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Hydrogenation of Chlorosilanes by $NaBH_4$

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Hydrogenation of Chlorosilanes by $NaBH_4$

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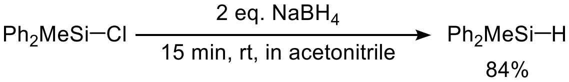
Hydrogenation of chlorosilane was achieved in acetonitrile using $NaBH_4$ being safe and easy to handle. This reaction converted Si-Cl portion(s) in organosilanes into Si-H portion(s) without hydrogenation of cyano, chloro, and aldehyde groups on an alkyl substituent of the Si reagents. In addition, the Si-Cl/Si-H exchange reaction was applicable to dichlorodisilane without Si−Si bond cleavage.

$LiAlH_4$ is one of the essential reagents for reduction of various chemicals.[1] However, the use of $LiAlH_4$ needs great care because of ignition and explosive nature. In addition, $LiAlH_4$ often causes undesired reduction at several functional groups.

Hydrosilane is known as a mild reducing reagent,[2] and therefore has been widely used as a starting compound in, for example, hydrosilylation,[3] C−H silylation[4] in order to obtain silyl-substituted organic compounds. Transition metal-, group 13 metal- and organo compound-catalyzed reactions using hydrosilane instead of $LiAlH_4$ as a reducing reagent have been developed toward alkyl halide,[5] aldehyde,[6] ketone,[7] ester,[8] amide,[9] epoxide,[10] nitro,[11,] CO_2,[12] nitrile,[7b, 8a, 13] etc. mainly from the safety reason. However, hydrosilane is generally prepared by hydrogenation of chlorosilane with $LiAlH_4$. Therefore, the use of hydrosilane in place of $LiAlH_4$ is not a basic solution for the purpose of avoiding the use of $LiAlH_4$. Now, safe and easy handling reagent for hydrogenation has been required. Sodium borohydride ($NaBH_4$) seems to be one of the candidates because it is a more handy reagent (much less risky than $LiAlH_4$). However, $NaBH_4$ has not been reported to hydrogenate chlorosilanes under normal conditions. Here, we describe the first example of preparation of hydrosilane from chlorosilanes using $NaBH_4$.

Diphenylmethylchlorosilane $Ph_2MeSiCl$ (0.5 mmol) was added dropwise to a suspension of $NaBH_4$ (1.0 mmol) in acetonitrile (0.5 mL) under nitrogen atmosphere, and the mixture was stirred at room temperature for 15 min (Scheme 1). After removal of the volatile materials under reduced pressure, *n*-hexane was added to the residue. The suspension was passed through a silica gel pad and removal of *n*-hexane under reduced pressure from the eluate afforded 84% of pure diphenylmethylhydrosilane Ph_2MeSiH. When the amount of $NaBH_4$ was reduced from 1.0 to 0.50 mmol, the yield of the product was diminished (65% isolated yield).[14]

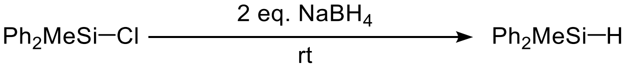


Scheme 1. Hydrogenation of $Ph_2MeSiCl$ by $NaBH_4$ in acetonitrile.

$$Ph_2MeSi{-}Cl \xrightarrow[\text{15 min, rt, in acetonitrile}]{\text{2 eq. }NaBH_4} Ph_2MeSi{-}H \quad 84\%$$

When THF was used instead of acetonitrile under the reaction conditions depicted in Scheme 1, the hydrogenation of chlorosilane took place although 5 h were needed to complete the reaction (Table 1, entry 2; 78% isolated yield). When the reaction was performed in other organic solvents such as toluene, dichloromethane and diethyl ether, the starting chlorosilane was not consumed at all (entries 3−5). The reaction under neat conditions also did not proceed (entry 6). Therefore, we believe that acetonitrile is the best solvent in this reaction and used it as a solvent hereafter.

Table 1. Solvent screening for the hydrogenation of chlorosilane by using $NaBH_4$.[a]



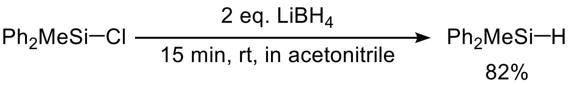
$$Ph_2MeSi{-}Cl \xrightarrow[\text{rt}]{\text{2 eq. }NaBH_4} Ph_2MeSi{-}H$$

Entry	Solvent	Reaction time /h	Isolated yield /%
1	acetonitrile	0.25	84
2	THF	5	78
3	Toluene	24	–
4	CH_2Cl_2	24	–
5	Et_2O	24	–
6	–	24	–

[a]Chlorosilane (0.5 mmol) and $NaBH_4$ (1.0 mmol) in 0.5 mL of an organic solvent.

In order to obtain insight into the role of the cation (Na^+), we examined the reaction using $LiBH_4$ instead of $NaBH_4$ under the conditions similar to those in entry 1 in Table 1; the reaction afforded the corresponding hydrosilane in 82% yield (Scheme 2). It strongly suggests that the cation in $[M][BH_4]$ does not play an important role in our reduction system.

