

Comparison of the reactivities of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ and $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{I}$

Abdulrahman I. Almansour

Department of Chemistry, College of Science, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia

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Abstract

The compound $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{I}$, **2**, reacts more readily than $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$, **1**, with electrophiles (AgNO_3 in MeCN; ICl in CH_2Cl_2) but less readily than **1** with the nucleophilic KSCN in MeCN, in keeping with the view that the former type of reaction involves anchimerically assisted formation of an alkyl-bridged cation in the rate-determining step and the latter direct nucleophilic attack at the functional silicon centre. Surprisingly, **2** is more reactive than **1** towards MeOH but less reactive than the latter towards H_2O –dioxane, adding to the enigma of the mechanism of such solvolyses. The reactions of the labelled compound $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{I}$ with MeOH or H_2O –dioxane take place at the same rate as that of **1** within the experimental uncertainty, and proceed without detectable formation of the rearranged products $(\text{Me}_3\text{Si})_2\text{C}[\text{Si}(\text{CD}_3)_2\text{Me}]\text{SiMe}_2\text{OX}$, $\text{X} = \text{Me}$ or H , confirming that the solvolyses do not involve cation formation. © 1997 Elsevier Science S.A.

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1. Introduction

In a series of studies it has been shown that for the iodide $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$, **1**, in which approach to the functional silicon centre is highly sterically hindered, three distinct mechanisms of substitution can be observed (see Ref. [1]).

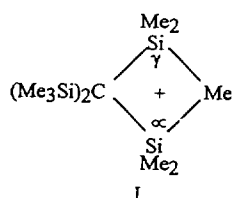
(a) Direct nucleophilic substitution. This is observed in reactions with, for example, CsF , NaN_3 , or KSCN in MeCN or, alongside other reactions, in MeOH [2,3]. The reactions have been shown to be of first order with respect to each reactant, and so can be assumed to be a bimolecular process of the $\text{S}_{\text{N}}2$ type (though possibly involving a five-coordinate intermediate) [4]. The reactions are slower by many powers of ten than those of simple trialkylsilyl iodides.

(b) Reaction via a cationic intermediate. This is observed, for example, in the reactions of **1** with silver salts AgX [5] or ICl [6], and appears to involve formation of the bridged cation **I**, which is then attacked by the nucleophile Y^- or Cl^- (at either the α - or γ -Si centre) to give $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Y}$ or $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Cl}$ respectively. (We have recently found that in such

reactions with $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{I}$, denoted below by **1-D**, less than the expected 50% of the rearranged product $(\text{Me}_3\text{Si})_2\text{C}[\text{Si}(\text{CD}_3)_2\text{Me}]\text{SiMe}_2\text{Y}$ or $(\text{Me}_3\text{Si})_2\text{C}[\text{Si}(\text{CD}_3)_2\text{Me}]\text{CSiMe}_2\text{Cl}$ is formed [7,8], suggesting that the mechanism is somewhat more complex than that outlined above, but we ignore this complication in the discussion below.)

(c) An undefined and very puzzling mechanism encountered in the reactions of **1** or the related more reactive compounds $(\text{Me}_3\text{Si})_3\text{CSiPhHI}$ [9] and $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{X}$, $\text{X} = \text{OCIO}_3$, OCN or OSO_2CF_3 , with MeOH or H_2O [10]. These reactions (unlike those of compounds $(\text{Me}_3\text{Si})_3\text{CSiPhHX}$ with, for example, $\text{X} = \text{Br}$ or Cl [8]) are not accelerated by addition of NaOMe or NaOH and so seem not to be simple nucleophilic substitutions, but the effects of the substituents Y in reactions of compounds of the types $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{Y})\text{HI}$ [11] and $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{C}_6\text{H}_4\text{Y})\text{SiMe}_2\text{I}$ [12] indicate that the solvent is nucleophilically involved in the rate-determining step. Certainly, it seems clear that the solvolyses do not involve a bridged cation, since no rearranged products are formed from $(\text{Me}_3\text{Si})_3\text{CSiEt}_2\text{I}$ or $(\text{Me}_3\text{Si})_3\text{CSiPh}_2\text{I}$

[13,14] (or, as we shall show below, from $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{I}$).



In an attempt to gain further information about these mechanisms we have now examined the reactions of the compound $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{I}$, in which the Pr^i group can be expected to cause a significant increase in the steric hindrance to direct attack at the $\text{Si}-\text{I}$ bond but on the other hand to provide a better bridge than Me in an intermediate cation, as it does in the case of 1,2-bridged alkyl cation. In terms of the mechanisms of reactions of **1** set out above, **2** would be expected to react more readily than **1** with silver salts or ICl , but less readily than **1** with KSCN in MeCN . The effect of the Pr^i groups on the third type of process could not be predicted with confidence, but in view of the seeming importance of the nucleophilic attack the additional steric hindrance seemed likely to lead to a lower rate.

