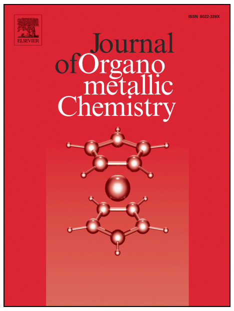

Building blocks for oligomeric siloxanes –selective chlorination of hydrido-siloxanes

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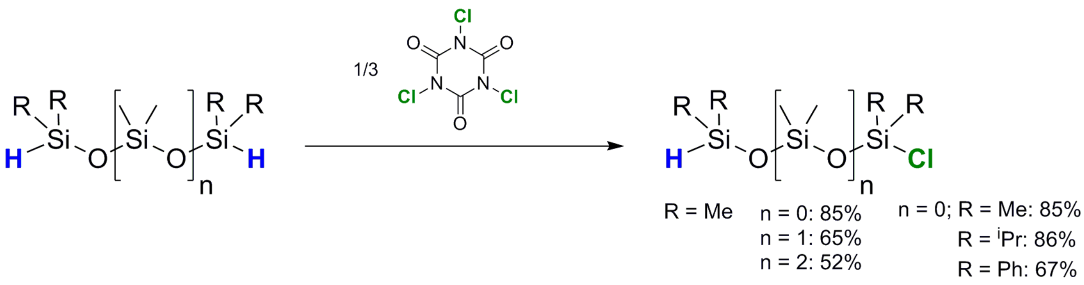
PII: S0022-328X(18)30465-0
DOI: 10.1016/j.jorganchem.2018.08.022
Reference: JOM 20549

To appear in: *Journal of Organometallic Chemistry*

Received Date: 8 June 2018
Revised Date: 6 August 2018
Accepted Date: 24 August 2018

Please cite this article as: T. Hafner, A. Torvisco, F. Uhlig, Building blocks for oligomeric siloxanes –selective chlorination of hydrido-siloxanes, *Journal of Organometallic Chemistry* (2018), doi: 10.1016/j.jorganchem.2018.08.022.


1/3
Cl
O
N
Cl
Cl
R
Si
O
H
n
R = Me
n = 0: 85%
n = 1: 65%
n = 2: 52%
n = 0; R = Me: 85%
R = ^{i}Pr: 86%
R = Ph: 67%

Building Blocks for Oligomeric Siloxanes – Selective Chlorination of Hydrido-Siloxanes

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Keywords

hydridosiloxanes, trichloroisocyanuric acid, TCCA, selective monochlorination

1. Abstract

A new method was developed to achieve highly selective monochlorination of α,ω-dihydridosiloxanes, ((H)Me_2SiO-$(SiMe_2O)_n$-$SiMe_2$(H), n = 0 - 2; (H)R_2Si-O-SiR_2(H); R = Me, ^{i}Pr, Ph; 3,5-dihydridooctamethyltetrasiloxane, Me_3SiO-$(Si(H)MeO)_2$-$SiMe_3$) with trichloroisocyanuric acid (TCCA). The dependence of the selectivity of the monochlorination on the siloxane chain length is also discussed.

