

Review

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

By Kohei TAMAO^{*1,*2,†}

(Communicated by Hitosi NOZAKI, M.J.A.)

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 R_nE 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 R_nEL, 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

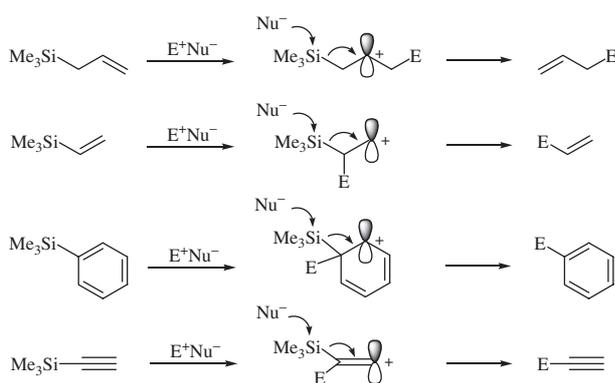
enhanced electrophilicity of the ligand L, the author has been interested in the latter concept for the enhanced nucleophilicity of the group R, especially in organosilicon compounds.

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 solution¹⁾ 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,²⁾ (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 S_N2 substitution reactions, penta- and hexa-coordinate silicon spe-

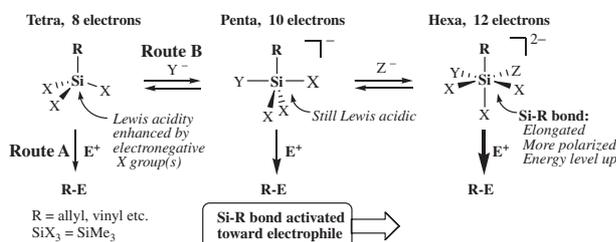
^{*1} Advanced Science Institute, RIKEN, Saitama, Japan.

^{*2} Recipient of the Japan Academy Prize in 2007.

[†] Correspondence should be addressed: K. Tamao, Advanced Science Institute, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan (e-mail: tamao@riken.jp).



Scheme 2.



Scheme 3.

In the former case, as shown in Scheme 2, electrophiles may first interact with the π electron moiety to form a carbocation β to silicon which is stabilized by the silyl group via the so-called σ - π conjugation, followed by nucleophilic attack on silicon to cleave the silicon-carbon bond, resulting in the formation of the product.⁸⁾ Thus, organosilicon compounds such as allylsilanes and vinylsilanes containing an “activated group” toward electrophiles have been well recognized as versatile synthetic reagents.

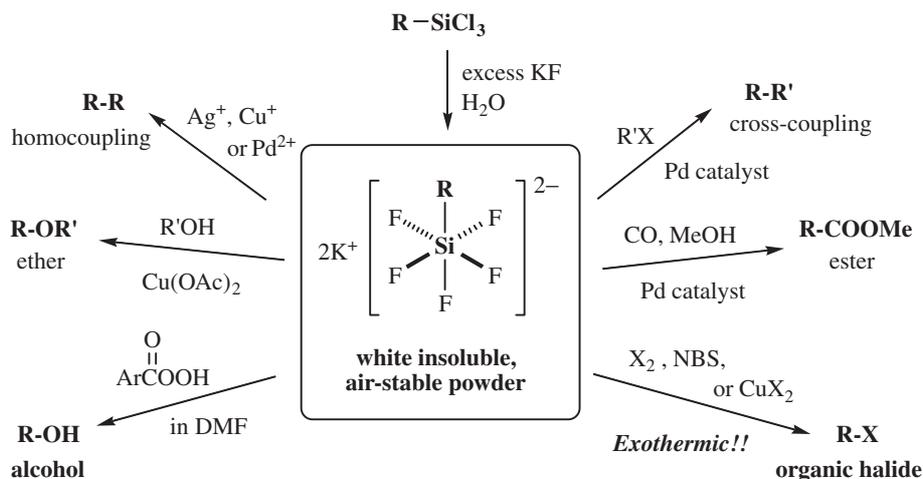
The latter concept has been developed for the activation of the silicon-carbon bond in simple “non-activated” alkyl-silanes via the formation of hyper-coordinate species. The complete view is summarized in Scheme 3. This is the main theme of our research in this field.

