Synthesis of Organofunctional Silicon Hydride Halides from Methylchlorosilane

Michael N. Missaghi,[†] Christopher M. Downing,[‡] Mayfair C. Kung,[†] and Harold H. Kung*,[†]

Departments of Chemical and Biological Engineering and Chemistry, Northwestern University, Evanston, Illinois 60208-3120

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Summary: The organofunctional silicon hydride halides R(CH₃)SiHCl were prepared in high yields from CH₃SiHCl₂, employing CH₃SiH₂Cl as an intermediate. CH₃SiHCl₂ was converted to CH₃SiH₂Cl by chloride−hydride redistribution in 41% yield (based on Si−H). The chloride substituent in CH₃SiH₂Cl reacted selectively with the Grignard reagent RMgX to form the corresponding dihydride R(CH₃)SiH₂, where R = H₂C═CH−, H₂C═C(CH₃)−, H₂C═CHCH₂−, (CH₃)₂CH−, H₂C═CHCH₂CH₂−, c-C₅H₉−, PhCH₂−, and p-Cl(C₆H₄)−. Cl(CH₂)₃(CH₃)SiH₂ was also prepared by reduction of the corresponding dichloride. Monohalogenation of R(CH₃)SiH₂ with CuCl₂/CuI in THF then gave CH₃RSiHCl in 60−88% overall yield (starting from CH₃SiH₂Cl).

Organofunctional siloxane materials have found a wide range of applications as adhesives,[1] biocompatible coatings,[2] composites and resins for microelectronics,[3] and acid−base bifunctional catalysts.[4,5] Generally, these polymers are produced by hydrolysis of chlorosilane or alkoxysilane precursors and homofunctional condensation of the resulting silanediols.[6] This method, while simple and inexpensive, does not permit synthesis of atomically defined siloxane oligomers or cyclic compounds, which requires silane monomers with functional groups of different reactivities.[7,8] An example of such a monomer is R(CH₃)SiHCl. The chloride ligand is a better leaving group than hydride, permitting stepwise addition of individual monomeric units to an oligomer in a manner similar to peptide synthesis.[9] In addition, R(CH₃)SiHCl can terminate polymer chains with retention of Si−H under mild polymerization conditions. The terminal hydride can then be utilized in postsynthesis modifications, such as hydrosilylation cross-linking.[10]

Although numerous examples of R(CH₃)SiHCl are known, only (CH₃)₂SiHCl and CH₃(C₆H₅)SiHCl are commercially available. Therefore, a general synthesis technique for these compounds, practical on both large and small scales, would be of great value in exploring the structure and reactivity of the corresponding oligomers and polymers. The most common synthesis procedure described in the literature is the slow addition of 1 equiv of RMgX to CH_3SiHCl_2, followed by fractional distillation of the product mixture.[11] While this is satisfactory for bulky R groups, the degree of substitution for unhindered R groups is difficult to control, and fractional distillation of the moisture-sensitive products is problematic, especially in small-scale preparations.[12] Here we report a versatile and scalable method to prepare R(CH₃)SiHCl.

Our method capitalizes on the fact that hydrides are poor leaving groups for Grignard substitution at Si, such that $CH_3SiH_xCl_{3-x}$ reacts with excess RMgX to form the organomethylsilane $R_{3-x}(CH_3)SiH_x$ selectively. Together with the electron-withdrawing effect of successive halogenations at Si that strongly favors monohalogenation, R(CH₃)SiH₂ (i.e., $x = 2$) could then be monohalogenated by a variety of techniques to obtain the desired R(CH₃)SiHCl. This general approach has been reported in the literature[13] but has not been widely utilized for the synthesis of R(CH₃)SiHCl, presumably due to the unavailability of CH_3SiH_2Cl.

Methylchlorosilane can be prepared using the well-known H/Cl redistribution of CH_3SiHCl_2, catalyzed by ca. 1% tetrabutylammonium chloride,[14] according to reactions 1 and 2.

$$2CH_3SiHCl_2 \rightleftarrows CH_3SiCl_3 + CH_3SiH_2Cl \quad (1)$$

$$2CH_3SiH_2Cl \rightleftarrows CH_3SiHCl_2 + CH_3SiH_3 \quad (2)$$

The low equilibrium concentration of CH_3SiH_2Cl (ca. 13 mol %[15]) in these redistribution reactions creates a significant challenge in product isolation and ordinarily limits the yield to 26 mol % (based on Si−H). To overcome these limitations, we studied the redistribution kinetics by ^{1}H NMR with the objective of shifting the equilibrium toward the desired product. A mixture of 0.8 g of CH_3SiHCl_2, 0.2 g of toluene-d_8, and 11 mg of Bu_4NCl (as catalyst) at 39 °C exhibited a $t_{1/2}$ value of 91 min for the conversion of CH_3SiHCl_2, while at 58 °C the process occurred twice as rapidly. Also, the redistribution rate was found to be first order in catalyst. Thus, by performing the redistribu-

* To whom correspondence should be addressed. E-mail: hkung@northwestern.edu.
[†] Department of Chemical and Biological Engineering.
[‡] Department of Chemistry.

