The Reactions of [Tris(trimethylsilyl)methyl]diphenylbromosilane and Tetra-n-butylphosphonium Chloride

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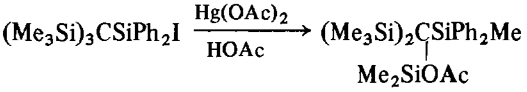
Abstract

Reaction between $(Me_3Si)_3CSiPh_2Br$ **3** and n-Bu_4PCl gives two products, $(Me_3Si)_3CSiPh_2Cl$ **4** and $(Me_3Si)_2CHSiPh_2OSiMe_3$ **5**, under hetero- and homogeneous conditions. The two products are quite unusual , the chloride **4** as one of the first examples of a direct nucleophilic displacement in the highly hindered trisyl system, the siloxane **5** as the first example of a new rearrangement. The nature of the oxygen impurity in Bu_4PCl which gives siloxane **5** is discussed as are the mechanisms of formation of both products.

Introduction

We recently reported some unusual reactions of [tris(trimethylsilyl)methyl] dimethylbromo- and chloro-silane**. Particularly important was the discovery that $TsiSiMe_2Br$ **1**, a compound normally quite unreactive [2], gave $TsiSiMe_2Cl$ **2** in high yield under heterogeneous reaction conditions with tetra-n-butylphosphonium chloride (eqn. 1). This reaction is unusual not only because of its relative rapidity, but also because of the nature of the interaction between n-Bu_4PCl and the starting bromosilane **1** [1]. Indeed, it represents the first reported example of a nucleophilic displacement in a trisyl compound [3]†. Because of the elegant work of Eaborn and coworkers [4, 5] on rearrangements of certain trisyl compounds (eqn. 2) and because **1** can only undergo degenerate rearrangement, we decided to study the reaction between tetra-n-butylphosphonium chloride and [tris(trimethylsilyl)methyl]-diphenylbromosilane **3**, a trisyl compound which can undergo rearrangement. We have examined this reaction under both hetero- and homogeneous conditions demonstrating that $TsiSiPh_2Cl$ **4** forms without rearrangement. Remarkably, however, this reaction takes a quite different course since **4** is not the major product. Rather, a new rearrangement [6] has been observed, resulting in the formation of the unexpected product $(Me_3Si)_2CHSiPh_2OSiMe_3$ **5**. In this paper, we describe our studies of this reaction along with speculations on the formation of **4** and **5** and the nature of the phosphonium chloride reactant.

$$\underset{\mathbf{1}}{(Me_3Si)_3CSiMe_2Br} + n\text{-}Bu_4PCl \xrightarrow[100^\circ]{\text{tetradecane}} \underset{\mathbf{2}}{(Me_3Si)_3CSiMe_2Cl} \qquad (1)$$



$$(Me_3Si)_3CSiPh_2I \xrightarrow[HOAc]{Hg(OAc)_2} (Me_3Si)_2\underset{\displaystyle Me_2SiOAc}{C}SiPh_2Me \qquad (2)$$

Experimental

General Remarks: The reactions studied have generally been carried out under atmospheric conditions, although we have demonstrated that the same results are obtained when such reactions are run in an inert atmosphere of dry nitrogen. A few reactions and transfers were carried out in a KSE dry-box, as indicated. Gas chromatographic analysis has been carried out using a Perkin-Elmer 3920B chromatograph with flame ionization detection. The columns

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**The [tris(trimethylsilyl)methyl] group, $(Me_3Si)_3C$, is generally named trisyl and abbreviated Tsi.

†Eaborn, in ref. 3, reports several nucleophilic displacements of iodine in $TsiSiMe_2I$. A footnote in Eaborn's paper suggests that our reaction between $TsiSiMe_2Br$ and Bu_4PCl is also a direct nucleophilic displacement.