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

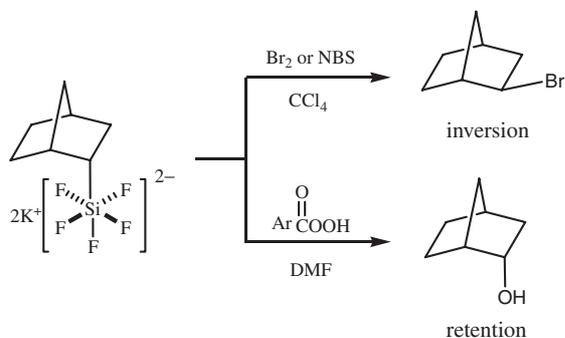
penta-coordinate silicon species. The resulting penta-coordinate silicon complex has 10 electrons around silicon, being two electrons more than the ordinary 8-electron state. These excess electrons are distributed onto the five ligands to enhance the electron density on the R group and thus the silicon-carbon (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 complex 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 1978.⁹⁾

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),10)} 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. Tansjoe¹⁶⁾ and some basic reactions were studied by R. Mueller¹⁷⁾ 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 *exothermically* reacts with NBS to form the organic bromide



Scheme 4.



Scheme 5.

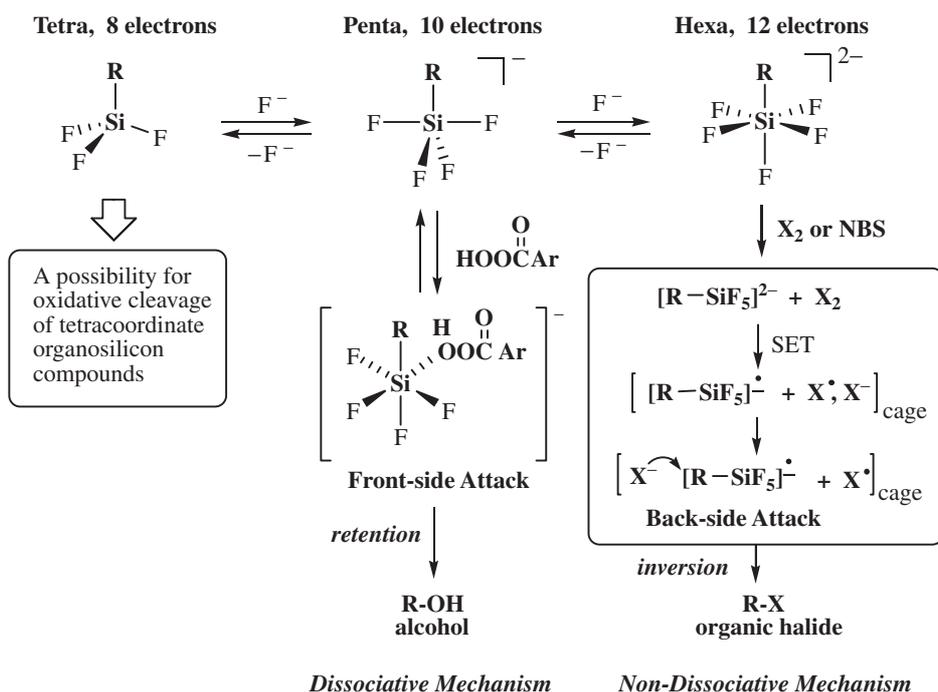
in an almost quantitative yield. Since the inorganic byproducts are also insoluble, simple filtration and concentration afford an almost pure organic bromide. Alcohols are also obtained by the reaction with *m*-chloroperoxybenzoic acid (MCPBA) in a polar solvent such as DMF. (c) Most important from a mechanistic point of view was the different stereochemical outcomes from the halogen or NBS cleavage¹⁸⁾ and the alcohol synthesis¹⁹⁾ 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 hexa-coordinate silicate to the halogen molecule; the resulting halide ion attacks the carbon atom from the back side to give the organic halide with

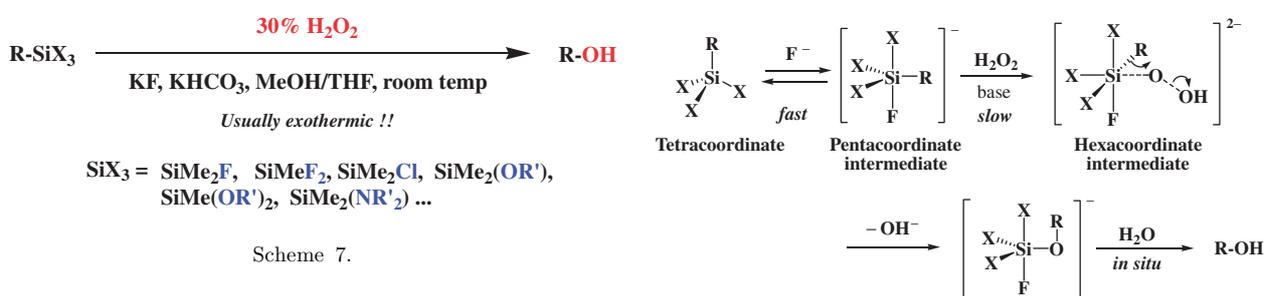
inversion of stereochemistry. In this connection, the high electron donating ability of the hexa-coordinate organosilicate has been confirmed by the reaction with tetracyanoethylene (TCNE); even in the solid state, deep-blue TCNE anion radicals were rapidly formed.²⁰⁾ In contrast, the peroxide oxidation 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 hexa-coordinate 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.¹⁹⁾



Scheme 6.



