-}SiPh_2[CH_2C(CH_3){=}CHCH_3]$			
18	$BF_3\cdot 2AcOH$ (0.05 M), CH_2Cl_2, r.t., 20 s (or −10 °C, 5 min)	[standard]	58,59
19	0.3 M HCl, MeOH, r.t., 3 h	[standard]	58
20	KBr, AcOOH, AcOH, NaOAc, r.t., 1 day (one pot)		58
21	KBr, H_2O_2, KF, $KHCO_3$, MeOH, THF, reflux (one pot)		58
			
22	TBAF	[basic]?	60
			
23	O_2, hν, Ph_4–porphyrin, −78 °C, 0.5 h	[standard]	61
			
24	CF_3CO_2H (×1.1), 0 °C, THF	[standard]	62
			
25	TBAF, DMF, r.t., 0.5 h	H_2O_2, KF, DMF	63
$R{-}SiMe_2(CH_2NR'_2)$			
26	H_2O_2, KF, $KHCO_3$, r.t. (2 steps in one pot)		64,65,66
$R{-}SiMe_2(CH_2SPh)$			
27	H_2O_2, KF, $KHCO_3$, r.t. (2 steps in one pot)		67
			
28	(1) $NaIO_4$, (2) heat in benzene	[standard]	68
			
29	TBAF	[basic]	68

(continued)

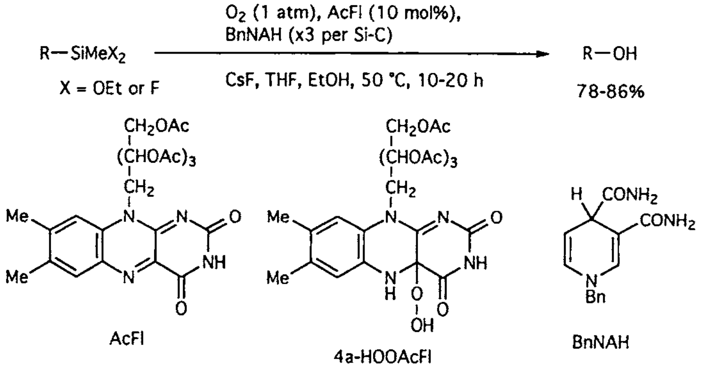
Table 2. (Continued)

Silyl Group	*Conditions*		
Entry	*1st step*	*2nd step*[a]	*Refs.*
$R–SiR'_2SiR''_3$			
$(–SiMe_2SiMe_3, –SiMe_2SiMe_2Ph, –SiPh_2SiMe_3)$			
30	TBAF, THF, r.t.	[basic]	69
31	(1) $AlCl_3$ or Br_2, (2) H_2O	[neural]	70
$R–Si(SiMe_3)_3$			
32	O_2, 2,3-Me_2-hydroquinone, TBAF, THF (one pot)		71

Note: [a] For abbreviations of the hydrogen peroxide oxidation, see Table 1.

A molecular oxygen oxidation of silicon–carbon bonds has been achieved by a biomimetic redox system consisting of a catalytic amount of tetraacetylriboflavin and a stoichiometric amount of a dihydronicotinamide derivative (Scheme 8).[75] The real oxidizing species may be 4a-hydroperoxyflavin or hydrogen peroxide generated therefrom. It has been claimed that this type of oxidation might afford a clue to clarify the decomposition pathways of organosilicon compounds in the environment.

The conditions listed in Tables 1 and 2 will be discussed mainly in terms of the nature of silyl groups in the Sections 3.1 and 3.2.



(ref. 75)

Scheme 8.

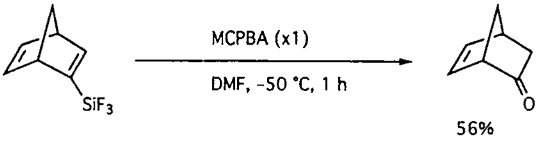
3.1. Oxidation Conditions for Heteroatom-Substituted Silyl Derivatives

3.1.1. *Fluorosilanes*

Almost all the conditions listed in Table 1 may be applied to the oxidation of fluorosilanes. One exception is that involving acidic conditions which do not oxidize monofluorosilanes such as $RSiMe_2F$.

Fluorosilanes are the most important class of compounds in the oxidative transformations since they are intermediates in many of the two-step procedures listed in Table 2: Further discussion of this phenomenon will be made in Section 3.2.

As summarized in Scheme 3, MCPBA oxidations are also useful for a variety of fluorosilanes. While an excess amount of KF is necessary for oxidation of monofluorosilanes (MCPBA/KF), a catalytic amount of KF is sufficient for difluorosilanes and no KF is needed for trifluorosilanes (MCPBA).[23] The extremely high reactivity of trifluorosilanes is demonstrated by the following oxidation which proceeds even at –50 °C in DMF by simply mixing with MCPBA (eq. 2).[43]

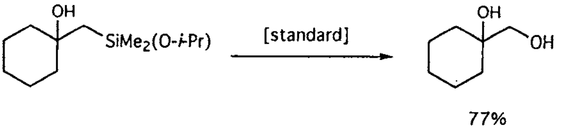


(2)[43]

3.1.2. *Alkoxysilanes, Acyloxysilanes, and Hydroxysilanes*

Oxidative cleavage of alkoxysilanes has been most frequently used in combination with a variety of alkoxysilane-based intramolecular transformations.

Mono-, di- and trialkoxysilanes are all oxidized by hydrogen peroxide under almost all the conditions listed in Table 1. The standard conditions of H_2O_2, $KHCO_3$, KF, THF, MeOH, r.t., 40 °C, however, is the first choice in many cases, as shown by several representative examples (eqs. 3,[76] 4,[77] and 5[78]) and as will be seen in many examples in this review. It is noted that eq. 4 demonstrates the inertness of the Me_3Si group towards



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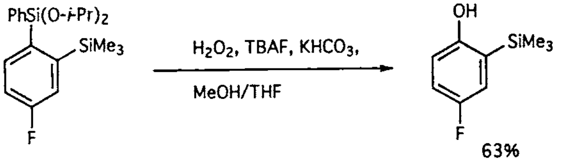

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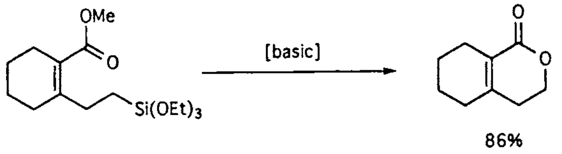

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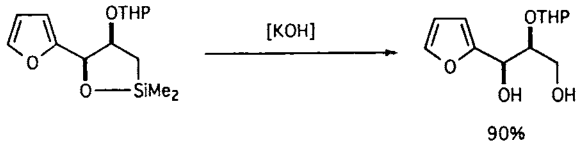
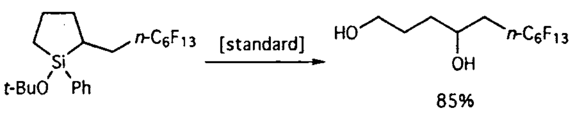


(6)[39]

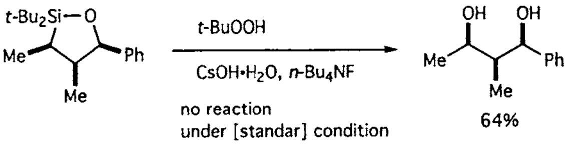
oxidation. However, this condition is not suitable for compounds containing silyl protecting groups on oxygen atoms, including TBS (*t*-BuMe$_2$Si) group, due to concomitant deprotection: the basic conditions with the omission of the KF should be used in such cases. The potassium hydroxide-mediated reaction conditions appear to be useful for cyclic alkoxysilanes such as those obtained by intramolecular hydrosilation procedures (eq. 6):[39] The acidic conditions are not suitable for oxidation of monoalkoxysilanes, because the monofluorosilane intermediate remains unchanged as mentioned above. It has recently been reported that cyanophenyl-silicon bonds in dialkoxysilanes are cleaved by bis(trimethylsilyl)peroxide in the presence of fluoride ion.[31a]

Sterically crowded (*t*-butoxy)silanes can also be oxidized under the standard conditions (eq. 7).[79] The *tert*-butylhydroperoxide conditions,[42] developed quite recently, seem to be the strongest reagent for the oxidation of sterically hindered alkoxysilanes such as di(*t*-butyl)(alkoxy)silanes[42,80] (eq. 8), which are generally inert under the standard and basic conditions.

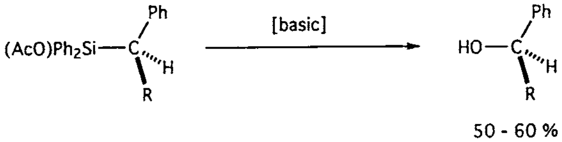
Acetoxysilanes can be directly subjected to hydrogen peroxide oxidation[81] as shown in eqs. 9[82,83] and 10.[84] Acetoxysilanes are also involved



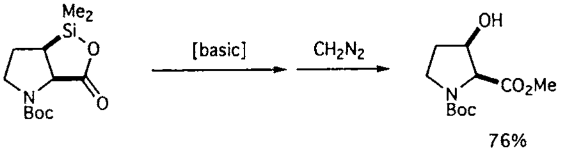
(7)[79]



(8)[42]



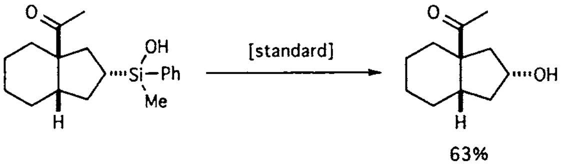
(9)[82,83]



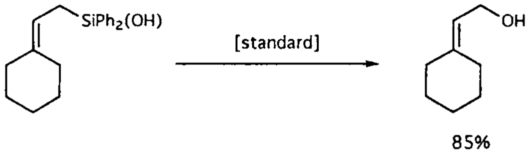
(10)[84]

as intermediates in the two-step oxidation of R–SiMe$_2$Ph via mercurodesilylation under the condition of entry 4 in Table 2.

Hydroxysilanes (silanols) are also oxidized under the standard conditions as shown in eqs. 11[55] and 12.[85] However, we have frequently encountered very sluggish reactions of R–SiPh$_2$OH; the reactivity appears to depend greatly on the structure of the R group.

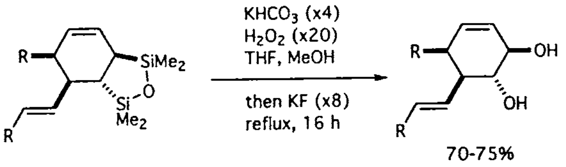


(11)[55]



(12)[85]

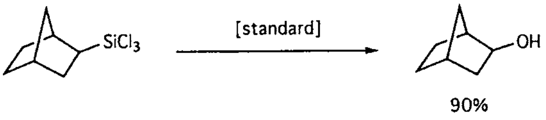
Disiloxanes are generally inert to the oxidation conditions listed in Table 1 and may be subjected to the two-step conversions under the conditions of entry 1 in Table 2, which will be discussed later. However, it has recently been shown that five-membered cyclic disiloxanes can be oxidized under a modification of the standard conditions where KF should be added last (entry 2, Table 2), as shown in eq. 13.[44]



(13)[44]

3.1.3. Chlorosilanes

While chlorosilanes may be oxidized in two steps by conversion into the corresponding alkoxysilanes and subsequent treatment with hydrogen peroxide under the various conditions described above for alkoxysilanes, they can also be oxidized in a one-pot manner with the basic or standard conditions. In the latter cases, however, excess amounts of bicarbonate salt must be used for neutralization of hydrogen chloride generated by the in situ alcoholysis: It is recommended that trichlorosilanes R–$SiCl_3$ are treated first with dry methanol and carbonate salt prior to addition of hydrogen peroxide.[38] An example is shown in eq. 14.[86]

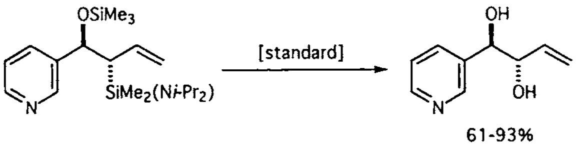


(14)[86]

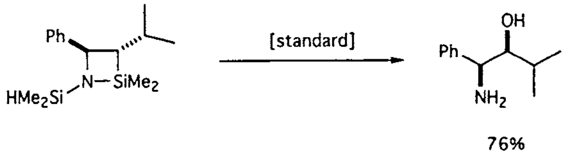
Bromosilanes should be the intermediates in the two-step oxidation of phenylsilyl- or allylsilyl-groups via halo-desilylation under the conditions of entries 3, 13, 17, 20, and 21 in Table 2.

