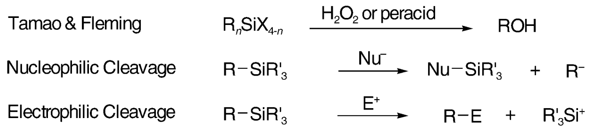
Synthesis of Silalactones

Electrophilic Cleavage of One Silicon–Carbon Bond of Pentacoordinate Tetraorganosilanes: Synthesis of Silalactones**

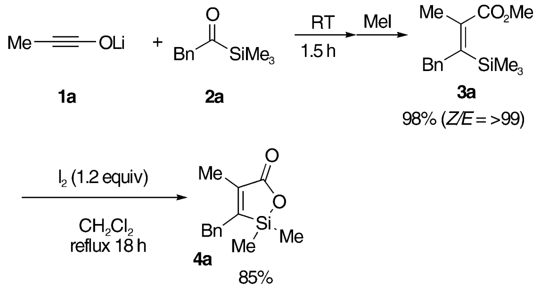
Mitsuru Shindo, Kenji Matsumoto, and Kozo Shishido*

The cleavage of silicon–carbon bonds is an important process in synthetic organic chemistry.[1] The Tamao–Fleming oxidation[2] is one general method for peroxide oxidation of organosilicon bearing at least one heteroatom or aromatic group, sometimes with the aid of a fluoride ion. In addition to the several published reports on intramolecular nucleophilic attack of an oxyanion on silicone leading to demethylation[3] or dephenylation,[4] there have also been some examples of electrophilic cleavage under strongly acidic conditions or by using fluorosilicates.[5] However, the selective cleavage of one carbon–silicon bond, especially the C(sp^3)–Si bond, in a tetraorganosilane is a challenging problem that has yet to be solved. Herein, we describe the direct electrophilic cleavage of one silicon–carbon bond activated by intramolecular pentacoordination of carbonyl oxygen, thus leading to the novel synthesis of silalactones (Scheme 1).



Scheme 1. Cleavage of Si–C bonds.

In the course of our studies on ynolates (**1**),[6] we found that a highly stereoselective olefination of acylsilanes (**2**) afforded (*Z*)-β-trialkylsilylacrylates (**3**).[7] When the desilyl-iodination of the acrylic acid ester **3a** upon treatment with iodine was attempted, the desired β-iodoacrylate was not produced at all, but the unexpected 2*H*-[1,2]oxasilol-5-one (silalactone **4a**) was obtained in good yield (Scheme 2).



Scheme 2. The unexpected formation of silalactone **4a** by the cleavage of a Si–C bond.

Silalactone **4a** was also obtained by using (*Z*)-β-trialkylsilylacrylic acid **5** as the substrate in the presence of iodine and pyridine under reflux in CCl_4 (Table 1). The fact that one equivalent of iodomethane was generated indicated that the silicon–carbon bond was cleaved electrophilically by iodine. This is one of only a few examples of direct electrophilic C(sp^3)–Si bond cleavage. These results prompted us to examine the generality of this oxidation reaction by using various types of (*Z*)-β-silyl-α,β-unsaturated acids.

As shown in Table 1, the silalactones were obtained in good to excellent yields using the acrylic acids bearing several types of substituents, including *o*-silylbenzoic acids. When *N*-iodosuccinimide (NIS) was used in place of iodine, the reaction proceeded faster at room temperature (entry 2, Method B), but in some cases, lower yields were obtained (entry 8). The ethyl, isopropyl, and phenyl groups, as well as the methyl group, were also cleaved (entries 4, 5 and 6). Since the substrate that have a terminal alkenyl group also furnished the silalactone **4h** (entry 10), the cleavage of the Me–Si bond proceeds faster than the iodination of the olefins. The methoxy and siloxy substituents were stable under these reaction conditions (entries 9 and 11). In the reaction of the substrate bearing the *tert*-butyldimethylsilyl group, the methyl group was selectively cleaved (entries 3 and 9). It is noteworthy that the methyl group rather than the phenyl group was selectively cleaved (entry 13).

