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# THE REACTIONS OF TRIS(TRIMETHYLSILYL)SILICON IODIDES AND HYDRIDES WITH IODINE MONOCHLORIDE *

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## Summary

The compounds $TsiSiPh_2I$ and TsiSiMeClI (Tsi = $(Me_3Si)_3C$) have been found to react readily with ICl with rearrangement to give $(Me_3Si)_2C(SiMe_2Cl)(SiPh_2Me)$ and $(Me_3Si)_2C(SiMe_2Cl)_2$, respectively. The compounds $TsiSiEt_2I$ and TsiSiEtMeI give approximately 25 and 35%, respectively, of the rearranged chlorides $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2Me)$ and $(Me_3Si)_2C(SiMe_2Cl)(SiEtMe_2)$, along with the unrearranged $TsiSiEt_2Cl$ and TsiSiEtMeCl. The reactions are suggested to proceed through methyl-bridged cationic intermediates in ion-pairs formed by abstraction of $I^-$ by ICl.

The hydride $TsiSiPh_2H$ reacts with a 2.2 molar equivalent of ICl to give the rearranged chloride $(Me_3Si)_2C(SiMe_2Cl)(SiPh_2Me)$ in good yield. The hydride TsiSiPhHI reacts with 1 mole of ICl to give some TsiSiPhICl along with the expected $TsiSiPhI_2$.

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## Introduction

Because of the large bulk of the $(Me_3Si)_3C$ group (the 'trisyl' group, often denoted below by Tsi), compounds of the type $(Me_3Si)_3CSiR_2X$ (e.g. X = halogen or H) undergo direct bimolecular nucleophilic displacements of X only with great difficulty, and this permits observations of other reactions not normally encountered [1—7]. For example, the iodides $(Me_3Si)_3CSiR_2I$ (R = Ph or Et) react with electrophilic species such as silver or mercury salts to give, wholly or in part, rearranged products of the type $(Me_3Si)_2C(SiMe_2Y)(SiR_2Me)$ [2,6,7]. We present below evidence that a corresponding rearrangement occurs when the iodides are treated with iodine monochloride.

This study began when it was observed that while use of one molar equivalent of ICl converted $TsiSiMe_2H$ into the iodide $TsiSiMe_2I$, use of a larger proportion of ICl led to formation also of $TsiSiMe_2Cl$, and that $TsiSiMe_2I$ is readily converted into $TsiSiMe_2Cl$ upon treatment with ICl [1].

## Results and discussion

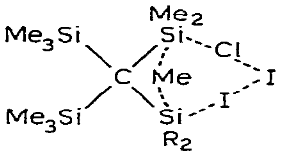
The rearranged chloride $(Me_3Si)_2C(SiMe_2Cl)(SiPh_2Me)$ was the exclusive or greatly dominant product when the iodide $TsiSiPh_2I$ was treated with one molar proportion of ICl, and also when the hydride $TsiSiPh_2H$ was treated with a 2.2 molar proportion of ICl. (See equations 1 and 2.) No unrearranged chloride, $TsiSiPh_2Cl$, was detected, but we cannot rule out the possibility that a small amount was formed.

$$(Me_3Si)_3CSiPh_2I + ICl \rightarrow (Me_3Si)_2C(SiMe_2Cl)(SiPh_2Me) \qquad (1)$$

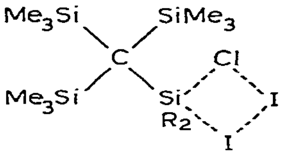
$$(Me_3Si)_3CSiPh_2H + 2\,ICl \rightarrow (Me_3Si)_2C(SiMe_2Cl)(SiPh_2Me) \qquad (2)$$

The reaction of $TsiSiEt_2Cl$ with ICl gave $TsiSiEt_2Cl$ and $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2Me)$ in roughly 65/35 ratio as indicated by the $^1H$ NMR spectrum of the product mixture. Similarly TsiSiEtMeI gave TsiSiEtMeCl and $(Me_3Si)_2C(SiMe_2Cl)(SiEtMe_2)$ in roughly 75/25 ratio. However, TsiSiMeClI gave exclusively the rearranged product $(Me_3Si)_2C(SiMe_2Cl)_2$.

