Hydrogenation of Chlorosilanes by NaBH₄

Masaki Ito, Masumi Itazaki, Takashi Abe, Hiroshi Nakazawa

Citation	Chemistry Letters, 45(12); 1434-1436
Issue Date	2016-10-13
Type	Journal Article
Textversion	Author
Supplementary	Supplementary file is available at https://doi.org/10.1246/cl.160808 .
Rights	© The Chemical Society of Japan. The following article has been accepted by Chemistry Letters. After it is published, it will be found at https://doi.org/10.1246/cl.160808
DOI	10.1246/cl.160808

Self-Archiving by Author(s)
Placed on: Osaka City University

Hydrogenation of Chlorosilanes by NaBH₄

Masaki Ito,¹ Masumi Itazaki,¹ Takashi Abe² and Hiroshi Nakazawa^{1*}

¹Department of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

²Advanced Materials Research Center, Nippon Shokubai Co., Ltd., 5-8 Nishi Otabi-cho, Suita, Osaka 564-8512, Japan

(Received <Month> <Date>, <Year>; CL-<No>; E-mail: <nakazawa@sci.osaka-cu.ac.jp>)

Hydrogenation of chlorosilane was achieved in acetonitrile using NaBH₄ 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 dichlorosilane without Si-Si bond cleavage.

LiAlH₄ is one of the essential reagents for reduction of various chemicals.¹ However, the use of LiAlH₄ needs great care because of ignition and explosive nature. In addition, LiAlH₄ 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 silylation⁴ in order to obtain silyl-substituted organic compounds. Transition metal-, group 13 metal- and organo compound-catalyzed reactions using hydrosilane instead of LiAlH₄ as a reducing reagent have been developed toward alkyl halide,⁵ aldehyde,⁶ ketone,⁷ ester,⁸ amide,⁹ epoxide,¹⁰ nitro,¹¹ CO₂,¹² nitrile,^{7b, 8a, 13} etc. mainly from the safety reason. However, hydrosilane is generally prepared by hydrogenation of chlorosilane with LiAlH₄. Therefore, the use of hydrosilane in place of LiAlH₄ is not a basic solution for the purpose of avoiding the use of LiAlH₄. Now, safe and easy handling reagent for hydrogenation has been required. Sodium borohydride (NaBH₄) seems to be one of the candidates because it is a more handy reagent (much less risky than LiAlH₄). However, NaBH₄ has not been reported to hydrogenate chlorosilanes under normal conditions. Here, we describe the first example of preparation of hydrosilane from chlorosilanes using NaBH₄.

Diphenylmethylchlorosilane Ph₂MeSiCl (0.5 mmol) was added dropwise to a suspension of NaBH₄ (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 Ph₂MeSiH. When the amount of NaBH₄ was reduced from 1.0 to 0.50 mmol, the yield of the product was diminished (65% isolated yield).¹⁴

Scheme 1. Hydrogenation of Ph₂MeSiCl by NaBH₄ in acetonitrile.

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 NaBH₄.^a

$\text{Ph}_2\text{MeSi-Cl} \xrightarrow[\text{rt}]{2 \text{ eq. NaBH}_4} \text{Ph}_2\text{MeSi-H}$			
Entry	Solvent	Reaction time /h	Isolated yield /%
1	acetonitrile	0.25	84
2	THF	5	78
3	Toluene	24	–
4	CH ₂ Cl ₂	24	–
5	Et ₂ O	24	–
6	–	24	–

^aChlorosilane (0.5 mmol) and NaBH₄ (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 LiBH₄ instead of NaBH₄ 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][BH₄] does not play an important role in our reduction system.

Scheme 2. Reaction of Ph₂MeSiCl with LiBH₄.

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

$\text{R}_{4-n}\text{SiCl}_n \xrightarrow[15 \text{ min, rt, in acetonitrile}]{2n \text{ eq. NaBH}_4} \text{R}_{4-n}\text{SiH}_n$			
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	$(n\text{-C}_6\text{H}_{13})_2\text{SiCl}_2$	$(n\text{-C}_6\text{H}_{13})_2\text{SiH}_2$	54
6	$(\text{PhC}_2\text{H}_4)\text{SiCl}_3$	$(\text{PhC}_2\text{H}_4)\text{SiH}_3$	(82)

^aChlorosilane (0.5/ n mmol) and NaBH_4 (1.0 mmol) in 0.5/ n mL of acetonitrile. ^bIsolated yield. ^cYield based upon ^1H NMR in parentheses.

Table 3. Hydrogenation of chlorosilane containing a functional group using NaBH_4 .^a

$\text{R}-\text{Si}(\text{Cl})(\text{Me})_2 \xrightarrow[15 \text{ min, rt, in acetonitrile}]{2 \text{ eq. NaBH}_4} \text{R}-\text{Si}(\text{H})(\text{Me})_2$		
Entry	Substrate	Product, Yield ^b / %
1		 92 ^c
2		 (81)
3		 (80)

^aChlorosilane (0.5 mmol) and NaBH_4 (1.0 mmol) in 0.5 mL of acetonitrile. ^bYield based upon ^1H NMR in parentheses. ^cIsolated yield.