Scheme 7.

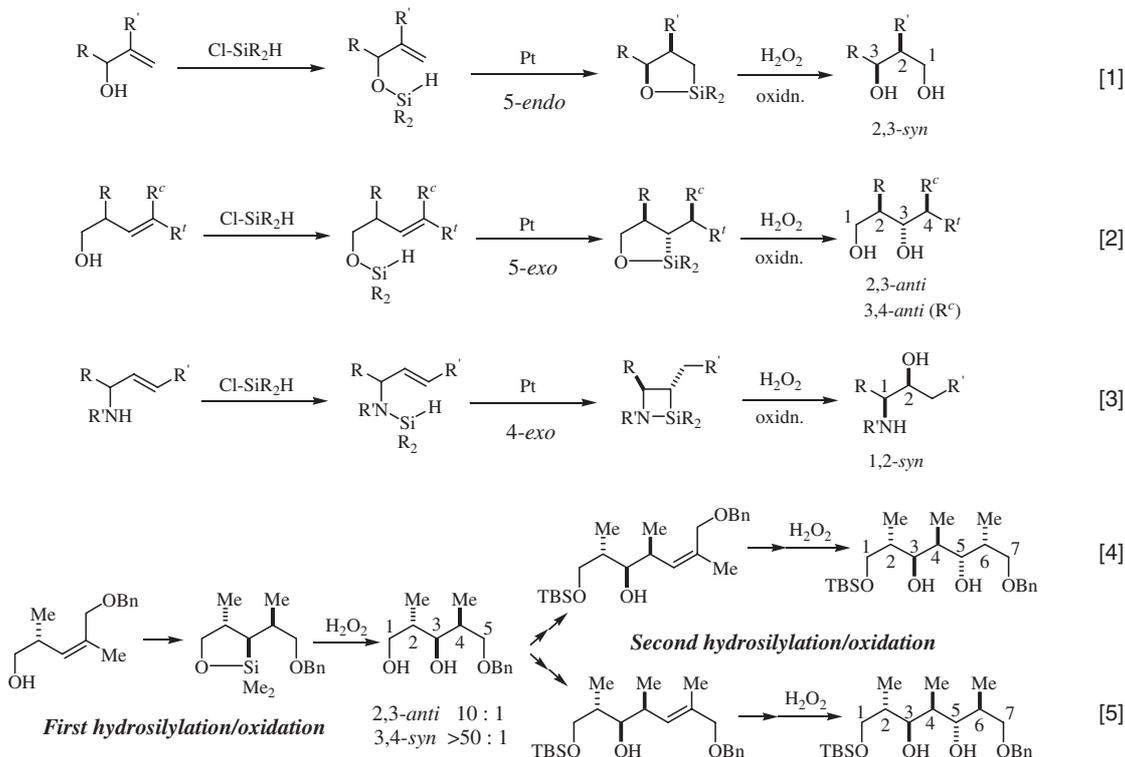
Scheme 8.

Development of the H₂O₂ oxidation of the silicon-carbon bond and its synthetic applications

Discovery of the H₂O₂ oxidation. Indeed, we soon found that the silicon-carbon bonds are readily cleaved by 30% H₂O₂ as the oxidant in the presence of a fluoride ion, as shown in Scheme 7.^{21),22)} In the first trials, we used 90% H₂O₂ with a greatest care for the oxidation, but finally found that the more practical 30% H₂O₂ was quite effective.

Several points deserve comment. First, the presence of at least one heteroatom, such as a fluorine and alkoxy 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 penta-coordinate 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.²³⁾ Fourth, it was confirmed that the H₂O₂ oxidation also proceeds with retention of configuration at the carbon center.^{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.

