Bull. Chem. Soc. Jpn., **70**, 945—955 (1997)

Accounts

Preparations and Reactions of Functionalized Silyllithiums

Atsushi Kawachi and Kohei Tamao*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

(Received December 16, 1996)

Several types of α-alkoxy and α-amino substituted silyllithiums have been prepared as the first members of stable and/or well-characterizable functionalized silyllithiums. Described herein are new aspects of (1) three methodologies for preparation of functionalized silyllithiums, (2) high stability of (aminosilyl)lithiums, (3) low stability of (monoalkoxysilyl)lithiums, behaving as silylenoid species, (4) high stability of (dialkoxysilyl)lithiums, (5) high stability of (2-alkoxydisilanyl)lithium, (6) first examples of [2,3]-sila-Wittig rearrangement, and (7) synthetic utilization of (aminosilyl)lithiums.

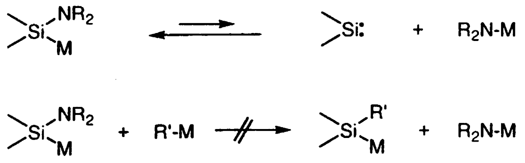
Carbanion chemistry plays a central role in the whole field of organic chemistry:[1] Much attention has been paid to functionalized carbanions, including α-heteroatom substituted carbanions **A** (Scheme 1). Extensive studies have revealed that the heteroatom on anionic carbon largely influences the nature of the carbanion. For example, α-phosphorus, α-sulfur, and α-selenium-substituted organolithiums are relatively stable, since the heteroatom effectively stabilizes the negative charge.[2] α-Amino substituted organolithiums have little stabilization effect from amino groups.[2] In contrast, α-oxygen and α-halogen substituted organolithiums are reactive, since the heteroatom works as a leaving group;[3] thus, they behave as carbenoids, which have both nucleophilicity and electrophilicity.

Silyl anions have been much less extensively studied than carbanions.[4] Synthetically useful silyl anions have long been limited only to several simple triorganosilyl anions such as Ph_3SiLi,[5] $Ph_2MeSiLi$,[5] $PhMe_2SiLi$,[5] and Me_3SiM (M = Li, Na, K).[6] Concerning functionalized silyl anions, $Cl_3Si^-HNR_3^+$,[7] $(RO)_nMe_{3-n}SiNa$,[8] HPh_2SiLi,[9] $H(Mes)_2SiLi$,[10] and $(MesCO)(Me_3Si)_2SiLi$[11] have been reported, where Mes stands for mesityl. The first two are the α-heteroatom-substituted species, which are highly reactive and generated in situ in the presence of tapping agents. HPh_2SiLi is obtained in about 10% yield and tends to polymerize readily. $H(Mes)_2SiLi$ and $(MesCO)(Me_3Si)_2SiLi$ are the only species which are well characterized. Under the circumstances we started to search for stable and tractable functionalized silyl anions of type **B** (Scheme 1). We anticipated that they would be practical building blocks in organosilicon chemistry and versatile reagents in synthetic organic chemistry.

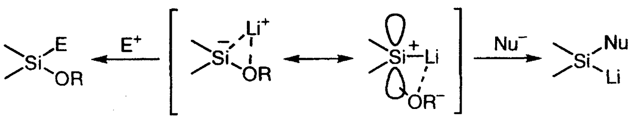
First, amino groups (X = NR_2) were chosen as functional groups on silicon because of their high stability towards organometallic reagents. We expected that aminosilyl anions should be stable with respect to both intramolecular α-elimination and intermolecular substitution (Scheme 2). We paid attention to some theoretical studies[12] which predicted the comparable stability between two model systems: MeH_2Si^- and $(H_2N)H_2Si^-$, and their much higher stability than the corresponding carbanions MeH_2C^- and $(H_2N)H_2C^-$.

Next, alkoxy groups (X = OR) were chosen as functional groups on silicon. We expected that (alkoxysilyl)lithiums could be "silylenoids", analogous to carbenoids,[3] since alkoxy group works as a leaving group (Scheme 3). Our special attention was focused on the electrophilic nature of the (alkoxysilyl)lithiums as the most diagnostic clue to the silylenoid character. Silylenoids have been postulated as reaction intermediates in reduction of dihalosilanes with alkali metals which affords polysilanes.[13] Thus, study on silylenoids may shed a new light on the mechanism of chain

Scheme 1.



Scheme 2.



Scheme 3.

elongation of polysilanes.

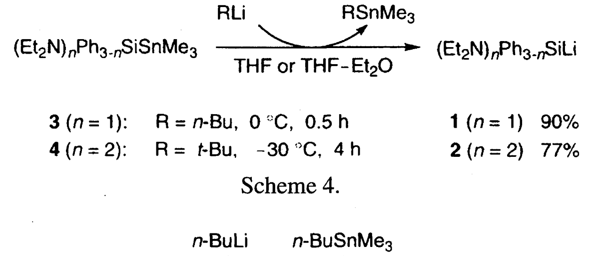
Moreover, some classes of α-oxygen and α-nitrogen-substituted organolithiums have been known to undergo Wittig rearrangement.[14] To investigate the scope and limitation of the functionalized silyl anion chemistry, we have developed its silicon analogs, that is, sila-Wittig rearrangements.

1. Preparation of Functionalized Silyllithiums

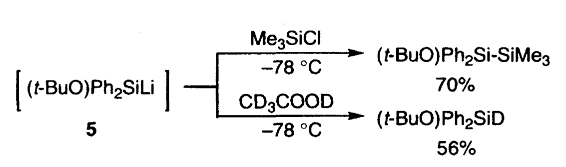
One of the most important problems in investigating the functionalized silyl anions is how to generate the silyl anions efficiently without significant side-reactions. Three methodologies have been examined to prepare the amino- and alkoxy-silyllithiums.

1-1. Tin-Lithium Exchange Reaction. To prepare (aminosilyl)lithiums **1** and **2**, we first examined tin-lithium exchange reactions[15] of the corresponding (aminosilyl)stannanes with butyllithiums as the most promising route, as shown in Scheme 4.[16] (Aminosilyl)stannane **3** was treated with n-BuLi in THF at 0 °C for 30 min to give a greenish solution. The reaction was quenched with Me_3SiCl to afford the corresponding aminodisilane in 90% yield, indicative of the formation of (aminosilyl)lithium **1** in solution. Similarly, (diaminosilyl)lithium **2** was obtained from reaction of **4** with t-BuLi in 77% yield.

An (alkoxysilyl)lithium was also prepared by a similar method. (t-Butoxysilyl)stannane was treated with 2 mol amt. of n-BuLi in THF at −78 °C for 3 h to give (t-butoxysilyl)lithium **5**, which was trapped with Me_3SiCl and acetic acid-d_4 to give the corresponding disilane in 70% yield and the deuterated silane in 56% yield, respectively (Scheme 5).[17] (Alkoxysilyl)lithium **5** was stable at −78 °C for at least 6 h, but it decomposed at 0 °C within 2 h (see Section 3). [(Allyloxy)silyl]lithiums and [(allylamino)silyl]lithiums were also prepared by a similar tin-lithium exchange reaction. The details are described in Section 4.



Scheme 4.



Scheme 5.

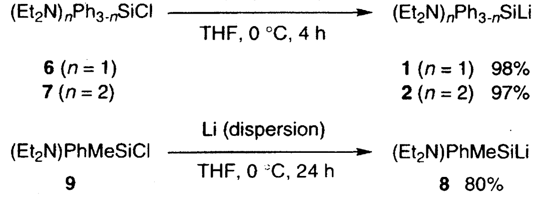
This method was not applicable to silylstannanes which have small substituents such as methyl group and methoxy group on silicon, because such silylstannanes underwent butylation on the silicon to give a stannyllithium instead of silyllithium. The successful results in some cases mentioned above, however, prompted us to examine simpler standard methods. We have found the following two procedures.

1-2. Reductive Lithiation of Chlorosilanes. As shown in Scheme 6, aminochlorosilanes **6** and **7** were treated with lithium metal in THF at 0 °C for 4 h to give (aminosilyl)lithium **1** and (diaminosilyl)lithium **2** as deep blue-green solutions in quantitative yields.[16] Methylphenyl derivative **8** could also be prepared from **9**, though it could not be obtained by the tin-lithium exchange reaction. Moreover, [(allylamino)silyl]lithiums were also prepared by a similar method (see Section 4).

