Review

Discovery and synthetic applications of novel silicon-carbon bond cleavage reactions based on the coordination number change of organosilicon compounds

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Abstract: Some synthetically useful transformations of organosilicon compounds have been developed since the mid 1970s, based on the new concept that the silicon-carbon bonds are activated toward electrophilic cleavage via the formation of penta- and hexa-coordinate species. This review mainly consists of the following aspects: (1) a general concept for the activation of the silicon-carbon bond via penta- and hexa-coordinate species, (2) synthetic application of hexa-coordinate organopentafluorosilicates, and (3) development of the H₂O₂ oxidation of the silicon-carbon bond and its synthetic applications via the intramolecular hydrosilylation, silicon-tethered intramolecular radical cyclization and Diels-Alder reaction, and some silicon-containing organometallic reagents for nucleophilic hydroxymethylation and hydroxyallylation synthons.

Keywords: organosilicon chemistry, hypercoordination, organopentafluorosilicate, hydrogen peroxide oxidation, intramolecular hydrosilylation

Introduction

The author was awarded the Japan Academy Prize 2007, together with Hisashi Yamamoto, University of Chicago, for the collaborative work, entitled “Exploitation of chemical and physical properties of main-group element compounds based on flexibility for high coordination”. The work is based on the following common features of main-group element compounds. Organic compounds RₙE of certain main group elements, especially heavy elements of groups 13 and 14, have electron-accepting molecular orbitals and thus the central element E behaves as a Lewis acidic center to accept a ligand L to form hyper-coordinate species RₙEL, increasing both the electrophilicity of the ligand L and the nucleophilicity of the group R; the electronic states and steric environments around the central element E can be tuned by appropriate modification to the R and/or L. While Yamamoto’s work is mainly based on the former concept for the enhanced electrophilicity of the ligand L, the author has been interested in the latter concept for the enhanced nucleophilicity of the group R, especially in organosilicon compounds.

A brief comparison of silicon with carbon in four categories is first made to determine key characteristic features of organosilicon compounds using the chart shown in Fig. 1. Among some similarities and differences between them, only several of the most striking features are mentioned as follows. (1) Size and electronegativity: silicon is larger and more electropositive than carbon, as shown in the central part, (2) reactive intermediates such as anion, radical, cation, and divalent species shown on the left side: among them, the trivalent silicocation can hardly be present as a free stable species in solution in which the vacant site is occupied by any basic species, suggesting that nucleophilic substitution reactions at silicon generally proceed not by a dissociative mechanism but by an associative mechanism, (3) high-coordinate species shown on the right side: this is the most important difference that while a penta-coordinate species of carbon corresponds to a high energy structure at a transition state of S₂N₂ substitution reactions, penta- and hexa-coordinate silicon spe-

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cies are stable enough to be isolated in many cases, and (4) unsaturated species, catenation and polymeric materials shown on the top and bottom: silicon-containing unsaturated compounds are so reactive that they can only be isolated through stabilization by introduction of bulky kinetically-protecting groups.

Obviously, most of these three features (2), (3) and (4) related to silicon-containing molecules are based on the feature (1) of the silicon atom. In particular, the large and electropositive silicon atom is the origin of the Lewis acid properties of organosilicon compounds to accept Lewis bases, resulting in the formation of hypercoordinate species. Since the mid 1970s, we have been interested in these inherent properties of organosilicon compounds with the objective of their application in organic syntheses.

This review summarizes several aspects obtained in our laboratories at Kyoto University where the author worked for 35 years, as listed below.

1. A general concept for the activation of the silicon-carbon bond via penta- and hexa-coordinate species
2. Synthetic application of hexa-coordinate organopentafluorosilicates
3. Development of the H$_2$O$_2$ oxidation of the silicon-carbon bond and its synthetic applications

A general concept for the activation of the silicon-carbon bond via penta- and hexa-coordinate species

A key step in the synthetic application of organosilicon compounds is the electrophilic cleavage of the silicon-carbon bond, where an electrophile links to the carbon center to form the desired product, while the counter nucleophile attacks the silicon atom, as shown in Scheme 1.

In principle, there are two extreme cases for activation of the silicon-carbon bond, depending on the timing of the interaction of the electrophilic part with the organic group and the nucleophilic part with the silicon center. One is the use of electron-rich organic groups, such as allyl and vinyl groups, and the other involves the formation of penta- and/or hexa-coordinate silicon species.

\[
\begin{align*}
X_3SiR & \quad + \quad E^+Nu^- \\
& \quad \xrightarrow{\text{X$_3$Si$\rightarrow$Nu$^-$}} \quad X_3SiNu^+ + RE
\end{align*}
\]

Scheme 1.