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generally used were 1/8″ × 6′ 10% OV-1 silicone oil on Chromosorb WHP. The yields reported are determined gas chromatographically unless otherwise specified. GC-MS analysis was carried out on a Finnigan 3200 with a Teknivent data system. NMR spectroscopy was done using Varian EM60, JEOL FX90Q, Bruker WM 250, and Bruker WM 360 spectrometers. ^{31}P NMR spectra are reported relative to external phosphoric acid. A Perkin-Elmer 237B IR spectrometer was used for IR analysis. Carbon-hydrogen analyses were carried out by Huffman Laboratories, Wheatridge, Colorado.

The trisyl compounds used in this study were prepared by the methods reported by Eaborn [7]. Tetra-n-butylphosphonium chloride was obtained commercially from Alfa and Strem Chemicals and prepared by us. All samples of it behaved in a similar manner.

Reaction of $TsiSiPh_2Br$ 3 and $n\text{-}Bu_4PCl$ in Heptane

In a typical reaction equimolar* quantities of $TsiSiPh_2Br$ **3** and Bu_4PCl were mixed in dry heptane (1 ml heptane/0.002 mol of reactants). The phosphonium salt formed a lower layer. Heating at 100° with magnetic stirring was required for reaction. Gas chromatographic analysis demonstrated the formation of two products subsequently identified as $TsiSiPh_2Cl$ **4** and $(Me_3Si)_2CHSiPh_2OSiMe_3$ **5**. The product ratios vary slightly with **5** generally forming in greater amounts. Typically, the **5**/**4** are between 1.4 and 1.0. Under these conditions, some starting material (between 5–15%) remains. The reaction time varies between 5–10 days.

Subsequent additions of tetra-n-butylphosphonium chloride cause the starting bromide **3** to be consumed while the ratio of **5**/**4** increases. Eventually, only **5** is present in the heptane layer. Large scale (**3**; 5g) reactions have been stopped at the stage when little starting **3** remained in order to isolate and identify **4**. Work-up has been accomplished by separation of the heptane and phosphonium chloride layers and thorough washing of the phosphonium salt layer with heptane. After drying the heptane layer ($MgSO_4$), it was rotovaped, leaving a yellow oil. From the oil, some crystals slowly precipitate. These are separated by washing with cold ethanol, in which the oil dissolves, but the crystals do not. The crystals were shown to be $TsiSiPh_2Cl$ **4** by comparison with an authentic sample [7].**

The other component, the yellow oil, was isolated and characterized under different conditions, ones where the amount of **4** was minimized. Thus, if the reaction is allowed to continue for between 30–40 days, with several additions of Bu_4PCl, essentially no **3** or **4** remain. Separation of the heptane layer, drying, and rotovaping gives a yellow oil (98% yield) which, by gas chromatographic and HLPC analysis, is essentially one peak. This material is purified by preparative HPLC (on an EM Reagents Lobar Si 60 column, CH_2Cl_2 diluent) giving an analytical sample of a viscous clear oil characterized as **5** as follows: *Anal.* calcd. for $C_{22}H_{23}Si_4O$: C, 61.32; H, 8.89. Found: C, 61.06; H, 8.76. NMR (^{13}C in $CDCl_3$): δ 2.151, 2.866, 4.752, 127.073, 128.699, 134.096, and 139.429. NMR (^{29}Si in $CDCl_3$): −12.923 (1 Si), −0.329 (2 Si) and 9.054 (1 Si). NMR (^1H, 360 MHz, in $CDCl_3$): −0.068 (18 H), 0.003 (1 H), 0.127 (9 H), and 7.3–7.5 (10 H). MS (chemical ionization with CH_4): two clusters, one at 415 (M-15) and one at 353 (M-77). IR (neat, NaCl) gave characteristic aliphatic and aromatic C–H as well as absorptions at 1430, 1260, and 1110 cm^{-1} assigned to Si–Ph, Si–CH_3, and Si–Ph, respectively.

