Deprotonation from Diphenylsilane with Organosilyllithium Agents

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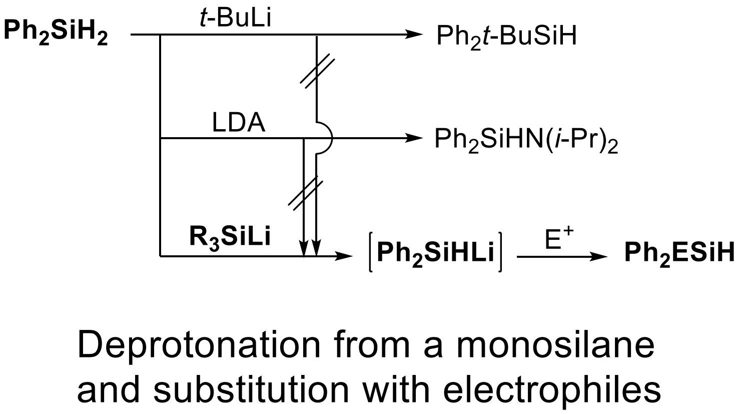
Supporting Information Placeholder

ABSTRACT: In contrast to their carbon analogs, there are only a few reports on deprotonation from silanes. This is because the normal polarization of a Si-H bond is Si(δ^+)-H(δ^-), while that of a C-H bond is C(δ^-)-H(δ^+). From a bond orbital perspective, a σ^*_{CH} orbital has greater expansion on hydrogen, while a σ^*_{SiH} orbital has greater expansion on Si. Thus, the lone pair of a base mainly attacks hydrogen of a C-H bond for deprotonation, but adds to the silicon atom of a Si-H bond. Previous reports showed that the assistance of negative hyperconjugation between the lone pair of the silyl anion and σ* orbitals on silyl substituent(s) or an intramolecular chelating group (a pincer ligand) is necessary for deprotonation from silanes. In fact, Kira et al. found that treatment of diphenylsilane with *t*-butyllithium or LDA resulted in nucleophilic substitution, not deprotonation, only to eliminate a hydride as a leaving group. Recently, we developed a silicon-homologation reaction by a deprotonation-nucleophilic substitution sequence. In that reaction, we assumed that disproportionation led to alkoxysilyllithium or a silenoid species generated *in situ*. We expected that a disproportionation approach could be applied to the deprotonation of monosilanes, such as diphenylsilane. Here we report the first successful approach to the deprotonation of monosilanes with no intramolecular chelation.



Deprotonation from a monosilane and substitution with electrophiles

1. INTRODUCTION

In organic chemistry, the introduction of substituents by the reaction of electrophiles with carbanions generated by deprotonation is a normal protocol. Especially for molecules with an electron-withdrawing group at the α position, we usually choose this procedure to introduce a substituent due to the ease of deprotonation.

On the other hand, the use of a silyl anion generated by deprotonation is scarcely employed for functionalization with electrophiles. Indeed, there have been only a few reports on the deprotonation of silanes.[1-4] The order of electronegativity is C(2.6) > H(2.2) > Si(1.9). Thus, the normal polarization of a C-H bond is C(δ^-)-H(δ^+), while that of a Si-H bond is Si(δ^+)-H(δ^-) (Figure 1). These values result in the greater expansion of a σ*-orbital of a C-H bond on hydrogen atom, which acts as the LUMO in the deprotonation reaction. In contrast, the σ^*_{SiH} orbital of a Si-H bond has a greater expansion on Si atom. The anionic species can attack hydrogen as a base to deprotonate in a C-H bond, while it should preferably attack the Si atom in a Si-H bond as a nucleophile, eliminating a hydride with nucleophilic substitution.

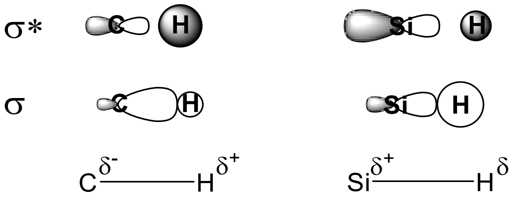


Figure 1. Bond polarization of C-H and Si-H bonds.

