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Reactions of H(PhMeSi)$_3$H with Triflic Acid: Evidence for Rearrangement Processes

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Summary: The reaction of the trisilane, H(PhMeSi)$_3$H, with 1 or 2 equiv of triflic acid (HOTf) followed by quenching with MeMgBr resulted in the formation of two isomers each of Ph$_2$Me$_4$Si$_3$H$_2$ and PhMe$_5$Si$_3$H$_2$, respectively. When H(PhMeSi)$_3$H was treated with 3 equiv of triflic acid and quenched with PhMgBr, two isomers of Ph$_3$Me$_3$Si$_3$H$_2$ were formed. The isomers formed in the sequence with 1 equiv of HOTf result from competitive cleavage of internal SiPh bonds vs terminal SiPh bonds, as demonstrated by labeling experiments. The products formed from reaction with a second and third equivalent of trific acid require a rearrangement process and may be rationalized through a common cationic intermediate, [HMe(TfO)SiSiMeSi(X)MeH]$^+$OTf$^-$ (X = Ph, OTf).

Development of the chemistry of oligosilanes has lagged behind that of cyclopolysilanes and polysilanes due, primarily, to the lack of synthetic methods for targeting short chains.[1] The general routes utilized for formation of oligomers have involved the condensation of halosilanes with alkali metals or magnesium (Wurtz-type coupling) or the ring-opening of a cyclopolysilane. In general, the former leads to organic "saturated" systems, R$_x$R$'_y$Si$_n$ ($x + y = n + 2$), and is usually employed in the synthesis of disilanes and trisilanes. The latter is used for oligomers with terminal functional groups, X(RR$'$Si)$_x$X (X is usually a halogen), and is of practical use for the range x = 4–6 due to low yields in the formation of the cyclic precursors when x = 3 or >6.

Two methods have been developed to introduce the more common silicon functional groups into organic "saturated" R$_x$R$'_y$Si$_n$ ($x + y = n + 2$) both of which rely on electrophilic cleavage of a phenyl group from silicon. The use of HX/AlX$_3$ does not appear to discriminate between phenyl group positions. As an example, in order to produce X(Ph$_2$Si)$_3$X it was necessary to prepare [(p-Tol)Ph$_2$Si]$_2$SiPh$_2$ in a multistep sequence which, when reacted with AlBr$_3$/HBr, resulted in the specific removal of the p-Tol groups to provide the 1,3-dibromotrisilane.[2] More recently, triflic acid (HOTf) has been utilized to remove phenyl groups and it has been shown that reaction of Ph$_8$Si$_3$ with 2 equiv of HOTf produced TfOPh$_2$SiSiPh$_2$SiPh$_2$OTf in a 90% yield.[3] It appears that replacement of one phenyl substituent at a silicon center with a triflate group deactivates that center toward additional substitution. Similar deactivation has been demonstrated in the rates of removal of two phenyl groups in PhMe$_2$Si(SiMe$_2$)$_x$SiMe$_2$Ph and in Me$_2$SiPh$_2$.[4] In no case has there been reported removal of a phenyl group from the internal silicon of a trisilane such as Ph$_3$SiSiPh$_2$SiPhMe$_2$, although Ph$_3$SiSiPh(OTf)SiPhRMe (R = Ph, Me) has been prepared by indirect methods.[3,5a] Recently, the use of triflic acid has been reported in the preparation of multifunctional disilanes,[5b] in the functionalization of polymers such as —[PhMeSiSiPhMe]$_n$—[6] and —[PhSi]$_n$—,[7] and in the preparation of the stereoisomers of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilanes utilized as starting materials for ring-opening polymerization to high molecular weight polysilylenes.[8]

An alternative to the Wurtz-type coupling approach to formation of oligomers is provided through the dehydrocoupling of secondary silanes in the presence of Cp$_2$MCl$_2$/nBuLi. The H(RR$'$Si)$_x$H products contain hydrogen functional groups which terminate the chains and thus provide a functional group for further chemical elaboration.[9a] Although mixtures of oligomers are usually formed, it is possible to generate each oligomer of H(PhMeSi)$_x$H (x = 2–4) in multigram quantities through suitable selection of the reaction conditions.[9b] However, the condensation of secondary silanes is limited in the range of substituents that are tolerated for condensation past the disilane stage. If it is possible to remove the phenyl groups in the readily prepared H(PhMeSi)$_x$H with triflic acid, then the triflates that would be formed, H(MeSiOTf)$_x$H, could provide an entry into a variety of oligomers with substitution patterns that are not found available with the present methodology. It was with this goal in mind that a study of the reactions of the trisilane, H(PhMeSi)$_3$H, with 1, 2, and 3 equiv of HOTf was initiated. In contrast to previous studies, competitive cleavage of internal and terminal SiPh bonds as well as rearrangement processes were observed and are described in this report.