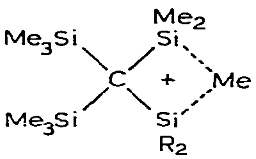
The rearrangement could be interpreted in terms of the multicentre process represented in I, in which there is concerted electrophilic attack of I of ICl at the I atom of the Si—I bond at Si(1), nucleophilic attack of the Cl of ICl at Si(3), and migration of an Me group from Si(3) to Si(1). In the case of the less hindered $TsiSiEt_2I$ and $TsiSiMe_2I$, this would have to be in competition with a corresponding four-centre process, II, wholly at Si(1).



(I)



(II)



$[III]^+$

It is much more likely, however, that the reaction proceeds through the bridged cationic intermediate of type $[III]^+$ which was proposed for the reactions of $TsiSiR_2I$ with silver and mercury(II) salts [2,7], the course of the reactions then being as in equations 3a and 3b. *

$$(Me_3Si)_3CSiR_2I + ICl \rightarrow [III]^+[I_2Cl]^- \qquad (3a)$$

$$[III]^+[I_2Cl]^- \rightarrow (Me_3Si)_3CSiR_2Cl + (Me_3Si)_2C(SiMe_2Cl)(SiR_2Me) \qquad (3b)$$

In the case of the species $[III]^+$ with $R_2 = Ph_2$, the substantially greater steric hindrance at Si(1) would be expected to favour greatly predominant attach-

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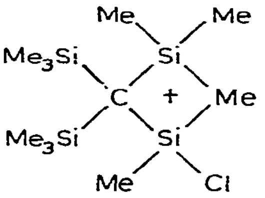
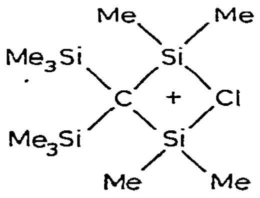
* For simplicity, we assume throughout that only one molecule of ICl is involved in the reaction. In the light of the knowledge that reactions of halogens in media such as $CCl_4$ are commonly of higher order than one with respect to halogen, it seems likely that additional ICl molecules will be present in the transition state; for example, the counter anion may be $[I_3Cl_2]^-$ rather than $[I_2Cl]^-$

ment of chlorine at Si(3), as observed for reactions of $TsiSiPh_2I$ with silver or mercury salts in polar media [2,7]. For $R_2 = Et_2$ or EtMe, however, there should be little difference in the case of attack at Si(1) and Si(3), and if the ion pair $[III]^+[I_2Cl]^-$ had a sufficiently long life, comparable amounts of attack at Si(1) and Si(3) would be expected, with the latter slightly predominating, again as observed in the reactions with silver and mercury salts [7]. However, in a non-polar medium such as $CCl_4$ the ion-pair would probably have only a very brief existence, with most of it collapsing by attachment of chloride ion at Si(1) before the counter anion $[I_2Cl]^-$ could migrate towards Si(3), and so the formation of only about 25—35% of rearranged chloride from $TsiSiEt_2I$ and TsiSiEtMeI is understandable.


$[IV]^+$


$[V]^+$

The exclusive or greatly predominant formation of the rearranged product $(Me_3Si)_2C(SiMe_2Cl)_2$ from the reaction of $(Me_3Si)_3CSiMeClI$ with ICl is especially interesting. In an intermediate of the type $[IV]^+$, nucleophilic attachment of $Cl^-$ at Si(1) rather than Si(3) should be slightly favoured on both steric and electronic grounds (the degree of positive charge being slightly greater at the silicon bearing the electronegative Cl ligand). It is possible, however, that in the medium used, which has a very low dielectric constant and in which there is little or no solvation of electron-deficient or electron rich centres, the electrostatic repulsion between the electron lone pair of the Cl ligand and the anion $[I_2Cl]^-$ is sufficient to expel the latter from the neighbourhood of Si(1). An alternative explanation is that the cation $[IV]^+$ undergoes rearrangement to $[V]^+$, which would be expected to be the more stable in view of the superior bridging ability of Cl than of Me in aluminium compounds [7]. (The analogy between the bridging in cations of type $[III]^+$ and that in $Al_2Me_6$ was pointed out previously [7].) The disadvantage of this proposal is that the cation $[IV]^+$ would have to exist for an appreciable time in order that complete conversion into $[V]^+$ could take place.