Fig. 1. A schematic comparison between carbon and silicon. $r_c$ and $\chi$ represent, respectively, the covalent radius and the electronegativity. Structures in parentheses are still unknown.
In the former case, as shown in Scheme 2, electrophiles may first interact with the \( /C25\) electron moiety to form a carbocation \( /C12\) to silicon which is stabilized by the silyl group via the so-called \( /C27\)–\( /C25\) conjugation, followed by nucleophilic attack on silicon to cleave the silicon-carbon bond, resulting in the formation of the product.

Thus, organo-silicon compounds such as allylsilanes and vinylsilanes containing an "activated group" toward electrophiles have been well recognized as versatile synthetic reagents.

The latter concept has been developed for the activation of the silicon-carbon bond in simple "non-activated" alkyl-silanes via the formation of hyper-coordinate species. The complete view is summarized in Scheme 3. This is the main theme of our research in this field.

In Scheme 3, while the route denoted as Route A corresponds to the former case for the activated organic groups discussed above, the route denoted as Route B is for the latter "non-activated" case (\( R = \) simple alkyl). In Route B, electronegative groups X are introduced on silicon to enhance the Lewis acidity of the silicon center and form the penta-coordinate silicon species. The resulting penta-coordinate silicon complex has 10 electrons around silicon, being two electrons more than the ordinary 8-electron state. These excess electrons are distributed onto the five ligands to enhance the electron density on the R group and thus the silicon-carbon (Si-R) bond becomes susceptible toward electrophilic cleavage. The silicon center in the penta-coordinate complex is still Lewis acidic to accept another Lewis base to form a hexa-coordinate silicon species of 12 electrons, in which the silicon-carbon bond is further activated toward electrophilic cleavage. In this way, the "non-activated" silicon-carbon bond may be activated for electrophiles up to a synthetically useful level. We have confirmed this concept by using hexa-coordinate organopentafluorosilicates as an extreme case since 1978.

### Synthetic application of hexa-coordinate organopentafluorosilicates

The silicon-carbon bond in hexa-coordinate organopentafluorosilicates \( K_2[RSiF_5] \) can readily be cleaved by a variety of electrophiles or oxidants including halogens,\(^9\) peracid,\(^11\) copper(II) halides,\(^12\) silver(I) halides,\(^13\) and palladium(II) salts,\(^14\) as summarized in Scheme 4.\(^15\) There are several points to be mentioned. (a) While organopentafluorosilicates were first reported in 1961 by L. Tansjoe\(^16\) and some basic reactions were studied by R. Mueller\(^17\) by the end of the 1960s, our work has shown that the silicon-carbon bonds therein are readily cleaved by a variety of electrophiles to give various functionalized products and carbon-carbon bond forming products up to a synthetically useful level. Worthy of note is that these transformations hardly occur with ordinary tetra-coordinate organosilicon compounds, demonstrating that the silicon-carbon bonds in the hexa-coordinate silicates are indeed highly activated toward electrophiles. (b) The organopentafluorosilicates are readily prepared from the corresponding organotrichlorosilanes by addition to an aqueous solution containing a large excess of potassium fluoride as air-stable, insoluble white powders. The most impressive example is the reaction with halogen or \( N\)-bromosuccinimide (NBS) to form the corresponding organic halides; even in a suspension of an organic solvent, the solid silicate \( \text{exothermically reacts with NBS to form the organic bromide} \).
in an almost quantitative yield. Since the inorganic byproducts are also insoluble, simple filtration and concentration afford an almost pure organic bromide. Alcohols are also obtained by the reaction with m-chloroperoxybenzoic acid (MCPBA) in a polar solvent such as DMF. (c) Most important from a mechanistic point of view was the different stereochemical outcomes from the halogen or NBS cleavage and the alcohol synthesis with inversion and retention at the carbon center, respectively, as shown in Scheme 5. Thus, the former must involve the back-side attack, while the latter alcohol synthesis must proceed through the front-side attack.

Plausible mechanisms are shown in Scheme 6. The halogen cleavage may be initiated by a single electron transfer from the electron rich hexacoordinate silicate to the halogen molecule; the resulting halide ion attacks the carbon atom from the back side to give the organic halide with inversion of stereochemistry. In this connection, the high electron donating ability of the hexacoordinate organosilicate has been confirmed by the reaction with tetracyanoethylene (TCNE); even in the solid state, deep-blue TCNE anion radicals were rapidly formed. In contrast, the peroxide oxidation reaction in a polar solvent may proceed through a penta-coordinate silicate formed by fluoride ion dissociation, to which the peracid oxygen atom links as the sixth ligand and within the resulting hexacoordinate silicate, the organic group migrates from silicon to the coordinating peracid oxygen atom to give an alkoxy-silicate and eventually the alcohol upon hydrolysis. The retention of configuration is explained by the intramolecular front side attack.