3.1.4. Aminosilanes

Aminosilanes are also oxidized by hydrogen peroxide under the standard conditions either directly[38,87] (eqs. 15[36] and 16[88]) or after conversion into alkoxysilanes.[87,89]



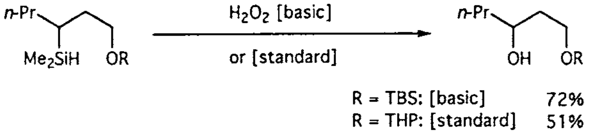
(15)[36]



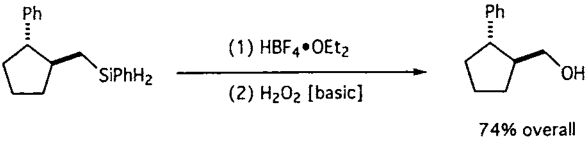
(16)[88]

3.1.5. Hydrosilanes

Hydrosilanes may be oxidized under the basic or the standard conditions,[38] but sometimes rather sluggishly (eq. 17).[35] Phenyl(hydro)silyl groups may be transformed into the OH group by two steps via removal of a benzene ring (eq. 18)[90] under the conditions of entry 7 in Table 2.



(17)[35]



(18)[90]

3.2. Oxidation Conditions for The Two-Step Cleavage

In most cases listed in Table 2, the second step of the two-step oxidation process involves the usual hydrogen peroxide oxidations listed under the various conditions in Table 1 and described above.

3.2.1. Disiloxanes

As mentioned briefly above, disiloxanes are generally oxidatively cleaved by a two-step procedure which involves the acid cleavage of the Si–O bond to an Si–F bond followed by oxidation under the basic or standard conditions (entry 1, Table 2).[38] See eq. 13 for the direct oxidation without acid treatment.

3.2.2. Phenylsilyl Groups

The $PhMe_2Si$ group is one of the most versatile silyl groups convertible to the OH group in two steps, as introduced and thoroughly investigated by Fleming. This group has the advantage that it can tolerate a variety of reaction conditions that would react with the heterosubstituted organosilanes described in Section 3.1. Since the scope and limitations have recently been discussed in detail by Fleming,[28] only a brief survey will be made in this review.

The phenyl group on silicon can be cleaved by protodesilylation (entries 7 and 8), halodesilylation (entries 3 and 9), or mercurodesilyla-

$$\text{R-SiMe}_2\text{Ph} \xrightarrow[\text{- PhH}]{\substack{\text{HBF}_4\text{•OEt}_2\text{ or}\\ \text{BF}_3\text{•2AcOH}}} \underset{(\text{X = F or OAc})}{\text{R-SiMe}_2\text{X}} \xrightarrow{[\text{O}]} \text{R-OH} \tag{19}$$

$$\text{R-SiMe}_2\text{Ph} \xrightarrow[\text{- PhH}]{\text{CF}_3\text{COOH (KHF}_2\text{)}} \underset{(\text{X = OCOCF}_3\text{ or F})}{\text{R-SiMe}_2\text{X}} \xrightarrow{[\text{O}]} \text{R-OH} \tag{20}$$

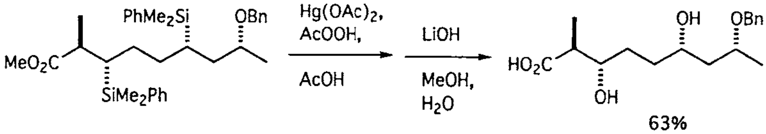
$$\text{R-SiMe}_2\text{Ph} \xrightarrow[\text{- PhBr}]{\text{Br}_2\text{ or KBr/AcOOH}} \text{R-SiMe}_2\text{Br} \xrightarrow{\text{AcOOH}} \text{R-OH} \tag{21}$$

$$\text{R-SiMe}_2\text{Ph} \xrightarrow[\text{- PhI}]{\text{ICl}} \text{R-SiMe}_2\text{Cl} \xrightarrow{\text{H}_2\text{O}_2} \text{R-OH} \tag{22}$$

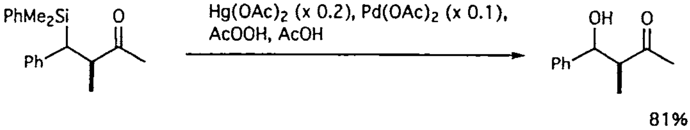
$$\text{R-SiMe}_2\text{Ph} \xrightarrow[\text{- PhHg(OAc)}]{\text{Hg(OAc)}_2} \text{R-SiMe}_2\text{(OAc)} \xrightarrow{\text{AcOOH}} \text{R-OH} \tag{23}$$

tion (entries 4, 5, and 6) to leave the corresponding fluorosilane, bromosilane, and acetoxysilane, respectively, as shown in eqs. 19–23. The fluorosilane can be oxidized under a variety of conditions using MCPBA or hydrogen peroxide, as listed in Table 2. The hydrogen peroxide oxidation under the standard or basic conditions may be the first choice as recommended by Fleming.[28]

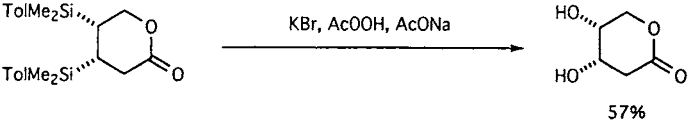
The halo- and mercurodesilylations are generally performed in situ; i.e. in the presence of peracetic acid and thereby the intermediates are readily oxidized to the alcohols.[28,45] These (entries 3–5) are sometimes referred to as the Fleming conditions. While the *p*-tolyl analogs, R–SiMe$_2$(Tol), are more reactive toward the halodesilylation/oxidation (entry 13),[53] the bulky phenylsilane R–SiPh$_2$(*t*-Bu) is stable to the halodesilylation conditions of entry 3[91] or only reluctantly cleaved under the mercurodephenylation conditions (entry 4).[92] Triphenylsilyl derivatives can also be oxidized via the mercurodephenylation (entry 14).[54] The mercurodephenylation can also be achieved more readily by using the stronger electrophilic agent Hg(OCOCF$_3$)$_2$ in CF$_3$COOH/AcOH, followed by peracetic acid oxidation (entry 6).[46] The mercurodesilylation method is applicable also to R–SiPh$_2$Me and –SiPh$_3$ derivatives (entry 14).[54] In entry 5, both Hg(OAc)$_2$ and Pd(OAc)$_2$ are used in catalytic amounts in the first mercurodesilylation step because the primary product PhHg(OAc) is converted back to Hg(OAc)$_2$ by reaction with Pd(OAc)$_2$; the latter is converted into PhPd(OAc) which is oxidatively decomposed by AcOOH/AcOH to regenerate Pd(OAc)$_2$ together with PhOAc.[28] Some typical examples are shown in eqs. 24–28.



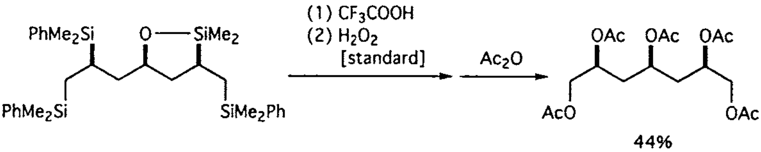
(24)[93]



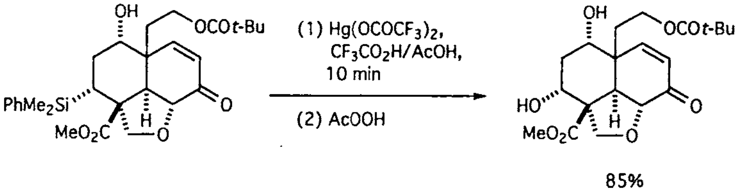
(25)[28]



(26)[53]



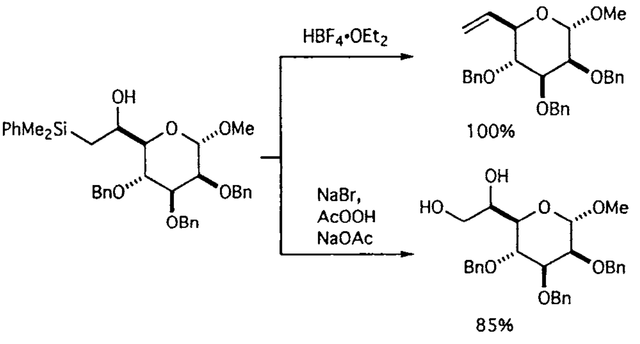
(27)[47]



(28)[46]

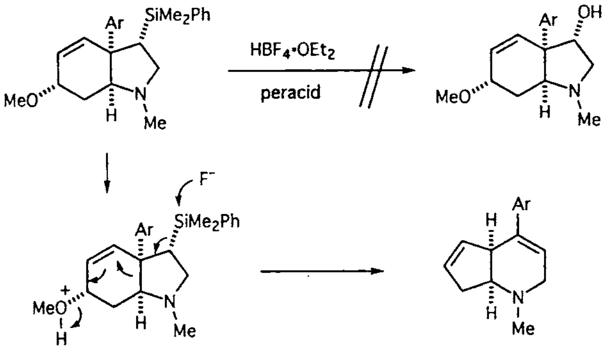
These procedures involve acid conditions, especially in the first step in the protodesilylation method in entries 7 and 8. There are some limitations under such acidic conditions. These are:

1. In (allyl)phenylsilanes, the protodesilylation occurs with the allyl–silicon bond much faster than with the phenyl–silicon bond. Similar problems have also been observed with (homoallyl)phenylsilanes.[28]
2. β-Oxysilanes (Scheme 9)[28,94,95] and the vinylogous analogs (Scheme 10)[96] undergo β-elimination readily to form olefins. However, the one-pot procedure using KBr/AcOOH (entry 3, Table 2) may be applicable to β-hydroxysilanes,[28] as also shown in Scheme 9.[94]
3. Cyclopropylsilanes, with[57] or without the β-oxy group,[97] are also sensitive to acidic conditions to give a mixture of ring-opening products, as shown in Scheme 11.[57]



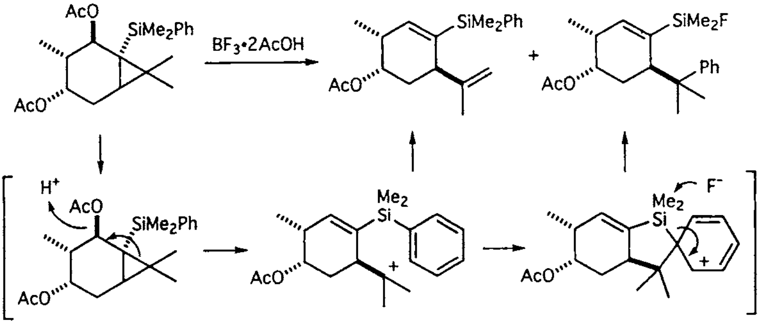
(ref. 92)

Scheme 9.



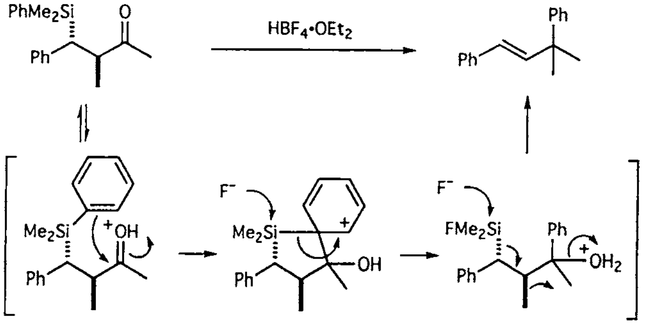
(ref. 94)

Scheme 10.