In related work, TsiSiPhHI was found to react with a 1 molar proportion of ICl to give the chloro-iodide TsiSiPhClI and the di-iodide $TsiSiPhI_2$ in ca. 35/65 ratio, whereas only the di-iodide was expected [1]. The formation of the chloro-iodide cannot be attributed to reaction of initially formed $TsiSiPhI_2$ with ICl, since some (probably predominant) rearrangement would be expected in such a reaction. The possibility was also considered that TsiSiPhHCl was formed by an initial reaction of TsiSiPhHI (though the absence of rearrangement argues against this) and then underwent iodination by the liberated iodine; this was ruled out by the observation that TsiSiPhHCl reacts much too slowly with $I_2$ (though some reaction does occur). It seems likely that the activation energy for interaction of $\equiv$SiH species with ICl to give $\equiv$SiI + HCl (the nature of which we have discussed [1]) is not much higher than that to give SiCl + HI, so that with TsiSiPhHI the hindrance to introduction of two iodine atoms is sufficient to divert reaction partly towards introduction of a chloride ligand.

No reaction was observed when $TsiSiPh_2I$ was treated with $Br_2$ or $I_2$ in $CCl_4$.

## Experimental

### *General*

The preparations of the compounds $TsiSiR_2I$ with $R_2 = Ph_2, Et_2$, EtMe, MeCl, and PhH have been described previously [1].

The $^1H$ NMR spectra were recorded at 60 MHz with solutions in $CCl_4$ containing $CH_2Cl_2$ as reference.

### *Reaction of $TsiSiPh_2I$ with ICl*

A solution of $TsiSiPh_2I$ (1.0 g, 1.85 mmol) in $CCl_4$ (20 $cm^3$) was added dropwise to a stirred solution of ICl (2.0 mmol) in $CCl_4$ (60 $cm^3$), and the mixture was set aside overnight. The solvent was then taken off and the residue treated with a 5% solution of sodium thiosulphate in water. Ether extraction, followed by washing, drying ($MgSO_4$) and removal of the solvent left a colourless solid, which was identified from its $^1H$ NMR spectrum as $(Me_3Si)_2C(SiMe_2Cl)(SiPh_2Me)$ (0.71 g, 84%); $\delta$ 0.18 (s, 18 H, $Me_3Si$), 0.58 (s, 6 H, $Me_2Si$), 1.03 (s, 3 H, SiMe), 8.01—7.75 ppm (m, 10 H, Ph). A sample recrystallized from methanol had m.p. 156°C (Found: C, 59.2; H, 8.1; $C_{22}H_{37}ClSi_4$ calcd.: C, 58.8; H, 8.3%).

### *Reaction of $TsiSiPh_2H$ with 2 equivalents of ICl*

A solution of ICl (5.3 mmol) in $CCl_4$ (60 $cm^3$) was added dropwise to a stirred solution of $TsiSiPh_2H$ (1.0 g, 2.4 mmol) in $CCl_4$ (20 $cm^3$), and the mixture was set aside overnight. Work-up as before gave $(Me_3Si)_2C(SiMe_2Cl)(SiPh_2Me)$ (0.82 g, 76%), identical with that described above.

### *Reaction of $TsiSiEt_2I$ with ICl*

A solution of $TsiSiEt_2I$ (45 mg, 0.10 mmol) and ICl (0.10 mmol) in $CCl_4$ (0.5 $cm^3$) was kept for 1 h at room temperature, and its $^1H$ NMR spectrum then recorded. This showed it to contain a mixture of $TsiSiEt_2Cl$ and $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2Me)$. A peak at $\delta$ 0.61 ppm was readily assigned to the $SiMe_2Cl$ group (cf. $\delta$ 0.61 ppm for the $SiMe_2$ protons in $TsiSiMe_2Cl$ [1]), and integration (specifically the ratio of $Si\mathit{Me}_2Cl$ to total $\mathit{Me}_3Si$ and $SiEt\mathit{Me}$ protons) indicated that ca. 30—35% of the $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2Me)$ had been formed. (By coincidental overlap, the $(\mathit{Me}_3Si)_3CSiEt_2Cl$ and $(\mathit{Me}_3Si)_2C(SiMe_2Cl)(SiEt_2\mathit{Me})$ protons gave rise to only one singlet, at $\delta$ 0.28 ppm, the value for the $Me_3Si$ peak in $TsiSiEt_2Cl$. The Et resonances appeared as a multiplet at $\delta$ 0.81—1.15 ppm.) The crude product mixture was recovered and sublimed, to give a sample (still a mixture of isomers) which gave the expected mass spectral peaks [viz. $(M - Me)^+$ at $m/e$ 337, and $(M - Et)^+$ at $m/e$ 323] and analysis (Found: C, 47.9; H, 10.6. $C_{14}H_{37}ClSi_4$ calcd.: C, 47.6; H, 10.6%).