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Table 1. Synthesis of $R(CH_3)SiH_2$ (1) and $R(CH_3)SiHCl$ (2) from Methylchlorosilane

		$R(CH_3)SiH_2$ (**1**)		$R(CH_3)SiHCl$ (**2**)	
compd	R	yield (%)[a]	^{29}Si NMR (δ, ppm)	yield (%)[a]	^{29}Si NMR (δ, ppm)
1a, 2a	vinyl	93 (78)	−39.9	81 (39)	0.9
1b, 2b	isopropenyl	93 (43)	−36.1	67 (30)	3.6
1c, 2c	allyl	78 (67)	−33.9	77 (59)	9.7
1d, 2d	isopropyl	92 (65)	−23.5	89 (38)	17.5
1e, 2e	3-butenyl	96 (47)	−33.0	92 (61)	13.4
1f, 2f	cyclopentyl	89 (65)	−28.3	92 (62)	14.6
1g, 2g	benzyl	(93)	−31.0	(67)	10.5
1h, 2h	4-chlorophenyl	(91)	−35.2	(93)	3.4
1i, 2i	3-chloropropyl[b]	86 (65)	−33.0	86 (48)	13.5

[a] Yields without parentheses are those of the THF product solutions, as determined by ^{1}H NMR with an internal standard. Yields in parentheses are those of isolated products. [b] Dihydride **1i** was prepared by reduction of (3-chloropropyl)dichloromethylsilane with lithium aluminum hydride; **2i** was prepared by the usual method.

tion reaction in the boiling flask of a fractional distillation apparatus, the continuous withdrawal of the lighter components (CH_3SiH_2Cl and CH_3SiH_3) gives a reasonable yield of CH_3SiH_2Cl. Redistribution is further accelerated as the residue boiling point increases and the catalyst becomes more concentrated. Indeed, by distilling slowly at atmospheric pressure under N_2, a 70% yield of crude CH_3SiH_2Cl (based on Si−H) was achieved from a 121 g batch of CH_3SiHCl_2 (27 g of CH_3SiH_2Cl, using 1 g of Bu_4NCl). Further purification of the obtained product by distillation gave 17.4 g of highly pure CH_3SiH_2Cl (41% yield). Methylchlorosilane can be handled as a refrigerated liquid (bp 8−9 °C), as a compressed liquid stored under its ca. 20 psig of vapor pressure at room temperature, or as a solution in THF. Methylsilane can form an explosive mixture with air (the flammability range is 1.3−88.9 vol % in air) and should be handled carefully. In our synthesis procedure, methylsilane generated during the redistribution was significantly diluted with a N_2 purge from the redistillation apparatus into the vent, away from spark and heat sources.

A wide variety of Grignard reagents react selectively with CH_3SiH_2Cl to form the corresponding organomethylsilanes **1a-h** (Table 1, column 2), according to reaction 3.

$$CH_3SiH_2Cl + RMgX \rightarrow \underset{\mathbf{1a-h}}{R(CH_3)SiH_2} + RMgClX \quad (3)$$

$$R = H_2C{=}CH- \ (\mathbf{a}),\ \ H_2C{=}(CH_3)- \ (\mathbf{b}),$$
$$H_2C{=}CHCH_2- \ (\mathbf{c}),\ \ (CH_3)_2CH- \ (\mathbf{d}),$$
$$H_2C{=}CHCH_2CH_2- \ (\mathbf{e}),\ \ c\text{-}C_5H_9- \ (\mathbf{f}),$$
$$PhCH_2- \ (\mathbf{g}),\ \ p\text{-}Cl(C_6H_4)- \ (\mathbf{h})$$

Only the chloride group was substituted, regardless of the specific Grignard reagent used; the hydride group remained unaffected under these conditions. For the more volatile products (bp_{760} <140 °C), simple vacuum transfer was sufficient to disengage product and solvent from the nonvolatile salts (MgClX and excess RMgX), and the products were then isolated from THF by binary fractional distillation. The isolated yields depended strongly on the boiling point separation between product and solvent. Isolation of less volatile products was accomplished by preliminary evaporation of THF, followed by water workup with a pH 6.8 buffer, extraction into petroleum ether, and evaporation to remove solvents. The molar yields after purification are shown in column 3 of Table 1 and were comparable for the two workup procedures when fractional distillation was carried out on a relatively large scale (>3 g) and with a low-holdup distillation column.