We have also taken the opportunity to examine the relevant reactivities of **1** and **1-D** in methanolysis and hydrolysis, and confirmed that the reactions do not involve an intermediate cation.

2. Experimental

2.1. General

Except for dioxane, which was used as-received, solvents were dried by standard methods and distilled from the drying agents immediately before use. The AgNO_3 and KSCN were dried by storage under vacuum (0.2 mmHg). The ^1H NMR spectra were recorded at 100 MHz for solutions in CDCl_3 , and IR spectra were recorded on a Perkin Elmer 883 spectrophotometer for solutions in CCl_4 . Mass spectra were obtained by electron impact at 70 eV; except for the $\text{M}-\text{Me}$ peak, only peaks of relative intensity $> 10\%$ are reported.

2.2. Preparations of compounds $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CH}$, $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{H}$, and $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{I}$

These were prepared as previously described [15]. A re-examination of the ^1H NMR spectra yielded the following data: for $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CH}$, δ -0.31 (1H, s, quat. CH), 0.095 (18H, s, SiMe_2), 0.96 (18H, s, Me_2C)

and 1.33 (3H, m, Me_2CH); for $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{H}$, δ 0.21 (18H, s, SiMe_2Pr^i), 0.36 (6H, d $J = 4$ Hz, SiMe_2H), 1.00 (18H, d $J = 5$ Hz, Me_2C), 1.21 (3H, m, Me_2CH) and 4.40 (1H, m, SiH); for $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{I}$, δ 0.35 (18H, s, SiMe_2Pr^i), 1.02 (6H, s, SiMe_2I), 1.14 (18H, d $J = 8$ Hz, Me_2C), and 1.40 (3H, m, Me_2CH). For the iodide m/z 457 (100, $\text{M}-\text{Pr}^i$), 373 (20, $\text{M}-\text{I}$), 341 (20), 313 (20), 299 (10), 257 (10), 215 (10), 201 (10), 187 (25), 171 (15), 129 (15), 73 (60), 59 (20) and 43 (10).

2.3. Preparations of compounds $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{X}$

2.3.1. $\text{X} = \text{Cl}$

A solution of ICl (0.12 g, 0.74 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of **2** (0.30 g, 0.60 mmol) in CH_2Cl_2 (10 cm^3) and the mixture was stirred at room temperature (ca. 24°C) for 20 h (probably much longer than necessary) then shaken with aqueous NaHSO_3 . The organic layer was separated, dried (MgSO_4) and evaporated under vacuum. The residue was sublimed (130°C at 0.5 mmHg) to give $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{Cl}$ (0.18 g, 74%), m.p. 185°C . (Anal. Found: C, 52.87; H, 11.02. Calc. for $\text{C}_{18}\text{H}_{45}\text{ClSi}_4$: C, 52.88; H, 11.02%.) δ_{H} 0.29 (18H, s, SiMe_2Pr^i), 0.72 (6H, s, SiMe_2Cl), 1.03 (18H, d $J = 6$ Hz, CMe_2) and 1.22 (3H, m, Me_2CH); mass spectrum: m/z 393 (5, $\text{M}-\text{Me}$), 365 (100, $\text{M}-\text{Pr}^i$), 347 (10), 323 (10), 201 (10), 187 (20), 73 (15) and 59 (10).

2.3.2. $\text{X} = \text{OH}$

A solution of **2** (0.30 g, 0.60 mmol) in dioxane (15 cm^3) containing 5 vol.% of water was stirred under reflux for 40 h. Charcoal was then added followed by MgSO_4 . Filtration and removal of the solvent under vacuum gave $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{OH}$ (0.16 g, 68%), a colourless oil. (Anal. Found: C, 55.37; H, 11.78. Calc. for $\text{C}_{18}\text{H}_{46}\text{OSi}_4$: C, 55.38; H, 11.79%.) δ_{H} 0.24 (18H, s, SiMe_2Pr^i), 0.41 (6H, s, SiMe_2O), 1.02 (18H, d $J = 5$ Hz, CMe_2) and 1.25 (3H, m, Me_2CH). IR spectrum: (OH) 3670 cm^{-1} . Mass spectrum: m/z 375 (5, $\text{M}-\text{Me}$), 347 (100, $\text{M}-\text{Pr}^i$), 331 (65), 187 (10), 73 (25) and 59 (10). Attempts to crystallize the product oil were unsuccessful.