2. Introduction

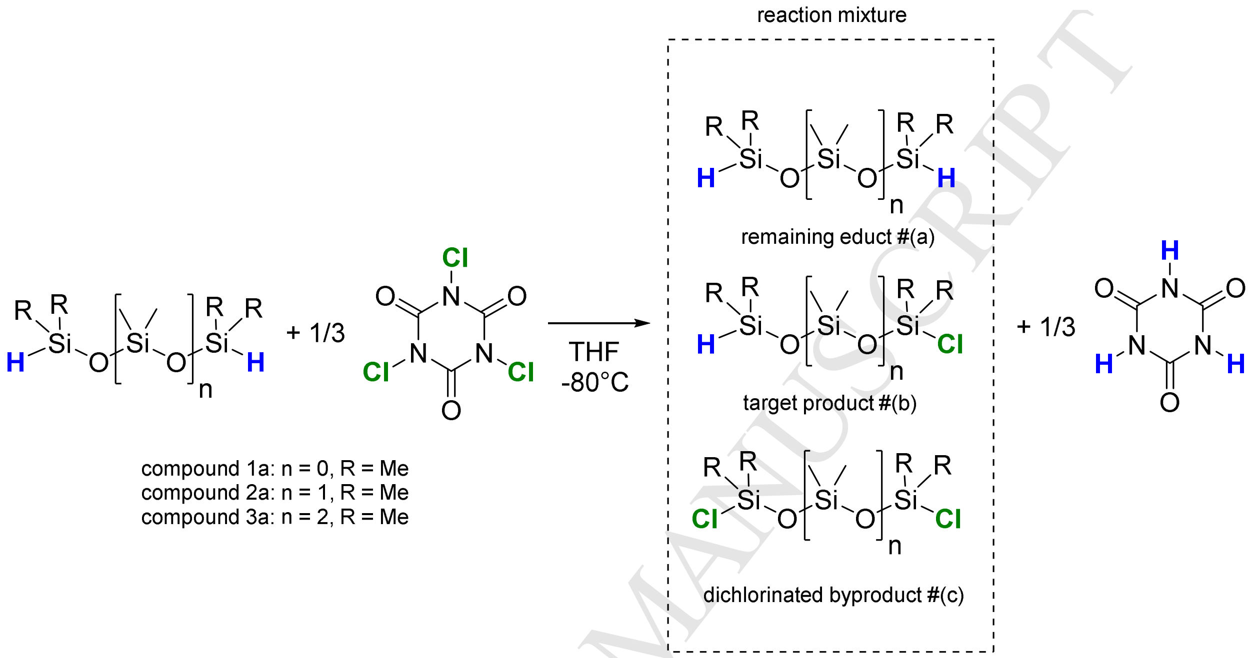
The conversion of the Si-H into Si-Cl bonds can be achieved by various methods and has been well established over the years using hydrochloric acid, chlorine gas, acetyl chloride, HCl in combination with $PdCl_2$ as catalyst [1], $CuCl_2$ [2], CCl_4 [3], PCl_3 [4] or PCl_5 [5]. Further advances deal with the dehalogenation of hexachlorocyclohexane catalyzed by rhodium complexes [6] or iron catalyzed ($FeCl_3$) based chlorination with acetyl chloride of Si-H bonds [7]. An overview of Si-H chlorination is given by Kunai and Oshita in 2003 [2].

Only a few examples of partial chlorination of compounds containing more than one Si-H bond are reported mainly due to the limited selectivity of the known methods. For example, tin tetrachloride has been used for chlorination in Bu_2O where $>SiH_2$ can be converted into >Si(H)Cl in approx. 60% yield [8]. Also, $CuCl_2$ was used for selective chlorination of R_2SiH_2 with Et_2O or THF as solvents, with optional addition of CuI as catalyst [9]. Disadvantages of such methods are often low yields, due to difficult workup, and therefore product isolation.

Trichloroisocyanuric acid (TCCA) [10] was reported for a full chlorination of the Si-H functions in siloxane hydrides [11]. First usage of TCCA for a selective chlorination of siloxanes containing more than one Si-H bond were performed by our group [12] and afterwards applied also for mono- [13] and disilanes [14]. Recently, a report using TCCA on the selective chlorination of $Naph_2SiH_2$ towards $Naph_2Si(H)Cl$ was published by Diemoz, Wilson and Franz [15]. The objective of this work was to develop and investigate this new chlorination method and provide a general synthetic method of using TCCA as a reagent to achieve a highly selective monochlorination in oligomeric siloxanes containing more than one Si-H unit.

3. Results

In a first step, the possibility of a selective monochlorination by TCCA on α,ω-dihydridosiloxanes with varying chain lengths ((H)Me_2SiO-$(SiMe_2O)_n$-$SiMe_2$(H) (n = 0 (**1a**), n = 1 (**2a**), n = 2 (**3a**)) was investigated (Scheme 1).



Scheme 1: Selective monochlorination of the linear α-ω dihydridosiloxanes 1-3a

In order to achieve selective monochlorination, a ratio of 1 mol siloxanes to $^{1}/_{3}$ mol TCCA was used. It could be clearly shown that the selectivity of the reaction depends strongly on the reaction conditions used. During chlorination, TCCA exchanges its chlorine atoms with the hydrogens from the educt, converting TCCA to TCCH and yields up to 85% of desired monochlorinated products (**1-3b**). In some cases, the desired product is accompanied by amounts of remaining starting materials (**1-3a**) and the dichloro-substituted byproducts (**1-3c**). Reactions were carried out in THF well below -20 ℃. Otherwise, the well-known chlorination of THF [11] takes place.

