

Utility of trichloroisocyanuric acid in the efficient chlorination of silicon hydrides

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Received 13 December 2006; received in revised form 21 December 2006; accepted 22 December 2006

Available online 9 January 2007

Abstract

The potential of trichloroisocyanuric acid (TCCA) as a chlorination agent for efficient conversion of Si–H functional silanes and siloxanes to the corresponding Si–Cl functional moieties was explored. In comparison to methods using other chlorinating agents, TCCA is inexpensive, results in a much faster reaction and produces a high purity product with a conversion that is essentially quantitative. A variety of chloro derivatives of linear and cyclic structures have been synthesized from silicon hydrides using this reagent with impressive yields that typically exceed 90%: PhSiCl₃ (97.5%); PhMeSiCl₂ (95.5%); Ph₃SiCl (97.5%); Vi₃SiCl (98.7%); (EtO)₃SiCl (99.7%); *t*-Bu₃SiCl (~100%); (MeClSiO)₄ (86.5%); (MeClSiO)₅ (95%); (MeClSiO)₇ (96.5%); Ph(OEt)₂SiCl (98%); ClMe₂SiOSiMe₂Cl (98.6%); ClMe₂SiO–SiMeClOSiMe₂Cl (94.6%); ClMe₂Si(OSiMeCl)₂OSiMe₂Cl (92.3%); (Me₃SiO)₃SiCl (97%); Me₃SiOSiClPhOSiMe₃ (99%); Me₃SiO(SiMeClO)₃SiMe₃ (95.7%); ClSi(OSiMe₃)₂OSi(OSiMe₃)₂Cl (93.6%).

For monohydrosilanes, dichloromethane (CH₂Cl₂) was a suitable solvent in which nearly quantitative conversion was observed within several minutes following the addition of the silanes to TCCA. For certain cyclic and linear siloxanes, and especially silanes containing multiple hydrogen atoms on the same silicon for which the reaction is sluggish in CH₂Cl₂, tetrahydrofuran (THF) was the preferred solvent. For a sterically demanding silane that did not undergo chlorination even in THF viz., HSi(OSiMe₃)₂O–Si(OSiMe₃)₂H, 1,2-dichloroethane was the best solvent.

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Keywords: Synthesis of chlorosilanes; Siliconhydrides; Trichloroisocyanuric acid; TCCA

1. Introduction

Among the organosilicon compounds, chlorosilane materials are the most frequently used for a variety of functional group transformations. Reactions involving nucleophilic attack by water, alcohols, organic acids, metallic oxides or organometallic reagents have been used in the synthesis of numerous substituted products. For example, introduction of a radioactive ¹⁴C-methyl group into organosilicon compounds is almost always accomplished by reaction of chlorosilanes with ¹⁴C-labeled methyl Grignard reagents [1a,1b]. The resulting ¹⁴C-labeled siloxanes

(for example, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, hexamethyldisiloxane, poly(dimethylsiloxanes) of various viscosities, etc.) are routinely utilized as tracers in environmental and toxicological investigations [2–10].

One of the common methods used to synthesize chlorosilanes of interest is via the silicon hydrides. Various chlorinating agents are used to transform the Si–H bond to Si–Cl: Cl₂, HCl, acetylchloride, phosphorous trichloride, allyl chloride in presence of activated charcoal on palladium etc [11a,11b,11c]. The draw backs in using these chlorinating agents can arise from one or more of the following: low yield, difficulty in handling the reagent, tedious workup procedures to obtain pure product.

In this context, the use of chloroimides was investigated. The driving force was the need to develop an efficient reaction involving a simple clean up procedure following the

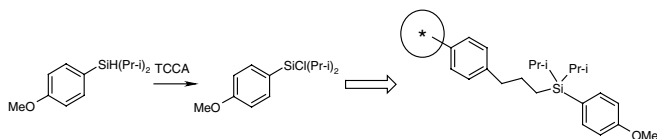
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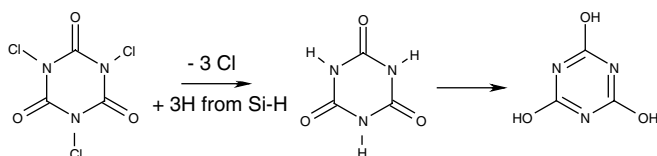
reaction which required just a filtration to remove the insoluble byproduct. Two chloroimides, *N*-chlorosuccinimide (NCS) and trichloroisocyanuric acid (TCCA) were investigated. We demonstrated that TCCA worked the best as a chlorinating agent transforming silicon hydrides to the chloro derivatives.