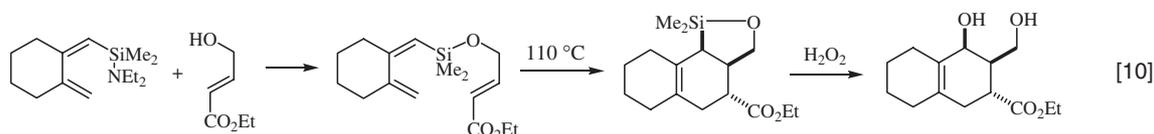
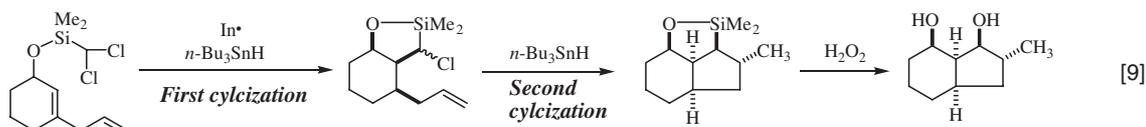
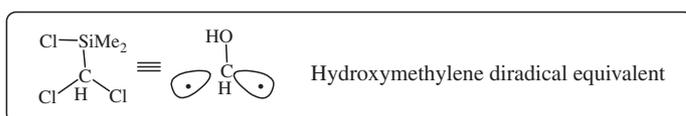
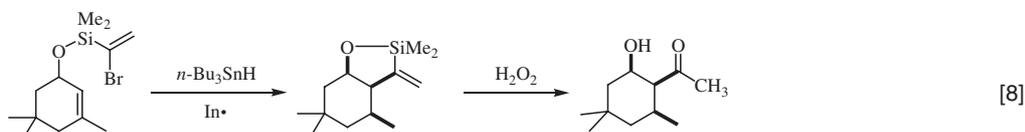
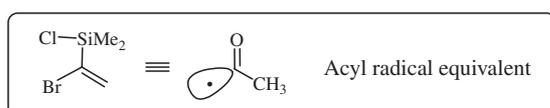
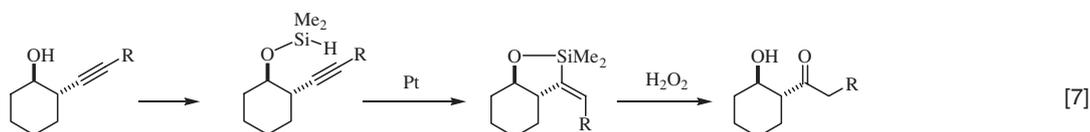
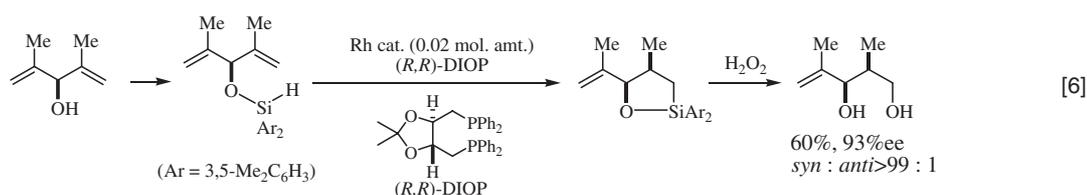
Synthetic application. With this new oxidation reaction in hand, we have developed a variety of new synthetic methodologies and new reagents, as summarized in Eqs. 1–16. Some characteristic features deserve more comment.

Intramolecular hydrosilylation. The intramolecular hydrosilylation of allyl alcohols and homoallyl alcohols followed by the H_2O_2 oxidation has provided a new methodology for the regio- and stereo-selective synthesis of 1,3-diol skeletons.²⁴⁾ In a typical example shown in Eq. 1,^{24b)-24d)} 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 H_2O_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),^{24b)} 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 amines, it proceeds in a 4-*exo* fashion to finally give a 1,2-aminoalcohol derivative with a high 1,2-*syn* stereoselectivity, as shown in Eq. 3.²⁵⁾