Silyl anion species generated from silanes are initially reported by use of (alkali metal) hydride, namely such as KH.[4] However, the mechanic study[5] showed that it is not a deprotonation process - nucleophilic attack of a hydride to afford pentavalent dihydridosilicates, which eliminate hydrogen to give the corresponding silyl anions. Corriu et al. reported that trialkylgermanes and –stannanes were more conveniently converted to the corresponding anionic species with KH or NaH.[6] Assuming this mechanism is also applicable for germanes and stannanes, we can understand that generation of (alkali metal) germides and –stannides should be more facile. Since the orbital energies of LUMO in these cases are much lower than that of silanes, nucleophilic addition should take place more easily.

Among the reported papers, Kira et al. reported the deprotonation of disilanes (Figure 2a,b).[7] Some bulky strong bases with low nucleophilicity, such as *t*-butyllithium and lithium diisopropylamide (LDA) can deprotonate disilanes, to react some electrophiles in good yields.

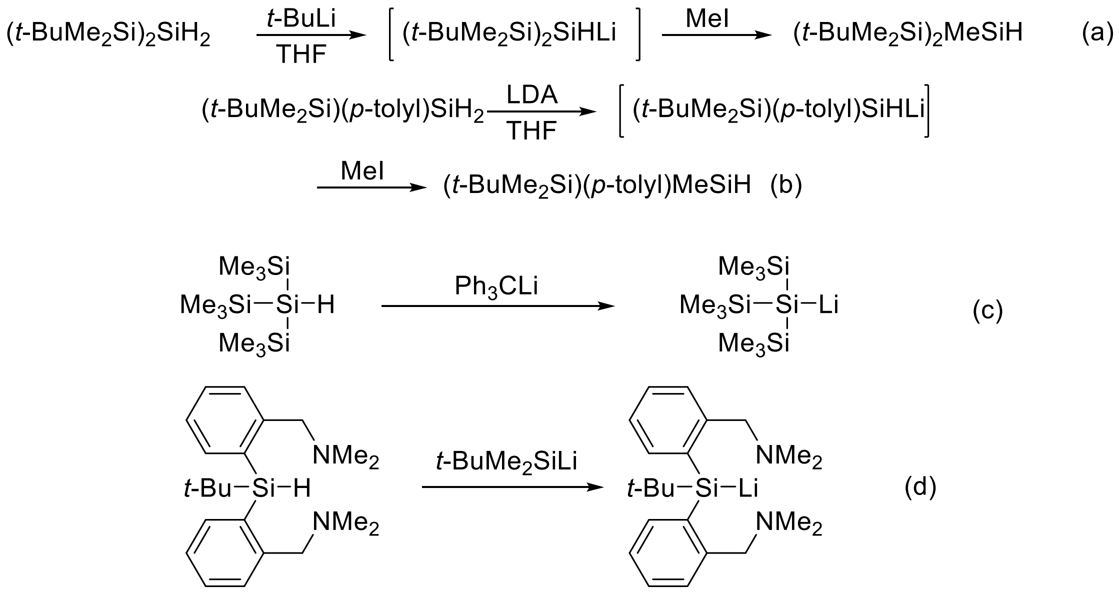
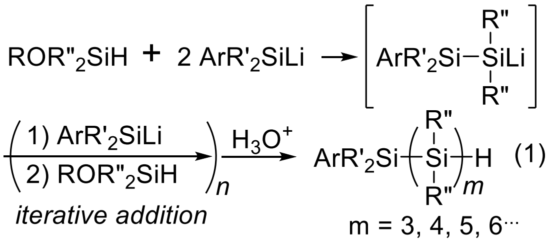


Figure 2. Deprotonation from di- and trisilanes, and a monosilane with pincer ligands.