Trichloroisocyanuric acid (TCCA) or 1,3,5-trichloro-1,3,5-2,4,6,-(1H,3H,5H)-trione, known since 1902, belongs to the large group of chloroimides. TCCA is produced in large quantities (>100,000 t/year) and is used primarily as a disinfectant in swimming pools and water treatment. It is also used as a dishwashing additive in hotel and food services. TCCA is seldom used in organic synthesis. In fact, a review article in 2002 [12] on TCCA deplored the fact “TCCA has never had a real breakthrough in organic chemistry laboratories. It has not found a way into text books of organic chemistry”. The following synthetic applications of TCCA have been reported: chlorination of cyclic ethers [13], benzene [14], alkenes [15] and ketones, benzylic chlorination [16], oxidation of secondary alcohols [17,18], aldehydes [19], oximes [20] and ethers [21], hypo-halogenation of unsaturated ethers [13] and alkenes [17], cleavage of acetals [22] and, dehydrogenations of various *N*-heterocycles [23,24].

The review article mentioned above has no specific citation of the utility of TCCA in Si–H to Si–Cl conversion. However, a single reference was noted in a multistep synthesis of an alkylsilyl-tethered polystyrene resin where TCCA was used on an intermediate containing Si–H moiety to introduce a chlorine atom following the reaction shown below [25].



Neither the potential of TCCA in achieving multiple halogenation onto a single silicon atom nor its utility to halogenate oligomeric linear and cyclic siloxanes containing Si–H have been explored. The striking aspect of this reagent is that all the three chlorine atoms present have comparable reactivity and are equally and completely available for reaction. This unique feature is due to the achievement of the lower energy state resulting from aromatization following the substitution of all 3 chlorine atoms by hydrogen atoms.



The objective of the paper is to explore the utility and scope of TCCA in the transformation of silicon hydrides to the corresponding chlorosilanes, since the latter are needed to synthesize various functional siloxanes and especially radioactive ¹⁴C-siloxanes involving Grignard reagents.

2. Experimental

2.1. Instrumentation

The Gas Chromatography–Mass spectrometer system components were as follows: Hewlett-Packard (HP) 5890 series II gas chromatograph; HP 7683 GC/SFC injector; HP 5970 series Mass Selective Detector. GC–MS system was equipped with electronic pressure control units. Data analyses were performed using a Microsoft® Windows-based Enhanced ChemStation software G1701BA, version B01.00 GC–MS Acquisition parameters are as follows:

GC-oven: Initial temperature, 70 °C; Initial time, 3 min; Ramps: 1. Rate, 20.00 °C/min to a final temperature of 210 °C. Held at 210 °C for 5 min; Ramp 2: Rate, 20.00 °C/min to a final temperature of 250 °C. Held at 250 °C for 5 min.

GC-Inlet settings: Temperature, 250 °C; Purge flow, 1.0 mL/min; Purge gas, Helium; Constant flow, ON; Initial pressure, 7.3 psi at 70 °C; Linear velocity, 39.1 cm/sec; GC column, HP-5 (5% phenylmethylsilicone) from Hewlett Packard; Column length, 30 meters; Column id, 0.25 mm; Film thickness, 0.25 micron. MS Detector (HP 5970 MSD): Detector temperature, 280 °C; Scan mass *m/z*, 50–550.

Removal of solvent from the products was carried out using a rotary evaporator of the following specifications: Buchi Rotavapor: R-205 ; Buchi Vacuum controller: V-800 ; Buchi Heating Bath: B-490.