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.^{24b)}



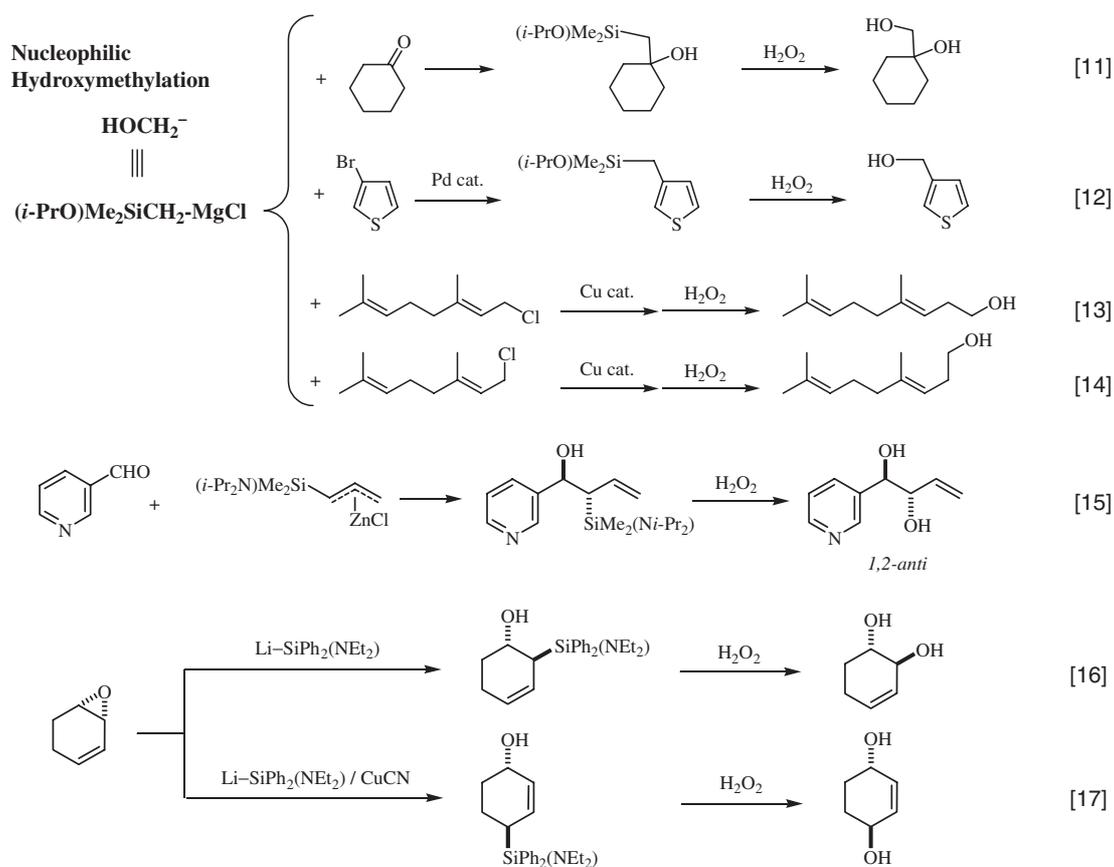
The catalytic asymmetric intramolecular hydrosilylation of an allylic alcohol is also possible to give an optically active 1,3-diol with a high stereoselectivity (Eq. 6).²⁶⁾ The intramolecular hydrosilylation of homopropargylic alcohols followed by the H₂O₂ oxidation provides a new regioselective functionalization of the acetylene group (Eq. 7).²⁷⁾

Silicon-tethered intramolecular radical cyclization and Diels-Alder reaction. The 1-bromovinylsilyl 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. 8²⁸⁾ and 9.²⁹⁾ 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 H₂O₂ oxidation, as an efficient method for the construction of poly-functionalized cyclohexane derivatives.³⁰⁾

Silicon-containing organometallic reagents for nucleophilic hydroxymethylation and hydroxyallylation and as a hydroxide ion equivalent. One of the interesting silicon reagents is the (isopropoxy)silylmethyl Grignard reagent (*i*-PrO)Me₂SiCH₂MgCl,³¹⁾ 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.^{31b)} The primary product contains a β -hydroxy-silicon moiety which might undergo β -elimination, known as the Peterson elimination,³²⁾ to form the corresponding olefin; however, under the H_2O_2 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 -enones has also been achieved.³³⁾

This reagent also undergoes a palladium catalyzed cross-coupling with aromatic halides, such as 3-bromothiophene, to give, after the H_2O_2 oxida-

tion, the hydroxymethylation products, as shown in Eq. 12.^{31a)} The copper-catalyzed cross-coupling reaction with allylic halides, followed by the H_2O_2 oxidation, affords the corresponding homoallylic alcohols, as shown by Eqs. 13 and 14. This approach significantly provides the most efficient, regio- and stereo-specific transformation of allylic halides to homoallylic alcohols without scrambling of the olefin geometry and the allylic position, as well as the one-carbon elongation of certain functionalized alcohols.³⁴⁾

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. 15.³⁵⁾

Aminosilyllithium reagents, the first stable functionalized silyllithiums which we found in 1992,³⁶⁾ act as a hydroxide ion synthon, as shown in Eqs. 16 and 17.³⁷⁾

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 article³⁾ 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.³⁸⁾ 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.

Acknowledgements

The research described in this review was performed at the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University. I would like to express my sincere thanks to all the former co-workers whose names appear in the references.