Another example is the deprotonation of tris(trimethylsilyl silane with triphenylmethyllithium, as reported by Apeloig et al. (Figure 2c).[8] This molecule is capable of negative hyperconjugation between the lone pair of the silyl anion and $\sigma^*_{\text{Si-C}}$ orbitals of three trimethylsilyl groups. They also reported the deprotonation of a silane bearing two pincer ligands of 2-(dimethylamino)phenyl group (Figure 2d).[9] In Kira's report,[7] the resulting silyl anion species are reacted with carbon electrophiles, such as iodomethane, to introduce a carbon substituent on the silicon atom.

However, there have been no reports on the deprotonation of monosilanes with no stabilizing silyl and/or pincer groups. Kira et al. attempted deprotonation from diphenylsilane, expecting that two phenyl groups could stabilize the resulting silyl anion.[7] However, they confirmed that no deprotonation occurred, and only nucleophilically-substituted products were obtained. Thus, deprotonation from monosilanes, even with aromatic substituents, is still a challenge.

Recently, we have developed a new one-silicon-homologation reaction by a deprotonation-nucleophilic substitution sequence to prepare oligosilanes (eq. 1).[10] In that reaction, we assumed that the silyllithiums deprotonate the alkoxysilane by disproportionation, to give alkoxysilyllithiums, a silenoid, *in situ*.



We supposed that at least some of the silane is deprotonated with silyllithium by disproportionation. Furthermore, deprotonated anion should react with the electrophile if the reactivity of the silyl bases is decreased due to the steric bulkiness of the substituents. Here we report our venture to deprotonate diphenylsilane using silyllithiums as a base.

2. THEORETICAL SIMULATION OF THE ACIDITY OF SILANES

Our initial concern was to determine the difference in acidity of trimethylsilane **1a** and trimethylsilyllithium **1b**, dimethylphenylsilane **2a** and its lithio-derivative **2b**, diphenylsilane **3a** and diphenylmethylsilane **4a**, and their lithio-congeners **3b** and **4b**. Apeloig et al. reported that tris(trimethylsilyl)silane **5a** has a pKa value of 29.4.[8] They also estimated the acidity by theoretical calculations, which gave a value similar to the experimental value. Thus, we also evaluated the acidity of these molecules by theoretical calculations in an isodesmic manner. We optimized them at the B3LYP/6-311+G(*d, p*) level in the gas phase, and compared the energies at the same level with a solvent effect of THF estimated by the polarizable continuum model (PCM). The lithio-derivatives **1b**-**5b** were calculated as dimers (Figure 3).[11,12]

1a	Me_3SiH	**1b**	Me_3SiLi
2a	$PhMe_2SiH$	**2b**	$PhMe_2SiLi$
3a	Ph_2SiH_2	**3b**	Ph_2SiHLi
4a	Ph_2MeSiH	**4b**	$Ph_2MeSiLi$
5a	$(Me_3Si)_3SiH$	**5b**	$(Me_3Si)_3SiLi$

$$Ph_2SiH_2\ \mathbf{3a} + 1/2(Me_3SiLi)_2\ \mathbf{1b} =$$

$$1/2(Ph_2SiHLi)_2\ \mathbf{3b} + Me_3SiH\ \mathbf{1a} + 11.1\ \text{kcal/mol} \quad (2)$$

$$Ph_2SiH_2\ \mathbf{3a} + 1/2(PhMe_2SiLi)_2\ \mathbf{2b} =$$

$$1/2(Ph_2SiHLi)_2\ \mathbf{3b} + PhMe_2SiH\ \mathbf{2a} + 6.8\ \text{kcal/mol} \quad (3)$$

$$Ph_2MeSiH\ \mathbf{4a} + 1/2(Me_3SiLi)_2\ \mathbf{1b} =$$

$$1/2(Ph_2MeSiLi)_2\ \mathbf{4b} + Me_3SiH\ \mathbf{1a} + 5.9\ \text{kcal/mol} \quad (4)$$

$$Ph_2MeSiH\ \mathbf{4a} + 1/2(PhMe_2SiLi)_2\ \mathbf{2b} =$$

$$1/2(Ph_2MeSiLi)_2\ \mathbf{4b} + PhMe_2SiH\ \mathbf{2a} + 1.6\ \text{kcal/mol} \quad (5)$$

$$(Me_3Si)_3SiH\ \mathbf{5a} + 1/2(Me_3SiLi)_2\ \mathbf{1b} =$$

$$1/2[(Me_3Si)_3SiLi)_2\ \mathbf{5b} + Me_3SiH\ \mathbf{1a} + 10.8\ \text{kcal/mol} \quad (6)$$