(ref. 57)

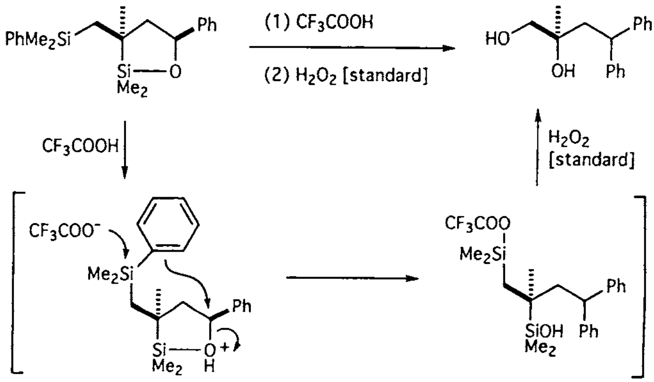
Scheme 11.



(ref. 28)

Scheme 12.

4. β-(Phenylsilyl)ketones undergo intramolecular migration of the phenyl group from silicon to the carbonyl carbon during the protodesilylation step, as shown in Scheme 12.[28]
5. A similar phenyl migration occurs from silicon to the benzylic cation generating from the benzyloxy moiety by protonolysis, as shown in Scheme 13.[47] This problem has been overcome by using ICl for the halodesilylation of the phenylsilane moiety (entry 9, Table 2), followed by hydrogen peroxide oxidation.[47]



(ref. 47)

Scheme 13.

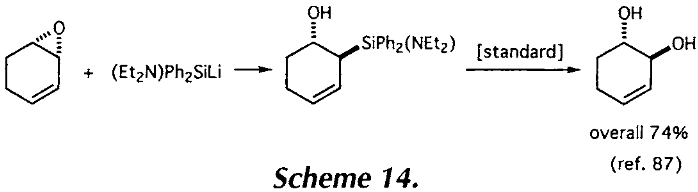
The most straightforward solution is, of course, the introduction of the heteroatom-substituted silyl groups ready for oxidation, in place of the $PhMe_2Si$ derivatives. A typical example may be the introduction of $(Et_2N)Ph_2SiLi$ in place of $PhMe_2SiLi$, as shown by the successful application to the compound which contains both the allylsilane and the β-hydroxysilane moieties (Scheme 14).[87,98]

Such silicon-functional reagents are however sometimes incompatible with multistep transformations in organic synthesis. Considerable effort has thus been devoted to development of simple, straightforward conditions for the dephenyl functionalization of the R–$SiMe_2Ph$ derivatives and introduction of other silyl groups which are stable enough for multistep transformations, but are readily convertible to functionalized silyl groups under mildly acidic or basic conditions. Almost all silyl groups and conditions from entry 9 listed in Table 2 have recently been introduced for these purposes.

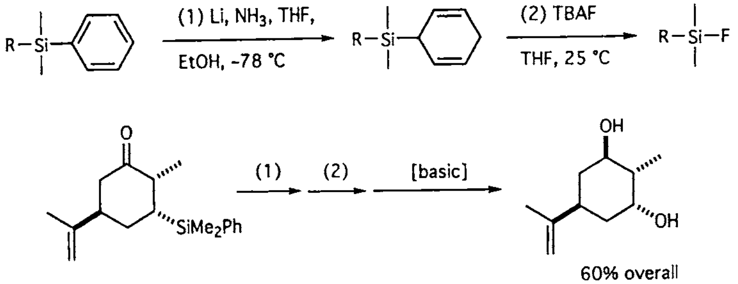
There have been three methods for dephenylation from R–$SiMe_2Ph$ under basic conditions (entries 10–12): in all cases the oxidations are performed by hydrogen peroxide under standard or basic conditions. The first (entry 10) is a two-step transformation consisting of the Birch reduction of the phenyl group followed by cleavage of the resulting allylic silane moiety by treatment with a fluoride ion, as shown in Scheme 15.[48] In this method, however, a carbonyl group is also reduced during the Birch reduction while keeping an olefin intact.

The second method is an intramolecular hydroxide ion assisted dephenylation which is induced by NaH,[50] TBAF (entry 11)[49] or *t*-BuOK in DMSO (entry 12),[51] as shown in Scheme 16.

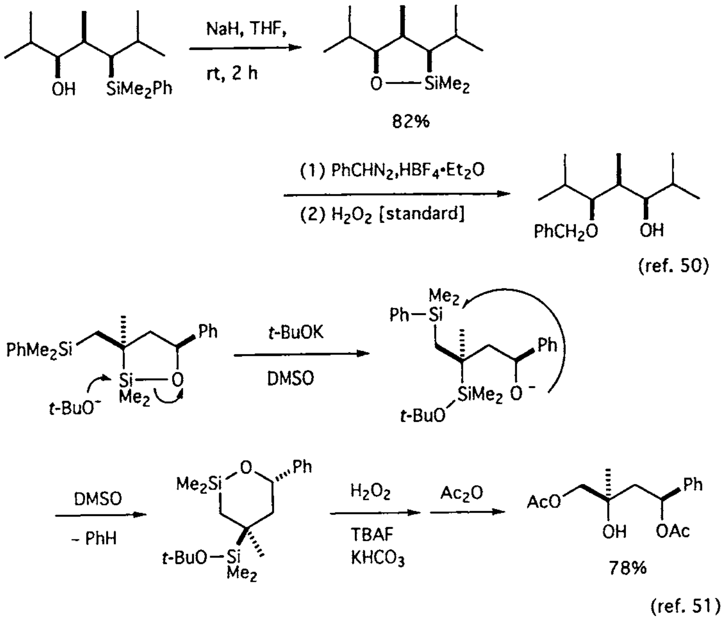
In the third method (entry 15), all three phenyl groups in R–$SiPh_3$ may be cleaved by an excess of TBAF in THF under reflux to afford probably the corresponding silanetriol, which is subjected to the hydrogen peroxide oxidation, as shown in Scheme 17.[55] This quite new methodology might be generally useful for phenylsilanes, except for allyl- and β-hydroxyalkyl–phenylsilanes where the allyl- and the β-hydroxyalkyl–silicon bonds can be readily cleaved by fluoride ion.



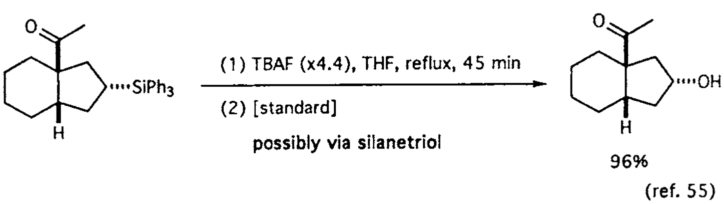
Scheme 14.



Scheme 15.



Scheme 16.

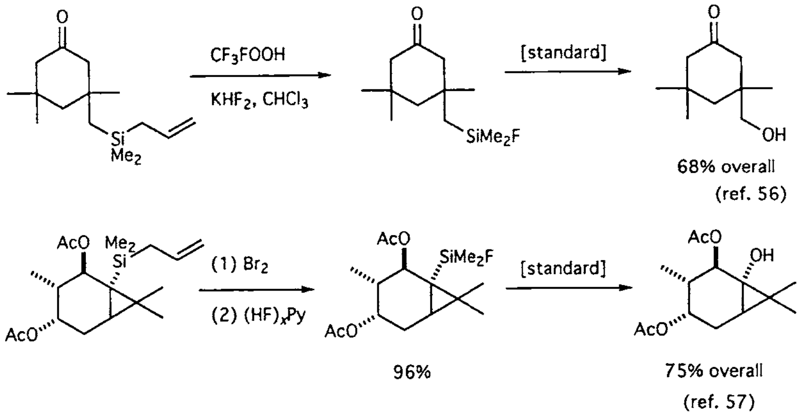


Scheme 17.

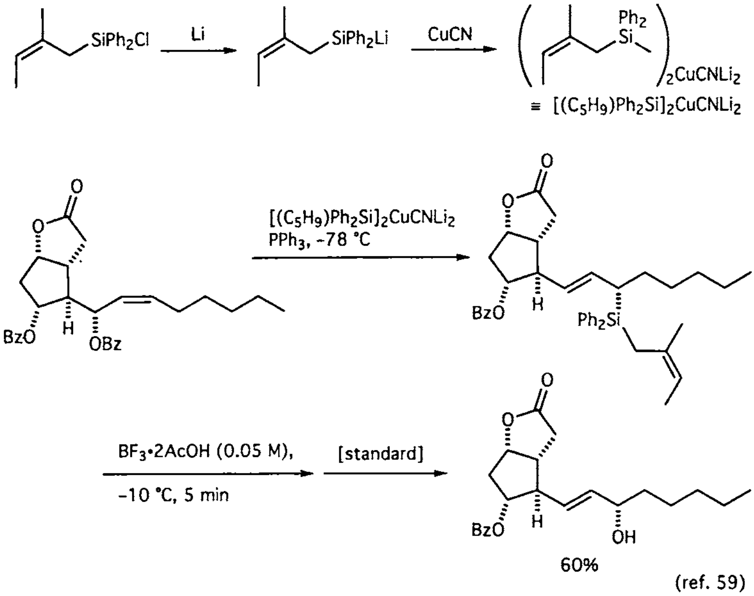
3.2.3. Allylsilyl Groups

Allyl–silicon bonds generally are more readily cleaved by electrophiles than is the phenyl–silicon bond. The parent allyl groups may be cleaved with CF_3COOH (entry 16)[56] or Br_2 (entry 17)[57] followed by fluoridation, as shown in Scheme 18. The subsequent oxidation can be performed with hydrogen peroxide. The last result shown in Scheme 18 should be compared with the $PhMe_2Si$ counterpart which gives no desired product (Scheme 11). It has been suggested that while the electrophilic attack on the ipso carbon in the $PhMe_2Si$ group is sterically hindered in such a highly congested system, electrophilic attack on the γ-position of the allyl–silicon moiety is much less susceptible to the steric hindrance.[57]

The (2-methyl-2-buten-1-yl)silyl group, $(C_5H_9)Ph_2Si$, has been introduced as the most reactive allylsilane moiety in which the allylic group can be readily removed under the mildly acidic or basic conditions listed in entries 18–21.[58] Therefore, other allylsilane and vinylsilanes can survive under these conditions. The lithium reagent $(C_5H_9)Ph_2SiLi$ has thus been developed to overcome the problems encountered with the $PhMe_2SiLi$ chemistry mentioned above. A representative example of applications is shown in Scheme 19,[59] which demonstrates the complete discrimination between two allylic silicon bonds.



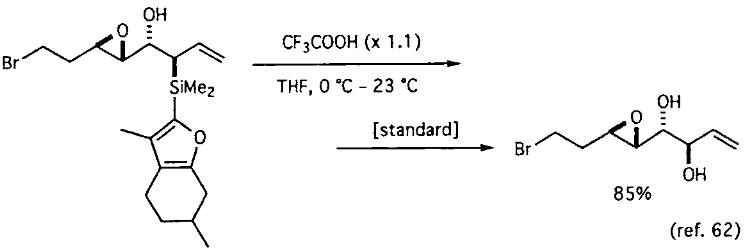
Scheme 18.



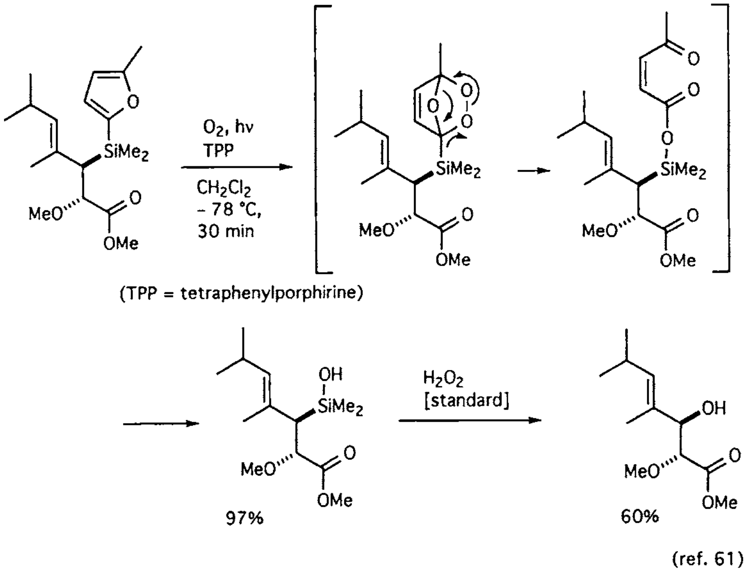
Scheme 19.