The reaction of H(PhMeSi)$_3$H with HOTf in a 1:1 molar ratio in toluene at 0 °C followed by quenching with an ether solution of MeMgBr resulted in the isolation of Ph$_2$Me$_4$Si$_3$H$_2$ in approximately 75% yield. Unexpectedly, two isomers of Ph$_2$Me$_4$Si$_3$H$_2$ were formed

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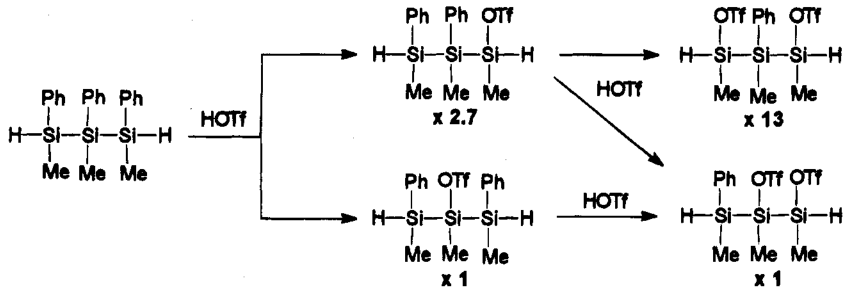

Figure 1. Sequential reaction of $H(PhMeSi)_3H$ with 1 and 2 equiv of HOTf followed by quenching with MeMgBr. The observed ratio between the isomers is included.

Table 1. ^{29}Si NMR Assignments for $Ph_xMe_{6-x}Si_3H_2$ (x = 1−3)[12]

	HPhMeSi		HMe₂Si	PhMeSi		Me₂Si	SiMeH	SiPh₂Me
compd	CDCl₃	C₆D₆	C₆D₆	CDCl₃	C₆D₆	CDCl₃	C₆D₆	C₆D₆
HPhMeSi(SiPhMe)SiMe₂H[a]	−33.30		−36.68	−45.45				
	−33.37	−36.82	−45.57					
HPhMeSi(SiMe₂)SiMePhH[b]	−34.14					−47.22		
	−34.15					−47.23		
HMe₂Si(SiMePh)SiMe₂H			−37.20	−45.47				
HPhMeSiSiPhMeSiPhMeH[c]	−34.06	−34.02[d]		−45.78	−45.85			
	−34.07	−34.10		−45.92	−46.00			
	−34.13			−46.11	−46.19			
	−34.20	−34.23						
HPhMeSiSiHMeSiPh₂Me[a]		−34.09[e]					−73.62	−17.72
							−73.80	−17.74

[a] Mixture of two diastereomers, both *d,l* pairs. [b] Mixture of two diastereomers, one *d,l* pair and one meso form. [c] Mixture of three diastereomers, two meso forms and one *d,l* pair. [d] In C_6D_6, the HSiPhMe region for $H(PhMeSi)_3H$ produced from dehydrocoupling exhibits only three signals: δ −34.00, −34.07, and −34.20. [e] Two signals should be observed; the second signal overlaps with the major isomer.

as indicated by the presence of three SiH regions in the ^{1}H NMR spectrum.[10] The expected product, $H(PhMeSi)(SiPhMe)(SiMe_2)H$, which would result from the cleavage of a terminal phenyl group, was the major isomer and exhibited SiH resonances (in $CDCl_3$) centered at δ 3.90 (HMe_2Si) and δ 4.47 (HPhMeSi). The minor product contained one SiH multiplet centered at δ 4.32 and was consistent with the formation of $(HPhMeSi)_2SiMe_2$ as the second isomer. Such a product would form if the central SiPh group of the starting trisilane was removed and subsequently replaced with a Me group. The ratio between the major and minor products was 2.7:1.

When $H(PhMeSi)_3H$ was reacted with 2 molar equiv of HOTf, followed by quenching with MeMgBr, two isomers of $PhMe_5Si_3H_2$ were produced.[11] The major isomer was assigned to $HMe_2SiSiPhMeSiMe_2H$ and resulted from the cleavage of both terminal phenyl groups. This isomer exhibited one SiH multiplet in the ^{1}H NMR spectrum, which in this case was a septet centered at δ 4.30 (in C_6D_6; or δ 3.93 in $CDCl_3$). The minor isomer, $HPhMeSiSiMe_2SiMe_2H$, contains two SiH resonances centered at δ 4.16 (HMe_2Si) and δ 4.71 (HPhMeSi). The integrated ratio (SiH) between the two isomers is 13:1.