The X-ray crystal structures[8] of (*Z*)-β-trimethylsilyl-α-methylcinnamic acid (**5 f**) may explain why the carbon–silicon bonds are unusually activated (Figure 1). The distance between the silicon atom and the carbonyl oxygen (Si–O2) is 2.826 Å, which is shorter than the sum of the van der Waals radii (3.35 Å) for the silicon and oxygen atoms, and the bond length of C9–Si is longer than that of the C13–Si or C14–Si bonds. The angles of C9-Si-C5, C9-Si-C13, and C9-Si-C14 are all slightly smaller (105.2–105.8) than those of a tetrahedral structure. From these values, it would seem that in the crystal structure, a weak intramolecular coordination of the neutral carbonyl oxygen to the tetraorganosilane, probably due to the rigid geometry, gives rise to the hypervalent silicon structure,[9] in which O2 and C9 are at apical positions. In the $CDCl_3$ solution structure, however, the ^{29}Si NMR spectra did not show a significant upfield shift,[10] which would generally be seen in a pentacoordinate silane,[11] relative to that observed in the corresponding tetrahedral analogues. Since even at −90 °C in CD_2Cl_2 only one singlet was observed in the ^{1}H NMR spectrum for the Me_3Si group, the C5–Si bond rotates freely. As a result, these compounds are not a perfect trigonal-bipyramidal pentacoordinated structure,[12] corre-

---

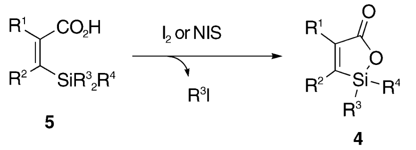
[*] Prof. Dr. M. Shindo, K. Matsumoto, Prof. Dr. K. Shishido
Institute for Medicinal Resources
University of Tokushima
Sho-machi 1, Tokushima 770-8505 (Japan)
Fax: (+81) 88-633-7294
E-mail: shindo@ph2.tokushima-u.ac.jp

[**] This work was supported in part by a Grant-in-Aid for Scientific Research in the Priority Area (A) "Exploitation of Multi-Element Cyclic Molecules" from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and PRESTO, JST. K.M. thanks the Japan Society for the Promotion of Science (JSPS) for a research fellowship.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200352705

Table 1: Cleavage of Si–C bonds of (*Z*)-β-silylacrylic acids **5** to provide silalactones **4**.



Entry	R^1	R^2	R^3	R^4	Method[a]	*t* [h]	4	Yield [%]
1	Me	Bn	Me	Me	A	29	**4a**	90[b]
2	Me	Bn	Me	Me	B	1	**4a**	96
3	Me	Bn	Me	*t*Bu	A	18	**4b**	81
4	Me	Bn	Et	Et	A	28	**4c**	94
5	Me	Bn	*i*Pr	*i*Pr	A	35	**4d**	74
6	Me	Bn	Ph	Ph	A	34	**4e**	87
7	Me	Ph	Me	Me	A	20	**4f**	95
8	Me	Ph	Me	Me	B	1.5	**4f**	65
9	Me	$MeOC_2H_4$	Me	*t*Bu	A	19	**4g**	85
10	Me	4-pentenyl	Me	Me	A	28	**4h**	65
11	PhCH(OTBS)	H	Me	Me	A	50	**4i**	64
12	*o*-silylbenzoic acid		Me	Me	A	28	**4j**	81
13	*o*-silylbenzoic acid		Me	Ph	A	23	**4k**	90

[a] Method A: I_2, pyridine in CCl_4 under reflux. Method B: NIS in CH_2Cl_2 at RT. Usually 0.1–0.5 mmol scale. [b] 82% yield for 10 mmol scale.