Scheme 2. Reaction of $Ph_2MeSiCl$ with $LiBH_4$.



$$Ph_2MeSi{-}Cl \xrightarrow[\text{15 min, rt, in acetonitrile}]{\text{2 eq. }LiBH_4} Ph_2MeSi{-}H \quad 82\%$$

Next, several chlorosilanes were examined to explore the scope of our hydrogenation reaction (Table 2). The desired reaction proceeded effectively for mono and trichlorosilanes (entries 1−3 and 6). Dichlorosilanes were converted into the corresponding dihydrosilanes (entries 4 and 5). These yields were moderate, but the starting dichlorosilanes were completely consumed. In the reaction of Ph_2SiCl_2 with $NaBH_4$, the reduction of the amount of $NaBH_4$ from 4 equiv (Table 2, entry 4) to 2 equiv against Ph_2SiCl_2 revealed that the products were a mixture of Ph_2SiHCl and Ph_2SiH_2 (1.3:1 molar ratio). The results show no big difference in the reaction rate between the first and the second reductions.

Next, we examined the hydrogenation of chlorosilanes having a functional group such as a cyano, chloro, or aldehyde group on an alkyl substituent of the Si reagent (Table 3).[15] These groups are well-known to be reduced by $LiAlH_4$. It should be noted that these groups could tolerate the hydrogenation by $NaBH_4$ with hydrogenation of the Si−Cl portion.

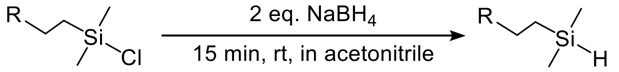
Table 2. Hydrogenation of chlorosilane by using $NaBH_4$.[a]

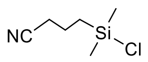
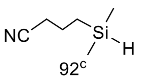
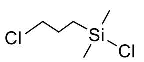
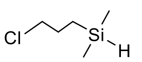
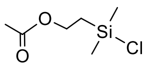
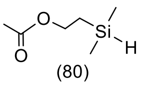
$$R_{4\text{-}n}SiCl_n \xrightarrow[\text{15 min, rt, in acetonitrile}]{2n\ eq.\ \mathrm{NaBH_4}} R_{4\text{-}n}SiH_n$$

Entry	Chlorosilane	Hydrosilane	Yield[b,c] /%
1	$Ph_2MeSiCl$	Ph_2MeSiH	84
2	Ph_3SiCl	Ph_3SiH	65
3	Et_3SiCl	Et_3SiH	(88)
4	Ph_2SiCl_2	Ph_2SiH_2	45
5	$(n\text{-}C_6H_{13})_2SiCl_2$	$(n\text{-}C_6H_{13})_2SiH_2$	54
6	$(PhC_2H_4)SiCl_3$	$(PhC_2H_4)SiH_3$	(82)

[a]Chlorosilane (0.5/*n* mmol) and $NaBH_4$ (1.0 mmol) in 0.5/*n* mL of acetonitrile. [b]Isolated yield. [c]Yield based upon ^1H NMR in parentheses.

Table 3. Hydrogenation of chlorosilane containing a functional group using $NaBH_4$.[a]



Entry	Substrate	Product, Yield[b] /%
1		 92[c]
2		 (81)
3		 (80)

[a]Chlorosilane (0.5 mmol) and $NaBH_4$ (1.0 mmol) in 0.5 mL of acetonitrile. [b]Yield based upon ^1H NMR in parentheses. [c]Isolated yield.

It was noteworthy that 1, 2−dichlorodisilane containing a Si−Si bond was also converted into the corresponding dihydrodisilane efficiently (Scheme 3) and no silyl compounds caused by Si-Si bond cleavage were detected. Moreover, monohydrogenated product ($HMe_2Si{-}SiMe_2Cl$) was not observed in the ^1H NMR spectrum. It should be noted in the reduction of an Si-Si bond containing compound that the quality of $NaBH_4$ is crucial for hydrogenation to occur, as $NaBH_4$ of lesser purity provided some undesired products.[15] The hydrogenation by $NaBH_4$ is expected to be a useful reduction method for polysilanes because a Si−Si bond being important in the field of materials chemistry remains intact.[16]

Scheme 3. Hydrogenation of 1,2−dichlorodisilane using $NaBH_4$ in acetonitrile.

$$ClMe_2Si{-}SiMe_2Cl \xrightarrow[\text{15 min, rt, in acetonitrile}]{\text{4 eq. NaBH}_4} HMe_2Si{-}SiMe_2H$$

72% (NMR yield)

In summary, we have developed a simple, efficient and safety reaction to access hydrosilanes from chlorosilanes. Moreover, some functionalized chlorosilanes can be converted into the corresponding hydrosilanes. The real reason why chlorosilanes can be converted into the corresponding hydrosilanes by $NaBH_4$ in acetonitrile is not clear at the moment. Further investigation of the reaction involving mechanistic consideration is in progress.

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