Early attempts for selective monochlorination of dihydridotetramethyldisiloxane ((H)Me_2Si-O-$SiMe_2$(H), (**1a**)) only yielded to a conversion of about 65-70% towards the monochlorinated product (**1b**) [12]. This method involved the slow addition of TCCA to a cooled mixture (below -20 ℃) of THF and **1a** in a concentration of about 20 ml THF for 5.6 mmol siloxane under intense stirring and inert conditions. TCCA was added in small amounts. Additional TCCA quantities were added only, when the previous ones were already in solution (Chlorination Method 1, see Experimental Section). However, this method still allowed for a local stoichiometric excess of TCCA promoting the formation larger amounts of the dichlorotetramethyldisiloxane (**1c**).

In order to circumvent the formation of the dichloro-substituted species **1c**, TCCA was first dissolved in THF at -80 ℃ and the solution added dropwise to a mixture of THF and **1a** also at -80 ℃ under intense stirring (Chlorination Method 2, see Experimental Section). In this respect a higher conversion rate of **1a** up to ~85% into the monochlorinated species (**1b**) can be observed. This procedure was applied also towards all siloxanes reported in this work.

The conversion of the α,ω-dihydridosiloxanes ($(H)Me_2SiO-(SiMe_2O)_n-SiMe_2(H)$; n = 0 (**1a**), n = 1 (**2a**), n = 2 (**3a**)) into the monochloro-substituted species are dependent on the chain length between the Si-H units (Figure 1). As mentioned above for dihydridotetramethyldisiloxane (**1a**), a conversion ratio to the desired monochlorinated species (**1b**) of 85% was observed. For the dihydrido-hexamethyltrisiloxane (**2a**), a decreased selectivity towards the desired mono-chlorinated species (**2b**) of 65% was observed in conjunction with increased 13% of **2a** and 22% of the dichloro-substituted species **2c**. In dihydridooctamethyl-tetrasiloxane (**3a**, $(H)Me_2SiO-(SiMe_2O)_2-SiMe_2(H)$) which displays the largest distance between the Si-H positions, the reduced selectivity is much more pronounced. The conversion ratio to the monochlorinated species (**3b**) is even further reduced to only 52%, with 35% remaining educt **3a** and 13% dichlorinated species **3c**.

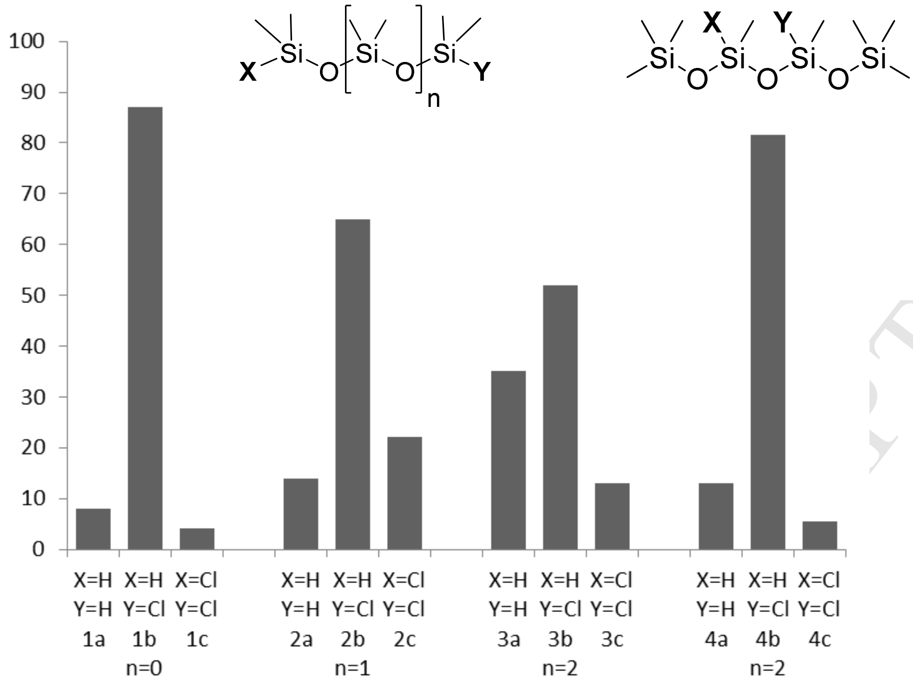


Figure 1: Conversion ratios of the methyl substituted α,ω-dihydridosiloxanes 1-4a

The influence of the chain length between the Si-H units and the selectivity can be emphasized by the monochlorination of 3,5-dihydridooctamethyltetrasiloxane ($Me_3SiO-(Si(H)MeO)_2-SiMe_3$, **4a**) which has the same chain length as **3a** but corresponding Si-H positions as compound **1a**, (Scheme 3). The conversion to the monochloro-substituted species (**4b**) is with a conversion ratio of 82% in a similar range like for **1b** (85%). Therefore, it can be stated that conversion ratios are not dependent on siloxane chain length, rather on the distances between the Si-H positions in the siloxane chain.