Obviously, these mechanistic considerations in Scheme 6 are traced back to the ordinary tetra-coordinate organosilicon compounds via the reverse route as discussed in Scheme 3, and thus strongly suggest the possibility for the oxidative cleavage of the silicon-carbon bonds in readily available tetra-coordinate silicon compounds under appropriate reaction conditions, if the silicon center is designed to be reasonably Lewis acidic by introduction of an electronegative group(s).

In 1983, with a strong certainty for this possibility, we started to survey the reaction conditions suitable for the oxidative cleavage reaction with hydrogen peroxide as the most readily available, practical oxidizing agent instead of peracids such as MCPBA.
Development of the $\text{H}_2\text{O}_2$ oxidation of the silicon-carbon bond and its synthetic applications

Discovery of the $\text{H}_2\text{O}_2$ oxidation. Indeed, we soon found that the silicon-carbon bonds are readily cleaved by 30% $\text{H}_2\text{O}_2$ as the oxidant in the presence of a fluoride ion, as shown in Scheme 7.\textsuperscript{21,22} In the first trials, we used 90% $\text{H}_2\text{O}_2$ with the greatest care for the oxidation, but finally found that the more practical 30% $\text{H}_2\text{O}_2$ was quite effective.

Several points deserve comment. First, the presence of at least one heteroatom, such as a fluorine and alkoxo and amino groups on the silicon, is essential for the oxidation. Second, the oxidation is highly accelerated by a fluoride ion, which has a strong affinity to silicon, to convert the silicon species to the activated penta-coordinate state. Third, in control experiments, the silicon-carbon bonds in some isolable pentacoordinate diorgano-trifluorosilicates were found to be easily cleaved under similar conditions but without an extra fluoride ion, demonstrating the penta-coordinate organosilicates to be actual reactive species.\textsuperscript{23} Fourth, it was confirmed that the $\text{H}_2\text{O}_2$ oxidation also proceeds with retention of configuration at the carbon center.\textsuperscript{21a} Thus, a plausible mechanism is shown in Scheme 8.
It should be noted that this discovery overturned the established common knowledge of organic chemists that silicon-carbon bonds are fairly resistant to oxidative cleavage.

**Synthetic application.** With this new oxidation reaction in hand, we have developed a variety of new synthetic methodologies and new reagents, as summarized in Eqs. 1–16. Some characteristic features deserve more comment.

**Intramolecular hydrosilylation.** The intramolecular hydrosilylation of allyl alcohols and homoallyl alcohols followed by the $\text{H}_2\text{O}_2$ oxidation has provided a new methodology for the regio- and stereo-selective synthesis of 1,3-diol skeletons. In a typical example shown in Eq. 1, the hydroxyl group of the 3-hydroxy-2-methyl-1-alkene skeleton is protected by a hydrosilyl group. Subsequent Pt-catalyzed hydrosilylation proceeds in a 5-endo mode to give a five-membered ring product with a high 2,3-syn stereoselectivity. Since the silicon moiety has the oxygen functionality, the resulting silicon-carbon bond is cleaved by the $\text{H}_2\text{O}_2$ oxidation with retention of configuration to form the corresponding 1,3-diol derivative with a high 2,3-syn stereoselectivity.

For homoallyl alcohols, such as the 1-hydroxy-2-methyl-3-alkenes (Eq. 2), they afford different stereoisomers of 1,3-diol; thus, the intramolecular hydrosilylation proceeds in a 5-exo mode to form a five-membered ring product, in which the 2,3-stereochemistry arising from the entering silyl group is controlled anti to the allylic methyl group and the stereochemistry on the 4-position depends on the olefin geometry of the starting material. These results observed with homoallylic alcohols have also provided two significant aspects from a mechanistic viewpoint: the first example of the direct hydrosilylation to an internal olefin without positional isomerization and the first clear-cut experimental evidence for the cis addition of the Si-H functionality to an olefin.

For the Pt-catalyzed hydrosilylation of allyl-amine, it proceeds in a 4-exo fashion to finally give a 1,2-aminoo alcohol derivative with a high 1,2-syn stereoselectivity, as shown in Eq. 3.