In addition, the heptane layer of reaction mixtures of this type have been extensively analyzed by GC-MS, affording us a fairly simple analytical scheme for compounds **4** and **5**, one used often in subsequent reactions.

Reaction of $TsiSiPh_2Br$ 3 and $n\text{-}Bu_4PCl$ in Toluene

In a typical experiment, equimolar* quantities of $TsiSiPh_2Br$ **3** and Bu_4PCl were dissolved in dry toluene (1 ml toluene/0.002 mol of reactants). GC and GC-MS analyses revealed that $(Me_3Si)_2CHSiPh_2OSiMe_3$ **5** was the major product, generally being present in amounts ten fold greater than those of $TsiSiPh_2Cl$ **4** and starting material **3**. Such reactions were carried at room temperature, with reaction times of 20–60 minutes.

Reaction of $TsiSiPh_2Br$ 3 and $n\text{-}Bu_4PCl$ in Methanol/Heptane and in Methanol/Toluene

Typically, equimolar* quantities of $TsiSiPh_2Br$ **3** and Bu_4PCl were added to either heptane or toluene in which methanol had been dissolved. Under the heterogeneous conditions with heptane, methanol was present in 4-fold molar excess of the starting bromide **3**; under homogeneous conditions with toluene, methanol was present in 12-fold molar excess. In heptane, the reaction was carried out at 100°; in toluene, at room temperature. Under both sets of reaction conditions, the results were no different from those obtained when methanol was absent. Detailed GC-MS analysis of the very minor peaks which are present in all of these reactions revealed nothing that could be interpreted as a methanol–silene adduct. Similarly, 250 MHz NMR analysis of reaction mixtures obtained by removal of solvent revealed no methanol adducts.

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*For the purpose of stoichiometric calculations, we have arbitrarily assumed that Bu_4PCl is pure.

**We wish to thank C. Eaborn for an authentic sample of the rearranged chloride.

Reaction of TsiSiMe$_2$Br 1 and n-Bu$_4$PCl in Methanol/Toluene Solution

When equimolar quantities of bromide **1** and tetra-n-butylphosphonium chloride were dissolved in a methanol/toluene solution containing a 12-fold molar excess of methanol (over bromide **1**), the room temperature reaction proceeded to give only TsiSiMe$_2$Cl **2** and unreacted starting bromide **3**, in a ratio of approximately 3 to 1.

Attempts to Dry n-Bu$_4$PCl

A. Heating/Vacuum Drying

Bu$_4$PCl was heated at 61° at 0.05 mm for 2½ days. The 'dried' material thus obtained when reacted with TsiSiPh$_2$Br **3** under N_2 gave results identical to those obtained with 'wet' Bu$_4$PCl.

B. Solutions of Methylene Chloride and Toluene/Molecular Sieves

Bu$_4$PCl dissolves in both methylene chloride and toluene. When such solutions are 'dried' with activated 4 Å molecular sieves and then tested for dryness by reaction with TsiSiPh$_2$Br **3**, we see no suppression in the formation of siloxane **5**.

C. Azeotropic Distillation of Toluene Solutions of n-Bu$_4$PCl

When a solution of Bu$_4$PCl in toluene was heated at reflux in a Dean-Stark apparatus, no water separated even over periods of several weeks.

Exchange Attempt Between D$_2$O and n-Bu$_4$PCl

Bu$_4$PCl (2 g) (Strem) was dissolved in D_2O (3 ml) and magnetically stirred for 4 days. The D_2O was removed by rotary evaporation and the resulting oily solid dissolved in dry toluene. The toluene solution after drying over molecular sieves was separated and evaporated. The resulting oily solid when analyzed by IR showed only O–H absorptions at 3375 cm^{-1}.