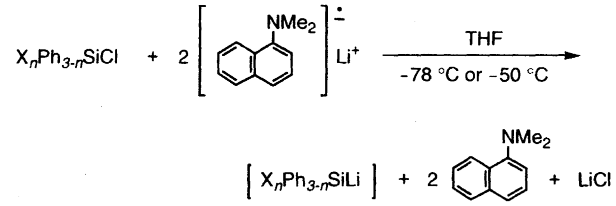
These reactions, however, proceed at or above 0 °C, at which temperatures (alkoxysilyl)lithiums such as **5** might decompose. Actually, the reaction of (t-BuO)Ph_2SiCl with lithium in THF at 0 °C gave no detectable amounts of **5** (see Section 3). We thus sought a low-temperature method for preparation of such reactive functionalized silyllithiums and found the following method.

1-3. Low Temperature Reduction of Chlorophenylsilanes with Lithium 1-(Dimethylamino)naphthalenide. We investigated reduction of functionalized chlorophenylsilanes with lithium salts of arene radical anions since the reduction was expected to occur at low temperatures.[18] Three reductants, lithium naphthalenide (LiNp), lithium 4,4′-di-t-butylbiphenylide (LDBB), and lithium 1-(dimethylamino)naphthalenide (LDMAN), have been examined.[1b,19,20] In model reactions, (t-BuO)Ph_2SiCl was reduced with LiNp in THF at −78 °C to give silyllithium **5** and homo coupling disilane [(t-BuO)Ph_2Si–]$_2$ in the ratio of 80 : 20. Stronger reductants LDBB and LDMAN suppressed the homo coupling reaction almost completely (> 98 : 2). LDMAN was chosen as reagent for our purpose in light of the high reactivity, the ready separability of the resulting aminonaphthalene, and economical reasons.

Scheme 7 summarizes representative results. In general procedures, a functionalized chlorosilane $X_nPh_{3-n}SiCl$ was added to a solution of excess LDMAN (4.5 mol amt.) in THF at −78 °C—−50 °C. This method has afforded the first successful access to less-bulky (alkoxysilyl)lithiums such as methoxy derivative (MeO)Ph_2SiLi (**10**) and to (dialkoxysilyl)lithium (t-BuO)$_2PhSiLi$ (**11**), as well as (aminosilyl)lithium **1** and (diphenylsilyl)lithium HPh_2SiLi, the yield of



Scheme 6.



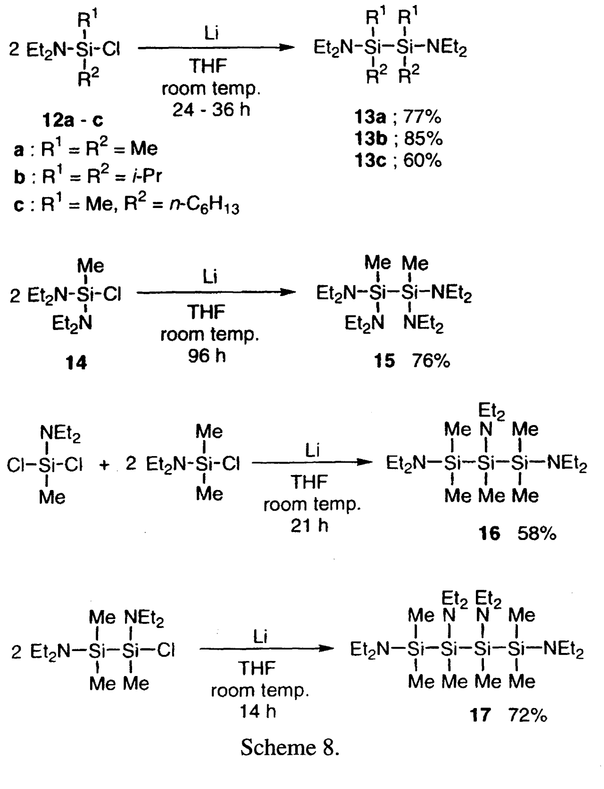
$(t\text{-}BuO)Ph_2SiLi$	(**5**)	93%
$(i\text{-}PrO)Ph_2SiLi$		81%
$(MeO)Ph_2SiLi$	(**10**)	46%
$(t\text{-}BuO)_2PhSiLi$	(**11**)	77%
$(Et_2N)Ph_2SiLi$	(**1**)	82%
HPh_2SiLi		40%

Yields are estimated after trapping with Me_3SiCl.

Scheme 7.

the last being higher than that obtained by reduction with lithium metal (11%).[5)]

1-4. Attempted Preparation of (Alkyl)aminosilyl Anions: Formation of Functionalized Alkyldisilanes. All of the silyllithiums prepared above possess at least one phenyl group on silicon. We attempted to prepare [alkyl(amino)silyl]lithiums from alkyl(amino)chlorosilanes by reductive lithiation with lithium metal and with LDMAN, but we found both methods unsuccessful. Instead, the action of lithium on alkyl(amino)chlorosilanes resulted in the formation of the coupling products, symmetrical polyfunctionalized disilanes,[21)] as shown in Scheme 8. The coupling reaction of dialkyl(amino)chlorosilanes **12** with lithium in THF proceeded at room temperature in 24—36 h to afford tetraalkyl(diamino)disilanes **13**: Alkyl groups on silicon are not only methyl (**a**) but also sterically crowded isopropyl (**b**) and long alkyl chain, hexyl group (**c**). (Diamino)chlorosilane **14** was considerably less reactive than **12** and required a longer period to give (tetraamino)dimethydisilane **15** in moderate yield. In a similar manner, trisilane **16** and tetrasilane **17** can be prepared.[22)] In contrast to this, reaction of the chloro(methyl)silane derivatives XMe_2SiCl (X=Me, *t*-BuO, and Et_2N) with LDMAN afforded neither the corresponding silyllithiums nor the homo coupling disilanes.[18)]



Scheme 8.

1-5. ^{29}Si Chemical Shifts of the (Aminosilyl)lithiums and (Alkoxysilyl)lithiums. The generation of these functionalized silyllithiums in solutions was confirmed by ^{29}Si NMR spectra. The chemical shifts are listed in Table 1. It is noteworthy that the spectra of the (aminosilyl)lithiums[23)] and (alkoxysilyl)lithiums[17,24)] exhibit downfield shifts compared to the corresponding chlorosilanes. For example, the chemical shift of $(Et_2N)Ph_2SiLi$ (**1**) was observed at $\delta=19.3$, which is a large downfield shift compared to that of $(Et_2N)Ph_2SiCl$ ($\delta=-6.8$)($\Delta\delta=+26.1$). This is in sharp contrast to the upfield shift of (triorganosilyl)lithiums compared to the corresponding chlorosilanes; for example, the chemical shift $\delta=-20.5$ for $Ph_2MeSiLi$ and $\delta=+10.0$ for $Ph_2MeSiCl$ ($\Delta\delta=-30.5$).[25)] The data suggest that the amino and alkoxy groups exert significant effect on the electronic structures of the functionalized silyllithiums; the origin of the effect, however, remains to be clarified by further studies.

2. Reactions of (Aminosilyl)lithiums

(Aminosilyl)lithium **1** in THF is stable at 0 °C for 6 d, and **2** and **9** are stable for 3 d without a drop in activity.[16)] Thus, these (aminosilyl)lithiums can be used as silylating agents in a variety of reactions.

2-1. As Reagents for Si–Si, Si–Ge, and Si–Sn Bond Formation. The versatility of the (aminosilyl)lithiums in organosilicon chemistry is apparent from some representa-

Table 1. ^{29}Si Chemical Shifts of the (Aminosilyl)lithiums and (Alkoxysilyl)lithiums[a)] and the Corresponding Chlorosilanes

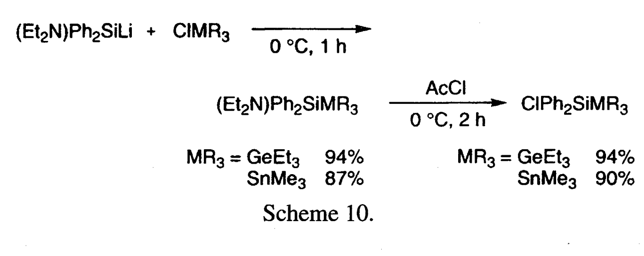
Compound		δ(ppm)	$\Delta\delta$(SiLi–SiCl)[b)]
$(Et_2N)Ph_2SiLi$	(**1**)	19.3	+26.1
$(Et_2N)_2PhSiLi$	(**2**)	27.9	+46.7
$(Et_2N)PhMeSiLi$	(**9**)	14.4	+12.1
$(t\text{-}BuO)Ph_2SiLi$	(**5**)	11.3[c)]	+34.6
$(t\text{-}BuO)_2PhSiLi$	(**11**)	41.8	+98.3
$(Et_2N)Ph_2SiCl$		−6.8	
$(Et_2N)_2PhSiCl$		−18.8	
$(Et_2N)PhMeSiCl$		2.3	
$(t\text{-}BuO)Ph_2SiCl$		−23.3	
$(t\text{-}BuO)_2PhSiCl$		−56.5	
$Ph_2MeSiLi$[d)]		−20.5	−30.5
$Ph_2MeSiCl$[d)]		10.0	

a) A 1.0 M THF solution with external Me_4Si as reference (0.0 ppm) at 273 K (1 M = 1 mol dm^{-3}). b) Positive signs denote downfield shifts. c) At 193 K. d) Ref. 25.