Monochlorination of polyhydridosilanes has been reported with $SnCl_4$,[16] $PhCH_2Cl/Pd$,[17] and a variety of other reagents[18] with varying selectivity. Here, the $CuCl_2/CuI$ system originally reported by Kunai et al.[19−21] was employed to monochlorinate $R(CH_3)SiH_2$. The reaction was found to proceed in THF (200/1 $CuCl_2/CuI$, 25 °C) according to reaction 4.

$$2CuCl_2 + \underset{\mathbf{1a-i}}{R(CH_3)SiH_2} \rightarrow 2CuCl + \underset{\mathbf{2a-i}}{R(CH_3)SiHCl} + HCl \quad (4)$$

$$R = Cl(CH_2)_3- (\mathbf{i})$$

The CuCl byproduct formed a white precipitate, and a full 1 equiv of HCl was observed as a broad singlet in ^{1}H NMR (THF-d_8). In all cases, the monochlorinated product was formed in high yield in less than 2 h (Table 1, column 5), as long as the molar ratio of $CuCl_2$ to $R(CH_3)SiH_2$ was controlled to avoid dichlorination. These results establish the functional-group tolerance of the $CuCl_2/CuI$ reagent toward a variety of olefins, alkyl halides, and Si−C linkages. As before, the volatile hydride halides were obtained as THF solutions by vacuum transfer, although the HCl byproduct was also transferred quantitatively to the receiving flask. Fractional distillation of $R(CH_3)SiHCl$ was found to be considerably more difficult than that of $R(CH_3)SiH_2$, due to moisture sensitivity and stronger intermolecular interaction with solvent, although all products were eventually isolated in 92−98% purity. For higher boiling products, evaporation of THF followed by resuspension in diethyl ether, syringe filtration, and removal of solvents gave the isolated products in the yields shown in Table 1.

The ^{29}Si NMR spectra of $R(CH_3)SiH_2$ and $R(CH_3)SiHCl$ are highly sensitive to the shielding characteristics of the organic substituents.[22] Electron-rich substituents, such as vinyl and isopropenyl, shift the ^{29}Si resonance significantly upfield relative to the isopropyl and cyclopentyl homologues. In all cases, replacement of H by Cl was accompanied by a downfield shift of 41−46 ppm. The conversion of Si from an achiral (SiH_2) to a chiral (SiHCl) center sometimes produced an observable nonequivalence in the NMR peaks of the organic substituent, as seen in the ^{13}C NMR spectra for (*i*-Pr)CH_3SiH_2 (two *i*-Pr

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^{13}C peaks in a 2/1 integral ratio) and (*i*-Pr)CH_3SiHCl (three *i*-Pr ^{13}C peaks in a 1/1/1 ratio). Control of the absolute configuration of Si centers in silanes and siloxanes, which remains an elusive goal due to the greater ease of racemization (e.g., by pseudorotation) for Si versus C, could be attempted through stereoinduction during the halogenation step, although a suitable reagent has yet to be identified.

Methylchlorosilane has previously been employed as a hydrosilylation agent to form $R(CH_3)SiHCl$ from the corresponding olefin substrate.[23] However, in our preliminiary experiments CH_3SiH_2Cl was found to poison Karstedt's catalyst upon addition to the reaction mixture (forming a soluble yellow complex), necessitating the use of high temperatures and long reaction times (70−80 °C for 16 h). A similar behavior has been noted previously for dichlorosilane.[24] These harsh reaction conditions often induce side reactions with functionalized olefins, such as allyl chloride.[25] We examined an alternative route, involving reduction of commercially available (3-chloropropyl)dichloromethylsilane with $LiAlH_4$,[26] followed by monohalogenation with $CuCl_2$/CuI. While this approach led to the successful preparation of 3-(chloropropyl)chloromethylsilane, direct hydrosilylation of methylchlorosilane is preferred when the desired functionality is sensitive to strong reducing agents.

In summary, we have described a method to produce $R(CH_3)SiHCl$ that employs commercially available starting materials (CH_3SiHCl_2, RMgX, and $CuCl_2$/CuI) and exhibits good reproducibility and high overall yield (average of 74% from CH_3SiH_2Cl before distillation), for which purification from nonvolatile byproducts is straightforward. Employing reactive fractional distillation to overcome the equilibrium-limited yield of CH_3SiH_2Cl makes the method even more productive in both laboratory and industrial settings. Although organomagnesium halides are incompatible with most protic and carbonyl-containing substituents, a variety of pro-functional groups can be incorporated into $R(CH_3)SiHCl$, as shown in Table 1. In particular, the olefin- and halogen-functional monomers are of use in the preparation of multifunctional organosiloxanes, since these groups can easily be transformed into coordination sites.[27] The utilization of $R(CH_3)SiH_2$ as an intermediate creates other synthetic possibilities, such as the preparation of $R(CH_3)SiHBr$ from $CuBr_2$/CuI[28] or of $R(CH_3)Si(OH)_2$ by catalytic oxidation with H_2O over Pd/C.[29] Since dichlorination proceeds rapidly in most cases, $R(CH_3)SiCl_2$ can also be prepared selectively via $R(CH_3)SiH_2$, as an alternative to adding 1 equiv of RMgX to CH_3SiCl_3.

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Supporting Information Available: Text giving experimental procedures and product characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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