Figure 1 summarizes the reactions of $H(PhMeSi)_3H$ with triflic acid. Further support for the assignments of the sequencing of silicon units in the trisilanes was obtained from ^{29}Si NMR data which are summarized in Table 1. The new trisilanes formed from the reaction of $H(PhMeSi)_3H$ with 1 equiv of HOTf are mixtures of two diastereomers, and two sets of signals are observed for these diastereomers for both $HPhMeSi(SiPhMe)SiMe_2H$ and $HPhMeSi(SiMe_2)SiMePhH$. The major isomer produced in the reaction of 2 equiv of triflic acid is achiral, and thus a single signal is observed for both the terminal and internal silicon centers. Data for the minor isomer were not obtained.

On the basis of literature precedence, the formation of structural isomers in the reaction of the trisilane is unexpected. Furthermore, the isomer ratio, 13:1, in the products formed in the reaction of 2 equiv of triflic acid with $H(PhMeSi)_3H$ does not reflect the 2.7:1 ratio of isomers produced with 1 equiv of triflic acid (see Figure 1). Since HPhMeSiSi(OTf)MeSiPhMeH can only react at a terminal silicon center and HMe(OTf)SiSiPhMeSiPhMeH can react at both an internal and a terminal silicon, the relative ratio of HMe(OTf)SiSiPhMeSi(OTf)MeH to HMe(OTf)SiSi(OTf)MeSiPhMeH should decrease below the 2.7:1 observed in the monotriflate precursor instead of the observed increase to 13:1 that is observed (as reflected in the quenched product, $PhMe_5Si_3H_2$). The observed results require either competitive cleavage of Ph—Si bonds (internal and terminal) and/or a rearrangement process.

To distinguish between these possibilities, the labeled trisilane $HPh_DMeSiSiPhMeSiPh_DMeH$[13] was prepared. Removal of a terminal $SiPh_D$ would provide $HPh_DMeSiSiPhMeSi(OTf)MeH$ (proton ratio:aromatic:SiMe:SiH = 5:9:2) plus C_6D_5H. Removal of an internal SiPh bond would generate $HPh_DMeSiSi(OTf)MeSiPh_DMeH$ (proton ratio:aromatic:SiMe:SiH = 0:9:2) plus C_6H_6. If only terminal Si—phenyl bonds are cleaved (followed by rearrangement) then the triflate should exhibit a proton integration ratio of arom:SiMe:SiH = 5:9:2. However, if cleavage of internal Si—phenyl bonds competes with terminal S—phenyl bonds, a weighted average of aro-

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[10] Reactions were conducted under an inert atmosphere in dried glassware, and full details are provided in the supplementary material.

[11] Reaction details and characterization data are provided in the supplementary material.

[12] ^{29}Si spectra were recorded on a Bruker ARX-500 spectrometer (99.36 MHz) using the INEPTRD (using a ^{1}H refocusing pulse) or DEPT pulse sequences.

[13] $HPh_DMeSiSiPhMeSiPh_DMeH$ was prepared from the reaction of $H(PhMeSi)_3H$ with 2 equiv of HOTf followed by reaction with Ph_DMgBr. Details are provided in the supplementary material.

matic protons should be observed. When the labeled trisilane was treated with 1 equiv of triflic acid in $\mathrm{CDCl_3}$ the integrated ratio of aromatic:SiMe:SiH was 6:10:2. After removal of volatiles (solvent and benzene) and redissolution of the product in $\mathrm{CDCl_3}$ the new ratio was 3.6:10:2. The intermediate value for the integration of the aromatic protons in the triflate corresponds to a ratio of Si—phenyl(terminal) to Si—phenyl(internal) cleavage of 2.6, close to the value obtained for the mixture of $\mathrm{Ph_2Me_4Si_3H_2}$ isomers produced on reaction of the triflate with MeMgBr. Thus, the labeling experiment supports the removal of both internal and terminal SiPh groups when 1 equiv of HOTf is added.[14] However, since the isomeric ratio of the trisilanes produced from the reaction with 2 equiv of HOTf does not reflect the ratio of isomers produced after 1 equiv of acid has been added, a rearrangement process is still required to explain the observed ratio of the $\mathrm{PhMe_5Si_3H_2}$ isomers produced.

The reaction of $\mathrm{H(PhMeSi)_3H}$ with 3 equiv of triflic acid followed by quenching with PhMgBr revealed the formation of two isomers of $\mathrm{Ph_3Me_3Si_3H_2}$.[15] In this case, the major product corresponded in both GC retention times and the ^{1}H NMR spectrum to the starting trisilane. On the basis of spectroscopic data the second isomer was assigned a structure where a terminal hydrogen had migrated to the central silicon, $\mathrm{HPhMeSiSiHMeSiPh_2Me}$. Confirmation of the structural assignment was obtained from the ^{29}Si spectrum, which shows a unique resonance about 40 ppm upfield of the region where terminal SiH resonances in the silicon oligomers are observed (see Table 1). The ^{29}Si resonances of the internal silicons in $\mathrm{R_3Si(SiR_2)_{\mathit{x}}SiR_3}$ (R = H, Me) appear upfield of the terminal silicon centers,[16] as is also the case in the recently reported spectrum of $\mathrm{HMe_2SiSiMeHSiMe_2H}$.[17]