Removal of Oxygen Reactant from n-Bu$_4$PCl by Reaction with TsiSiPh$_2$Br 3

In a typical experiment, TsiSiPh$_2$Br (1.0 g; 0.002 mol) and Bu$_4$PCl (0.6 g; 0.002 mol) were reacted under dry nitrogen in refluxing heptane (5 ml) for about 1 month. During this period small quantities of TsiSiPh$_2$Br were added to insure that all the oxygen in the Bu$_4$PCl was removed by formation of siloxane **5**. Careful decantation of the mixture and repeated washings with dry heptane afforded a viscous liquid, physically indistinguishable from the starting Bu$_4$PCl. This material, called deoxygenated Bu$_4$PCl for simplicity, was divided and reacted as described below. All work-up, dividing operations, and sample preparations were carried out in a dry box.

A sample of this material was dissolved in CDCl$_3$ for ^{31}P NMR analysis. NMR (^{31}P in CDCl$_3$, 250 MHz): 33.6 ppm.

Reaction of Deoxygenated n-Bu$_4$PCl and TsiSiPh$_2$-Br 3

Deoxygenated Bu$_4$PCl (0.10 g; 0.0003 mol) and TsiSiPh$_2$Br (0.17 g; 0.0003 mol) were dissolved in toluene (3 ml). Only a small amount of siloxane **5** (10–15%) forms, suggesting that all the oxygen has not been removed from the Bu$_4$PCl. This reaction, however, is markedly different from those with unaltered Bu$_4$PCl, where siloxane **5** forms in large amounts.

Reaction of Deoxygenated n-Bu$_4$PCl and TsiSiMe$_2$Br 1

Deoxygenated Bu$_4$PCl (0.10 g; 0.0003 mol) and TsiSiMe$_2$Br (0.13 g; 0.0003 mol) were dissolved in toluene (3 ml). No reaction could be detected either at room temperature or after refluxing for several days.

Preparation of n-Bu$_4$PCl

Tributylphosphine (Aldrich; 3.1 g; 0.015 mol) and freshly dried and distilled 1-chlorobutane (Aldrich; 1.4 g; 0.015 mol) were charged into a dry glass bomb. All operations and sample preparations were carried out in a dry box. The bomb was stoppered and heated between 100° and 120° in the dry box for 3 days. On cooling a white precipitate formed in an oily matrix. Repeated additions of dry heptane followed by decantation afforded a nicely crystalline, white precipitate whose reactivity was identical to the commercial samples used in these studies.

A sample of this material was prepared for NMR analysis. NMR (^{31}P in CDCl$_3$, 250 MHz): 33.8 ppm.

Phosphorus-31 NMR Studies

Samples of n-Bu$_4$PCl and Bu$_3$P were submitted to ^{31}P NMR analysis. Commercially available Bu$_4$PCl (Strem), Bu$_4$PCl prepared by us, and deoxygenated Bu$_4$PCl each gave a single peak ^{31}P NMR spectrum with resonances at 33.8, 33.8, and 33.6 ppm, respectively. Commercial Bu$_3$P (Aldrich) had a major resonance at –29.7 ppm, but, in addition, there were five other resonances at 57.8, 48.7, 38.8, 35.2, and –68.4 ppm.

Results and Discussion

Reaction between $TsiSiPh_2Br$ **3** and $n\text{-}Bu_4PCl$ has been carried out under both homogeneous (toluene) and heterogeneous (heptane) conditions (eqn. 3).

$$\underset{\mathbf{3}}{(Me_3Si)_3CSiPh_2Br} + n\text{-}Bu_4PCl \longrightarrow \underset{\mathbf{4}}{(Me_3Si)_3CSiPh_2Cl} + \underset{\mathbf{5}}{(Me_3Si)_2CHSiPh_2OSiMe_3} \qquad (3)$$

Under a variety of such conditions, the reaction takes a course leading to only **4** and **5**. When equimolar * quantities of the starting materials were dissolved in toluene and allowed to stir at room temperature for 20–60 min., siloxane **5** was obtained in about a 10-fold excess over $TsiSiPh_2Cl$ **4** and starting material **3**. The addition of excess Bu_4PCl gave an identical result. Increases in temperature and/or reaction time did not result in any significant changes.