2.2. Materials

The following organosilanes were purchased from Gel-est: Ph₃SiH, V₃SiH, *t*-Bu₃SiH, and Ph(OEt)₂SiH. The silanes purchased from Aldrich Chemical Co are the following: PhSiH₃, PhMeSiH₂ and (Me₃SiO)₃SiH. The following were available from Dow Corning Corporation: (MeHSiO)₄, (MeHSiO)₅, (MeHSiO)₇, HSiMe₂OSiMe₂H, HMe₂SiOSiMeHOSiMe₂H, HMe₂Si(OSiMeH)₂OSiMe₂H, Me₃Si(OSiMeH)₃OSiMe₃, Me₃SiOSiHMeOSiMe₃ and Me₃SiOSiPhHOSiMe₃. The solvent CH₂Cl₂ was distilled over phosphorous pentoxide. Pentane, THF and 1,2-dimethoxyethane were distilled over lithium aluminum hydride. 1,2-dichloroethane was distilled over calcium hydride. The distilled solvents were stored over molecular sieve, 4 Å (4–8 mesh).

2.3. General note on the experimental

The reactions were conducted in oven dried glassware under a dry nitrogen atmosphere. To realize high yields, care must be exercised to prevent moisture getting into the system throughout the entire procedure until isolation. Although the reactions require stoichiometric amounts of the reagents, a slight excess (10 mole%) of TCCA is preferred.

2.4. The order of addition

When using CH_2Cl_2 as the solvent, the silanes were added to a slurry of TCCA in CH_2Cl_2 . A similar procedure was used for reactions in 1,2-dimethoxyethane and 1,2-dichloroethane. However, when THF was used, the reagents were added in reverse. TCCA was added by means of a solid addition funnel to the silane dissolved in THF cooled to -20°C . The change in the order of addition for reactions in THF was necessary to minimize chlorination of THF by TCCA.

2.5. Procedure for reactions in CH_2Cl_2

The solvent was placed in a 50 mL, 14/20 two-necked round-bottom flask equipped with a magnetic stir-bar, a rubber-septum and a condenser. The condenser in turn was attached in series to a gas-inlet and gas bubbler. TCCA was then added and the slurry of TCCA in CH_2Cl_2 was stirred at ambient temperature. Under a blanket of nitrogen, the organosilane (either as neat or as a solution in the reaction medium) was added dropwise by means of a gas-tight syringe at a rate to maintain a steady reflux of the solvent. After the addition was over, the flask was heated, if necessary, in an oil bath maintained at 40°C until the GC–MS analysis of a 5–10 μL aliquot of the reaction mixture indicated complete conversion to the product.

2.6. Procedure for reactions in THF

For reactions in THF, the organosilane and THF were placed in the reaction flask. The flask was cooled to -20°C in an acetone bath, the temperature of which was maintained by the addition of controlled amounts of dry ice. TCCA was then added in installments via a solid addition funnel. After the addition was over, the cold bath was removed and the reaction mixture was allowed to warm to ambient temperature. The stirring was continued until GC–MS analysis indicated a complete conversion of the organosilane to the desired product.

2.7. Monitoring the progress of the reaction

The reaction mixture (5–10 μL aliquot) was withdrawn by means of a gas-tight syringe and diluted with dry pentane (1–2 mL) in a 7 mL vial with a screw cap. The vial was centrifuged for a minute and the clear solution analyzed by GC–MS. If the mixture remained turbid, Celite[®] or anhydrous MgSO_4 can be added and the contents centrifuged again. Once it was determined that the reaction is complete, the entire reaction mixture can be worked up by one of the three methods described below depending upon the volatility of the product and the difference between the boiling point of the product and the solvent.

2.8. Workup method A

To isolate products of very high to moderate volatility, the condenser on the reaction flask was replaced with a short-path distillation unit with a vigreux column. The receiver flask (100 mL, 14/20 round-bottom flask) was attached to a vacuum manifold. The receiver flask was cooled to -78°C in a dry ice/acetone bath under nitrogen. The nitrogen line was closed and the vacuum was applied carefully and gently to collect volatiles (solvent and the product). Heating was then applied to the distillation flask either via a heat gun or an oil bath until the residue in the flask (excess TCCA and the byproduct) turned to a dry solid which indicated a complete removal of the product. The solvent in the receiver flask was removed using a rotary evaporator or by simple distillation at atmospheric pressure to obtain the product.