The observation of the second isomer in the reaction of the trisilane with 3 equiv of triflic acid also suggests a rearrangement reaction. Both rearrangements may occur through a cationic species where the charge is located on the central silicon of the trisilane intermediate. The cationic intermediate may be formed either in the protodesilylation of the Si—Ph bond or from ionization of a bound triflate. The rearrangement of a phenyl group in $\mathrm{[HMe(TfO)SiSiMeSiPhMeH]^+OTF^-}$ to the internal silicon would give the 1,3-ditriflate which, when quenched with MeMgBr, would provide $\mathrm{(HMe_2Si)_2SiPhMe}$, the major product observed in this reaction. Likewise, rearrangement of a hydride in the $\mathrm{[HMe(OTf)SiSiMeSiMeHOTf]^+OTf^-}$ intermediate produced from reaction of 3 equiv of triflic acid would provide the 1,1,3-tritriflate which leads to the minor product, $\mathrm{HPhMeSiSiHMeSiPh_2Me}$, observed on quenching with PhMgBr. The combination of the results observed for the reaction of $\mathrm{H(PhMeSi)_3H}$ with 2 and 3 equiv of triflic acid suggests that the migratory aptitude of substituents is $\mathrm{Ph > H \gg Me}$.

Although controversy exists over the nature of isolated silicon cations,[18] evidence has been presented recently for the formation in solution of solvated silicenium ions from hydride abstraction reactions and from solvolysis reactions.[19] Most studies aimed at the generation and identification of silicenium ions have involved the study of monosilane precursors. However, in the reaction of $\mathrm{R_3SiH}$ with $\mathrm{Ph_3C^+[B(C_6F_5)_4]}$, which produced $\mathrm{Ph_3CH}$ and the silylium salts, the formation of cationic species is suggested from the downfield shift of the ^{29}Si resonance. The largest differences in the ^{29}Si chemical shifts between $\mathrm{R_3SiH}$ and $\mathrm{R_3Si^+}$ were found for $\mathrm{R = SiMe_3}$, that is, in the formation of $\mathrm{(Me_3Si)_3Si^+}$ which could be viewed as a substituted trisilane, $\mathrm{[Me_3SiSiRSiMe_3]^+}$ and thus related to the trisilanes described in this report.[20] The formation of silicenium ions as intermediates may occur more frequently than is currently recognized. In a recent study of the chlorodephenylation of $\mathrm{[(tBu)PhSi]_4}$ with $\mathrm{HCl/AlCl_3}$ the product formed is the *all-trans*-$\mathrm{[(tBu)ClSi]_4}$ independent of the stereochemistry of starting material (*cis,cis,trans, cis,trans,cis,* or *all-trans*).[21] A tentative suggestion was made by the authors that trivalent silicon cations may be intermediates in this reaction.

The reactions of $\mathrm{H(PhMeSi)_3H}$ with successive increments of triflic acid have demonstrated that cleavage of internal PhSi bonds can compete with the cleavage of terminal SiPh bonds and that rearrangement of substituents occurs in cases where triflate groups are present on adjacent silicon centers. This observation suggests that the use of triflic acid in the cleavage of PhSi bonds in polysilanes may lead to additional changes in the sequencing of silicon units in the oligomer or polymer products. Our preliminary studies demonstrate that reaction of $\mathrm{H(PhMeSi)_2H}$ with HOTf does not lead to isomeric products but that reactions of $\mathrm{H(PhMeSi)_4H}$ appear to resemble those described here for the trisilane. Whether such rearrangements are unique to the hydrogen-terminated oligomers that were the focus of this study requires further investigation.

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Supplementary Material Available: Text giving experimental details for the reactions of $\mathrm{H(PhMeSi)_3H}$ with 1, 2, and 3 equiv of HOTf and characterization data for selected products produced from quenching with RMgX and Figures 1–3 of sample ^{1}H NMR spectra (12 pages). Ordering information is given on any current masthead page.

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[14] A simultaneous rearrangement process cannot be completely eliminated. The ratio of $\mathrm{SiPh_{D(terminal)}}$ to $\mathrm{SiPh_{(terminal)}}$ is ~27:1, and $\mathrm{SiPh_{(internal)}}$ to $\mathrm{SiPh_D}$(internal) is ~13:1, and will influence the measured proton loss in a minor fashion.

[15] A mixture of isomers was formed from $\mathrm{H(PhMeSi)_3H}$ with 3 equiv of HOTf followed by reaction with PhMgBr. Details are provided in the supplementary material.

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