3.2.4. Furylsilyl Groups

The parent furyl–silicon bond can be cleaved with TBAF (entry 22), followed by the hydrogen peroxide oxidation.[60] The furyl–silicon bonds, especially the menthofuryl–silicon bond (entry 24), are much more sensitive toward protodesilylation conditions and can be cleaved with CF_3COOH in the presence of the allyl–silicon bond as well as the β-hydroxy–silane moiety, as shown in Scheme 20.[62]



Scheme 20.

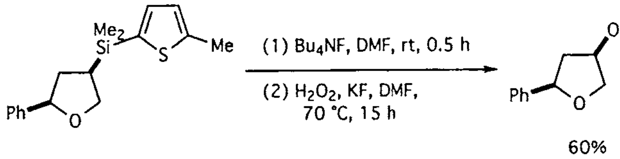


Scheme 21.

A furyl group can also be removed from silicon under neutral condition by the singlet oxygen oxidation (entry 25), as shown in Scheme 21.[61]

3.2.5. *Thienylsilyl Group*

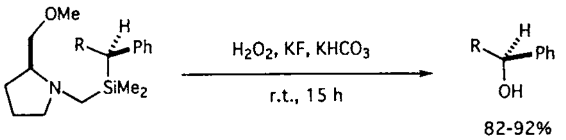
The 2-thienyl–silicon bond is more stable under acidic conditions than the furyl–silicon bonds, but is readily cleaved by TBAF in DMF (entry 25), as shown in eq. 29.[63]



(29)[63]

3.2.6. *Aminomethylsilyl Groups*

Aminomethylsilyl groups have been found to be converted into the OH group in a one-pot procedure by hydrogen peroxide oxidation under the standard conditions (entry 26),[64–66] as exemplified by the conversion shown in eq. 30.[64] Although the mechanism has not been clarified, the

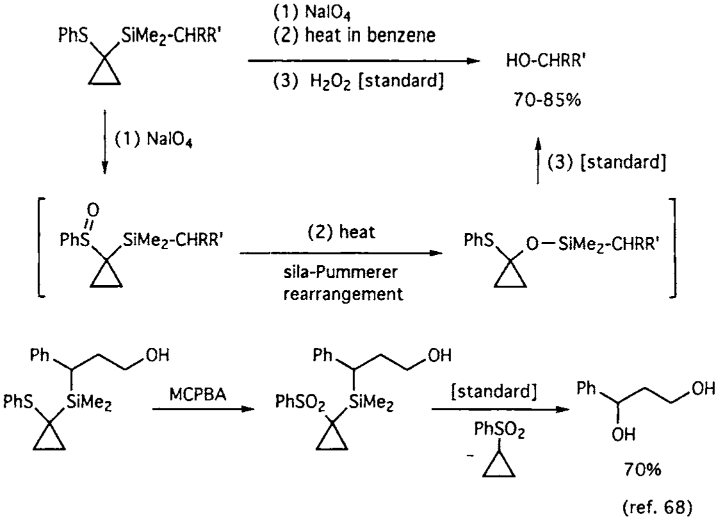


(30)[64]

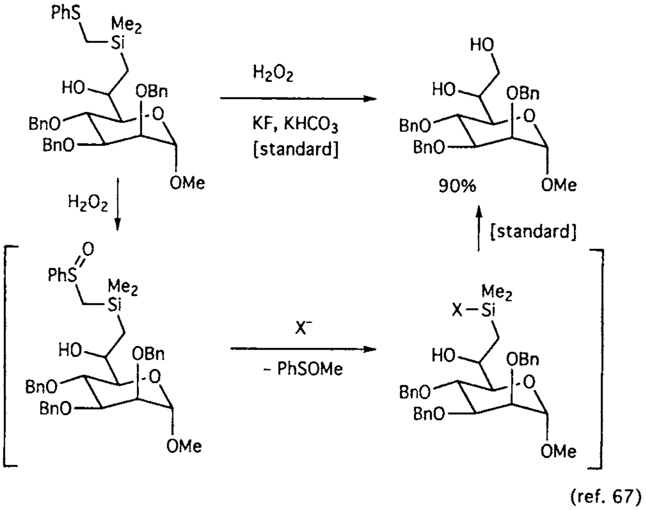
oxidation may be considered to proceed in two steps: cleavage of the aminomethyl–silicon bond and subsequent oxidation of the resulting fluorosilane derivatives. The low oxidation potentials of the nonbonding electrons on nitrogen in the silylmethylamine skeletons[99] might be responsible for the first step; thus the amine moiety may be oxidized first by hydrogen peroxide to facilitate the fluoride ion-induced cleavage of the aminomethyl–silicon bond.

3.2.7. Thiomethylsilyl and Related Groups

A thiocyclopropylsilyl group has been used as the OH equivalent after oxidation with a periodate salt followed by heating (entry 28) to ensure the sila-Pummerer rearrangement[4] (cf. the second equation in Scheme 2) which converts the Si–C bond into the Si–O bond necessary for oxidation, as shown in Scheme 22.[68] Alternatively, the sulfide may be oxidized with MCPBA to sulfone which is subjected to hydrogen peroxide oxidation directly or after treatment with TBAF (entry 29); the sulfonylalkyl–



Scheme 22.



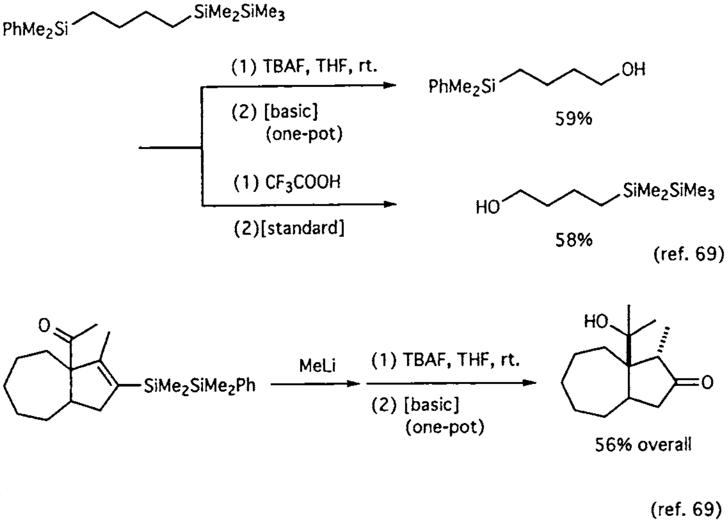
Scheme 23.

silicon bond is readily cleaved by the fluoride ion present in the reaction mixture, as also shown in Scheme 22.[68]

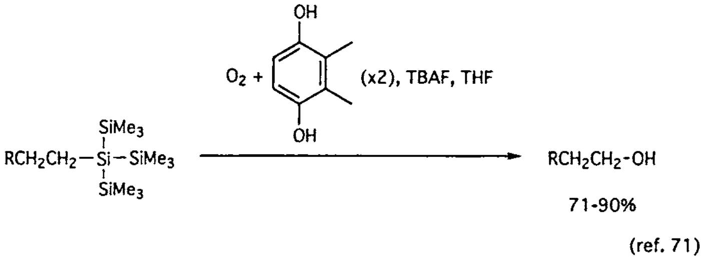
More conveniently, a thiomethylsilyl group can also be converted into the OH group in a one-pot procedure by hydrogen peroxide oxidation under the standard conditions (entry 27),[28] as shown in Scheme 23. The first step may involve the oxidation of the sulfide to its sulfoxide followed by the fluoride-ion-induced cleavage of the resulting sulfoxymethyl–silicon bond: cleavage of the sulfoxide appears to be faster than the sila-Pummerer rearrangement.

3.2.8. Disilanyl and Related Groups

Since the Si–Si bond is cleaved by a fluoride ion (TBAF),[100] the disilanyl groups (entry 30)[69] and a related oligosilanyl group (entry 32)[71] can serve as the OH equivalent in combination with the hydrogen peroxide oxidation. The oxidation can be performed in a one-pot manner, as shown in Schemes 24 and 25. It should be noted that the disilanyl groups are tolerated during some synthetic elaborations using organometallic reagents and stable toward acidic conditions: the disilanyl groups may thus be useful complementarily to the $PhMe_2Si$ group,[69] as also shown in Scheme 24. The Si–Si bond can also be cleaved with aluminum chloride or bromine prior to the oxidation (entry 31) (see eq. 37).[70]



Scheme 24.



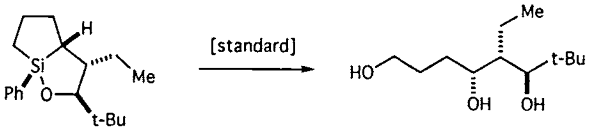
Scheme 25.

4. ORGANIC GROUPS AND OXIDATION CONDITIONS

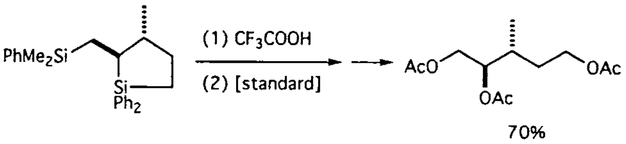
4.1. Cleavage of All Organic Groups on Silicon

All the organic groups, up to three, on silicon can be converted into alcohols as exemplified by the MCPBA oxidation shown in eq. 31.[23] Therefore, silacycloalkanes[47,101,102] afford the corresponding diols efficiently as exemplified by eqs. 32[102] and 33[47] (see also eqs. 7 and 36).

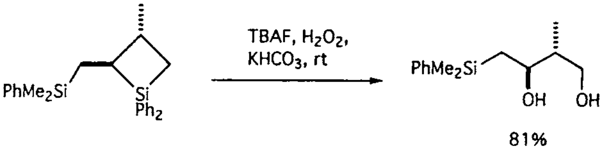
$$(n\text{-}C_8H_{17})_3SiF \;+\; 3\ \text{MCPBA} \xrightarrow[\text{DMF, 50 °C, 5 h}]{\text{KF (x 2)}} \underset{72\%}{3\ n\text{-}C_8H_{17}OH} \qquad (31)^{23}$$



(32)[102]



(33)[47]



(34)[47]

In this connection, it should be noted that four-membered silacyclobutane rings without any heteroatom on silicon can be oxidized directly by hydrogen peroxide oxidation in the presence of TBAF, as shown in eq. 34.[47] This high reactivity of silacyclobutanes may be ascribed to the high Lewis acidity[103] of the silicon center which is favorable for the formation of the penta- and hexacoordinate silicon species, as well as ring strain. It should be noted that while in eq. 33 all silicon moieties are converted into OH groups, in eq. 34 the ordinary alkyl–$SiMe_2Ph$ group remains intact.

4.2. Reactivity Order of Organic Groups on Silicon

In connection with the mechanistic studies of hydrogen peroxide oxidation, the reactivity order of organic groups on silicon has been determined by intermolecular and intramolecular competition experiments.[31,104]

In the intermolecular competition experiments, an equimolar mixture of $R^1MeSi(OCH_2CH_2OMe)_2$ and $R^2MeSi(OCH_2CH_2OMe)_2$ was treated at 10 °C for 1 h with 30% H_2O_2 (0.5 molar equiv), $KHCO_3$ (1 molar equiv) and CsF (2 molar equiv) in a 20:1 (v/v) homogeneous mixed solvent of $MeOCH_2CH_2OH$ and water. The relative reactivity is roughly as follows: Me (1.0), 5-decenyl (1.0), 2-octyl (1.1) < 1-octyl (1.7), 1-octenyl (1.8) < Ph (2.7). While the reactivity difference is not so large, three general tendencies are deduced: (1) the Me group is least reactive, (2) aromatic and alkenyl C(*sp*^{2}) groups are more reactive than aliphatic

sp^3 C groups, and (3) terminal alkyl or alkenyl groups are more readily cleaved than internal groups.