2.9. Workup method B

For products of low volatility (high boiling point), the solvent was removed under vacuum at ambient temperature following the method A. The residue in the reaction flask was treated with dry pentane and the contents were transferred into a centrifuge tube under nitrogen atmosphere. The contents were centrifuged and the clear organics decanted into another 14/20 one-necked flask. Pentane extraction of the residue must be repeated twice for complete removal of the products. The combined extracts were subjected to rotary evaporation to remove the solvent.

2.10. Workup method C

The contents of the flask can be transferred directly into a filtration apparatus containing a bed of Celite[®]. The filtration apparatus is a coarse sintered funnel fitted with 14/20 joints to facilitate direct transfer of the contents from the reaction flask and allow filtration under vacuum into a 14/20 receiver flask. The filtrate collected is removed of the solvent using a rotary evaporator. This method is suitable for isolation of volatile as well as non-volatile products.

2.11. Workup method D (a special case for $(\text{MeSiClO})_4$)

The solvent was removed under vacuum following the procedure in method A. The distillation unit was replaced with a sublimation apparatus which was connected to a vacuum manifold. Vacuum was applied and the flask heated with a heat gun to sublime the product on to the cold surface maintained at -10°C by a circulating bath. The sublimation unit was placed in a nitrogen glove bag and product was scrapped off the cold surface using a spatula.

3. Results and discussion

Typically, to convert Si–H functional silanes and siloxanes to the corresponding Si–Cl analogs, chlorine gas, or

allylchloride in presence of palladium on charcoal is used. The method using chlorine gas has been described in detail previously [1]. In compounds containing multiple hydrogen atoms, for example (MeHSiO)₄, three of the four hydrogen atoms were readily replaced with chlorine atom, whereas substitution of the fourth hydrogen atom was very sluggish. The same was true of the chlorination of (MeHSiO)₅ with chlorine. The experimental set up using chlorine gas is somewhat involved: (a) dilution of Cl₂ with nitrogen or argon was necessary to moderate the exothermic reaction, (b) the by-product HCl had to be effectively removed from the solution and trapped, and (c) temperature control was necessary to avoid side chain halogenation.

Chlorination using allyl chloride in presence of palladium on charcoal can mitigate some of the inconveniences mentioned above. However, allyl chloride, a lachrymator is required in a large excess, and its removal from the products can be cumbersome. It was also observed that contamination from palladium and charcoal is a frequent occurrence necessitating additional purification.

In view of the issues cited above, chloroimides were considered for use as chlorination agents. It is known that the byproducts (imides) are quite insoluble in nonpolar solvents. Hence following chlorination with such reagents, the byproducts can simply be filtered off to obtain the product in the reaction medium. The workup to isolate the product is very much simplified. In this regard use of *N*-chlorosuccinimide (NCS) and TCCA were investigated as chlorinating agent. It became apparent from preliminary experiments that TCCA chlorinated Si–H compounds quite rapidly and NCS was relatively sluggish. Consequently the focus was shifted to utilizing TCCA for chlorination and establishing the experimental procedure.

The various silanes converted to the corresponding chlorosilanes are given in Table 1. Though the reaction requires a stoichiometric amount of TCCA, a slight excess of the latter was used. For reactions using 5–20 mmol of the silane, 20–30 mL of solvent was sufficient.

Table 1
The list of silanes that were converted to the corresponding chlorosilanes