In a second step, the influence of the substituents attached to a series of dihydridosiloxanes ($(H)R_2Si-O-SiR_2(H)$; R = Me (**1a**), R = ^{i}Pr (**5a**), R = Ph (**6a**)) was also investigated (Figure 2). While monochlorination conversion ratios of the ^{i}Pr substituted dihydridosiloxane (**5a**) (86%) compares well to compounds **1a** and **4a**, the phenyl substituted dihydridosiloxane (**6a**) shows a decreased monochlorination conversion ratio of 65% probably due to the more electron withdrawing effect of the phenyl groups.

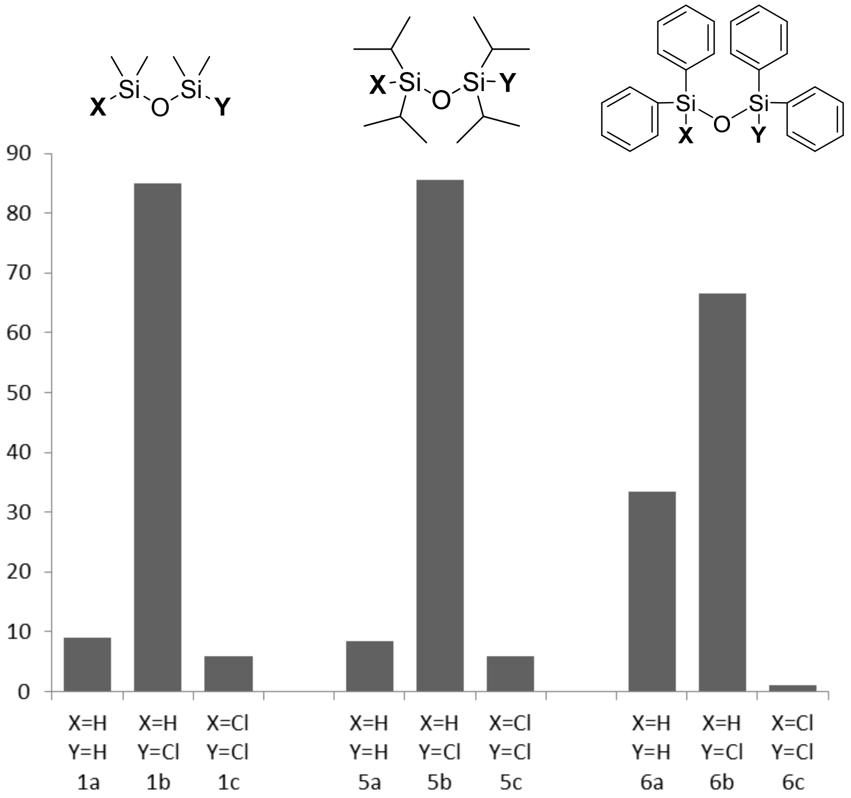


Figure 2: Conversion ratios in the 1,2-dihydridotetraorganodisiloxanes 1a, 5a and 6a

Hydrido- as well as chloro-substituted siloxanes such as compounds **1**-**6** are often causing difficulties in GC measurements due to their sensitivity towards column materials. Therefore, ^{1}H-NMR, ^{13}C-NMR, and ^{29}Si-NMR measurements were also used for determining the yields of the reported reactions. Detailed description on product separation and characterization are described in the Supplementary Material. The results were not only compared to the literature known chemical shifts [16] [17] [18] but also a complete chlorination of all Si-H bonds *via* TCCA was performed to verify the corresponding shifts of the dichloro-substituted species (Supplementary Information). In any cases combinations of spectroscopical methods were used to distinguish between the different products.

4. Conclusion

It was shown that trichloroisocyanuric acid (TCCA) is a highly useful reagent in performing selective chlorinations of Si-H bonds in dihydridosiloxanes. While the monoselective chlorination of the α,ω-dihydridosiloxanes ($(H)Me_2SiO-(SiMe_2O)_n-SiMe_2(H)$) is selective for n = 0 and 1, for n = 2, a substantial loss in selectivity is observed leading to a statistically expectable product mixture only. In addition, the influence of different substituents at the silicon atoms (Me, ^{i}Pr, Ph) on selective monochlorination of 1,3-dihydridodisiloxanes was examined. Through the use of this novel selective chlorinating method, novel mono-functionalized building blocks for the synthesis of short chain siloxanes could be synthesized. The use of those building blocks will be discussed in an upcoming publication.