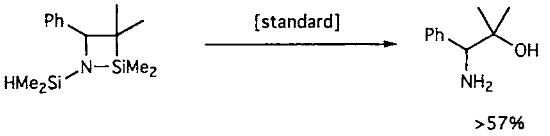
The last tendency is reversed in the intramolecular competition experiments using $R^1R^2Si(OCH_2CH_2OMe)$ under the same conditions as described above. Thus, the relative reactivity order in the intramolecular competitions is roughly as follows: 1-octyl (1) < 2-octyl (10); Me (1) < 1-octyl (10) and Me (1) < Ph (12). The Me group is again the least reactive group in the oxidation.

All the results are consistent with the proposed mechanism shown in Scheme 6. Thus, while in the intermolecular competitions a steric hindrance effect may be operative in the F^- and/or H_2O_2 attacking steps, in the intramolecular competitions bulkier secondary alkyl groups may migrate from silicon to oxygen much faster to release the steric crowding within the sterically congested hexacoordinate silicon species.

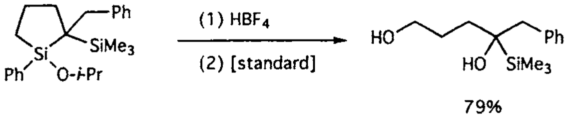
The intramolecular reactivity order of sec-alkyl > phenyl ≥ primary-alkyl > Me is far more important from a synthetic point of view. Thus, for example, while in the dimethylsilyl compounds, $R–SiMe_2X$, the R–Si bond would be oxidized much faster than the remaining Me–Si bonds, in the oxidation of diphenyl counterparts, $R–SiPh_2X$, the Ph–Si bonds would compete with or would be cleaved faster than the R–Si bond. In the latter cases, therefore, the oxidizing agent must be used in excess to ensure the oxidative cleavage of all the organic groups.

4.3. Steric Effects in the Oxidative Cleavage of Organic Groups on Silicon

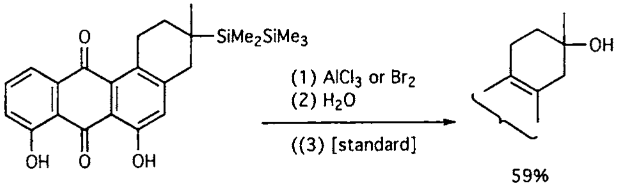
The reactivity orders mentioned above suggest that bulky organic groups may be oxidatively cleaved faster than other groups once the hypercoordinate silicon species is formed. In fact, while the reactivity order of the *tert*-alkyl–silicon bonds has not yet been determined, several successful cases[51,57,70,88,100,105] have been reported as shown by repre-



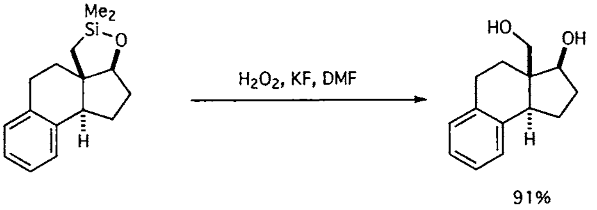
(35)[88]



(36)[101]



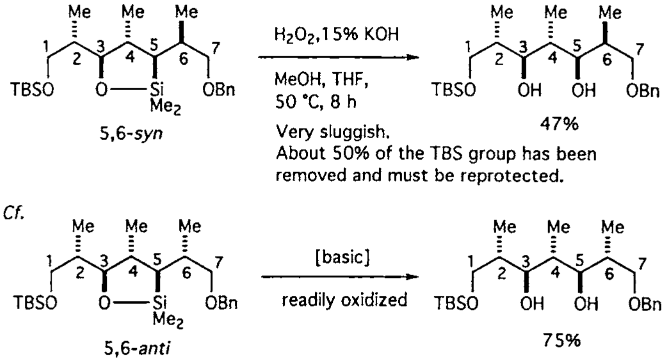
(37)[70]



(38)[106]

sentative examples in eqs. 35,[88] 36,[100] and 37[70] (see also Schemes 16 and 18). Neopentyl-type silicon moieties[23,46,106–108] are also cleaved without difficulty as exemplified by eq. 38[106] (see also eq. 28).

Unexpected steric hindrance effects have sometimes been observed in the oxidation step. For example, in the tetraol synthesis shown in Scheme 26, only the 5,6-*syn* isomer has been found to be much less reactive than the several other diastereoisomers represented by the 5,6-*anti* isomer. Thus, the former is almost recovered unchanged under the mild basic conditions, under which the latter has been completely oxidized.[34,39] Oxidation of the former is still very sluggish and incomplete under more drastic conditions such as the [KOH] condition. The



Very sluggish.
About 50% of the TBS group has been removed and must be reprotected.

(ref. 34)

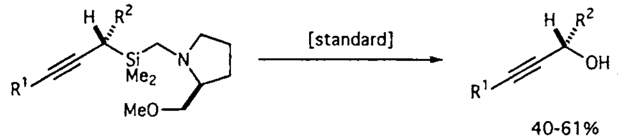
Scheme 26.

observed large steric effect caused by such a small structural difference as the side-chain 6-epimers is totally unexpected.

4.4. Oxidative Cleavage of Allylsilanes, Propargysilanes, Alkenylsilanes, Epoxysilanes, and Related α-Functional Silicon Compounds

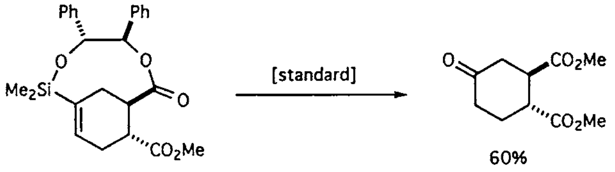
The regiochemistry concerning the oxidation of allylsilanes deserves comment. Thus, unlike the traditional allylsilane chemistry where electrophiles attack on the γ-position of the allyl group to give the allylic-transposition products, the oxidative cleavage reaction proceeds without transposition, i.e. the oxygen functionality is introduced directly onto the silicon-bearing carbon atom (so-called α-position) regioselectively, as already shown in eqs. 12, 13, and 15 and Schemes 14, 19, 20, and 21.

Propargylsilanes also give propargyl alcohols regioselectively as shown in eq. 39.[109] The compatibility of an allenyl group[110] (not allenylsilane moiety) with hydrogen peroxide oxidation may be noted herein.

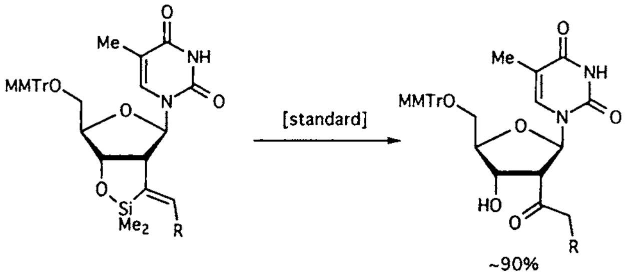


(39)[109]

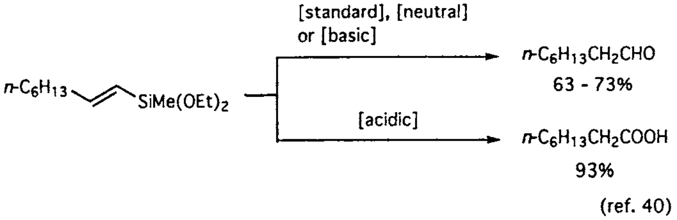
Alkenylsilanes are oxidized into carbonyl compounds probably via enol intermediates.[33,40] In addition to the examples illustrated in eq. 2 and Scheme 24, further examples[89,111–113] have been reported, as shown in eqs. 40[112] and 41.[113]



(40)[112]



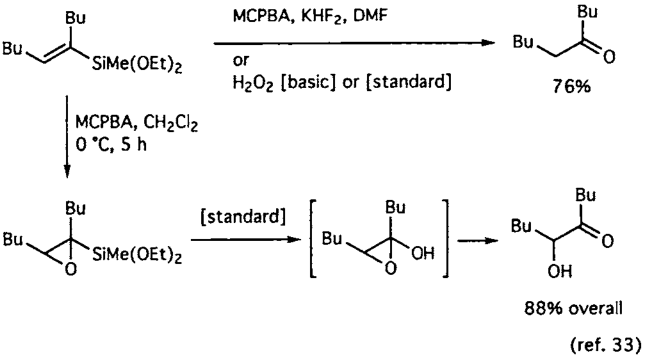
(41)[113]



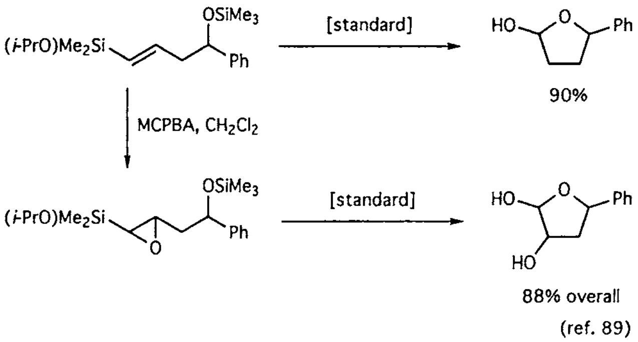
Scheme 27.

Terminal alkenylsilanes are converted into aldehydes with hydrogen peroxide oxidation under the standard conditions, but under the [acidic] conditions the aldehydes are further oxidized to carboxylic acids, as shown in Scheme 27.[40]

Solvent effects on the MCPBA oxidation of alkenylsilanes may be noted. While MCPBA in dichloromethane gives the epoxide, this reagent in DMF gives no epoxide, probably due to the disruption of the intramolecular hydrogen bond in the peracid by the more polar solvent.[114] Alkenylsilanes can thus be converted into either the carbonyl compounds by direct oxidation of the silicon–carbon bond or α-(hydroxy)carbonyl compounds via epoxidation of the alkenyl group: the latter transformation involves the oxidation of the epoxysilanes to (hydroxy)epoxides which isomerize to α-(hydroxy)carbonyl compounds, as shown in Schemes 28[33] and 29.[89]

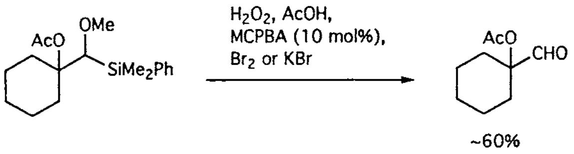


Scheme 28.

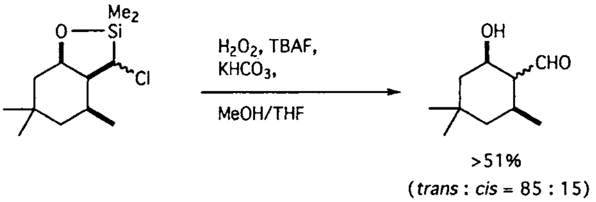


Scheme 29.

α-Alkoxy-[115] and α-chloroalkylsilanes[116] are oxidized to the corresponding aldehydes via hemiacetals and α-chlorohydrins, respectively, as shown in eqs. 42 and 43.



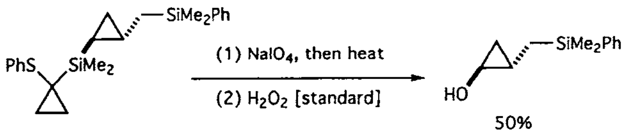
(42)[115]



(43)[116]

4.5. Cyclopropysilanes and Cyclobutylsilanes

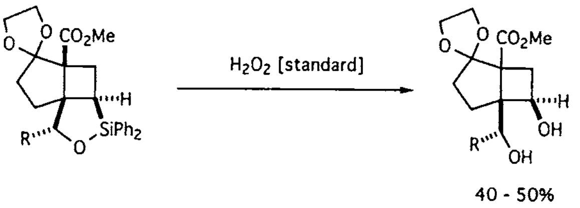
As mentioned above, cyclopropylsilanes are so acid-sensitive that peracetic acid oxidations (entries 3 and 4, Table 2)[97] and an acid treatment (entry 7, Table 2)[57] give ring opening products. However, hydrogen peroxide oxidation seems to be applicable to conversion of cyclopropylsilanes to cyclopropanols,[57,68,117] as shown in eq. 44 (see also Scheme 18).