In contrast, the equimolar* heterogeneous reaction in heptane at 100° gives a product distribution only slightly favoring siloxane **5** (a large number of such reactions have yielded **5/4** product rations between 1.4 and 1) with between 5 and 15% starting bromide **3** left unreacted. It generally requires 5–10 days to reach the stage where no further starting bromide **3** is consumed. Subsequent additions of $n\text{-}Bu_4PCl$ cause the unreacted starting bromide **3** to be consumed as the **5/4** ratio increases. Eventually, after as long as 30–40 days, the siloxane **5** is the only product.

Both of the products of reaction (3) are remarkable, $TsiSiPh_2Cl$ 4 because it is the first example of a direct nucleophilic displacement on silicon in a diphenylbromo-substituted trisyl systym [3] and $(Me_3Si)_2CHSiPh_2OSiMe_3$ **5** because of its unusual and unexpected structure. Indeed, characterization of the unrearranged chloride **4** has been very carefully carried out by comparison with authentic samples of $TsiSiPh_2Cl$ [7] and $(Me_3Si)_2C(SiMe_2Cl)SiPh_2Me$**; we see no evidence that any rearranged chloride forms. Other studies of trisyl systems under nucleophilic attack [2b, 8] have been carried out in strongly basic media, leading to products thought to have formed by an eliminative reaction scheme (eqn. 4). Our reaction conditions were selected to force nucleophilic reaction under presumably non-basic conditions. We wondered whether the severe steric constraints of the Tsi group would allow any nucleophilic displacement recognizing that typical optically active bromosilanes (unhindered ones) undergo nucleophilic displacement with inversion [9, 10]. It is highly unlikely that $TsiSiPh_2Cl$ **4** forms with inversion; we believe it is far more likely that it results from a frontal attack at silicon. Since no rearrangement occurs, it also seems clear that substitution is not occurring by a dissociative process through a cationic intermediate.

$$\begin{tikzcd}
(Me_3Si)_3CSiR_2X \arrow[r, "MeO^-", "MeOH"'] & {} \\
{[Me_3SiOMe + (Me_3Si)_2C{=}SiR_2 + X^-]} \arrow[d, "MeOH"] & (4) \\
(Me_3Si)_2CHSiR_2OMe &
\end{tikzcd}$$

The formation of siloxane **5** occurs under all of the conditions we have investigated. Various observations suggest that $n\text{-}Bu_4PCl$, though the source of oxygen leading to siloxane **5**, is not contaminated by bulk water. For example, while infrared analysis of solutions of $n\text{-}Bu_4PCl$ reveal O–H stretching bonds centered at 3375 cm^{-1}, attempts to exchange the O–H with D_2O have failed as have several drying methods including azeotropic distillation of a solution of $n\text{-}Bu_4PCl$ in toluene. Phosphorous-31 NMR spectra of samples of Bu_4PCl both commercially supplied and prepared by us from Bu_3P and BuCl show a single resonance at 33.8 ppm, consistent with literature reports [11]. We have also prepared a deoxygenated Bu_4P^+ species by reaction of $TsiSiPh_2Br$ **3** and either commercially supplied or synthetic Bu_4PCl in heptane. When the reaction is complete (*i.e.* when incremental additions of **3** yield no more siloxane **5**), all those species soluble in heptane are removed, leaving a deoxygenated phosphonium species. Phosphorus-31 NMR of this material shows a single resonance at 33.6 ppm, strongly suggesting that the $n\text{-}Bu_4P^+$ moiety is intact. We have found that this material is essentially unreactive with both $TsiSiMe_2Br$ **1** and $TsiSiPh_2Br$ **3** in toluene. Thus, both reaction (1) and (3) require the fully constituted Bu_4PCl, *i.e.* either the commercial or synthetic samples we have used which contain large amounts of some oxygen species. We do not believe that the oxygen species is water bound to the Bu_4P^+ primarily because the ^{31}P NMR shifts of the Bu_4PCl samples and the deoxygenated material are essentially identical. Were water somehow strongly bound to Bu_4P^+, we would expect a large chemical shift difference between the oxygenated and deoxygenated materials. We are at present unable to shed any additional light on the phosphorus species which brings about reaction (3) although we are actively pursuing this question. We know of no other reactions of Bu_4PCl in which oxygen containing products are obtained; we are, however, suggesting that some of the reported reactions [12] involving Bu_4PCl may result from the oxygen impurities which are seemingly present in many samples of this material. Finally, the persistent nagging question about why $TsiSiMe_2Br$ **1** gives no oxygenated products in reaction 1 while $TsiSiPh_2$-