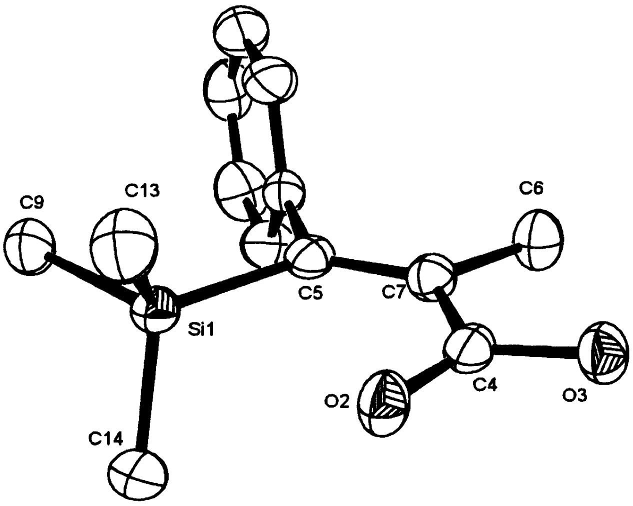


Figure 1. ORTEP drawing of the X-ray crystal structure of **5f** (thermal ellipsoids set at the 50% probability level) selected distances [Å] and angles [°]: Si1-O2, 2.826(1); Si1-C9, 1.875(2); Si1-C13, 1.862(2), Si1-C14, 1.865(2); Si1-C5, 1.922(2); C5-Si1-C9, 105.26(9); C9-Si1-C13, 105.8(1); C9-Si1-C14, 105.5(1).

sponding to an intermediate at the early stage of the S_N2 reaction at the silicon.

From this spectral information, the reaction mechanism can be elucidated based on the cooperative push–pull mechanism, which involves the double activation of the C9–Si bond mainly by the electrophilic iodine (pull) and secondarily by the nucleophilic oxygen (push). Since the methyl group was preferentially cleaved rather than the phenyl group, the electrophile would directly attack the $C(sp^3)$–Si σ bond bearing the higher HOMO energy rather than the $C(sp^2)$–Si σ bond, in contrast to *ipso* substitution.[13] And, the steric hindrance of the *t*Bu group would prevent its cleavage. Because the electron deficient alkene bears the ester group, the electrophilic iodine attacks only the R group, not the alkene (Figure 2).

The reactivity and synthetic utility of the silalactones are not well known.[14] Reduction by $LiAlH_4$ gave the cyclic silyl ether **6** in good yield. Grignard reagents attack the silicon selectively to afford the (*Z*)-β-silylacrylic acids (Scheme 3). Palladium catalyzed cross-coupling reactions (Hiyama coupling)[15] of the silalactone with aryl iodides furnishes the (*Z*)-β-arylacrylic acid in good yield without the use of a fluoride source. These transformations indicate the synthetic utility of the silalactones.

In conclusion, we have found a new methodology for the direct electrophilic cleavage of C–Si bonds activated by the formation of pentacoordinate organosilanes. This can be considered as an activation method for stable C–Si bonds. The silalactones would be useful for the preparation of multisubstituted alkenes and silicon-containing compounds.

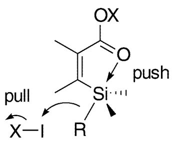
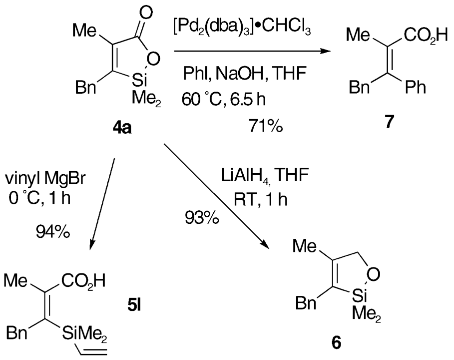


Figure 2. The push–pull mechanism.



Scheme 3. Transformations of silalactone **4a**.

Received: August 22, 2003 [Z52705]

Keywords: cleavage reaction · hypervalent compounds · iodine · silalactones · silanes

---

[1] For a review, see: G. R. Jones, Y. Landais, *Tetrahedron* **1996**, *52*, 7599-7662.

[2] a) K. Tamao, N. Ishida, M. Kumada, *J. Org. Chem.* **1983**, *48*, 2120–2122; b) I. Fleming, R. Henning, H. Plaut, *J. Chem. Soc.*

Chem. Commun. **1984**, 29; c) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, **2000**.

[3] For examples, see: a) W. Kirmse, F. Söllenböhmer *J. Chem. Soc. Chem. Commun.* **1989**, 774–775; b) C. Eaborn, P. B. Hitchcock, *J. Chem. Soc. Perkin Trans. 2* **1991**, 1137–1141; c) P. F. Hudrlik, Y. M. Abdallah, A. M. Hudrlik, *Tetrahedron Lett.* **1992**, *33*, 6743–6746; d) H. Taguchi, K. Ghoroku, M. Tadaki, A. Tsubouchi, T. Takeda, *Org. Lett.* **2001**, *3*, 3811–3814; e) S. K. Tipparaju, S. K. Mandal, S. Sur, V. S. Puranik, A. Sarkar, *Chem. Commun.* **2002**, 1924–1925. For the report by Hudrlik et al on debenzylation and deallylation, albeit in moderate yields, see: f) P. F. Hudrlik, Y. M. Abdallah, A. M. Hudrlik, *Tetrahedron Lett.* **1992**, *33*, 6747–6750.