(44)[46]

Cyclopropane rings far from the silyl groups are generally stable[118] (see also eq. 51).

Cyclobutylsilanes are also oxidized to cyclobutanols by hydrogen peroxide oxidation under the standard conditions, as shown in eq. 45.[119]



(45)[119]

4.6. Polysilylated Compounds

Since several examples have already been illustrated in Schemes 13 and 16 and eqs. 13, 24, 26, 27, 32, 33, 34, and 36, all the silyl groups in disilyl to tetrasilyl derivatives, including geminal disilyl derivatives, can be converted into the corresponding polyols.

5. FUNCTIONAL GROUP COMPATIBILITY

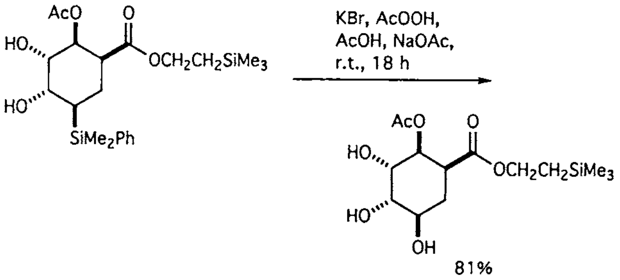
While a variety of functional groups are compatible with oxidation conditions, appropriate conditions must be chosen for some reactive functional groups. Some data for incompatibility of carbonyl, acetoxy, and alkoxy groups in the protodesilylation steps of the $PhMe_2Si$ moiety have already been mentioned in Schemes 9–13. Other comments will be described in this section.

Since a silyl group on carbon α to the carbonyl group is readily cleaved under both acidic and basic conditions to form protodesilylation compounds, the following discussions are only applicable to carbonyl derivatives containing silyl groups on the β-position or beyond:

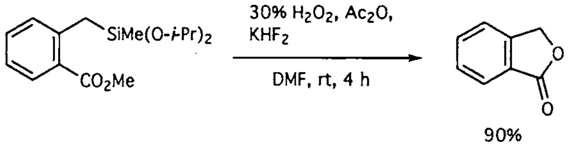
- **Aldehydes** are compatible with hydrogen peroxide oxidation, but are further oxidized to carboxylic acids in the presence of peracids as mentioned above (see Scheme 27).
- **Ketones** can survive even the peracid oxidation under the Fleming conditions (entries 3–5 and 7 in Table 2) and the MCPBA oxidation in DMF ([MCPBA] and [MCPBA/KF] in Table 1), as well as the hydrogen peroxide oxidations: no Baeyer–Villiger oxidation has been observed during these oxidations. In addition to some exam-

ples shown in eqs. 11,[55] 25,[28] and 28[46] and Schemes 17[55] and 18,[56] many reactions have been reported to show the compatibility of ketones.[48,69,107,119–122]

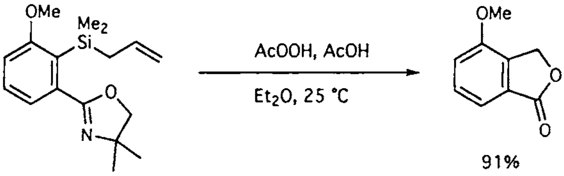
- **Ester** groups are usually stable under hydrogen peroxide oxidation, except the highly basic conditions (such as [KOH] in Table 1), and Fleming oxidation conditions, as seen from examples in eqs. 10,[84] 26,[53] 28,[46] 40,[113] 42,[115] and 45[119] and Schemes 18,[57] 19,[59] and 21,[61] and other reports.[35,58,60,98,111,112,122–133] The compatibility of the 2-(trimethylsilyl)ethyl ester under Fleming oxidation conditions may be noted as shown in eq. 46.[95] In those cases where the new hydroxy group is generated on the γ-position of the ester group, the final product may be the γ-lactones, as shown in eqs. 5[78] and 47:[123] a similar γ-lactone formation has also been observed with certain oxazole derivatives as shown in eq. 48.[57] γ-,[59,134] δ-,[52,53,135] and ε-Lactones[136] and cyclic carbonates[137] are all stable under oxidations. The compatibility of the free carboxylic acid under the Fleming conditions has been reported.[138]



(46)[95]

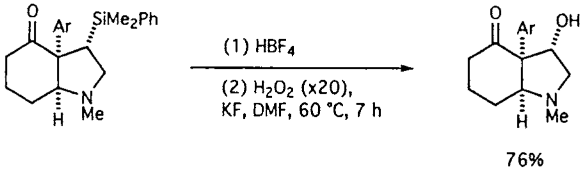


(47)[123]

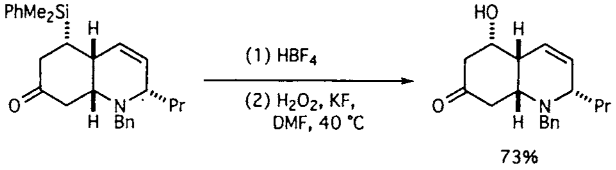


(48)[57]

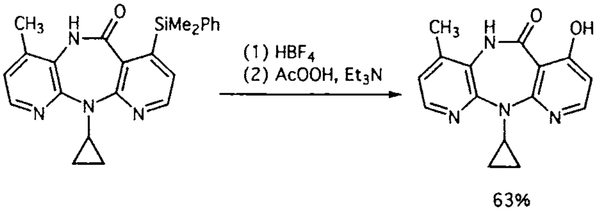
- **Amines** are not oxidized under the conditions of hydrogen peroxide oxidation, as shown for primary amines[47,139] (eqs. 16[88] and 35[88]), secondary amines,[139,140] pyrrolidine rings[141] (eq. 49),[121] pyperidine



(49)[121]



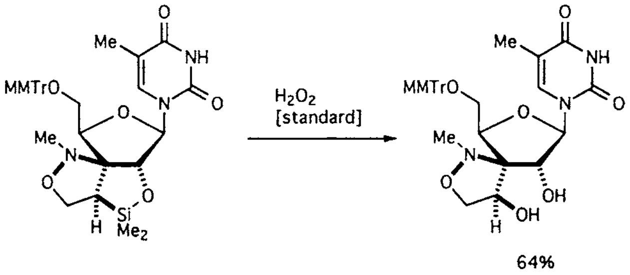
(50)[142]



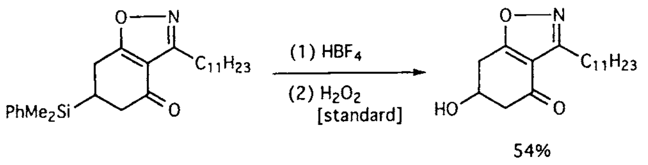
(51)[143]

rings (eq. 50),[142] cyclopropylamine (eq. 51),[143] and pyridine[123,143] (eq. 15);[36] the latter two amino groups can be tolerated even under a peracid oxidation condition, while MCPBA in DMF oxidizes tertiary amines to amine oxide.[28] Interestingly, the result in eq. 51 also indicates that the protodesilylation has occurred selectively with the Si–Ph bond rather than the Si–pyridine ring containing an acyl group. Primary amino groups may be protected as ammonium mesylates by treatment with methane sulfonic acid prior to the Hg(OAc)$_2$/AcOOH oxidation.[139]

- **Isoxazolidine** rings (eq. 52)[144] and **isoxazole** rings (eq. 53)[145] are also stable to the oxidation conditions.
- **Lactams**,[125] including N-protected and N-unprotected β-lactams[146–148] can survive the acidic Fleming conditions as shown in

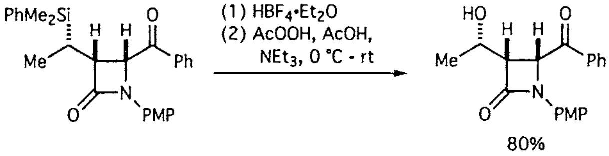


(52)[144]



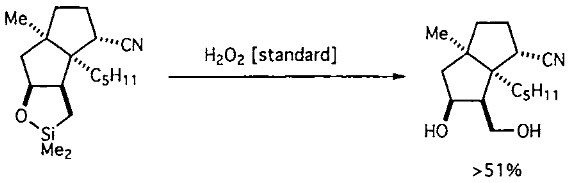
(53)[145]

eq. 54.[148] Common amides, including NBoc (Boc = *t*-BuOCO)[84,149] and NCbz (Cbz = $PhCH_2OCO$)[150] are all compatible with the oxidation conditions.

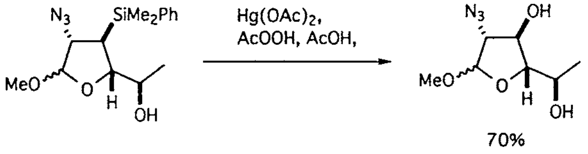


(54)[148]

- **Nitriles**[123,151] (eq. 55)[152] and **azides** (eq. 56)[153] are also stable.

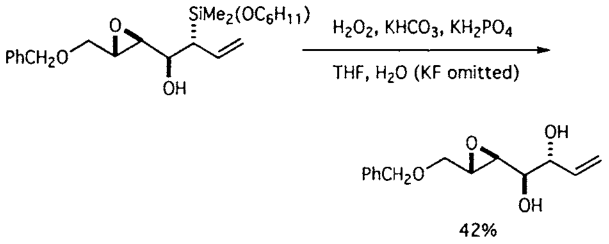


(55)[152]



(56)[153]

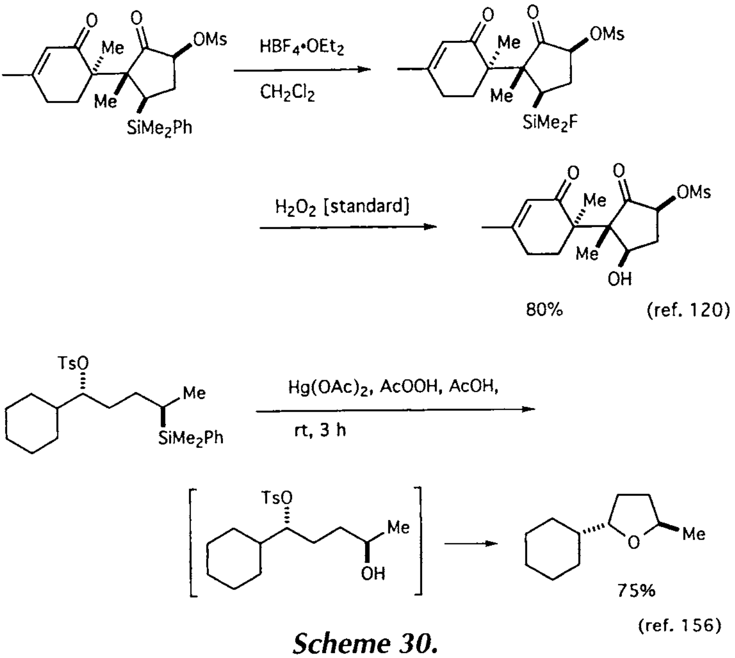
- As mentioned above, hydroxy groups β to the silyl groups may undergo β-elimination under strongly acidic conditions (see Scheme 9), but may be compatible with milder conditions such as hydrogen peroxide oxidation even in the presence of KF, standard conditions (see eqs. 3 and 15 and Schemes 14, 19, 23), and also Fleming peracetic acid oxidation (see also Scheme 9). Such a β-elimination, however, seems to be highly dependent on the stereochemistry (Peterson elimination: *syn*-isomer 4 times faster than *anti*-isomer)[154] and substituents around these two functional groups. For example, an extremely high tendency towards elimination has been noted for the isomer shown in eq. 57, for which has been developed a much milder condition omitting KF and using KH_2PO_4



(57)[155]

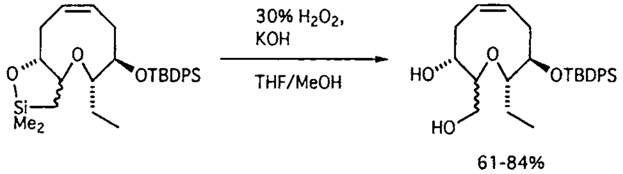
as a buffer to give the desired diol in fair yields, but a significant amount of elimination still occurs.[155]