Figure 3. Calculated free energy differences (B3LYP/6-311+G(*d, p*)(PCM:THF)//B3LYP/6-311+G(*d, p*)).

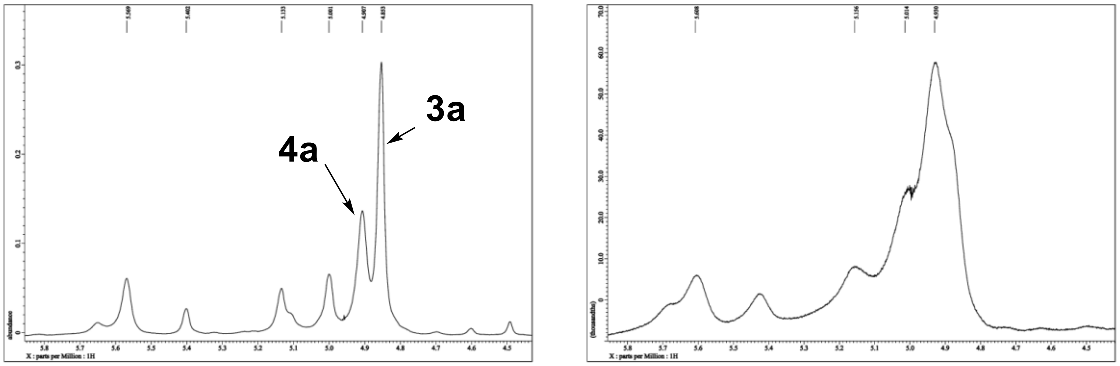
Disproportionation of diphenylsilane **3a** and trimethylsilyllithium **1b** to diphenylsilyllithium **3b** and trimethylsilane **1a** was calculated to be an exothermic reaction with ΔG = 11.1 kcal/mol (298.15 K, eq. 2). Use of dimethylphenylsilyllithium **2b** leads to ΔG = 6.8 kcal/mol (eq. 3). These values correspond to differences in pKa (ΔpKa) of 8.1 and 5.0, respectively. Interestingly, the energy difference at the equilibrium between tris(trimethylsilyl)silane **5a** with trimethylsilyllithium **1b** and trimethylsilane **1a** with tris(trimethylsilyl)silyllithium **5b** is ΔG = 10.8 kcal/mol (eq. 6). Thus, the silanes **3a** and **5a** have pKa values in almost the same range because there is a difference (ΔΔG(pKa)) of only 0.28 kcal/mol. Apeloig et al. reported that the pKa value of tris(trimethylsilyl)silane **5a** was 29.4[8]. Considering eqs. 3 and 6, the pKa values for **3a** and **4a** were estimated to be 29.2 and 33.4, respectively. Trimethylsilyllithium **1b** should be a far superior base than dimethylphenylsilyllithium **2b**. However, **2b** should still be a very good base for deprotonation.

Although the model is too preliminary to estimate the acidity of silanes under the reaction conditions, we can expect that considerable deprotonation of diphenylsilanes should occur by disproportionation with dialkylphenyl- and trialkylsilyllithiums. Dialkylphenylsilyllithiums are very easy to prepare. They only require mixing of the corresponding silyl halides and granular lithium in THF. We expected that we can control reactivity of the silyllithium base to the electrophiles. Increased steric bulkiness of alkyl group(s) in dialkylphenylsilyllithium should reduce reactivity to the electrophile, to improve the yields of the substituted products.