References

- 1) Kim, K.-C., Reed, C. A., Elliott, D. W., Mueller, L. J., Tham, F., Lin, L. and Lambert, J. B. (2002) Crystallographic Evidence for a Free Silylium Ion. *Science* **297**, 825–827.
- 2) Holmes, R. R. (1990) The Stereochemistry of Nucleophilic Substitution at Tetracoordinated Silicon. *Chem. Rev.* **90**, 17–31.
- 3) Chuit, C. C., Corriu, R. J. P., Reye, C. and Young, J. C. (1993) Reactivity of Penta- and Hexacoordinate Silicon Compounds and Their Role as Reactive Intermediates. *Chem. Rev.* **93**, 1371–1448.
- 4) Tamao, K., Hayashi, T., Ito, Y. and Shiro, M. (1992) Electronic and Steric Effects in Anionic Pentacoordinate Diorganotrifluorosilicates: X-ray Structures and ¹³C NMR Studies for Evaluation of Charge Distribution in Aryl Groups on Silicon. *Organometallics* **11**, 182–191.
- 5) Okazaki, R. and West, R. (1996) Chemistry of Stable Disilenes. *Adv. Organomet. Chem.* **39**, 231–274.
- 6) Colvin, E. (1981) *Silicon in Organic Synthesis*. Butterworths, London.
- 7) Tamao, K. (1985) Silafunctional Compounds in Organic Synthesis. *In Organosilicon and Bioorganosilicon Chemistry* (ed. Sakurai, H.). Ellis Horwood, Chichester, UK, pp. 231–242.
- 8) a) Hosomi, A. (1988) Characteristics in the Reactions of Allylsilanes and Their Applications to Versatile Synthetic Equivalents. *Acc. Chem. Res.* **21**, 200–206; b) Fleming, I., Dunogues, J. and Smithers, R. (1989) The Electrophilic Substitution of Allylsilanes and Vinylsilanes. *Org. React.* **37**, 57–575; c) Fleming, I., Barbero, A. and Walter, D. (1997) Stereochemical Control in Organic Synthesis Using Silicon-Containing Compounds. *Chem. Rev.* **97**, 2063–2192.
- 9) Tamao, K., Yoshida, J., Takahashi, M., Yamamoto, H., Kakui, T., Matsumoto, H., Kurita, A. and Kumada, M. (1978) A Novel General and Practical Method for Anti-Markownikoff Hydrohalogenation of Olefins via Organopentafluorosilicates Derived from Hydrosilylation Products. *J. Am. Chem. Soc.* **100**, 290–291.
- 10) a) Tamao, K., Yoshida, J., Murata, M. and Kumada, M. (1980) Stereochemistry at Carbon in Cleavage of the Carbon-Silicon Bond in *exo*- and *endo*-2-Norbornylpentafluorosilicates by Various Brominating Agents. *J. Am. Chem. Soc.* **102**, 3267–3269; b) Tamao, K., Yoshida, J., Yamamoto, H., Kakui, T., Matsumoto, H., Takahashi, M., Kurita, A., Murata, M. and Kumada, M. (1982) Preparation of Organopentafluorosilicates and Their Cleavage Reactions by Halogens and *N*-Bromosuccinimide. Synthetic and Mechanistic Aspects. *Organometallics* **1**, 355–368.
- 11) Tamao, K., Kakui, T. and Kumada, M. (1978) A Convenient Procedure for Preparing Primary Alcohols from Olefins. A Novel Facile Oxidative Cleavage of Carbon-Silicon Bonds by *m*-Chloroperoxybenzoic Acid. *J. Am. Chem. Soc.* **100**, 2268–2269.
- 12) Yoshida, J., Tamao, K., Kakui, T., Kurita, A., Murata, M., Yamada, K. and Kumada, M. (1982) Copper(II) Oxidation of Organopentafluorosilicates. *Organometallics* **1**, 369–380.
- 13) Tamao, K., Matsumoto, H., Kakui, T. and Kumada, M. (1979) A Stereoselective Synthesis of Symmetrical (*E,E*)-1,3-Dienes by Silver(I)-Promoted Homo Coupling of (*E*)-Alkenylpentafluorosilicates. *Tetrahedron Lett.* 1137–1140.
- 14) Yoshida, J., Tamao, K., Yamamoto, H., Kakui, T., Uchida, T. and Kumada, M. (1982) Organo-