- In addition to the high stability of acetoxy groups already described above (see esters), compatibility of more reactive sulfonate esters such as **mesylates** OMs (OSO_2Me)[120] and **tosylates** OTs ($OSO_2C_6H_4Me$-*p*)[156] should be mentioned herein, as shown in Scheme 30. In the latter example, it seems reasonable that the tosylate group survives during Fleming oxidation and then is substituted by the newly generated hydroxy group intramolecularly with inversion of configuration to give the tetrahydrofuran ring.[156]
- While **ethers** are generally stable under the usual oxidation conditions,[35] two points may be noted. First, deprotection of a benzyl



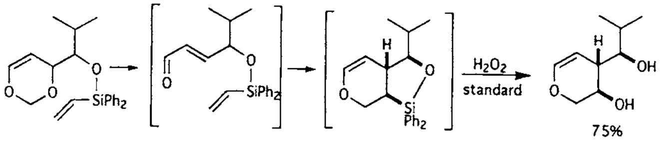
Scheme 30.

ether has been observed during the halo-deallylation of the proximate allylsilane moiety.[57] Second, silyl ethers are desilylated under the conditions using fluoride ions. Thus, in the presence of even the bulky TBS (t-BuMe$_2$Si) ethers, the hydrogen peroxide oxidation under the basic condition omitting fluoride ions must be used (see Scheme 26).[34,35,131,155] The TBDPS (t-BuPh$_2$Si) ether is compatible even with the [KOH] condition (eq. 58).[157,158]

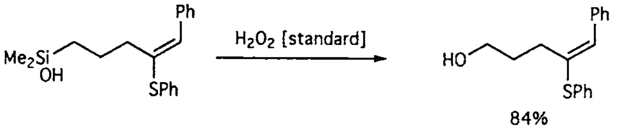


(58)[157,158]

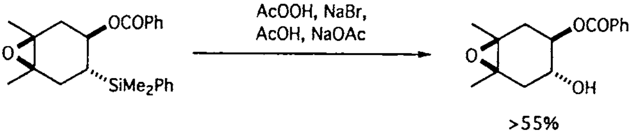
- **Epoxides**[62,155,159,160] (Scheme 20 and eq. 57), a cyclic **vinyl ether** (eq. 59),[161] **furan** (eq. 6),[37] **thiophene**,[36,123] and **sulfides**[110] (eq. 60)[101] are stable under hydrogen peroxide oxidations. The compatibility of epoxides even with Fleming peracetic acid oxidation is noteworthy (eq. 61).[160]



(59)[161]



(60)[101]



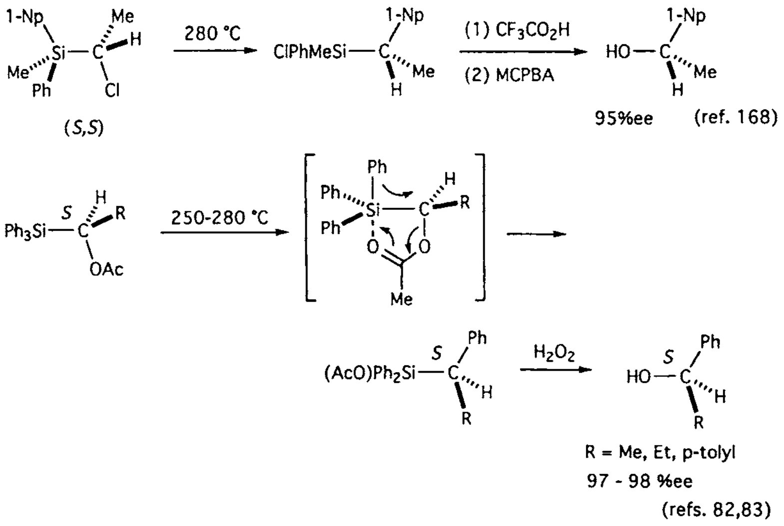
(61)[160]

- **Acetals** and **ketals** including common protecting groups such as acetonide, OMOM, and OTHP are all stable under hydrogen peroxide oxidation conditions.[35,39] Some of them, such as acetonides and acetals incorporated in sugar skeletons, also survive acidic conditions such as proteodesilylation of a phenyl or a furyl group with $BF_3 \cdot 2AcOH$[122] or CF_3COOH[62] and Fleming peracetic acid oxidation (cf. Scheme 9).[94,122,162] Since tetrahydrofuran and tetrahydropyran rings are also stable, the oxidative cleavage reactions have found a wide applicability in carbohydrate chemistry.[67,78,94,162–167] (see Schemes 8 and 23 and eqs. 41, 52, and 56).

6. SYNTHETIC APPLICATIONS

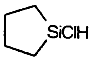
A wide variety of functionalized organosilicon compounds have been used for organic synthesis in combination with the oxidative cleavage of the silicon–carbon bond. While detailed descriptions of their synthetic applications and transformations are not the purpose of this review, comprehensive compilation of the synthetic applications has been attempted. Table 3 lists the silicon reagents, their synthetic equivalents after oxidation of the appropriate Si–C bonds, their synthetic applications, and references.

There are, however, several silicon compounds and reactions which cannot simply be categorized into any groups listed in Table 3. These are described briefly.



Scheme 31.

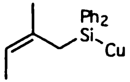
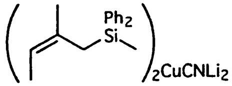
Table 3. Silicon Reagents: Their Synthetic Equivalents after Oxidation and Synthetic Applications

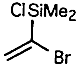
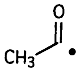
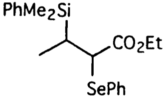
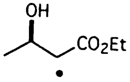
Silicon Reagent[a]	*Synthetic Equivalent(s)*[b]	*Synthetic Application*	*Ref.*[c]
Hydrosilanes			
$HSiCl_3$	H, OH	Pd-catalyzed asymmetric hydrosilation	86, 133, 170(r), 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183
$HSiMeCl_2$	H, OH	Pd-catalyzed asymmetric hydrosilation	183
		$AlCl_3$-catalyzed hydrosilation	184
$HSiMe_2Cl$	H, OH	intramolecular hydrosilation	84, 88, 185, 186
		Rh-catalyzed asymmetric intramolecular hydrosilation	187, 188, 189, 190
		carbene insertion	191
$HSiMe_2(CH_2Cl)$	H, $^+CH_2OH$	hydrosilation to acetylene, followed by $AlCl_3$-catalyzed rearrangement	117
$(HMe_2Si)_2NH$	H, OH	Rh or Pt-catalyzed intramolecular hydrosilation	34, 39, 84, 157, 158, 192, 193, 194, 195
	H, OH	Rh-catalyzed asymmetric intramolecular hydrosilation	188, 189, 190, 196
	H, OH	Rh-catalyzed asymmetric intramolecular hydrosilation	188, 189, 190, 196
$HSiMe(OEt)_2$	H, OH	Pt or Rh-catalyzed hydrosilation	24, 33, 40
H_3SiPh	H, OH	Y-catalyzed hydrosilation	90

$HSi(i\text{-}Pr)_2Cl$	H, OH	Rh-catalyzed intramolecular hydrosilation	185
		Rh-catalyzed asymmetric intramolecular hydrosilation	188, 189
$HSiMe_2(NEt_2)$	H, OH	Rh or Pt-catalyzed intramolecular hydrosilation	197
		intramolecular hydrosilation of acetylene	198
$HSiMe_2Ph$	H, OH	carbene insertion	191
$HSiPh_2Cl$	H, OH	Rh-catalyzed asymmetric intramolecular hydrosilation	187, 188, 189, 190
$HSiAr_2Cl$ (Ar = 3-MeC_6H_4, 4-MeC_6H_4, 3,5-$Me_2C_6H_3$)	H, OH	Rh-catalyzed asymmetric intramolecular hydrosilation	187
$HSi(SiMe_3)_3$	$H^\bullet$, $OH^\bullet$	radical addition	8
Chlorosilanes and alkoxysilanes			
$ClSiMe_2(OMe)$	OH^+	reaction with RLi	199
$(MeO)_3SiMe$	OH^+	reaction with RMgX	200
$ClSiMe_2(O\text{–}i\text{-}Pr)$	OH^+	reaction with RLi	201
$ClSiMe_2Ph$	OH^+	reaction with RLi	143
Silyl anions			
$Me_3SiSiMe_2Li$	OH^-	conjugate addition	70, 202
$(PhMe_2Si)_2Cu(CN)Li_2$	OH^-	conjugate addition	28(r), 48, 93, 120, 125, 127, 128, 139, 145, 203(r), 204, 205, 206, 207
		allylic substitution	208
		asymmetric conjugate addn.	93, 148, 209

(continued)

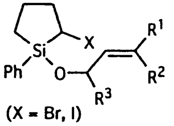
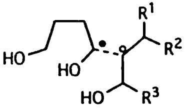
Table 3. (Continued)

Silicon Reagent[a]	*Synthetic Equivalent(s)*[b]	*Synthetic Application*	*Ref.*[c]
$(Et_2N)Ph_2SiLi$	OH^-	conjugate addition	87, 98
		allylic substitution	87
$[(Et_2N)Ph_2Si]Cu(CN)Li$	OH^-	conjugate addition	87
		addition to acetylene	87
		allylic substitution	87, 98
	OH^-	allylic substitution	58, 59
	OH^-	conjugate addition	58
		addition to acetylene and allene	58
		allylic substitution	58, 59
Ph_3SiLi	OH^-	reaction with R^*Cl (inversion)	210
Disilanes			
$Cl_3Si–SiMe_3$	OH^-	silylation of π-allyl-Pd complex	211
$ClMe_2Si–SiMe_2(O–$*i*-Pr)	HO,OH	Pd-catalyzed intramolecular bis-silylation	47, 212(r)
$PhCl_2Si–SiMe_3$	OH^-	Pd-catalyzed asymmetric allylic substitution	213
	OH^-	Pd-catalyzed asymmetric addition to enones	214, 215, 216
$ClMe_2Si–SiMe_2Ph$	HO,OH	Pd-catalyzed intramolecular bis-silylation	47, 51, 212(r)

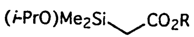
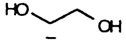
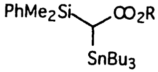
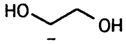
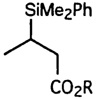
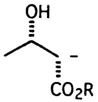
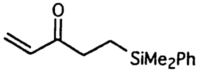
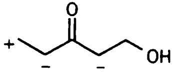
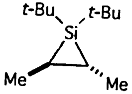
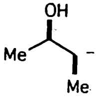
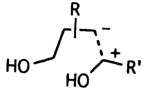
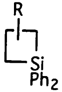
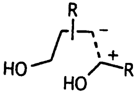
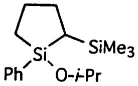
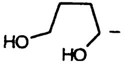
$ClPh_2Si–SiMe_2Ph$	HO,OH	Pd-catalyzed intramolecular bis-silylation	47, 212(r)
Carbofunctional silanes for radical reactions			
$ClMe_2SiCH_2Br$	$HOCH_2^\bullet$	radical cyclization of allylic alcohol	217(r), 218(r)
		5-*exo* for acyclic olefin	219
		5-*exo* for cyclic olefin	118, 131, 151, 164, 165, 220, 221, 222, 223, 224, 225
		5-*exo* for angular position	106, 107, 108
		6-*exo* for acyclic olefin	225
		6-*endo* for cyclic olefin	107, 226
		6-*endo* for acyclic olefin	227, 228, 229
		7-*endo* for acyclic olefin	227
		radical cyclization of propargyl alcohol	151, 230(r)
$PhMe_2SiCH_2COOH$	$HOCH_2^-$	Kolbe electrolysis	134
$ClMe_2SiCHCl_2$	$O{=}CH^\bullet$	radical cyclization of allylic alcohol	116
	$HOCH^{\bullet/\bullet}$	radical cyclization of dien-ol	116
$ClMe_2SiCH_2CH_2Cl$	$HOCH_2CH_2^\bullet$	6-*endo* radical cyclization of enol silyl ether	231
		radical cyclization of allylic alcohol	232
		allylation with allylstannane	129

(continued)

Table 3. (Continued)