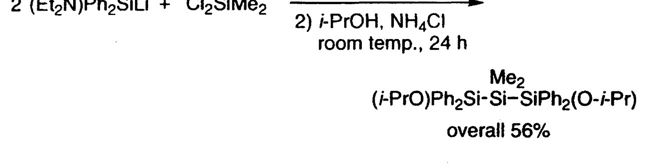
tive transformations shown in Scheme 9. The (aminosilyl)lithiums undergo smooth reactions with a variety of chlorosilanes to form the corresponding disilanes;[16] the Si–N bonds in the primary products can be converted into Si–Cl bonds by mixture with an acyl chloride. These methods are applicable to the synthesis of functionalized Si–Ge and Si–Sn compounds, as shown in Scheme 10.[26]

A one-step introduction of two functionalized silyl groups into a dichlorosilane and a stepwise Si–Si chain elongation by sequential treatment of a chlorosilane with the (aminosilyl)lithiums are exemplified by the formation of trisilanes shown in Scheme 11.[16] Most of the functionalized disilanes and trisilanes prepared herein are structurally simple, but not easily accessible by conventional methods.

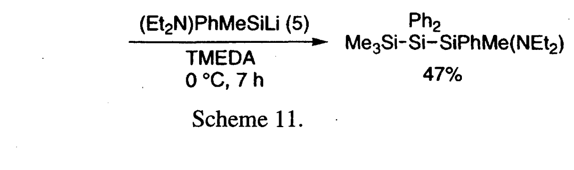
2-2. Reactivity Control of Silyl Anions. For preparation of oligosilanes,[27] reaction of silyllithiums with (chloro)oligosilanes is a standard method. The (aminosilyl)lithiums in THF, however, often cleave the Si–Si bonds of the oligosilanes. To overcome this trouble, we tried to control the reactivity of aminosilyl anions by covering the counter cation (Li^+) into other metals. There has been a practical hint that alkyl Grignard reagents efficiently alkylate the silicon in oligosilanes without the Si–Si bond cleavage, while alkyllithiums often cleave the Si–Si bonds.[28] Among some metals so far examined, we have found that alkyl(aminosilyl)magnesiums are most suitable for this purpose.[29] As shown in Scheme 12, alkyl(aminosilyl)magnesiums can be prepared in situ by just mixing the (aminosilyl)lithiums with isopropyl Grignard reagent at 0 °C, based on the report by Nozaki, Oshima, and their co-workers.[30] These silylmagnesium reagents exhibit a sufficient reactivity toward chlorosilanes without formation of isopropylsilanes (Scheme 13), and, as expected, caused no undesired Si–Si bond cleavage. This method has thus been successfully applied to the preparation of functionalized oligosilanes, as shown in Scheme 14.



Scheme 9.



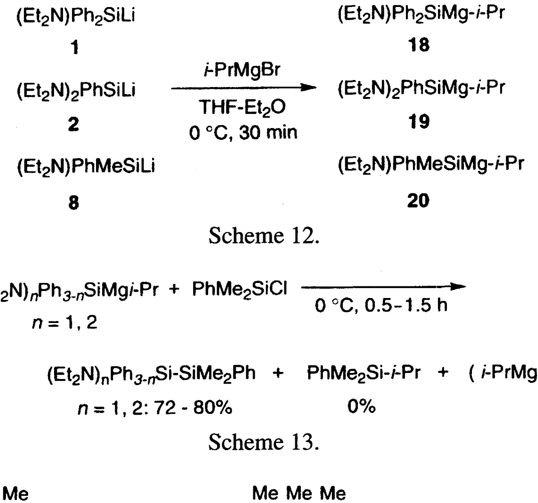
Scheme 10.



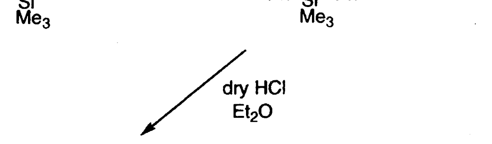
Scheme 11.

3. Reactions of (Alkoxysilyl)lithiums: The Chemistry of Silylenoids

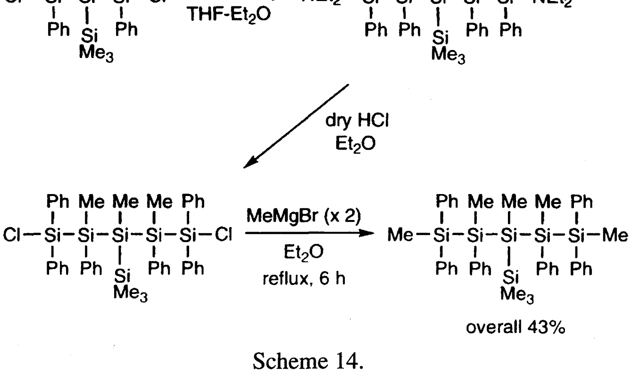
α-Heteroatom substituted organolithiums which exhibit both nucleophilicity and electrophilicity have been known as carbenoids.[3] Over the past few decades, a considerable number of studies have been made on carbenoids. In contrast to this, the silicon analogues, silylenoids, have rarely been studied. To date only one theoretical study has been



Scheme 12.



Scheme 13.



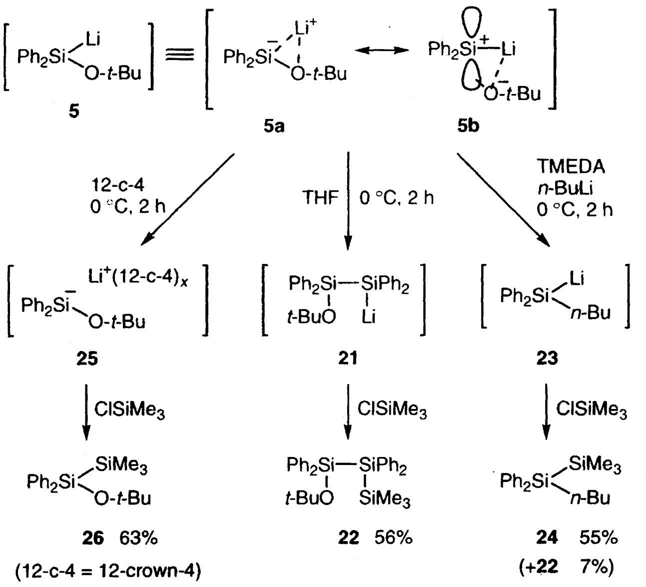
Scheme 14.

performed on a (lithium)(fluoro)silylenoid FH_2SiLi.[31] The result indicates that the Si–F bond is weakened when the electropositive lithium atom is bonded to the silicon, resulting in the enhanced electrophilicity of the silicon. Described herein are the first experimental aspects of silylenoid in the chemistry of (alkoxysilyl)lithiums.

3-1. Silylenoid Character of (*t*-Butoxysilyl)lithium. Self-Condensation: As described previously in Section 1-1 and Scheme 5, (*t*-butoxysilyl)lithium **5** was stable at −78 °C for at least 6 h, but it decomposed completely at 0 °C within 2 h. This finding is a striking contrast to the high stability of (aminosilyl)lithiums **1**, **2**, and **9**, which are stable at 0 °C for several days. Analysis of the decomposition products disclosed the ambiphilic nature of **5**, as summarized in Scheme 15.[17] At 0 °C, **5** was found to undergo bimolecular self-condensation, via nucleophilic substitution of the *t*-butoxy group by another molecule of **5**, giving (2-*t*-butoxydisilanyl)lithium **21**, which was trapped as (*t*-butoxy)trisilane **22** in 56% yield. Note that one molecule of **5** behaves as a nucleophile and the other as an electrophile.

The ambiphilic nature of **5** could be accounted for by contribution of two extreme electronic structures, that is, a nucleophilic silyl anion structure **5a** and an electrophilic silylenoid structure **5b**, as shown in Scheme 15, by analogy with the carbenoid chemistry.[2] In the latter **5b**, the electropositive lithium atom bound to the silicon ionizes and activates the silicon–oxygen bond,[32] so that the silicon becomes more susceptible to nucleophiles than that in the neutral alkoxysilanes counterparts.