3. DISPROPORTIONATION EXPERIMENT WITH DIPHENYLSILANE AND TRIMETHYLSILYLLITHIUM

In a previous chapter, we discussed the possibility of deprotonation from diphenylsilane **3a** with a silyllithium agent due to the large difference in pKa. We examine this notion by using an NMR analysis.

Sakurai[13] reported that trimethylsilyllithium **1b** showed methyl groups at δ 0.21 ppm in toluene-d_8, prepared from bis(trimethylsilyl)mercury and Li, while those in **1b**·(THF)$_n$ were at -0.29 ppm in THF-d_8. Since the SiH signal for **3a** in $CDCl_3$ is reported to be δ 4.93, we expected that we would be able to distinguish them by ^1H NMR. In fact, we observed that diphenylsilane **3a** and diphenylsilyllithium **3b**, prepared from chlorodiphenylsilane and lithium[14], showed SiH peaks at δ 4.85 and 4.91 ppm in THF-d_8, respectively (Figure 4). However, considerable broadening of the peaks was observed when the measurements were performed at 0 °C.



(a)

(b)

Figure 4. Observed ^1H NMR spectra of a mixture of **3a** and **4a** prepared from chlorodiphenylsilane and Li in THF-d_8 in the presence of HMPA: (a) at rt and (b) at 0 °C.

We chose trimethylsilyllithium **1b** as the base. Preparation of **1b** was achieved in THF-d_8 by mixing hexamethyldisilane and MeLi in diethoxymethane (DEM) in the presence of HMPA.[15] Thus, there is a considerable amount of hexamethyldisilane and by-product of Me_4Si. Furthermore, there is a large amount of DEM and HMPA as solvents in the reaction mixture.

The ^1H NMR observation was impaired by the strong signals from these compounds. The signals for the methyl groups in trimethylsilane **1a**, trimethylsilyllithium **1b** and hexamethyldisilane are so close to each other that we gave up trying to estimate the consumption of **1b** based on a decrease in the methyl signal. On the other hand, observed ^1H NMR signals for the hydrido group in **3a** (at δ 4.96 ppm) and **3b** (at δ 4.98 ppm) were broadened by coupling from $^{6/7}Li$ and a low S/N ratio. Thus, we could confirm that diphenylsilyllithium was generated *in situ* by mixing of **1b** and **3a**. Although we observed a shoulder peak of **3a** when we introduced additional **3a** to the reaction mixture, we could not determine the time-dependence of the conversion of **3a** to **3b.** We evaluated disproportionation by an increase in the hydrido signal of **1a**, a decaplet observed at δ 3.95 ppm. Integration was measured relative to the methylene signal of DEM (Table 1 and Figure 5). The disproportionation should be a relatively fast process, since the reaction should be almost completed within 30 min.

Table 1. Time-dependence of ^1H NMR integration of **1a** (relative to CH_2 group in DEM as 100) in the disproportionation equilibrium between **1b** and **3a**.

Time/min	^1H integration of **1a**
(0)	(0)
30	2.47
40	2.51
60	2.66
75	2.72
90	2.81
105	2.83
120	2.87

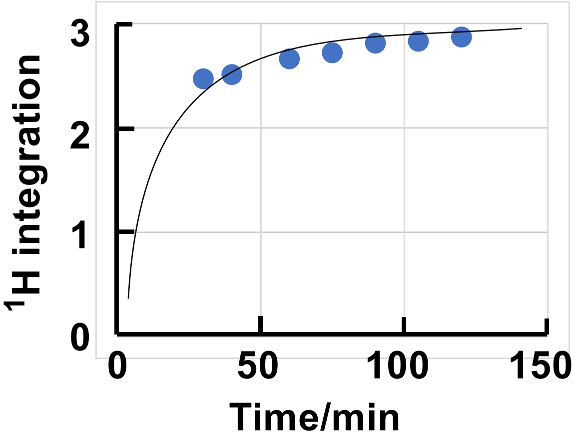


Figure 5. Time-dependence of ^1H NMR integration of **1a** in disproportionation equilibrium between **1b** and **3a**.