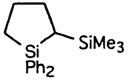
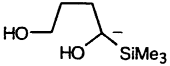
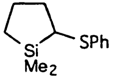
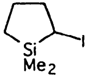
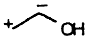
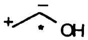
Silicon Reagent[a]	*Synthetic Equivalent(s)*[b]	*Synthetic Application*	*Ref.*[c]
		radical cyclization	102
(Silyl)methyl anions			
(i-PrO)Me_2SiCH_2MgCl	$HOCH_2^-$	nucleophilic hydroxymethylation	76
		addition to carbonyl group	76, 159, 167, 233, 234, 235, 236, 237
		coupling with halide, tosylate, epoxide	123, 238, 239
(i-PrO)Me_2SiCH_2MgCl/CuI	$HOCH_2^-$	conjugate addition to enoate	135
[(i-PrO)$Me_2SiCH_2]_2Zn$	$HOCH_2^-$	coupling with halide	240, 241
(i-PrO)$_2MeSiCH_2MgCl$	$HOCH_2^-$	coupling with halide, phosphate	123
$(CH_2{=}CHCH_2)Me_2SiCH_2MgCl$	$HOCH_2^-$	Cu-catalyzed conjugate addition to enone	56
$PhMe_2SiCH_2MgCl$	$HOCH_2^-$	addition to carbonyl group	94, 162, 165, 242
$PhMe_2SiCH_2MgCl/CeCl_3$ or CuI	$HOCH_2^-$	addition to imine	150
$(PhSCH_2)Me_2SiCH_2MgCl$	$HOCH_2^-$	addition to carbonyl group	67
$PhMe_2SiCH_2OMe$/s-BuLi	$O{=}CH^-$	addition to ketone	115
$RPh_2SiCHPh(SPh)$/Li/Naph. (R = Me, Ph)	$HOCHPh^-$	reaction with epoxide	54
$(R_2{}^*NCH_2)Me_2SiCH_2Ph$/$s$-BuLi	$HOCHPh^{*-}$	reaction with halide, epoxide	64, 65(r), 243

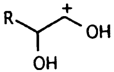
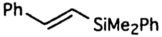
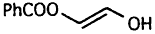
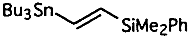
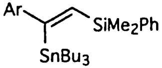
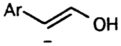
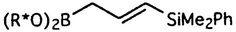
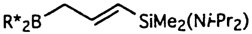
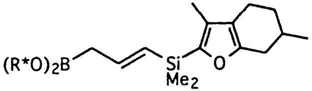
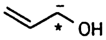
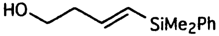
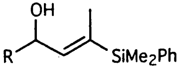
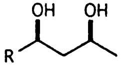
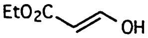
(Silyl)alkyl anions and related compounds

 /(Me$_3$Si)$_2$NLi		coupling with halide, then LAH	244
		reaction with imine, then LAH	140
$OHCCH_2CH_2SiMe_2Ph$	$OHCCH_2CH_2OH$	reaction with enolate	147
		reaction with aldehyde or imine	146, 147
		Robinson annelation	122
		addition to aldehyde (inversion)	42
		addition to aldehyde R′CHO	245, 246(r)
		reaction with carbenoid, Li(X)CHR	246(r), 247
 /*t*-BuLi		coupling with halide	101, 246(r)

(continued)

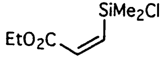
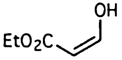
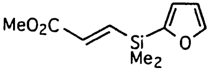
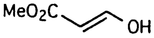
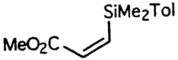
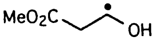
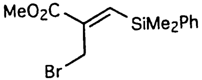
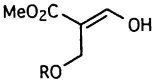
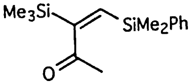
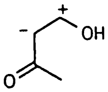
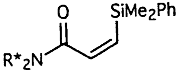
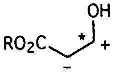
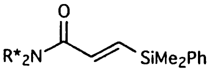
Table 3. (Continued)

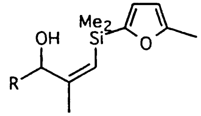
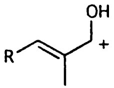
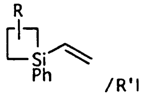
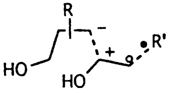
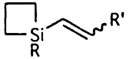
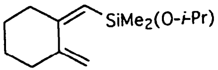
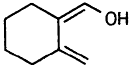
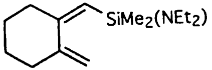
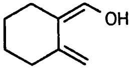
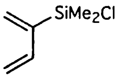
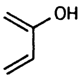
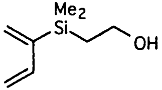
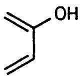
Silicon Reagent[a]	*Synthetic Equivalent(s)*[b]	*Synthetic Application*	*Ref.*[c]
 /*t*-BuLi		reaction with aldehyde	101, 246(r)
 /*t*-BuLi		reaction with aldehyde (+ Peterson olefination)	101, 246(r)
 /*t*-BuLi		reaction with aldehyde (+ Peterson olefination)	247
Vinylsilanes			
$CH_2{=}CHSiCl_3$	$CH_2{=}CH(OH)$	Diels–Alder dienophile	248
$CH_2{=}CHSiMe_2Cl$	$CH_2{=}CH(OH)$	intramolecular Diels–Alder dienophile	249
		intramolecular [2+3] dipolar addition	144
$CH_2{=}CHSiMe(OEt)_2$		conjugate addition of RMgX	250
$CH_2{=}CHSi(OEt)_3$	$CH_2{=}CH(OH)$	Ru-catalyzed C–H insertion	78
$CH_2{=}CHSiPh_2Cl$	$CH_2{=}CH(OH)$	intramolecular Diels–Alder dienophile	161
		intramolecular [2+2] cycloaddition	119
$CH_2{=}CHSiMe(NR^*_2)$		conjugate addition of RMgX	251

		epoxidation and reaction with RMgX/CuCN	37
		[2+3] dipolar addition	141
		Diels–Alder dienophile	160
		oxy-Cope	142
		aza-Cope/Mannich cyclization	121
		reaction with aldehyde	155
		reaction with aldehyde	155
		reaction with aldehyde	149, 252, 253
		reaction with aldehyde	62
		radical cyclization	254
		OH-directed hydrogenation	255
		intramolecular Diels–Alder dienophile	249

(continued)

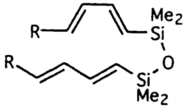
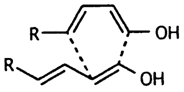
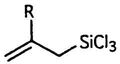
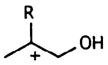
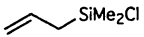
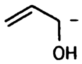
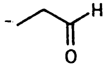
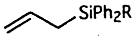
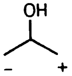
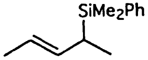
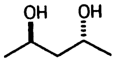
Table 3. (Continued)

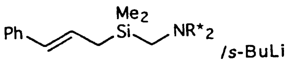
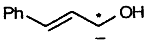
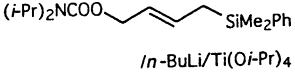
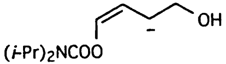
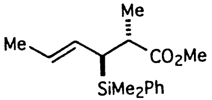
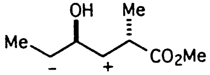
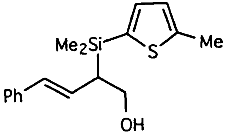
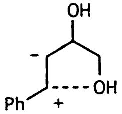
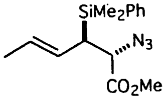
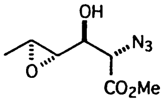
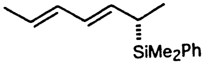
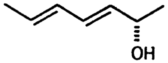
Silicon Reagent[a]	*Synthetic Equivalent(s)*[b]	*Synthetic Application*	*Ref.*[c]
		intramolecular Diels–Alder dienophile	249
		Diels–Alder dienophile	60
		SmI_2-promoted dimerization	52, 53, 136
		SmI_2-promoted dimerization	52, 53, 136
		intramolecular Diels–Alder dienophile	46, 256
		conjugate addition of enolate	257
		conjugate addition of RCu	138
		conjugate addition of RCu	124

		[3,3] sigmatropic rearrangement	61
		radical addition and rearrangement	79, 246(r)
 (R = Me, Ph)		epoxidation, rearrangement (with subsequent Peterson olefination)	246(r), 258
(Dienyl)silanes			
		Diels–Alder reaction	95
		Diels–Alder reaction	260
		intramolecular Diels–Alder reaction	260
		intramolecular Diels–Alder reaction	112
		intramolecular Diels–Alder reaction	111

(continued)

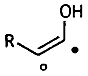
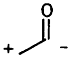
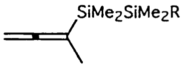
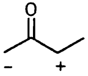
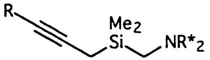
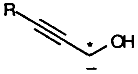
Table 3. (Continued)

Silicon Reagent[a]	*Synthetic Equivalent(s)*[b]	*Synthetic Application*	*Ref.*[c]
 (R= Ar, (*E*)-PhCH=CH-)		intramolecular Diels–Alder reaction	44
Allylsilanes			
 (R = H, Me)		Friedel–Crafts reaction	248
		intramolecular [2+2] cycloaddition	119
		intramolecular radical cyclization	163
 *n*-BuLi/ZnCl2		*anti* addition to aldehyde	36
 *n*-BuLi/CuCN		addition to aldehyde	89
 (R = Me, Ph)		cycloaddition to enone via silyl migration	55
 (various allylsilanes)	 (isomeric 1,3-diols)	diastereoselective hydroboration	260, 261

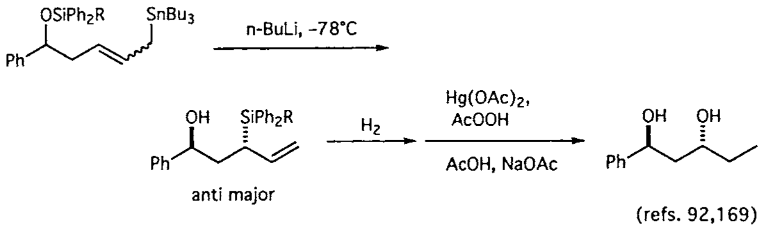
		coupling with halide	65(r), 262
		reaction with aldehyde	132
		diastereoselective cylcoaddition with aldehyde via silyl migration	126
		PhSe$^+$ induced cyclization	63
		OsO$_4$-catalyzed epoxidation	153
		Diels–Alder diene	263
Ethynyl-, allenyl- and propargyl-silanes			
HC≡CSiCl$_3$	HC≡C(OH)	Diels–Alder dienophile	43

(continued)

Table 3. (Continued)

Silicon Reagent[a]	*Synthetic Equivalent(s)*[b]	*Synthetic Application*	*Ref.*[c]
$R-C\equiv C-SiMe_2(NEt_2)$ (R = Ph, Me_3Si, $TBSOCH_2$)		intramolecular radical cyclization	113
$H-C\equiv C-SiMe_2(OR)$ (R = *n*-Bu, *i*-Pr)		conjugate addition of RCu	264
		cycloaddition to enone via silyl migration	69
 /*s*-BuLi		coupling with halide	65(r), 109

Notes: [a] Compounds are listed roughly in the order of the complexity in each group.
[b] For notations • and ° in radical reactions, see ref. 265.
[c] Reviews are shown as (r).



Scheme 32.

The stereospecific oxidative cleavage of the silicon–carbon bond has also provided a useful method for mechanistic studies in organosilicon chemistry. Thus, the stereochemical pathway of the thermal intramolecular rearrangement of optically active α-chloro-[168] and α-acetoxyalkyl[82,83] silicon compounds has been determined to proceed with >95% inversion of configuration at carbon, as shown in Scheme 31. It has also been reported that the retro-[1,4]-Brook rearrangement preferentially forms 1,3-*anti*-isomers, as shown in Scheme 32.[92,169]

7. CONCLUSIONS

Almost 13 years have passed since the first practical methods for the oxidative cleavage of the silicon–carbon bond were discovered and reported. The reactions are now recognized as the only existing method for the conversion of an aliphatic carbon–silicon bond to the oxygen functionality with complete retention of configuration. In addition to the mechanistic importance, the synthetic applications of the oxidation reactions will certainly continue to expand.

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