It was noteworthy that 1, 2-dichlorodisilane containing a Si-Si bond was also converted into the corresponding dihydrosilane efficiently (Scheme 3) and no silyl compounds caused by Si-Si bond cleavage were detected. Moreover, monohydrogenated product ($\text{HMe}_2\text{Si-SiMe}_2\text{Cl}$) 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.

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.

This work was supported by a Challenging Exploratory Research Grant (No. 15K13662), a Grant-in-Aid for Science Research Japan (C) (No. 16K05728), a Grant-in-Aid for Scientific Research on Innovative Area “Stimuli-responsive Chemical Species for the Creation of Function Molecules (No. 2408)” (JSPS KAKENHI Grant Number JP15H00957) from MEXT Japan and the Sasakawa Scientific Research Grant from The Japan Science Society.

References and Notes

- 1 a) *SYNTHETIC REAGENTS Volume 1, Lithium Aluminium Hydride* ed. by J. S. Pizey, John Wiley & Sons, 1974, 104. b) *Reductions in Organic Chemistry* ed. by M. Hudlicky, John Wiley & Sons, 1984.
- 2 a) Y. Nagai, *Org. Prep. Proced. Int.* **1980**, 12, 13. b) G. L. Larson, J. L. Fry, *Org. React.* **2008**, 71, 1.
- 3 a) B. Marciniec, *Coord. Chem. Rev.* **2005**, 249, 2374. b) B. Marciniec, J. Guliński, W. Urbaniak, Z. W. Kornetka, in *Comprehensive Handbook on Hydrosilylation* ed. by Pergamon, Oxford, **1992**. c) A. K. Roy, *Adv. Organometal. Chem.* **2008**, 55, 1.
- 4 Recent reviews of silylation using hydrosilane: a) C. Cheng, J. F. Hartwig, *Chem. Rev.* **2015**, 115, 8946. b) Q.-A. Chen, H. F. T. Klare, M. Oestreich, *Chem. Rev.* **2016**, 138, 7868.
- 5 For examples, see: a) K. Miura, M. Tomita, Y. Yamada, A. Hosomi, *J. Org. Chem.* **2007**, 72, 787. b) G. Meier, T. Braun, *Angew. Chem. Int. Ed.* **2009**, 48, 1546. c) T. Stahl, H. F. Klare, M. Oestreich, *ACS Catal.* **2013**, 3, 1578. and references therein. d) Z. Chen, C.-Y. He, Z. Yin, L. Chen, Y. He, X. Zhang, *Angew. Chem. Int. Ed.* **2013**, 52, 5813.
- 6 For examples, see: a) Z. Li, G. Deng, Y.-C. Li, *Synlett* **2008**, 3053. b) N. Sakai, Y. Nonomura, R. Ikeda, T. Konakahara, *Chem. Lett.* **2013**, 42, 489. b) J. Zheng, C. Darcel, J.-B. Sortais, *Catal. Sci. Technol.* **2013**, 3, 81. c) S. R. Roy, S. C. Sau, S. K. Mandal, *J.*