Starting silane	The chlorosilane product	Isolated yield %
PhSiH ₃	PhSiCl ₃	97.5
PhMeSiH ₂	PhMeSiCl ₂	95.5
Ph ₃ SiH	Ph ₃ SiCl	97.5
Vi ₃ SiH	Vi ₃ SiCl	98.7
(EtO) ₃ SiH	(EtO) ₃ SiCl	99.7
(MeHSiO) ₄	(MeClSiO) ₄	86.5
(MeHSiO) ₅	(MeClSiO) ₅	95.0
(MeHSiO) ₇	(MeClSiO) ₇	96.5
Ph(OEt) ₂ SiH	Ph(OEt) ₂ SiCl	98.0
HMe ₂ SiOSiMe ₂ H	ClMe ₂ SiOSiMe ₂ Cl	98.6
HMe ₂ SiOSiMeHOSiMe ₂ H	ClMe ₂ Si(OSiMeCl)OSiMe ₂ Cl	94.6
HMe ₂ Si(OSiMeH) ₂ OSiMe ₂ H	ClMe ₂ Si(OSiMeCl) ₂ OSiMe ₂ Cl	92.3
(Me ₃ SiO) ₃ SiH	(Me ₃ SiO) ₃ SiCl	97.0
Me ₃ SiOSiHPhOSiMe ₃	Me ₃ SiOSiClPhOSiMe ₃	99.0
Me ₃ SiO(SiMeHO) ₃ SiMe ₃	Me ₃ SiO(SiMeClO) ₃ SiMe ₃	95.7
O[SiH(OSiMe ₃) ₂] ₂	O[SiCl(OSiMe ₃) ₂] ₂	93.6

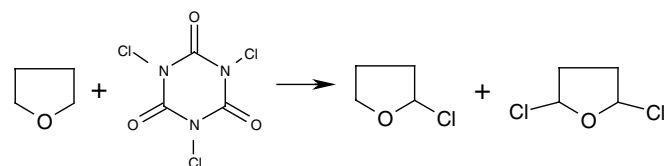
3.1. Reaction medium

Time and temperature required for completion of the chlorination reaction was strongly dependant on the medium used for the reaction. In the case of simple silanes containing a single hydrogen on a silicon atom, which are not sterically demanding (Ph₃SiH, Vi₃SiH, (EtO)₃SiH, etc.), chlorination was found to take place in CH₂Cl₂ almost instantly. The reactions were exothermic and the rate of addition of silane to TCCA was controlled to maintain a gentle reflux of the solvent. At the 10 mmol scale of the silanes, the reaction mixtures could be worked up anywhere from 10 min to an hour of stirring after the addition of the reagent.

In CH₂Cl₂ as the reaction medium, silanes containing more than one hydrogen atom per silicon required longer reaction time and higher temperature for completion. PhSiH₃, for example, required 5 h of heating at reflux temperature in CH₂Cl₂ for 95% completion. For such silanes, THF was found to be a more suitable solvent. In THF, PhSiH₃ underwent complete chlorination in 10 min at ambient temperature. Similarly, cyclic siloxanes in CH₂Cl₂ also required longer reaction time and heating at reflux temperature for completion. However, in THF the chlorination proceeded much more rapidly. A 30 min heating at reflux in THF resulted in complete conversion of (MeHSiO)₇ to the perchlorinated product, whereas in CH₂Cl₂, a 5 h heating at reflux was needed.

For a relatively crowded internal Si–H materials, such as Me₃SiO(SiMeHO)₃SiMe₃, only 68% of the theoretical trichloro substituted product was formed in CH₂Cl₂ after one hour at ambient temperature. It required an hour of reflux and overnight stirring at ambient temperature for complete conversion. In contrast, 92% of the trichloro substituted product was formed in 10 min at ambient temperature when the chlorination was conducted in THF. Heating at 40 °C for 20 min led to complete conversion. The three hydrogen atoms in the sterically less demanding HMe₂SiOSiMeHOSiMe₂H were substituted with chlorine atoms within an hour of stirring at ambient temperature.

It must be noted that reactions in THF must be started at or below –20 °C, and then allowed to warm to room temperature. This is to control the very exothermic reaction, and to prevent chlorination, to a small extent, of THF. At ambient temperature, in the absence of any silane, TCCA reacted with THF exothermically to form mono and disubstituted products shown in the equation below:



However, no such products were observed when the ingredients were mixed at 0 °C. Therefore, it is critical that the reactions in THF are conducted at well below 0 °C before warming to ambient temperature.