The change in integration should be well described by simple decay. Thus, our preliminary calculations showed a good direction to prove our ideas.

4. DEPROTONATION FROM DIPHENYLSILANE WITH (DIALKYLPHENYLSILYL)LITHIUMS AND THE INTRODUCTION OF SUBSTITUENTS WITH ELECTROPHILIC AGENTS

After we confirmed deprotonation from diphenylsilane with a silyllithium agent, we could expect that deprotonation should proceed cleanly to give the corresponding diphenylsilyllithiums. Gilman reported that diphenylsilyllithium could be prepared by reductive cleavage of 1,1,2,2-tetraphenyldisilane with lithium and, alternatively, reaction of chlorodiphenylsilane with lithium.[14] However, the corresponding diphenylsilyllithium reacted with chlorotriphenylsilane, only to give pentaphenyldisilane in low yields. In a previous chapter, we discussed the possibility of deprotonation from diphenylsilane **3a** with a silyllithium agent due to the large difference in pKa. Thus, we could expect that deprotonation should proceed cleanly to give the corresponding diphenylsilyllithiums. We investigated deprotonation with dialkylphenylsilyllithiums **2b**, **2ba** and **2bb** to confirm our idea experimentally (eq. 6). Dialkylphenylsilyllithiums **2ba** and **2bb** were prepared from the corresponding chlorosilanes and granular lithium in THF. Chlorodi-*i*-propylphenylsilane **6a** was prepared from di-*i*-propylphenylsilane **2aa** using a procedure similar to that used to prepare chlorodi-*t*-butylphenylsilane **6b** from di-*t*-butylphenylsilane **2ab**.[15]

Initially, we used dimethylphenylsilyllithium **2b** as a base. However, only a trace amount of the product was obtained, accompanied by a considerable amount of by-products. One of the main by-products was phenyltrimethylsilane, as determined by MS, which was produced by nucleophilic addition of dimethylphenylsilyllithium **2b** to iodomethane **7a**. We supposed that **2b** reacts with **7a** faster than bulky **3b** does. With consumption of **2b**, fast equilibrium would regenerate **2b** from **2a** and **3b**, which would lead to considerable production of phenyltrimethylsilane. Thus, we expected that an increase in the steric bulkiness of silyllithiums should suppress alkylation to a silyllithium base. We used di-*i*-propylphenylsilyl- **2ba** and di-*t*-butylphenylsilyllithium **2bb** for this purpose.

Diphenylsilane **3a** was treated with a slight excess of di-*i*-propylphenylsilyllithium **2ba** in THF at 0°C. After 2 h, iodomethane **7a** was introduced as an electrophile, and the reaction solution was then warmed to r.t. (eq. 7). Diphenylmethylsilane **4a** was obtained in 15% yield (Table 2).

$$Ph_2SiH_2\ \mathbf{3a} \xrightarrow{R_3SiLi} \left[\ Ph_2SiHLi\ \right] \xrightarrow{\text{electrophile } E^+} Ph_2ESiH\ \ \mathbf{4a},\ \mathbf{4aa\text{-}e} \qquad (7)$$

7a MeI
7b MeOTf
7c EtI
7d *n*-HexBr
7e *n*-OctBr
7f $PhCH_2Br$
7g AllylBr

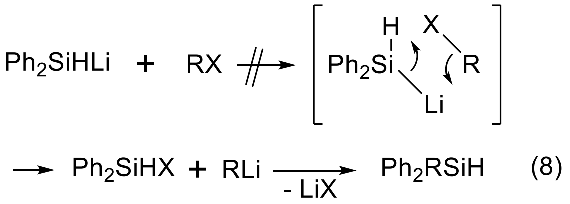
Table 2. Deprotonation of diphenylsilane 3a with (dialkylphenylsilyl)lithiums and reaction of the corresponding anion with electrophiles