- Org. Chem.* **2014**, *79*, 9150. d) B. Chatterjee, C. Gunanathan, *Chem. Commun.* **2014**, *50*, 888.
- 7 For more recent examples, see: a) T. Bleith, H. Wadepohl, L. H. Gade, *J. Am. Chem. Soc.* **2015**, *137*, 2456. b) M. Pérez, Z.-W. Qu, C. B. Caputo, V. Podgorny, L. J. Hounjet, A. Hansen, R. Dobrovetsky, S. Grimme, D. W. Stephan, *Chem. Eur. J.* **2015**, *21*, 6491. c) T. T. Metsänen, D. Gallego, T. Szilvási, M. Driess, M. Oestreich, *Chem. Sci.* **2015**, *6*, 7143. d) M. Szewczyk, F. Stanek, A. Bezlada, J. Mlynarski, *Adv. Synth. Catal.* **2015**, *357*, 3727. e) S. Hosokawa, K. Teramoto, Y. Motoyama, *ChemistrySelect*, **2016**, *1*, 2594. f) T. C. Jung, G. Argouarch, P. van de Weghe, *Catal. Commun.* **2016**, *78*, 52.
- 8 For recent examples, see: a) D. Addis, S. Das, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2011**, *50*, 6004. and references therein. b) D. Bézier, G. T. Venkanna, L. C. M. Castro, J. Zheng, T. Roisnel, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* **2012**, *354*, 1879. c) C. Chen, M. Brookhart, *Angew. Chem. Int. Ed.* **2012**, *51*, 9422. d) S. Das, Y. Li, K. Junge, M. Beller, *Chem. Commun.* **2012**, *48*, 10742. e) H. Li, L. C. M. Castro, J. Zheng, T. Roisnel, V. Dorcet, J.-B. Sortais, C. Darcel, *Angew. Chem. Int. Ed.* **2013**, *52*, 8045. f) F. A. Westerhaus, B. Wendt, A. Dumrath, G. Wienhöfer, K. Junge, M. Beller, *ChemSusChem* **2013**, *6*, 1001. g) O. O. Kovalenko, H. Adolfsson, *Chem. Eur. J.* **2014**, *21*, 2785.
- 9 For more recent examples, see: a) O. O. Kovalenko, A. Volkov, H. Adolfsson, *Org. Lett.* **2015**, *17*, 446. b) S. Das, Y. Li, C. Bornschein, S. Pisiewicz, K. Kiersch, D. Michalik, F. Gallou, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2015**, *54*, 12389. c) P.-Q. Huang, Q.-W. Lang, Y.-R. Wang, *J. Org. Chem.* **2016**, *81*, 4235. d) F. Tinnis, A. Volkov, T. Slagbrand, H. Adolfsson, *Angew. Chem. Int. Ed.* **2016**, *55*, 4562. e) S. Das, Y. Li, L.-Q. Lu, K. Junge, M. Beller, *Chem. Eur. J.* **2016**, *22*, 7050. f) J. Pesti, G. L. Larson, *Org. Process Res. Dev.* **2016**, *20*, 1164. and references therein.
- 10 a) H. Nagashima, A. Suzuki, T. Iura, K. Ryu, K. Matsubara, *Organometallics* **2000**, *19*, 3579. b) S. Park, M. Brookhart, *Chem. Commun.* **2011**, *47*, 3643.
- 11 For recent examples, see: a) L. Pehlivan, E. Métay, S. Laval, W. Dayoub, P. Demonchaux, G. Mignani, M. Lemaire, *Tetrahedron Lett.* **2010**, *51*, 1939. b) L. Pehlivan, E. Métay, S. Laval, W. Dayoub, P. Demonchaux, G. Mignani, M. Lemaire, *Tetrahedron* **2011**, *67*, 1971. c) S. Park, I. S. Lee, J. Park, *Org. Biomol. Chem.* **2013**, *11*, 395. d) M. Sutter, L. Pehlivan, R. Lafon, W. Dayoub, Y. Raoul, E. Métay, M. Lemaire, *Green Chem.* **2013**, *15*, 3020. e) N. Sakai, S. Asama, T. Konakahara, Y. Ogiwara, *Synthesis* **2015**, *47*, 3179. f) D. Porwal, M. Oestreich, *Eur. J. Org. Chem.* **2016**, 3307.
- 12 For recent examples, see: a) F. J. Fernández-Alvarez, A. M. Aitani, L. A. Oro, *Catal. Sci. Technol.* **2014**, *4*, 611. and references therein. b) M. L. Scheuermann, S. P. Semproni, I. Pappas, P. J. Chirik, *Inorg. Chem.* **2014**, *53*, 9463. c) T. T. Metsänen, M. Oestreich, *Organometallics* **2015**, *34*, 543. d) K. Motokura, M. Naijo, S. Yamaguchi, A. Miyaji, T. Baba, *Chem. Lett.* **2015**, *44*, 1217. e) Z. Lu, H. Hausmann, S. Becker, H. A. Wegner, *J. Am. Chem. Soc.* **2015**, *137*, 5332. f) S. Bontemps, *Coord. Chem. Rev.* **2016**, *308*, 117. and references therein. g) J. Chen, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 5321.
- 13 a) S. Das, B. Wendt, K. Möller, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2012**, *51*, 1662. b) C. Bornschein, S. Werkmeister, K. Junge, M. Beller, *New J. Chem.* **2013**, *37*, 2061. c) S. Laval, W. Dayoub, L. Pehlivan, E. Métay, D. Delbrayelle, G. Mignani, M. Lemaire, *Tetrahedron Lett.* **2014**, *55*, 23. d) M. Ito, M. Itazaki, H. Nakazawa, *ChemCatChem* **2016** accepted (DOI: 10.1002/cctc.201600940R1).
- 14 When 0.5 mmol NaBH₄ was used, the chlorosilane was not consumed completely and some unidentified signals in the ¹H NMR spectrum of the reaction mixture were observed.
- 15 Supporting Information is also available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- 16 R. D. Miller, J. Michl, *Chem. Rev.* **1989**, *89*, 1359.

NOTE The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge.

For publication, electronic data of the colored G.A. should be submitted. Preferred data format is EPS, PS, CDX, PPT, and TIFF.

If the data of your G.A. is "bit-mapped image" data (not "vector data"), note that its print-resolution should be 300 dpi.

You are requested to put a brief abstract (50-60 words, one paragraph style) with the graphical abstract you provided, so that readers can easily understand the graphic shows.

Graphical Abstract	
Textual Information	
A brief abstract (required)	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.
Title(required)	Hydrogenation of Chlorosilanes by NaBH_4
Authors' Names(required)	Masaki Ito, Masumi Itazaki, Takashi Abe and Hiroshi Nakazawa
Graphical Information	