5. Experimental – General Remarks

All reactions were moisture and air sensitive and were carried out under inert-atmosphere using Schlenk-techniques unless otherwise stated. Different procedures where applied, depending if the target compound has to be selectively or fully chlorinated. Also, the workup is dependent on the volatility of the target compound. All products are colorless oils with different viscosity.

^1H (300.22 MHz), $^{13}C\{^1H\}$ (75.50 MHz) and $^{29}Si\{^1H\}$ (59.6 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25 °C. Chemical shifts are given in parts per million (ppm) relative to TMS (δ= 0 ppm) regarding ^{13}C and ^1H and relative to $SiMe_4$ in the case of ^{29}Si. Coupling constants (*J*) are reported in Hertz (Hz). For more details see supplementary material.

Two different selective chlorination methods were applied:

Chlorination method 1 for selective monochlorination

Chlorination where Si-H bonds had to be chlorinated selectively were performed analog to Chlorination Method 1, but TCCA was used with (1/3 eq. TCCA / 1 eq. siloxane). A flask was filled with educt and THF and cooled down to -20°C. (20 ml

THF/g educt). TCCA was added in small portions, under intense stirring. New TCCA portions were added only, if the last portions already went into solution. After TCCA addition was completed, stirring was continued for 15 minutes, afterwards, the cooling bath was removed and the solution was allowed to come room temperature.

Chlorination method 2 for selective chlorination

TCCA was used in the following equivalents: $^1/_3$ eq. TCCA / 1 eq. siloxane. A three-neck flask was filled with THF (100 ml THF/g educt) and cooled down to -80 ℃ under intense stirring. TCCA was added in small portions until everything was dissolved. A second flask was filled with the educt/THF mixture (50 ml/g educt) and also cooled down to -80 ℃. The receiving flask was kept under constant stirring. At this point, the THF/TCCA solution was transferred slowly (drop wise) into the educt/THF flask with a syringe while maintaining the temperature at -80 ℃. The reaction vessel was kept under stirring until room temperature was reached.

Example for selective chlorination – chlorotetramethyldisiloxane (1b)

Starting materials: 46.1 g **1a** (0.34 mol); 26.6 g (0.11 mol) TCCA. Chlorination procedure 2 was used. The conversion rate determination was done by ^{29}Si-NMR before distillation. Removal of unreacted TCCA and TCCH was achieved by use of a condensation bridge to transfer the THF and product mixtures into a liquid N_2 cooled flask under moderate heating (water bath with 60 ℃) to avoid decomposition processes. THF removal was achieved by standard distillation and the remaining product mixtures were separated by fractional distillation. A filling material column was used for distillation. After distillation, 41 g (0.24 mol, 71%) of chlorotetramethyldisiloxane **1b** as colorless liquid was isolated. Boiling Point: 103-105 ℃ (see also literature [17])

^{1}H-NMR (C_6D_6) δ: 0.145 (d, 6 H, $-Si(C\underline{H}_3)_2H$), $^3J_{H\text{-}H}$ = 2.72 Hz; 0.27 (s, 6H, $-Si(C\underline{H}_3)_2Cl$); 4.92 (h, 1H, $\underline{Si}H$) $^3J_{H\text{-}H}$ = 2.72 Hz, $^1J_{Si\text{-}H}$ = 208 Hz; **^{13}C-NMR** (C_6D_6) δ: 0.5 (s, 2C, $-Si(\underline{C}H_3)_2H$), $^1J_{Si\text{-}C}$ = 59.65 Hz; 3.8 (s, 2C, $-Si(\underline{C}H_3)_2Cl$), $^1J_{Si\text{-}C}$ = 71.58 Hz; **^{29}Si^{DEPT}-NMR** (C_6D_6) δ -2.9 (s, $\underline{Si}H$); 6.0 (s, $-\underline{Si}Cl$).

6. Acknowledgements

The authors are grateful to the Graz University of Technology and the NAWI Graz project for support.

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Highlights

1. High yield selective chlorination of oligomeric siloxanes containing more than one Si-H unit.
2. Selectivity is depending on the chain length between the Si-H units.
3. Selectivity is depending on the organic substituents at the silicon atoms.
4. Easy to use, upscaling possible, TCCA is inexpensive and non-toxic.
5. Workup and chlorination procedures are depending on the desired target compounds.