- fluorosilicates in Organic Synthesis. Carbon-Carbon Bond Formation Promoted by Palladium Salts. *Organometallics* **1**, 542–549.
- 15) Kumada, M., Tamao, K. and Yoshida, J. (1982) Chemistry of Organopentafluorosilicates. *J. Organomet. Chem.* **239**, 115–132.
- 16) Tansjoe, L. (1961) On the Reactions of N-substituted Alkyltriaminosilanes. V. *Acta Chem. Scand.* **15**, 1583–1594.
- 17) Mueller, R. (1966) Über Organofluorosilicate und Ihre Verwendung zur Darstellung Metallorganischer Verbindungen. *Organometal. Chem. Rev.* **1**, 359–377.
- 18) Tamao, K., Yoshida, J., Murata, M. and Kumada, M. (1980) Stereochemistry at Carbon in Cleavage of the Carbon-Silicon Bond in *exo*- and *endo*-2-Norbornylpentafluorosilicates by Various Brominating Agents. *J. Am. Chem. Soc.* **102**, 3267–3268.
- 19) Tamao, K., Kakui, T., Akita, M., Iwahara, T., Kanatani, R., Yoshida, J. and Kumada, M. (1983) Oxidative Cleavage of the Silicon-Carbon Bonds in Organosilicon Fluorides to Alcohols. *Tetrahedron* **39**, 983–990.
- 20) Yoshida, J., Tamao, K., Kumada, M. and Kawamura, T. (1980) Alkylation of TCNE with Organopentafluorosilicates: Implication of One-Electron Transfer Mechanism. *J. Am. Chem. Soc.* **102**, 3269–3270.
- 21) a) Tamao, K., Ishida, N., Tanaka, T. and Kumada, M. (1983) Hydrogen Peroxide Oxidation of the Silicon-Carbon Bond in Organoalkoxysilanes. *Organometallics* **2**, 1694–1696; b) Tamao, K. and Ishida, N. (1984) Silyl Groups Synthetically Equivalent to the Hydroxy Group. *J. Organomet. Chem.* **269**, C37–C39; c) Tamao, K., Kumada, M. and Maeda, K. (1984) Hydrogen Peroxide Oxidation of Alkenyl(alkoxy)silanes. *Tetrahedron Lett.* **25**, 321–324.
- 22) a) Tamao, K. (1996) Oxidative Cleavage of the Silicon-Carbon Bond: Development, Mechanism, Scope and Limitations. *In Advances in Silicon Chemistry* (ed. Larson, G. L.). Vol. 3, Jai Press, 1–62; b) Jones, G. R. and Landais, Y. (1996) The Oxidation of the Carbon-Silicon Bond. *Tetrahedron* **52**, 7599–7662.
- 23) Tamao, K., Hayashi, T. and Ito, Y. (1991) Hydrogen Peroxide Oxidation of the Silicon-Carbon Bond: Mechanistic Studies. *In Frontiers of Organosilicon Chemistry* (eds. Bassindale, S. R. and Gasper, P. P.). The Royal Society of Chemistry, UK, pp. 197–207.
- 24) a) Tamao, K., Tanaka, T., Nakajima, T., Sumiya, R., Arai, H. and Ito, Y. (1986) Intramolecular Hydrosilation of Alkenyl Alcohols: A New Approach to the Regioselective Synthesis of 1,2- and 1,3-Diols. *Tetrahedron Lett.* **27**, 3377–3380; b) Tamao, K., Nakajima, T., Sumiya, R., Arai, H., Higuchi, N. and Ito, Y. (1986) Stereocontrol in Intramolecular Hydrosilation of Allyl and Homoallyl Alcohols: A New Approach to the Stereoselective Synthesis of 1,3-Diol Skeletons. *J. Am. Chem. Soc.* **108**, 6090–6091; c) Tamao, K., Nakagawa, Y., Arai, H., Higuchi, N. and Ito, Y. (1988) Intramolecular Hydrosilation of α -Hydroxy Enol Ethers: A New Highly Stereoselective Route to Polyhydroxylated Molecules. *J. Am. Chem. Soc.* **110**, 3712–3713; d) Tamao, K., Nakagawa, Y. and Ito, Y. (1995) Regio- and Stereoselective Intramolecular Hydrosilation of α -Hydroxy Enol Ethers: 2,3-*syn*-2-Methoxymethoxy-1,3-nonanediol. *Org. Synth.* **73**, 94–109.
- 25) Tamao, K., Nakagawa, Y. and Ito, Y. (1990) Platinum-Catalyzed Intramolecular Hydrosilation of Allylamines: Formation of 1-Aza-2-silacyclobutanes and Application to Stereoselective Synthesis of 2-Amino Alcohols. *J. Org. Chem.* **55**, 3438.
- 26) Tamao, K., Tohma, T., Inui, N., Nakayama, O. and Ito, Y. (1990) Catalytic Asymmetric Intramolecular Hydrosilation. *Tetrahedron Lett.* **31**, 7333–7336.
- 27) Tamao, K., Maeda, K., Tanaka, T. and Ito, Y. (1988) Intramolecular Hydrosilation of Acetylenes: Regioselective Functionalization of Homopropargyl Alcohols. *Tetrahedron Lett.* **29**, 6955–6958.
- 28) Tamao, K., Maeda, K., Yamaguchi, T. and Ito, Y. (1989) 1-Silylvinyl Radical Cyclization: Silicon-Mediated Regio- and Stereo-Selective Hydroacylation and Hydrovinylation of Allyl Alcohols. *J. Am. Chem. Soc.* **111**, 4984–4985.
- 29) Tamao, K., Nagata, K., Ito, Y., Maeda, K. and Shiro, M. (1994) (Dichloromethyl)dimethylsilyl Group as a Hydroxymethylidene Diradical Equivalent: Radical Annulation of Dienols and Its Application to the Stereoselective Synthesis of *cis*- and *trans*-Hydrindan Ring Systems. *Synlett*, 257–259.
- 30) Tamao, K., Kobayashi, K. and Ito, Y. (1989) Nickel(0)-Catalyzed Cyclization of 1,7-Diynes via Hydrosilation: One-Step Synthesis of 1,2-Dialkylidene-cyclohexanes with a *Z*-Vinylsilane Moiety. *J. Am. Chem. Soc.* **111**, 6478–6479.
- 31) a) Tamao, K., Ishida, N. and Kumada, M. (1983) (Diisopropoxymethylsilyl)methyl Grignard Reagents: A New, Practically Useful Nucleophilic Hydroxymethylating Agent. *J. Org. Chem.* **48**, 2120; b) Tamao, K. and Ishida, N. (1984) (Isopropoxydimethylsilyl)methyl Grignard Reagent: A New Nucleophilic Hydroxymethylating Agent for Aldehydes and Ketones. *Tetrahedron Lett.* **25**, 4245–4248; c) Tamao, K., Ishida, N., Ito, Y. and Kumada, M. (1990) Nucleophilic Hydroxymethylation of Carbonyl Compounds: 1-(Hydroxymethyl)cyclohexanol. *Org. Synth.* **69**, 96–105.
- 32) Ager, D. J. (1990) The Peterson Olefination Reaction. *Org. React.* **38**, 1–223.
- 33) Tamao, K. and Ishida, N. (1984) Conjugate Addition of a Hydroxymethyl Anion Synthone to α,β -Enones. *Tetrahedron Lett.* **25**, 4249–4252.
- 34) Tius, M. A. and Fauq, A. (1986) Total Synthesis of (–)-asperdiol. *J. Am. Chem. Soc.* **108**, 6389–