2.3.3. $\text{X} = \text{OMe}$

A solution of **2** (0.30 g, 0.60 mmol) in MeOH (45 cm^3) was stirred under reflux for 42 days. The solvent was removed under vacuum and the residue was sublimed (135°C at 0.5 mmHg) to give $(\text{Pr}^i\text{Me}_2\text{Si})_3\text{CSiMe}_2\text{OMe}$ (0.19 g, 79%), m.p. 217°C . (Anal. Found: C, 56.44; H, 11.87. Calc. for $\text{C}_{19}\text{H}_{48}\text{OSi}_4$: C, 56.44; H, 11.88%.) δ_{H} 0.20 (18H, s, SiMe_2Pr^i), 0.33 (6H, s, SiMe_2O), 0.98 (18H, d $J = 6$ Hz, CMe_2), 1.26 (3H, m, Me_2CH) and 3.33 (3H, s, OMe). Mass spectrum: m/z 389 (10, $\text{M}-\text{Me}$), 361 (100, $\text{M}-\text{Pr}^i$).

2.3.4. $X = \text{NCS}$

A mixture of **2** (0.30 g, 0.60 mmol) and KSCN (0.60 g, 6.2 mmol) in MeCN (30 cm³) was stirred under reflux for 2 h and the solvent then removed under vacuum. The residue was shaken with a mixture of water and CH₂Cl₂ and the organic layer was separated, washed, dried (MgSO₄) and evaporated under vacuum. The residue was sublimed (150 °C at 0.5 mmHg) to give (Pr¹Me₂Si)₃CSiMe₂NCS (0.20 g, 76%), m.p. 249 °C. (Anal. Found: C, 52.90; H, 10.44; N, 3.25. Calc. for C₁₉H₄₅NSSi₄: C, 52.90; H, 10.44; N, 3.25%.) δ_{H} 0.27 (18H, s, SiMe₂Pr¹), 0.60 (6H, s, SiMe₂N), 1.03 (18H, d $J = 5$ Hz, CMe₂) and 1.28 (3H, m, Me₂CH). IR: (NCS) 2080 cm⁻¹. Mass spectrum: m/z 416 (5, M – Me), 388 (100, M – Pr¹), 272 (15), 244 (20), 229 (10), 201 (10), 187 (25), 129 (10), 73 (65), 59 (25) and 43 (10).

2.3.5. $X = \text{ONO}_2$

A mixture of **2** (0.30 g, 0.60 mmol) and AgNO₃ (0.20 g, 1.2 mmol) in MeCN (30 cm³) was stirred vigorously at room temperature under nitrogen with protection from light for 25 h and the solvent then removed under vacuum. The residue was extracted with hexane, the extract filtered and evaporated under vacuum. The residue was sublimed (140 °C at 0.5 mmHg) to give (Pr¹Me₂Si)₃CSiMe₂ONO₂ (0.17 g, 66%), m.p. 235 °C. (Anal. Found: C, 49.65; H, 10.34; N, 3.22. Calc. for C₁₈H₄₅NO₃Si₄: C, 49.66; H, 10.34; N, 3.22%.) δ_{H} 0.29 (18H, s, SiMe₂Pr¹), 0.74 (6H, s, SiMe₂O), 1.01 (18H, d $J = 5$ Hz, CMe₂) and 1.22 (3H, m, Me₂CH). Mass spectrum: m/z 420 (10, M – Me), 392 (100, M – Pr¹), 376 (15), 248 (15), 205 (10), 187 (15) and 73 (20).

2.4. Rate comparisons

In each case the extent of reaction was determined from the relative integrals of the ¹H NMR signals from the (Me₃Si)₃C or (Pr¹Me₂Si)₃C protons. Reactions of **1**, (**1**-D) and **2** were carried out at the same time alongside one another under conditions as similar as possible. The comparisons were all repeated, and no significant differences in the results were observed.

2.4.1. Reaction with KSCN

A mixture of the relevant iodide (0.20 mmol) and KSCN (0.20 g, 2.11 mmol) in MeCN (10 cm³) was stirred under reflux for 15 min then cooled quickly to room temperature. The solvent was then rapidly evaporated under vacuum at room temperature and the residue extracted with hexane. The extract was filtered and evaporated, the residue dissolved in CDCl₃, and the ¹H NMR spectrum recorded. This showed that ca. 70% of **1** and 45% of **2** had reacted.

2.4.2. Reaction with AgNO₃

The relevant iodide (0.20 mmol) was stirred with MeCN (20 cm³) for 1 h at room temperature to ensure that dissolution was complete, and finely powdered AgNO₃ (0.070 g, 0.41 mmol) was then added. The mixture was stirred vigorously for 4 h at room temperature (ca. 24 °C) under nitrogen with protection from light, after which the solvent was then rapidly evaporated under vacuum at room temperature. The residue was extracted with hexane, the extract filtered and evaporated, and the residue dissolved in CDCl₃, for recording of the ¹H NMR spectrum. This showed that ca. 20% of **1** and 85% of **2** had reacted.