Nucleophilic Alkylation: The enhanced electrophilicity of silicon in **5** has been demonstrated by ready nucleophilic alkylation. Thus, **5** underwent concomitant nucleophilic butylation with external *n*-BuLi in the presence of TMEDA at 0 °C to afford (butyldiphenylsilyl)lithium **23**, which was trapped as disilane **24** (Scheme 15),[17] together with the self-condensation product **22** in the ratio of 89 : 11. The activation of the silicon–oxygen bond toward nucleophilic substitution was confirmed by the following control experiments.[17] A counter model compound (*t*-BuO)Ph_2SiMe, where the neutral methyl group is attached to the silicon, was very slightly butylated with *n*-BuLi (5 mol amt.) at 0 °C for 10 min in the presence of TMEDA, giving *n*-$BuPh_2SiMe$ in only 4% yield. Under the same condition, **5** was butylated to give **24** in 24% yield, together with **22** in 9%, after the quenching with Me_3SiCl. The silicon–oxygen bond in **5** is thus 8—9 times more reactive towards the nucleophiles than that in the neutral counter model compound.



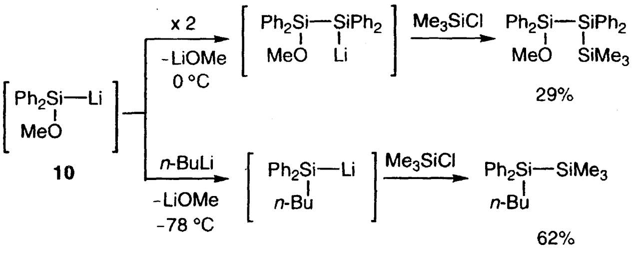
Scheme 15.

Disappearance of the Electrophilicity: The electrophilicity of **5** completely disappeared by addition of a crown ether which was expected to convert **5** into a "solvent-separated ion pair" **25**, as shown in Scheme 15.[17] In the presence of 12-crown-4, **25** was stable even at 0 °C for 2 h and underwent neither self-condensation nor any butylation, but behaved as silyl anion only. Upon trapping with Me_3SiCl, only **26** was thus obtained in 63% yield. The nature of the silicon–lithium bond plays a decisive role in the ambiphilicity: The lithium cation which is surrounded by the crown ether has no significant interaction with the oxygen atom on silicon, resulting in little or no activation of the silicon–oxygen bond.

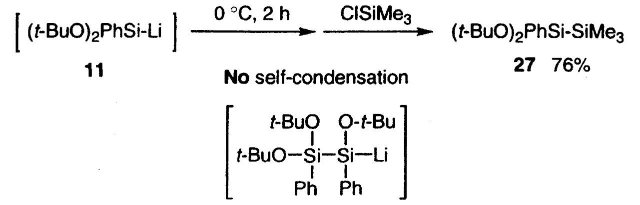
3-2. Effect of the Size and the Number of Alkoxy Group(s). The methoxy analog (MeO)Ph_2SiLi (**10**; see Scheme 7) underwent self-condensation in the same manner but more rapidly at 0 °C within 10 min to give the corresponding (methoxy)trisilane after the quenching with Me_3SiCl in 29% yield and also underwent butylation with *n*-BuLi even at −78 °C within 30 min (Scheme 16).[18]

In contrast to the ambiphilic behavior of the (monoalkoxysilyl)lithiums, a (dialkoxysilyl)lithium was found to behave predominantly as a silyl anion.[18] Thus, a solution of (*t*-BuO)$_2$PhSiLi (**11**), prepared at −50 °C according to the procedure in Scheme 7, was warmed to 0 °C for 2 h, followed by addition of Me_3SiCl, to form the silyllithium-trapped disilane **27** solely in 76% yield (Scheme 17). No self-condensation product was detected at all, even after a longer period was employed. The (dialkoxysilyl)lithium **11** thus turned out to be stable even at 0 °C.

The (dialkoxysilyl)lithium **11** underwent butylation with a large excess of *n*-BuLi at 0 °C to give the dibutylated product **28** (**29** after trapping) in 12% yield together with unchanged **11** (**27** after trapping): No monobutylated product **30** (**31** after trapping) was obtained at all (Scheme 18).[24] These results indicate that, while the first butylation of dialk-



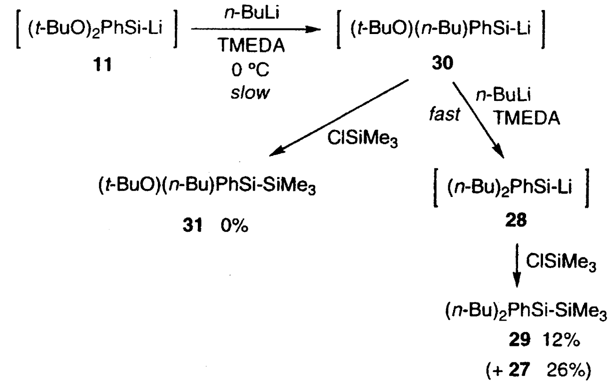
Scheme 16.



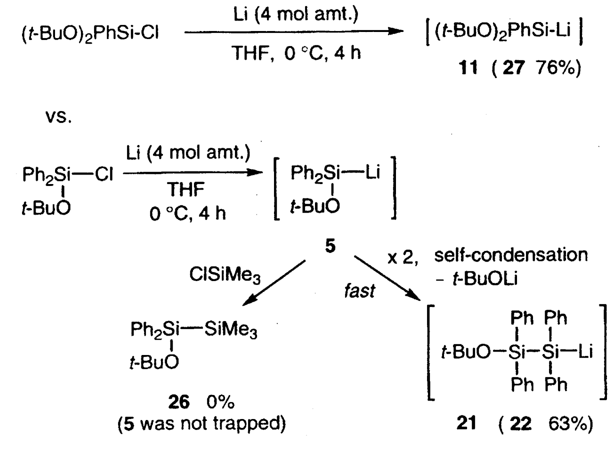
Scheme 17.

oxy species **11** proceeds slowly, the second butylation of the resulting monoalkoxy species **30** is much faster, which is in accordance with the higher electrophilicity of the (monoalkoxysilyl)lithiums. The reason for the decrease in the electrophilicity of the silicon atom in **11** is not clear, but steric factors as well as electronic factors should be considered.

3-3. Different Modes of Reactions of Monoalkoxy- and Dialkoxychlorophenylsilanes with Lithium Metal. The contrasting behavior of the monoalkoxy- and dialkoxy-silyllithiums as described above are clearly reflected in reaction modes of monoalkoxy- and dialkoxy-chlorosilanes with lithium metal,[24] as summarized in Scheme 19. Thus, while reaction of (dialkoxy)chlorosilane $(t\text{-BuO})_2\text{PhSiCl}$ with lithium in THF at 0 °C afforded (dialkoxysilyl)lithium **11**, which was tapped as disilane **27** in 45% yield, a similar reaction of (monoalkoxy)chlorosilane $(t\text{-BuO})\text{Ph}_2\text{SiCl}$ afforded disilanyllithium **21**, which was trapped as trisilane **22** in 63% yield, with no trace of **26** arising from the (alkoxysilyl)lithium. In the latter case, it is likely that the lithium (alkoxy)silylenoid **5** is generated first and then it rapidly undergoes bimolecular self-condensation. These reactions, as a result, provide the selective formation of (dialkoxysilyl)lithium **11** and [2-(alkoxy)disilanyl]lithium **21** from the corresponding, readily available (alkoxy)chlorosilanes.[27] It should be noted here that the [2-(alkoxy)disilanyl]lithium **21** is stable and shows little tendency for β-elimination at 0 °C within a few hours, while the carbon analogs undergo β-elimination readily to form olefins.



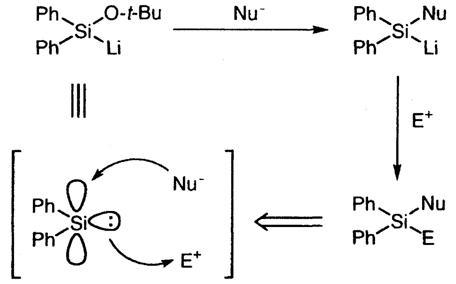
Scheme 18.



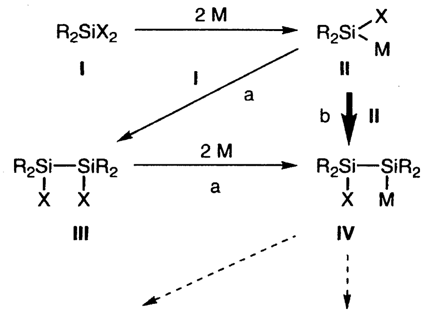
Scheme 19.