- 6391.
- 35) Tamao, K., Nakajo, E. and Ito, Y. (1987) Metalated (Allyl)aminosilanes: A New, Practical Reagent for the Stereoselective α -Hydroxyallylation of Aldehydes to *erythro*-1,2-Diol Skeletons. *J. Org. Chem.* **52**, 957–968.
- 36) a) Tamao, K., Kawachi, A. and Ito, Y. (1992) The First Stable Functional Silyl Anions: (Aminosilyl)lithiums. *J. Am. Chem. Soc.* **114**, 3989–3990; b) Kawachi, A. and Tamao, K. (1997) Preparations and Reactions of the Functionalized Silylithiums. *Bull. Chem. Soc. Jpn.* **70**, 945–955.
- 37) Tamao, K., Kawachi, A., Tanaka, Y., Ohtani, H. and Ito, Y. (1996) Synthetic Applications of Functionalized Silyl Anions: Aminosilyl Anions as Hydroxy Anion Equivalent. *Tetrahedron* **52**, 5765–5772.
- 38) a) Fleming, I., Henning, R., Parker, D. C., Plaut, H. E. and Sanderson, P. E. (1995) The Phenyl-dimethylsilyl Group as a Masked Hydroxy Group. *J. Chem. Soc., Perkin Trans. 1*, 317–337; b) Fleming, I. (1996) Silyl-to-Hydroxy Conversion in Organic Synthesis. *Chemtracts, Org. Chem.* **9**, 1–64.

(Received Jan. 25, 2008; accepted Feb. 25, 2008)

Profile

Kohei Tamao received his B. Eng., M. Eng., and Ph.D. of Eng. from Kyoto University under the direction of Professor Makoto Kumada in 1961, 1967, and 1971, respectively. He became an Assistant Professor at Kyoto University in 1970 and was promoted to Associate Professor in 1987, and then to Professor in 1993 at Institute for Chemical Research, Kyoto University. He served as Director of the Institute for two years from 2000. In 2005, he was awarded the title of Professor Emeritus at Kyoto University. He is the present Director of the RIKEN Advanced Science Institute. He received the Chemical Society of Japan Award in 1999, The American Chemical Society, Frederic Stanley Kipping Award in 2002, The Toray Science & Technology Prize in 2002, The Asahi Prize in 2003, Medal of Honor with Purple Ribbon in 2000, and The Japan Academy Prize in 2007. He served as a research leader of the Kyoto University COE (Center of Excellence) "Elements Science" supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (2000–2004). His current research interests are organosilicon chemistry and related elemento-organic chemistry, σ - and π -conjugated electronic materials, reactive intermediates, and transition metal catalysis.