2.4.3. Reaction with ICl

A solution of ICl (0.20 mmol) in CH₂Cl₂ (5 cm³) was added to a solution of the relevant iodide (0.20 mmol) in CH₂Cl₂ (5 cm³) and the mixture was shaken at room temperature for 1 min then quickly added to cold aqueous NaHSO₄ and shaken vigorously with it. The organic layer was then separated, dried (MgSO₄) and evaporated, and the residue dissolved in CDCl₃ for recording of the ¹H NMR spectrum. This showed that ca. 55% of **1** and 75% of **2** had reacted.

2.4.4. Hydrolysis

A solution of the relevant iodide (0.20 mmol) in 5 vol.% of water in dioxane (5 cm³) was stirred under reflux. The solvent was then rapidly evaporated under vacuum at room temperature, the residue dissolved in CDCl₃, and the ¹H NMR spectrum recorded. After 15 h ca. 88% of **1** and 62% of **2** had reacted, and after 5 h 53% of **1**-D and 49% of **1**. After complete reaction (50 h) there was no detectable amount of rearranged hydroxide from **1**-D.

2.4.5. Methanolysis

A mixture of the relevant iodide (0.20 mmol) in MeOH (15 cm³) was kept under nitrogen in a thermostatted bath at 52 ± 0.3 °C for 1 h, after which the iodide had completely dissolved. The solvent was then rapidly evaporated under vacuum at room temperature, the residue dissolved in CDCl₃, and the ¹H NMR spectrum determined. After 7 days ca. 28% of **1** and 50% of **2** had reacted, and after 15 days 53% of **1**, 76% of **2**, and 54% of **1**-D had reacted. After complete reaction (100 h) there was no detectable amount of rearranged methoxide from **1**-D.

3. Results and discussion

The preparation of the iodide **2** was described in an earlier report [14]. The puzzling ¹H NMR data presented there were in error, and correct data are given above in Section 2.

We first compared the reactivities of **1** and **2** (0.20 mmol) towards an excess of KSCN (2.1 mmol) in MeCN (10 cm³) under reflux. After 15 min ca. 70% of **1** and 45% of **2** had reacted, indicating that **1** is ca. three times the more reactive, in keeping with the greater steric hindrance in **2**.

We next examined the reactions of **1** and **2** (0.20 mmol) with AgNO₃ (0.41 mmol) in MeCN at room temperature. After 4 h, ca. 85% of **2** but only 20% of **1** had reacted, indicating that **2** is rather more than ten times the more reactive. We note, however, that the AgNO₃ was not completely dissolved, and this could give rise to significant uncertainty in the quantitative comparison, but virtually identical results were obtained in repeat experiments and there seems no doubt that **2** is at least a few times the more reactive. (It would have been better in principle to carry out a competition experiment between the two iodides in the one solution, but overlapping of the NMR signals used for the analyses prevented that.) Subsequently, a solution of ICl (0.20 mmol) in CH₂Cl₂ (5.0 cm³) was added to a solution of **1** or **2** (0.20 mmol) in CH₂Cl₂ (5.0 cm³) and the mixture was shaken at room temperature (ca. 24 °C) for 1 min then quickly shaken with an excess of aqueous sodium thiosulfate and the organosilicon mixture isolated from the organic layer. The ¹H NMR spectra showed that ca. 75% of **2** and 55% of **1** had reacted. There is obviously a substantial margin of error in these figures because of the short reaction time, but there is no doubt that **2** is significantly the more reactive, in keeping with the result for the silver salt reaction.

The studies of the solvolyses produced a surprise. In the reaction with 5 vol.% H₂O in dioxane at the reflux temperature, after 15 h 88% of **1** and 62% of **2** had been converted into the corresponding hydroxide, indicating that **1** was ca. 2.2 times the more reactive, consistent with the predominance of nucleophilic attack. However, in the reaction with MeOH at 52 °C, after 7 days 50% of **2** had been converted into the corresponding methoxide, but only 28% of **1**. After 15 days the corresponding figures were 76% and 53%. Thus **2** is ca. three times the more reactive. This result was so surprising that we carried out the comparison several times, always obtaining essentially similar results. We cannot at present suggest any satisfactory explanation of this finding, which only adds to the enigma [10] of the mechanism of this type of process.

We took the opportunity to examine the solvolyses of

the labelled iodide (Me₃Si)₃CSi(CD₃)₂I. **1-D**. After 15 days in MeOH at 52 °C, 54% had reacted, identical within experimental error with the result for **1**.

Similarly, after 5 h under reflux in the H₂O–dioxane medium 53% of **1-D** had reacted, implying a rate constant equal within the experimental uncertainty to that for **1**. In each case, after complete reaction there was no detectable amount (i.e. ca. < 5%) of rearranged product, confirming that the solvolyses do not involve an intermediate bridged cation.

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