3-4. Further Comments on the Silylenoid Chemistry. Two further points on the silylenoids deserve comment. First, the ambiphilicity of the silylenoids allows the successive introduction of a nucleophile (Nu^-) and of an electrophile (E^+) to a silylene moiety, as shown in Scheme 20.[33] The important point is that a nucleophile is introduced first with ease because of the high electrophilicity of the silylenoid, which makes a sharp contrast to the conventional transformations involving ordinary silyl anions to which only an electrophile is introduced. This new reaction pattern may suggest a potential synthetic utility of silylenoids.

Second, the behavior of the silylenoids may offer a new clue to explain the mechanism[13] of chain elongation of polysilanes via reductive coupling of dihalosilanes **I** with alkali metal M, as shown in Scheme 21.[17] The first step is the formation of metal halosilylenoid **II**. It has been so far proposed that the coupling reaction of **II** with **I** affords 1,2-dihalodisilane **III**, which is then metalated to give the second reactive species, 1-halo-2-metallodisilane **IV** (path a). The present results, however, strongly suggest a new possibility for the direct conversion of the initially formed silylenoid species **II** into **IV** via self-condensation (path b), which would proceed much faster than the reaction of **II** with **I**. This step has not previously been proposed for the mechanism of chain



Scheme 20.



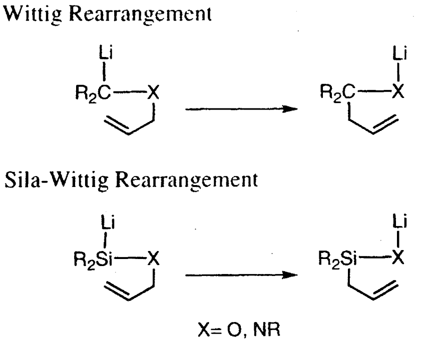
Scheme 21.

elongation of polysilanes.

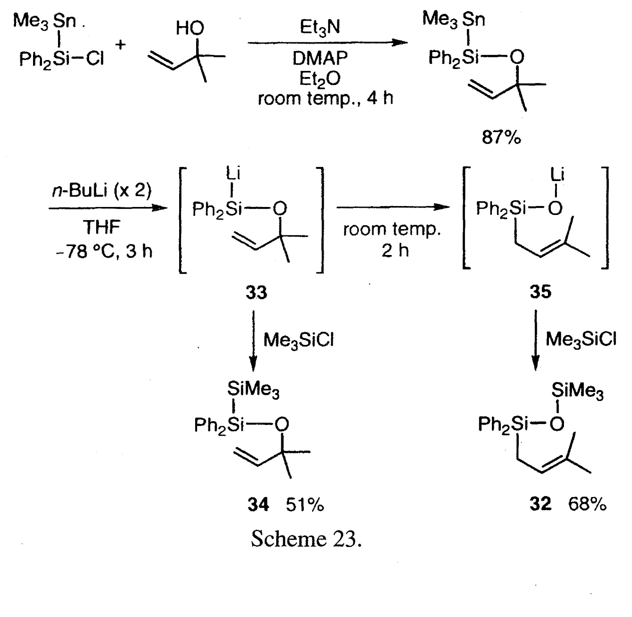
4. Reactions of [(Allyloxy)silyl]lithiums and [(Allylamino)silyl]lithiums: The Sila-Wittig Rearrangement

The Wittig rearrangement is one of the most important reactions of α-oxygen and α-nitrogen substituted carbanions. Much attention has been paid especially to the [2,3]-Wittig rearrangements since they serve as regio- and stereoselective C–C bond forming reactions (Scheme 22).[14,34,35] In contrast, silicon analogues to the [2,3]-Wittig rearrangements have never been reported so far.[36] In the course of our study of amino- and alkoxy-silyllithiums, we have found the first examples of [2,3]-sila-Wittig and aza-sila-Wittig rearrangements.[37] They involve intramolecular migration of an allyl group from an oxygen or nitrogen to silicon in [(allyloxy)silyl]lithium or [(allylamino)silyl]lithium, as shown in Scheme 22.

4-1. [2,3]-Sila-Wittig Rearrangement. The tin–lithium exchange reaction is applicable to the preparation of [(allyloxy)silyl]lithiums. A typical example is shown in Scheme 23. [(Allyloxy)silyl]stannane in THF was treated with n-BuLi (2.0 mol amt.) at −78 °C for 3 h. Then the reaction mixture was stirred at room temperature for 2 h and the reaction was quenched with Me_3SiCl to give the rearrangement product, allylsilane-containing disiloxane **32**, in 68% yield. No [1,2]-rearrangement product was detected at all. The intermediate formation of the (allyloxysilyl)lithium **33** has been confirmed by quenching the reaction at −78 °C to give the corresponding allyloxydisilane **34**. The rearrangement was greatly enhanced by addition of 12-crown-4 to the solution of **33** to give only the rearrangement product **32** via **35** in 55% yield even at −78 °C within 1 h.[38]



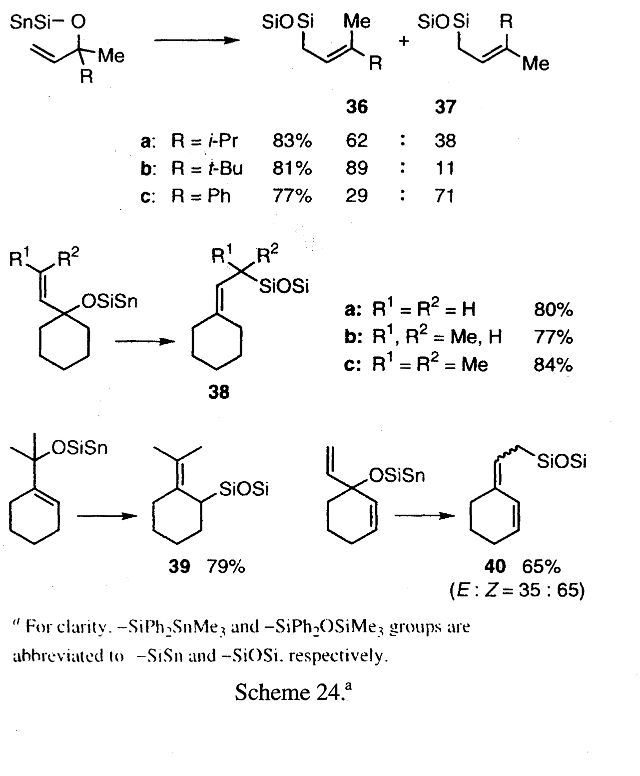
Scheme 22.



Scheme 23.

Some other representative results are summarized in Scheme 24; three points deserve comment. (1) An olefinic stereoselection[14,39] has been investigated on [(allyloxy)silyl]lithiums which have a chiral *tertiary* allylic carbon center. The rearranged allylsilanes preferentially have (E)-olefin moieties (**36**) with an increase in the bulkiness of the allylic alkyl substituent, but the reversed Z-selectivity (**37**) is observed in the phenyl case. Whereas the E-selectivity is similar to the general tendencies observed for the [2,3]-Wittig rearrangement,[39] the Z-selectivity implies a mechanistic complexity in the present silicon version. (2) In addition to the rearrangement from *tertiary* allyloxy[40] to *primary* allylsilanes (**38a**) (abbreviated as *tert*-to-*prim*), *tert*-to-*sec* (**38b**), and *tert*-to-*tert* (**38c**) rearrangements proceed smoothly. (3) Exocyclic allyloxy-silane is converted into endocyclic allylsilane **39**. Further noted is the regioselectivity observed in the last example, which exclusively undergoes migration to the exocyclic olefin (**40**) with the endocyclic olefin intact.

The present method, however, is applicable only to *tertiary* allyloxy derivatives. Some attempted transmetalations of [(*prim*-allyloxy)silyl]- and [(*sec*-allyloxy)silyl]stannanes were unsuccessful, because butyllithiums tend to attack the sterically less bulky silicon atom rather than the tin atom. This limitation has been partially overcome by a reductive lithiation method,[18] as shown in Scheme 25. Thus, a (*sec*-allyloxy)chlorosilane was treated with lithium naphthalenide



[a] For clarity, $-SiPh_2SnMe_3$ and $-SiPh_2OSiMe_3$ groups are abbreviated to –SiSn and –SiOSi, respectively.