silyllithiums	eq.	Temp./°C	Electrophile (eq.)	Product	Yield (%)
PhMe$_2$SiLi 2b	**1.2**	**0**	**MeI 7a (1.1)**	**4a (E = Me)**	**trace**
Ph(*i*-Pr)$_2$SiLi 2ba	**1.2**	**0**	**7a (1.3)**	**4a**	**15**
	1.2	**0**	**7a (1.3)[a]**	**4a**	**17**
	1.2	**-40**	**7a (1.3)**	**4a**	**17**
Ph(*t*-Bu)$_2$SiLi 2bb	**1.1**	**0**	**7a (1.1)**	**4a**	**30**
	2.0	**0**	**7a (3.0)**	**4a**	**31**
	1.2	**0**	**MeOTf 7b (1.3)**	**4a**	**13**
	1.2	**0**	**EtI 7c (1.3)**	**4aa (E = Et)**	**trace**

[a]HMPA (2.0 eq) was added.

With di-*t*-butylphenylsilyllithium **2bb**, the yield was considerably improved to 30%. However, the yield was still not sufficient. An excess of silyllithium and use of HMPA did not improve the yield.

We wondered if the introduction of an alkyl group could result in the initial exchange of lithium atom on the silyllithium with the leaving group of the alkylating agent to generate the corresponding alkyllithium, which attacks the silicon atom, releasing the leaving group (eq. 8). However, since the use of methyl triflate also resulted in methylation, in which the yield was still moderate, we assume that this exchange mechanism should be unlikely. We concluded that the use of bulky dialkylphenylsilyllithium could not further improve the yields.



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5. DEPROTONATION FROM DIPHENYLSILANE WITH TRIMETHYLSILYLLITHIUM AND INTRODUCTION OF SUBSTITUENTS WITH ELECTROPHILIC AGENTS

In the previous chapter, we used dialkylphenylsilyllithiums as a base, only to produce the corresponding product in low to fair yield. Thus, we further investigated the alkylation of diphenylsilane **3a** with more basic silyllithium agents.

We selected trimethylsilyllithium **1b**. Trimethylsilyllithium **1b** can be easily prepared *in situ* by the addition of hexamethyldisilane to MeLi in the presence of HMPA.[16] Thus, it should be less convenient than the use of dialkylphenylsilyllithiums. However, we can expect that trimethylsilyllithium **1b** should show greater basicity than phenylsilyllithiums due to a lack of conjugation, as confirmed by the theoretical calculations. Furthermore, trimethylsilane **1a** has a boiling point of ca. 6 °C at atmospheric pressure. Thus, it should be considerably removed from the system under the reaction conditions (stirring at 0 °C). The product yields should be considerably improved.

To a THF solution of trimethylsilyllithium **1b**, freshly prepared from hexamethyldisilane in THF with MeLi (DME solution) in the presence of HMPA[16,17], was introduced diphenylsilane **3a** in THF at 0 °C, followed by the corresponding electrophilic agent. Overall, the yield was considerably improved compared to the case of dialkylphenylsilyllithiums. We tried generation of **1b** using MeLi-LiBr complex in diethyl ether instead of MeLi in DME, to give almost the same results. When MeI **7a** was used as an electrophile, diphenylsilane **3a** was converted to diphenylmethylsilane **4a** in 67 % yield. Iodoethane **7c** was a superior electrophilic agent to afford the corresponding ethylated product **4aa** quantitatively. Alkyl halides with longer carbon chains still react. However, the yields were considerably lowered. We tested a variety of carbon electrophiles to confirm that the corresponding products were obtained in moderate to excellent yield.

In most cases, the yields are further improved with the reaction temperature at -10°C. Table 3 summarizes the results.