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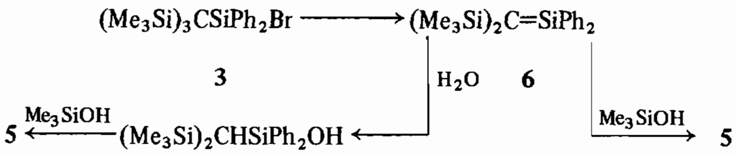
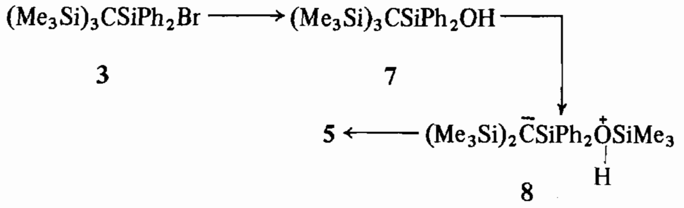
*,**See footnotes page 70.



(5)



(6)

Br 3 gives siloxane 5 remains. We believe its unraveling requires a reasonable grasp of what the Bu_4PCl oxygen impurities are.

Without knowing the nature of the phosphonium species involved in reaction (3), we can still comment on some aspects of the mechanism of formation of siloxane **5**. Two possibilities are suggested (eqns. 5 and 6). In reaction (5), an intermediate silene **6** could form, presumably generated by either a thermal elimination of Me_3SiBr followed by its conversion to Me_3SiOH or by hydroxide ion promoted elimination of Me_3SiOH and Br^-. We do not favour this, because we have been unsuccessful in trapping silene **6** with methanol*. Instead, we favor a mechanism related to reaction (6), recognizing that details of this unusual rearrangement are yet unknown. The intermediate oxygen-containing species 7 has recently been prepared by Eaborn and undergoes an analogous rearrangement with NaOMe [13]. In addition, other examples of such rearrangements have been reported jointly by Eaborn and us [6]. Among the most important factors favoring such rearrangements are the proximity of a nucleophilic group on the $SiPh_2$ moiety to a trimethylsilyl group (suggesting a relief of strain upon rearrangement) and the stabilization of a carbanionic species like 8 by three adjacent silyl substitutions.

In summary, we have reported the unusual reaction between $TsiSiPh_2Br$ **3** and Bu_4PCl. The formation of both products, the unrearranged $TsiSiPh_2Cl$ **4** and the siloxane **5**, have been discussed. The chloride **4** is believed to form by frontal nucleophilic attack at silicon while the siloxane **5** forms by rearrangement probably from an intermediate oxygen-containing species like $TsiSiPh_2OH$ 7. Introduction of oxygen into the silicon products by the Bu_4PCl is also considered, but any detailed mechanism must await a proper characterization of the oxygen impurity in Bu_4PCl.

Acknowledgements

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*Attempts to trap a silene intermediate, in reaction (1), have also been unsuccessful.