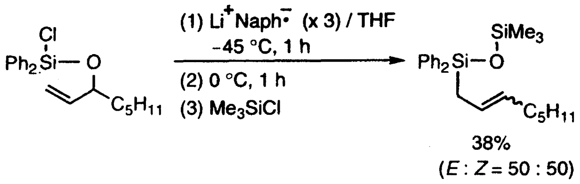
Scheme 24.[a]

(3.0 mol amt.) in THF at −45 °C for 1 h, followed by stirring at 0 °C for 1 h and by trapping with Me_3SiCl, to afford the rearrangement product in 38% yield as a mixture of olefinic stereoisomers.[37)]

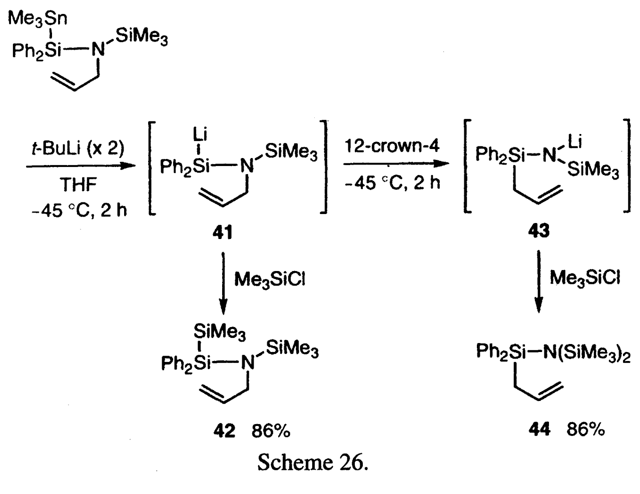
4-2. [2,3]-Aza-Sila-Wittig Rearrangement. We next turned our attention to the aza-sila-Wittig rearrangement, in which the oxygen atom is replaced by a nitrogen atom.[37)] A typical example is shown in Scheme 26. Transmetalation of [(allylamino)silyl]stannane with *t*-BuLi (2.0 mol amt.) was complete at −45 °C in 2 h to give [(allylamino)silyl]lithium **41**, which was trapped as **42** in 86% yield. By addition of 12-crown-4, **41** smoothly underwent the rearrangement at −45 °C to form lithium (allylsilyl)amide **43**, which was trapped with Me_3SiCl to give the allylsilane **44** in 86% yield. The crown ether was essential for this rearrangement;[38)] in the absence of the crown ether, the rearrangement proceeded in only 10% yield even by warming to −20 °C; at higher temperatures, a complex mixture resulted.

A direct reductive lithiation was also successful for the aza-sila-Wittig rearrangement.[41)] As shown in Scheme 27, reaction of (allylamino)fluorosilanes with lithium in THF at 0 °C for 4 h, followed by trapping with Me_3SiCl, gave the rearranged allylsilanes **45** in moderate yields. In this method, 12-crown-4 was not required, perhaps because the reaction temperature was higher than that in the transmetalation method.

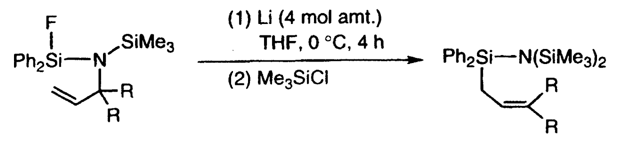
These sila-Wittig rearrangements are considered to be thermodynamically favorable since they convert the silyllithiums into the more stable lithium oxides and lithium amides. The enthalpy for the model reaction, $(CH_2{=}CH{-}CH_2{-}O){-}Ph_2Si{-}Li \rightarrow (Li{-}O)Ph_2Si{-}CH_2{-}CH{=}CH_2$, was estimated to be about −40 kcal mol^{-1} by PM3 calculation.[37)] The sila-Wittig rearrangements offer a novel route from allyl alcohols or allylamines to sila-functionalized allylsilanes in a regiocontrolled fashion, which are hardly accessible by conventional methods.



Scheme 25.



Scheme 26.



45a; R = H 41%
45b; R = Me 54%

Scheme 27.

5. Synthetic Applications of the Functionalized Silyl Anions: Aminosilyl Anions as Hydroxide Ion Equivalent

Silyl anions have been known to serve as a hydroxide ion equivalent, because functionalized silyl groups in organosilicon compounds can be converted into the hydroxy group by oxidation.[42)] In the conventional $PhMe_2Si$ anion chemistry,[43)] the silicon–carbon bond can be oxidatively cleaved only after the phenyl group is replaced with a heteroatom by acid treatment. This methodology involving the acid treatment, however, cannot be applied to at least three types of silanes, that is, allylsilane, vinylsilane, and *β*-hydroxy silane, because the acid might cleave the silicon–allyl and –vinyl carbon bonds much faster than the silicon–phenyl carbon bond[44)] or might cause Peterson olefination of the *β*-hydroxy silane.[45)]

The aminosilyl anion chemistry has afforded a solution to this problem.[46)] Thus, no acid treatment is required since the silyl group is already nitrogen-functionalized. For synthetic applications, (aminosilyl)lithium **1** has been converted into the copper reagent **46** and the magnesium reagent **47**, as shown in Scheme 28.[30,43)] These reagents can be applied to regio- and stereoselective synthesis of allylsilanes, *β*-hydroxy silanes, and vinylsilanes, which are converted into the corresponding alcohols and aldehyde,[47)] as summarized in Scheme 29.

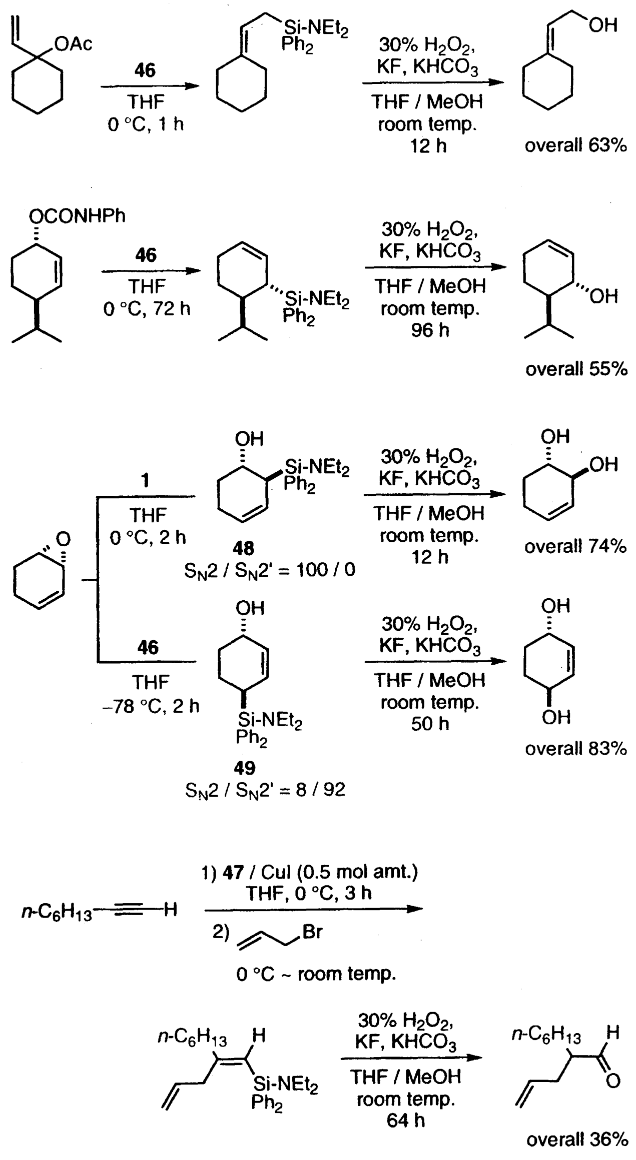
Allylsilanes via Allylic Substitution: (Aminosilyl)cuprate **46** underwent the S_N2' allylic substitution reaction[48)] with 1-vinylcyclohexyl acetate to give amino-substituted [2-(cyclohexylidene)ethyl]silane, which was converted into the corresponding allyl alcohol in 63% yield. Similarly, 2-cyclohexenyl carbamate was transformed into an isomeric allylic alcohol in a highly regio- and stereoselective fashion.

***β*-Hydroxy Silane via Ring-Opening of Epoxides:** Monoepoxide of 1,3-cyclohexadiene[49)] was converted into 1,2- and 1,4-diols in a completely regio- and stereoselective fashion by use of **1** and **46** via an S_N2 type and an S_N2' type

$$\underset{\mathbf{1}}{(Et_2N)Ph_2SiLi} + CuCN \xrightarrow[0\ ^\circ C,\ 1\ h]{THF} \underset{\mathbf{46}}{(Et_2N)Ph_2SiCu(CN)Li}$$

$$\underset{\mathbf{1}}{(Et_2N)Ph_2SiLi} + MeMgBr \xrightarrow[\substack{0\ ^\circ C,\ 1\ h \\ -\ LiBr}]{THF} \underset{\mathbf{47}}{(Et_2N)Ph_2SiMgMe}$$

Scheme 28.



Scheme 29.

ring opening, respectively. It is noted that the primary products **48** and **49** have allylsilane moieties as well as β-hydroxy (or vinylogous β-hydroxy) silane moieties, but these can be subjected directly to the oxidation reaction.