The intramolecular hydrosilylation/oxidation sequence can be repeatedly performed in a stepwise fashion to construct polyols, such as polypropionate skeletons, as shown in Eqs. 4 and 5.
The catalytic asymmetric intramolecular hydrosilylation of an allylic alcohol is also possible to give an optically active 1,3-diol with a high stereoselectivity (Eq. 6). The intramolecular hydrosilylation of homopropargylic alcohols followed by the \( \text{H}_2\text{O}_2 \) oxidation provides a new regioselective functionalization of the acetylene group (Eq. 7).

### Silicon-tethered intramolecular radical cyclization and Diels-Alder reaction

The 1-bromo-movynilsilyl and dichloromethylsilyl groups have been found to be useful as a synthetic equivalent, respectively, to the acetyl radical and the hydroxymethylene diradical, as exemplified by the silicon-tethered radical cyclization/oxidation sequence of allylic alcohols, as shown in Eqs. 8 and 9. The latter example demonstrates that the high regio- and stereoselective stepwise radical cyclization can provide four new chiral centers from one chiral center, accompanied by a new carbon-ring annulation.

Eq. 10 represents the first example of the silicon-tethered intramolecular Diels-Alder reaction, followed by the \( \text{H}_2\text{O}_2 \) oxidation, as an efficient method for the construction of poly-functionalized cyclohexane derivatives.

Silicon-containing organometallic reagents for nucleophilic hydroxymethylation and hydroxallylation and as a hydroxide ion equivalent. One of the interesting silicon reagents is the (isopropoxy)silylmethyl Grignard reagent (\( \text{i-PrO} \)\( \text{Me}_2\text{SiCH}_2\text{MgCl} \)), because this reagent contains both a carbon nucleophilic center and a leaving group on silicon, but is quite stable as it...
can be stored in THF even at room temperature; the isopropoxy group is probably bulky enough to prevent the intermolecular nucleophilic substitution at the silicon. This reagent is used as the nucleophilic hydroxymethylating agent for carbonyl compounds, as shown in Eq. 11. The primary product contains a β-hydroxy-silicon moiety which might undergo β-elimination, known as the Peter-son elimination, to form the corresponding olefin; however, under the H₂O₂ oxidation conditions even in the presence of fluoride ions, the oxidative cleavage of the silicon-carbon bond preferentially proceeds, without any such elimination, to form the corresponding 1,2-diol derivative in high yields. In connection with this, it has been reported that the conjugate addition of a hydroxymethyl anion synthon, namely the (allyldimethylsilyl)methyl Grignard reagent, to α,β-enzyme has also been achieved. This reagent also undergoes a palladium catalyzed cross-coupling with aromatic halides, such as 3-bromothiophene, to give, after the H₂O₂ oxidation, the hydroxymethylation products, as shown in Eq. 12. The copper-catalyzed cross-coupling reaction with allylic halides, followed by the H₂O₂ oxidation, affords the corresponding homoallyl alcohols, as shown by Eqs. 13 and 14. This approach significantly provides the most efficient, regio- and stereo-specific transformation of allylic halides to homoallyl alcohols without scrambling of the olefin geometry and the allylic position, as well as the one-carbon elongation of certain functionalized alcohols.

A metallated (allyl)aminosilane is a practical reagent for the stereoselective α-hydroxyallylation of aldehydes to form erythro-1,2-diol skeletons, as shown in Eq. 15. Aminosilyllithium reagents, the first stable functionalized silylithiums which we found in 1992, act as a hydroxide ion synthon, as shown in Eqs. 16 and 17.

**Conclusion**

In this review, we have concentrated on our
own work, but our concept about the activation of the silicon-carbon bond via hypercoordination and the H₂O₂ oxidative cleavage of the silicon-carbon bond have been widely recognized as a new general concept and a new synthetically useful transformation.

The first point has clearly been described by R. Corriu and his co-workers in their review article as follows: “This was the first demonstration of the synthetic applications of hypercoordinate organosilicon compounds and stimulated other chemists to use the same idea that the silicon-carbon bonds are highly activated by hypercoordination. This idea has now become a widely accepted basic concept in synthetic organic chemistry.”

The second point, i.e., the synthetic usefulness of the H₂O₂ oxidation of the silicon-carbon bond, was recognized by many synthetic chemists soon after the discovery by our group, together with a similar oxidative cleavage reaction independently developed by I. Fleming. We are proud of the fact that the oxidation reaction is now generally known as the “Tamao oxidation” and/or “Tamao-Fleming oxidation”. As reference data, the citation number of our first paper published in 1983 has reached 300 times by the end of 2007.

All results described in this review are rather old, but the author is convinced that the concept and the information are still very informative for synthetic organic chemists.

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Profile

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