Among the organosilanes investigated, $\text{H}(\text{OSiMe}_3)_2\text{-SiOSi}(\text{OSiMe}_3)_2\text{H}$ was found to be most sterically demanding. In both CH_2Cl_2 and THF, <10% of the completely chlorinated product was formed after an hour of heating at the respective reflux temperatures. Prolonged heating failed to improve the conversion. Hence, two other solvents – $\text{ClCH}_2\text{CH}_2\text{Cl}$ in place of CH_2Cl_2 and $\text{MeOCH}_2\text{-CH}_2\text{OMe}$ (DME) in place of THF were attempted. DME was found to be unsuitable due to incomplete conversion. However, in $\text{ClCH}_2\text{CH}_2\text{Cl}$, a complete conversion to the desired product was noted after heating for an hour at 80 °C.

3.2. Product isolation

If a stoichiometric amount of TCCA was used for the chlorination, all that was required, following the completion of chlorination, was to filter off the insoluble by-product (see Method C), cyanuric acid (1,3,5-triazine-2,4,6-triol). Celite[®] as a filter aid may be necessary in instances where the byproduct was very fine and passed through the filter disk. If an excess of TCCA was used, the isolation procedures were modified slightly to enable removal of the trace level of the sparingly soluble TCCA present in the reaction medium along with the desired product (see Methods A and B).

If the product was distillable under low pressure, the solvent and the product were collected in a dry flask cooled to –78 °C. During the flash distillation, the distillation flask can be heated rapidly either using an oil bath or by gently waving a heat gun. It is critical, for quantitative recovery of product, that the residue (cyanuric acid and the excess TCCA) in the distillation flask turns very dry to indicate complete transfer of the product. Cyanuric acid and TCCA did not distill over under these conditions. The solvent from the distillate was then removed using a rotary evaporator to obtain the product. Product purity was 95% or greater in almost all cases, and further purification was not necessary.

For products such as $(\text{MeClSiO})_7$ that are not readily distillable, and where filtration was required, it was preferred to distill off the solvent (CH_2Cl_2 or THF) first. The residue was then triturated with dry pentane. Cyanuric acid and the excess TCCA are practically insoluble in pentane. Both pentane and the insoluble residue were transferred under nitrogen into a centrifuge tube. Following centrifugation, the clear pentane extract was collected and the pentane removed using a rotary evaporator to obtain the product.

The isolation method for $(\text{MeClSiO})_4$ is a special case since it sublimes readily. In this case, a sublimation unit was placed on the reaction flask. THF was removed under

Table 2
Experimental condition on the synthesis of chlorosilanes

Starting silane	Amount silane (g)	Amount TCCA (g)	Reaction medium	Workup method	Conditions for solvent removal
PhSiH_3	2.07	4.91	CH_2Cl_2	A	$P = 150$ mbar $T = 35$ °C
PhMeSiH_2	2.4	3.41	CH_2Cl_2	B	$P = 200$ mbar $T = 23$ °C
Ph_3SiH	2.6	0.85	CH_2Cl_2	B	$P = 150$ mbar $T = 35$ °C
Vi_3SiH	1.1	0.85	CH_2Cl_2	A	$P = 150$ mbar $T = 4$ °C
$(\text{EtO})_3\text{SiH}$	3.28	1.7	CH_2Cl_2	A	$P = 200$ mbar $T = 5$ °C
$(\text{MeHSiO})_4$	2.4	3.4	THF	D	$P = 150$ mbar $T = 35$ °C
$(\text{MeHSiO})_5$	3	4.3	THF	A	$P = 150$ mbar $T = 35$ °C
$(\text{MeHSiO})_7$	2.1	2.98	THF	B	$P = 200$ mbar $T = 35$ °C
$\text{Ph}(\text{OEt})_2\text{SiH}$	1.96	2.57	CH_2Cl_2	A	$P = 200$ mbar $T = 23$ °C
$\text{HMe}_2\text{SiOSiMe}_2\text{H}$	1.61	1.86	CH_2Cl_2	A	$P = 400$ mbar $T = 23$ °C
$\text{HMe}_2\text{SiOSiMeHOSiMe}_2\text{H}$	1.94	2.64	CH_2Cl_2	A	$P = 200$ mbar $T = 10$ °C
$\text{HMe}_2\text{Si}(\text{OSiMeH})_2\text{OSiMe}_2\text{H}$	2.54	3.41	THF	A	$P = 200$ mbar $T = 23$ °C
$(\text{Me}_3\text{SiO})_3\text{SiH}$	2.22	1.74	CH_2Cl_2	A	$P = 400$ mbar $T = 23$ °C
$\text{Me}_3\text{SiOSiHPhOSiMe}_3$	2.84	2.6	CH_2Cl_2	A	$P = 200$ mbar $T = 23$ °C
$\text{Me}_3\text{SiO}(\text{SiMeHO})_3\text{SiMe}_3$	3.42	2.6	THF	A	$P = 75$ mbar $T = 35$ °C
$\text{O}[\text{SiH}(\text{OSiMe}_3)_2]_2$	2.15	0.85	$\text{ClCH}_2\text{CH}_2\text{Cl}$	A	$P = 50$ mbar $T = 37$ °C