Vinylsilane by Addition to Alkyne: It has been reported that silylcuprates[50] and silylmagnesium species[30] undergo regioselective addition to alkynes. (Aminosilyl)cuprate **46**, however, underwent addition to 1-alkyne with low regioselectivity, together with deprotonation on the terminal carbon atom. In contrast, (aminosilyl)magnesium species **47** performed stereo- and regioselective addition to 1-alkyne in the presence of CuI to give the vinylsilane, which afforded the corresponding aldehyde by hydrogen peroxide oxidation in 36% overall yield.

Concluding Remarks

We have developed four types of functionalized silyllithiums: that is, amino-, alkoxy-, allyloxy-, and allylaminosilyllithiums. The present chemistry has opened up the possibility of preparing a variety of functionalized organosilicon compounds as well as preparing new synthetic reagents for organic synthesis. We should say, however, that we are just on the starting point to a new field of organosilicon reactive species. Much remains to be investigated, including the crystal structure analysis,[51] stereochemical analysis of the functionalized silyllithiums, and introduction of other heteroatoms, such as P, S, Se, and halogens, on the silicon in silyllithiums.

We thank Prof. Y. Ito, Kyoto University, for useful discussions. We are also grateful to the Ministry of Education, Science, Sports and Culture, for Grant-in-Aids for Scientific Research.

References

1) a) "Comprehensive Carbanion Chemistry," ed by E. Buncel and T. Durst, Elsevier, Amsterdam, Part A (1980) and Part B (1984); b) B. J. Wakefield, "Organolithium Methods," Academic Press, London (1988); c) P. G. Williard, "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), Vol. 1, pp. 1—47.

2) a) P. Beak, W. J. Zajdel, and D. B. Reitz, *Chem. Rev.*, **84**, 471 (1984); b) G. Boche, *Angew. Chem., Int. Ed. Engl.*, **28**, 277 (1989); α-Aminoorganolithiums: c) I. Coldham, R. Hufton, and D. J. Snowden, *J. Am. Chem. Soc.*, **118**, 5322 (1996).

3) Reviews: a) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **11**, 473 (1972); b) A. Maercker, *Angew. Chem., Int. Ed. Engl.*, **32**, 1023 (1993); α-Alkoxyorganolithiums: c) G. Boche, F. Bosold, J. C. W. Lohrenz, A. Opel, and P. Zulauf, *Chem. Ber.*, **126**, 1873 (1993); α-Chloroorganolithiums: d) D. Seebach, H. Siegel, J. Gabriel, and R. Hässig, *Helv. Chim. Acta*, **63**, 2046 (1980); e) A. Müller, M. Marsch, K. Harms, J. C. W. Lohrenz, and G. Boche, *Angew. Chem., Int. Ed. Engl.*, **35**, 1518 (1996).

4) Reviews: a) I. Fleming, "Comprehensive Organic Chemistry," ed by E. Barton and W. D. Ollis, Pergamon Press, Oxford (1979), Vol. 3, pp. 664—669; b) M. Fujita and T. Hiyama, *J. Synth. Org. Chem. Jpn.*, **42**, 293 (1984); c) J. B. Lambert and W. J. Schulz, Jr., "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, Wiley, Chichester (1989), pp. 1007—1010; d) K. Tamao and A. Kawachi, *Adv. Organomet. Chem.*, **38**, 1 (1995); e) P. D. Lickiss and C. M. Smith, *Coord. Chem. Rev.*, **145**, 75 (1995).

5) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

6) a) M=Na: H. Sakurai, A. Okada, M. Kira, and K. Yonezawa, *Tetrahedron Lett.*, **12**, 1511 (1971); b) M=Li: W. C. Still, *J. Org. Chem.*, **41**, 3063 (1976); c) M=K: R. J. P. Corriu, C. Guerin, and B. Kolani, *Bull. Soc. Chim. Fr.*, **1985**, 974.

7) a) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Jpn.*, **29**, 322 (1956); b) R. A. Benkeser, *Acc. Chem. Res.*, **4**, 94 (1971); c) C. S. Li, D. F. Ehler, and R. A. Benkeser, *Org. Synth.*, Coll. Vol. 6, 747 (1988); d) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).

8) H. Watanabe, K. Higuchi, Y. Goto, T. Muraoka, J. Inose, M. Kageyama, Y. Iizuka, M. Nozaki, and Y. Nagai, *J. Organomet. Chem.*, **218**, 27 (1981).

9) H. Gilman and W. Steudel, *Chem. Ind.* (*London*), **1959**, 1094.

10) D. M. Roddick, R. H. Heyn, and T. D. Tilley, *Organometallics*, **8**, 324 (1989).

11) a) J. Ohshita, Y. Masaka, S. Masaoka, M. Ishikawa, A. Tachibana, T. Yano, and T. Yamabe, *J. Organomet. Chem.*, **473**, 15 (1994); b) J. Ohshita, Y. Masaka, S. Masaoka, M. Ishikawa, A. Tachibana, T. Yano, and T. Yamabe, *Organometallics*, **15**, 3136 (1996).

12) a) A. C. Hopkinson and M. H. Lien, *Tetrahedron*, **37**, 1105 (1981); b) E. Magnusson, *Tetrahedron*, **41**, 2945 (1985).

13) a) R. West, *J. Organomet. Chem.*, **300**, 327 (1986); b) C. L. Smith and R. Gooden, *J. Organomet. Chem.*, **81**, 33 (1974); c) P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrusciel, and K. R. Anderson, *Angew. Chem., Int. Ed. Engl.*, **27**, 1355 (1988); d) T. Tsumuraya, S. A. Batcheller, and S. Masamune, *Angew. Chem., Int. Ed. Engl.*, **30**, 902 (1991); e) R. J. P. Corriu, G. Lanneau, C. Priou, F. Soulairol, N. Auner, R. Probst, R. Conlin, and C. J. Tan, *J. Organomet. Chem.*, **466**, 55 (1994).

14) Reviews: a) J. A. Marshall, "Comprehensive Organic Synthesis," ed by B. M. Trost, I. Fleming, and G. Pattenden, Pergamon Press, Oxford (1991), Vol. 3, pp. 975—1014; b) T. Nakai and K. Mikami, *Chem. Rev.*, **86**, 885 (1986); c) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **18**, 563 (1979).

15) B. H. Lipshutz, D. C. Reuter, and E. L. Ellsworth, *J. Org. Chem.*, **54**, 4975 (1989).

16) K. Tamao, A. Kawachi, and Y. Ito, *J. Am. Chem. Soc.*, **114**, 3989 (1992).

17) K. Tamao and A. Kawachi, *Angew. Chem., Int. Ed. Engl.*, **34**, 818 (1995).

18) K. Tamao and A. Kawachi, *Organometallics*, **14**, 3108 (1995).

19) a) For LDMAN: T. Cohen, J. P. Sherbine, J. R. Matz, R. R. Hutchins, B. M. McHenry, and P. R. Willey, *J. Am. Chem. Soc.*, **106**, 3245 (1984); b) For LDBB: P. K. Freeman and L. L. Hutchinson, *J. Org. Chem.*, **45**, 1924 (1980).

20) A stannylsodium was obtained by reduction of a stannyl chloride with sodium naphthalenide: J. C. Podestá, N. N. Giagante, A. E. Zuñiga, G. O. Danelon, and O. A. Mascaretti, *J. Org. Chem.*, **59**, 3747 (1994).

21) K. Tamao, A. Kawachi, and Y. Ito, *Organometallics*, **12**, 580 (1993).

22) K. Tamao, G-R. Sun, A. Kawachi, and S. Yamaguchi, *Organometallics*, **16**, 780 (1997).

23) The ^{29}Si shift of the silyllithium **1** was reported uncorrectly in the original paper (Ref. 16) and reinvestigated in 1994.

24) A. Kawachi and K. Tamao, *Organometallics*, **15**, 4653 (1996).

25) a) G. A. Olah and R. Hunadi, *J. Am. Chem. Soc.*, **102**, 6989 (1980); b) E. Buncel, T. K. Venkatachalan, B. Eliasson, and U. Edlund, *J. Am. Chem. Soc.*, **107**, 303 (1985); c) U. Edlund, T. Lejon, T. K. Venkatachalam, and E. Buncel, *J. Am. Chem. Soc.*, **107**, 6408 (1985).

26) K. Tamao, A. Okamoto, T. Kobayashi, A. Kawachi, and Y. Ito, unpublished results.

27) Recent works on preparation of oligosilanyllithiums and oligosilanes: a) A. Sekiguchi, M. Nanjo, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **117**, 4195 (1995); b) A. Sekiguchi, M. Nanjo, C. Kabuto, and H. Sakurai, *Organometallics*, **14**, 2630 (1995).

28) Y. Apeloig, "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, Wiley, Chichester (1989), pp. 655—761.