Table 3. Deprotonation of diphenylsilane 3a with trimethylsilyllithium 1b and reaction of the corresponding anions with electrophiles

silyllithium	Electrophile (eq.)	Product	Condition A[a] Yield (%)	Condition B[a] Yield(%)

Me_3SiLi 1b	**MeI 7a (1.3)**	**4a (E = Me)**	**67**	**89**
	EtI 7c (1.3)	**4aa (E = Et)**	**quant.**	**97**
	n-HexBr 7d (1.3)	**4ab (E = n-Hex)**	**57**	**89**
	n-OctBr 7e (1.3)	**4ac (E = n-Oct)**	**48**	**96**
	$PhCH_2Br$ 7f (1.3)	**4ad (E = $PhCH_2$)**	**28**	**42**
	AllylBr 7g (1.3)	**4ae (E = allyl)**	**73**	**67**

[a]Condition A: Use of 1.2 equiv. silyllithium; Reaction temp. 0°C, Condition B: Use of 1.2 equiv. silyllithium; Reaction temp. -10°C.

6. DEPROTONATION-ALKYLATION FROM ALKYLDIPHENYLSILANES

Deprotonation from methyldiphenylsilane **3a** is also possible. However, due to steric congestion of tertially substitution, alkylation with alkyl halides gave quite low yields. However, use of methyl triflate **7b** as an electrophile gave dimethyldiphenylsilane **8a** in a fair yield of 52% (eq. 9). Improved yield (57%) of **8b**[18] was achieved with ethyl triflate **7h**. Table 4 summarizes the results. We assume that the slow alkylation rate for tertially-substituted silyllithiums, lithium-halide exchange between silyllithiums and alkyl halides, and faster lithium-hydrogen exchange between the resulting silyllithiums and trimethylsilane lowered the yields of the corresponding products.

$$\mathrm{Ph_2MeSiH}\ \mathbf{4a} \xrightarrow[\text{2) E}^+]{\text{1) Me}_3\text{SiLi } \mathbf{1b}} \mathrm{Ph_2MeRSi}\ \mathbf{8} \quad (9)$$

$\mathbf{8a}$ R = Me
$\mathbf{8b}$ R = Et

Table 4. Deprotonation of **4a** followed by alkylation

Electrophile E^+	product	Yield(%)
MeI 7a	**8a**	**19**
MeOTf 7b		**52**
EtI 7c	**8b**	**16**
EtOTf 7h		**57**

7. CONCLUSION

Deprotonation from a silane is still a challenge. Normally, a Si-H bond has a polarity of Si(δ^+)-H(δ^-), so that the LUMO of σ^*_{SiH} has greater expansion on the Si atom. Thus, the anion attacks the Si atom, not hydrogen as a base for deprotonation, to give a silicate anion, followed by the elimination of a hydride to afford the substituted product.

We expected that a silane and a silyllithium could disproportionate in the reaction mixture, so that (some of) the silane should undergo deprotonation. The resulting silyl anion species are expected to react with the electrophilic agents.

We investigated diphenylsilane, which is known to be undeprotonated with bulky strong bases, such as *t*-BuLi and LDA. We evaluated the relative acidity by theoretical calculations to show that trimethylsilyllithium and dialkylphenylsilyllithium can deprotonate diphenylsilane.

We confirmed our idea experimentally. We believe this procedure can be useful for introducing substituents on silanes.

Supporting Information

The Supporting Information (Experimental procedures and ^{1}H, ^{13}C and ^{29}Si NMR charts, and the optimized structures, PDF) is available free of charge on the ACS Publications website.

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Author Contributions

All authors have approved this version of the manuscript.

Notes

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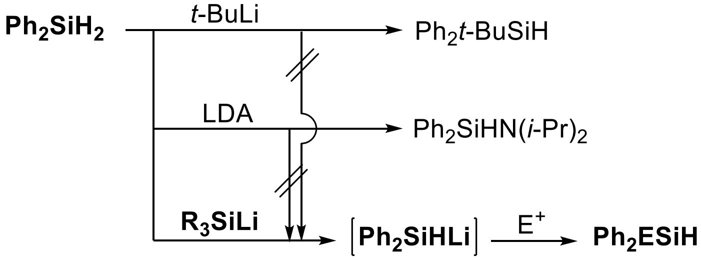

Deprotonation from a monosilane
and substitution with electrophiles

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