Table 3
Mass spectral characteristics of chlorosilanes

Chlorosilane synthesized	GC–MS retention time (min)	Prominent mass spectral characteristics; m/z
PhSiCl ₃	6.17	210 (M, the parent ion), 175 (M–Cl), 133, 112, 77
PhMeSiCl ₂	6.19	190 (M), 175, 77
Ph ₃ SiCl	15.07	294 (M), 217 (M–Ph), 154
Vi ₃ SiCl	2.44	129, 116, 91, 63, 53
(EtO) ₃ SiCl	3.74	197 and 199 (M), 183, 169, 155, 139, 125, 97
(MeClSiO) ₄	6.76–7.07 (isomers)	361 (M–CH ₃), 311, 233, 174
(MeClSiO) ₅	8.38–8.63 (isomers)	455 & 457 (M–CH ₃), 329, 397, 291, 255, 233, 93
(MeClSiO) ₇	Centered at 11.13	647 (M–CH ₃), 517, 389, 367, 343, 307, 247, 207, 187, 113, 93
Ph(OEt) ₂ SiCl	7.78	230 (M), 185 (M–OEt), 157, 137, 121, 105, 77, 63
ClMe ₂ SiOSiMe ₂ Cl	2.74	187 (M–CH ₃), 167 (M–Cl), 151, 137, 113, 93, 63, 45
ClMe ₂ Si(OSiMeCl)OSiMe ₂ Cl	5.57	283 (M–CH ₃), 261, 229, 187, 153, 93
ClMe ₂ Si(OSiMeCl) ₂ OSiMe ₂ Cl	7.69	375 (M–CH ₃), 247, 93
(Me ₃ SiO) ₃ SiCl	6.62	315 (M–CH ₃), 207, 191, 73
Me ₃ SiOSiClPhOSiMe ₃	8.32	303 (M–CH ₃), 267, 251, 193, 135, 126, 91, 73
Me ₃ SiO(SiMeClO) ₃ SiMe ₃	8.46	429 & 431 (M–CH ₃), 321, 301, 269, 249, 167, 93 and 73
O[SiCl(OSiMe ₃) ₂] ₂	8.81	483 (M–CH ₃), 375, 287, 267, 147 73

low pressure at ambient temperature. The sublimation unit was then cooled to $-10\text{ }^{\circ}\text{C}$ or less and the distillation flask heated either with a heat gun or an oil bath. The product was scrapped off the sublimation apparatus inside a nitrogen glove bag. The experimental details on the reactions and mass spectra characteristics of the products are given in Tables 2 and 3 respectively.

4. Conclusion

An efficient synthetic methodology was developed for the conversion of silicon hydrides to chlorosilanes using inexpensive trichloroisocyanuric acid (TCCA) as the chlorination agent. The conversions were essentially quantitative, and in general, the isolated product yields were 90% or greater. The workup after the reaction was quite simple, requiring only a removal of the very insoluble byproduct. Since the products formed are of high purity (>95%), an additional purification step (such as distillation) was not necessary.

With TCCA, complete chlorination occurred rapidly, requiring a few minutes to an hour depending upon the steric demand of the starting silane. For compounds that reacted sluggishly in CH_2Cl_2 as the solvent medium, use of THF drastically reduced the reaction time. For sterically demanding silanes, chlorination was accomplished using $\text{ClCH}_2\text{CH}_2\text{Cl}$ as the solvent.

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