[4] M. Murakami, M. Suginome, K. Fujimoto, H. Nakamura, P. G. Andersson, Y. Ito, *J. Am. Chem. Soc.* **1993**, *115*, 6487–6498.

[5] For examples of the acidic or electrophilic C–Si bond cleavage, see: a) C. Eaborn, *J. Chem. Soc.* **1949**, 2755–2764; b) M. Ishikawa, M. Kumada, H. Sakurai, *J. Organomet. Chem.* **1970**, *23*, 63–69; c) K. Tamao, J. Yoshida, H. Yamamoto, T. Kakui, H. Matsumoto, M. Takahashi, A. Kurita, M. Murata, M. Kumada, *Organometallics* **1982**, *1*, 355–368; d) M. Demuth, G. Mikhail, *Synthesis* **1982**, 827; e) M. Bordeau, S. M. Djamei, J. Dunogues, R. Calas, *Bull. Soc. Chim. Fr.* **1982**, II159–160; f) K. Tamao, T. Hayashi, Y. Ito, *Bull. Soc. Chim. Fr.* **1995**, *132*, 556–558; g) M. Mutahi, T. Nittoli, L. Guo, S. McN. Sieburth, *J. Am. Chem. Soc.* **2002**, *124*, 7363–7375. See also: h) Y. Yamamoto, Y. Takeda, K. Akiba, *Tetrahedron Lett.* **1989**, *30*, 725–728; i) K. Itami, K. Terakawa, J. Yoshida, O. Kajimoto, *J. Am. Chem. Soc.* **2003**, *125*, 6058–6059.

[6] For reviews, see: a) M. Shindo, *Chem. Soc. Rev.* **1998**, *27*, 367–374; b) M. Shindo, *J. Synth. Org. Chem. Jpn.* **2000**, *58*, 1155–1166; c) M. Shindo, *Yakugaku Zasshi* **2000**, *120*, 1233–1246.

[7] M. Shindo, K. Matsumoto, S. Mori, K. Shishido, *J. Am. Chem. Soc.* **2002**, *124*, 6840–6841.

[8] CCDC-218067 (**5 f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[9] For pentacoordinate tetraorganosilanes, see: a) K. Jurkschat, C. Mugge, J. Schmidt, A. Tzschach, *J. Organomet. Chem.* **1985**, *287*, C1-C4; b) M. Weinmann, A. Gehrig, B. Schiemenz, G. Huttner, B. Nuber, G. Rheinwald, H. Lang, *J. Organomet. Chem.* **1998**, *563*, 61–72. For selected reviews on extracoordinate silanes, see: c) C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371–1448; d) R. R. Holms, *Chem. Rev.* **1996**, *96*, 927–950.

[10] The chemical shift of compounds **5** in the ^{29}Si NMR is $+4 \sim -8$ ppm, like that of vinyltrimethylsilanes.

[11] A. I. Albanov, L. I. Gubanova, M. F. Larin, V. A. Pestunovich, M. G. Voronkov, *J. Organomet. Chem.* **1983**, *244*, 5–16.

[12] The pentacoordination character TBPa is 20% and TBPe 37% according to the Tamao equation: K. Tamao, T. Hayashi, Y. Ito, *Organometallics* **1992**, *11*, 2099–2114.

[13] The electrophilic selective cleavage of the Ph–Si bond would be an *ipso* substitution mechanism involving a cation intermediate.[2b,5f,g] The Tl^{II}-mediated direct cleavage of the Me–Si bond in preference to the Ph–Si bond was reported, see: F. Kakiuchi, K. Furuta, S. Murai, Y. Kawasaki, *Organometallics* **1993**, *12*, 15–16.

[14] For preparation of unsaturated silalactones, see: U. Wannagat, R. Schrader, *J. Organomet. Chem.* **1988**, *341*, 95–108.

[15] For a review, see: Y. Hatanaka, T. Hiyama, *Synlett* **1991**, 845–853.