29) A. Kawachi and K. Tamao, unpublished results; The term "silyl(alkyl)magnesium" does not represent the "real" structure, but is used for species consisting of a 1 : 1 mixture of silyllithium and alkylmagnesium halide.

30) H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, and H. Nozaki, *J. Am. Chem. Soc.*, **105**, 4491 (1983).

31) T. Clark and P. v. R. Schleyer, *J. Organomet. Chem.*, **191**, 347 (1980).

32) In carbenoid chemistry, ionization of this type is sometimes called "metal-assisted ionization" which involves a definite heteroatom-metal interaction, see: M. Topolski, M. Duraisamy, J. Rachon, J. Gawronski, K. Awronska, V. Goedken, and H. M. Walborsky, *J. Org. Chem.*, **58**, 546 (1993).

33) For an example of successive introduction of a nucleophile and an electrophile to carbenoids in organic synthesis, see: P. Knochel, N. Jeong, M. J. Rozema, and M. C. P. Yeh, *J. Am. Chem. Soc.*, **111**, 6474 (1989).

34) Recent reports on Wittig rearrangement: a) K. Tomooka, P-H. Keong, and T. Nakai, *Tetrahedron Lett.*, **36**, 2789 (1995); b) A. R. Katritzky, H. Wu, and L. Xie, *J. Org. Chem.*, **61**, 4035 (1996).

35) Aza-Wittig rearrangement: a) T. Durst, R. V. D. Elzen, and M. LeBelle, *J. Am. Chem. Soc.*, **94**, 9261 (1972); b) C. Broka and T. Shen, *J. Am. Chem. Soc.*, **111**, 2981 (1989); c) I. Coldham, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1275; d) J. Åhman and P. Somfai, *J. Am. Chem. Soc.*, **116**, 9781 (1994); e) J. Åhman and P. Somfai, *Tetrahedron Lett.*, **36**, 303 (1995); f) J. C. Anderson, D. C. Siddons, S. C. Smith, and M. E. Swarbrick, *J. Chem. Soc., Chem. Commun.*, **1995**, 1835; g) I. Coldham, A. J. Collis, R. J. Mould, and R. E. Rathmell, *J. Chem. Soc., Perkin Trans. 1*, **1995**, 2739; h) R. E. Gawley, Q. Zhang, and S. Campagna, *J. Am. Chem. Soc.*, **117**, 11817 (1995); i) J. Anderson, D. C. Siddons, S. C. Smith, and M. E. Swarbrick, *J. Org. Chem.*, **61**, 4820 (1996).

36) For a review on rearrangements involving silicon, see: a) A. G. Brook and A. R. Bassindale, "Rearrangements in Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), pp. 149—227; The term sila-Wittig rearrangement is used to differentiate the present reaction from the silyl-Wittig rearrangement (reversed Brook rearrangement): b) A. Wright and R. West, *J. Am. Chem. Soc.*, **96**, 3214, 3222, and 3227 (1974).

37) A. Kawachi, N. Doi, and K. Tamao, *J. Am. Chem. Soc.*, **119**, 233 (1997).

38) A similar solvent effect has been well documented in the Wittig rearrangements of carbanions. a) G. Wittig and E. Stahnecker, *Justus Liebigs Ann. Chem.*, **605**, 69 (1957); b) K. Mikami, T. Kasuga, K. Fujimoto, and T. Nakai, *Tetrahedron Lett.*, **26**, 4185 (1986). See also Ref. 35i.

39) a) W. C. Still and A. Mitra, *J. Am. Chem. Soc.*, **100**, 1927 (1978); b) Y-D. Wu, K. N. Houk, and A. Marshall, *J. Org. Chem.*, **55**, 1421 (1990); c) R. Hoffmann and R. Brückner, *Angew. Chem., Int. Ed. Engl.*, **31**, 647 (1992); d) E. J. Verner and T. Cohen, *J. Am. Chem. Soc.*, **114**, 375 (1992); e) K. Mikami, T. Uchida, T. Hirano, Y-D. Wu, and K. N. Houk, *Tetrahedron*, **50**, 5917 (1994).

40) The term "tertiary allyl" means that the allylic carbon is tertiary. The terms primary and secondary are used in a similar way in this paper.

41) A. Kawachi, N. Doi, and K. Tamao, unpublished results.

42) a) K. Tamao, N. Ishida, T. Tanaka, and M. Kumada, *Organometallics*, **2**, 1694 (1983); b) I. Fleming, *Chemtracts, Org. Chem.*, **9**, 1 (1996); c) G. Jones and Y. Landais, *Tetrahedron*, **37**, 7599 (1996); d) K. Tamao, "Advances in Silicon Chemistry," ed by G. Larson, JAI Press, Greenwich, Connecticut (1996), Vol. 3, pp. 1—62.

43) For examples; a) R. A. N. C. Crump, I. Fleming, J. H. M. Hill, D. Parker, N. L. Reddy, and D. Waterson, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 3277; b) I. Fleming, *Pure Appl. Chem.*, **60**, 71 (1988), and references cited therein.

44) a) I. Fleming, J. Dunogues, and R. Smithers, *Org. React.*, **37**, 57 (1989); b) S. S. Magar and P. L. Fuchs, *Tetrahedron Lett.*, **32**, 7513 (1991).

45) D. J. Ager, *Org. React.*, **38**, 1 (1990).

46) Recently, Fleming et al. have found another solution to this problem by use of a well-designed (allylsilyl)lithium: An allyl group, 2-methyl-2-butenyl group, on the silicon can be removed selectively with very weak acids with other allyl-, vinyl-, and β-hydroxy-silane moieties intact. I. Fleming and S. B. D. Winter, *Tetrahedron Lett.*, **34**, 7287 (1993).

47) K. Tamao, A. Kawachi, Y. Tanaka, H. Ohtani, and Y. Ito, *Tetrahedron*, **52**, 5765 (1996).

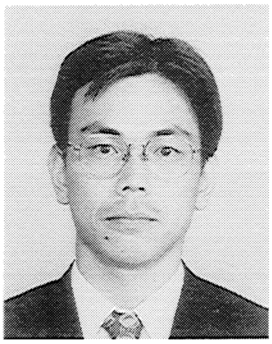
48) a) I. Fleming and T. W. Newton, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 1805; b) I. Fleming and A. P. Thomas, *J. Chem. Soc., Chem. Commun.*, **1986**, 1456.

49) J. A. Marshall, *Chem. Rev.*, **89**, 1503 (1989), and references cited therein.

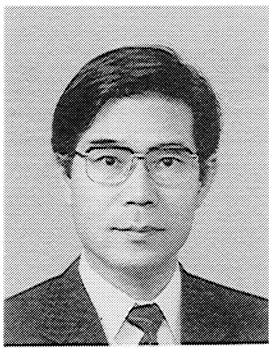
50) I. Fleming, T. W. Newton, and F. Roessler, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 2527.

51) Note added in proof: After submission of this manuscript, we have succeeded in the X-ray crystal structure determination of an (aminosilyl)lithium, monomeric $(Ph_2N)Ph_2SiLi(thf)_3$, at −70 °C ($R = 0.056$, $R_w = 0.080$), where Si–N 1.824(3) Å, Si–Li 2.732(7) Å, and N–Si–Li 115.8(2)°. The Si–N and the Si–Li bonds are respectively longer than 1.755(4) Å observed in the precursor $(Ph_2N)Ph_2SiSnMe_3$ and 2.67 Å observed in $Ph_3SiLi(thf)_3$.[52] A. Kawachi, M. Shiro, and K. Tamao, unpublished results (1997).

52) H. V. R. Davis, M. M. Olmstead, K. Ruhlandt-Senge, and P. P. Power, *J. Organomet. Chem.*, **462**, 1 (1993).



Atsushi Kawachi was born in Sendai, Japan, in 1966. He graduated from Kyoto University in 1990 and received a Ph. D. degree in 1996 under the direction of Professor K. Tamao from Kyoto University. Since November 1993 he has been Assistant Professor at Institute for Chemical Research, Kyoto University. He is currently an Alexsander von Humboldt research fellow as a postdoctoral associate with Professor Gernot Boche, Philipps-Universität Marburg, Germany.



Kohei Tamao was born in Kagawa, Japan, in 1942. He graduated from Kyoto University in 1965 and received a Ph. D. degree in 1971 under the direction of Prof. M. Kumada from Kyoto University. He was appointed as Assistant Professor in 1970 and as Associate Professor in 1987 at the Faculty of Engineering, Kyoto University. He spent one year from 1973 as a postdoctral associate at the State University of New York at Binghamton. In 1993, he moved to the present position as Professor. His current research interests are organosilicon chemistry, transition metal catalysis, and π-conjugated electronic materials.