### *Reaction of TsiSiEtMeI with ICl*

The TsiSiEtMeI (43 mg, 0.10 mmol) and ICl (0.10 mmol) were dissolved in

$CCl_4$ (1.6 $cm^3$) and the solution was kept at room temperature for 30 min. A little $CH_2Cl_2$ was added as a reference, and the $^1H$ NMR spectrum determined. There were two singlets in the ClSiMe region, at $\delta$ 0.58 and 0.61 ppm, and the latter was assigned to $SiMe_2Cl$ by comparison with the spectrum of $TsiSiMe_2Cl$. From the heights of these two peaks it was concluded that the ratio of the rearranged $(Me_3Si)_2C(SiMe_2Cl)(SiEtMe_2)$ to the unrearranged TsiSiEtMeCl was about (25 ± 5)/(75 ± 5). The product mixture was sublimed, and the sample obtained gave the expected mass spectral peaks (viz. $(M - Me)^+$ at $m/e$ 323 and $(M - Et)^+$ at 309), but a poor analysis (Found: C, 43.6; H, 9.4. $C_{13}H_{33}ClSi_4$ calcd.: C, 46.0; H, 10.4%), suggesting that some unchanged starting material remained. (This would not, however, affect the determination of the product ratio as described above.)

### *The reaction of TsiSiPhHI with ICl*

A solution of TsiSiPhHI (64 mg, 0.14 mmol) and ICl (0.14 mmol) in $CCl_4$ (0.85 $cm^3$) (containing a little $CH_2Cl_2$ as NMR reference) was set aside at room temperature for 30 min., after which the $^1H$ NMR spectrum indicated that no significant amount of starting material remained. The solvent was removed, and the residue subjected to TLC ($SiO_2$ gel, hexane as eluent), mainly to remove the traces of iodine. Only one spot developed, and the solid recovered gave an $^1H$ NMR spectrum [$\delta$ 0.34 (s, 27 H, $Me_3Si$), 7.25—8.25 ppm (m, 5 H, Ph)] which indicated that no $SiMe_2Cl$ or $SiMe_2I$ groups were present. The $^{13}C$ NMR spectrum initially gave, in addition to Ph resonances, one singlet (at 70.9 ppm upfield from internal $CDCl_3$), but upon expansion this was resolved into two very close singlets in roughly 2/1 ratio. The mass spectrum showed peaks for $(TsiSiPhI_2 - Me)^+$ (at $m/e$ 575) and $(TsiSiPhICl - Me)^+$ (at $m/e$ 483). From the relative abundance of the ions at 463 [$(TsiSiPhI_2 - I)^+$] and 371 [$(TsiSiPhICl - I)^+$] it was tentatively assumed that $TsiSiPhI_2$ and TsiSiPhICl were present in ca. 65/35 ratio. The analysis was in good agreement with this (Found: 34.8; H, 6.0. Calcd: C, 34.6; H, 5.8%).

A sample (168 mg) of a mixture obtained as above was treated with an excess of $LiAlH_4$ in THF for 3 h, and the standard work-up gave $TsiSiPhH_2$ (56 mg, ca. 50%), identical with an authentic specimen. (This result confirms the absence of any rearrangement to give products containing $SiMe_2X$ groups.)

An authentic sample of TsiSiPhICl was prepared by treatment of TsiSiPhHI with $PCl_5$ in $CCl_4$ and gave $^1H$ NMR and mass spectral data consistent with the above results: $\delta$ 0.35 (s, 27 H, $Me_3Si$) and 7.21—8.21 ppm (m, 5 H, Ph): $m/e$ 483 $(M - Me)^+$, 463 $(M - Cl)^+$, 371 $(M - I)^+$.

### *Reaction of TsiSiPhHCl with $I_2$*

A solution of TsiSiPhHCl in $CCl_4$ (3 $cm^3$) was treated with an excess of $I_2$ at room temperature. The $^1H$ NMR spectrum showed only a small decrease in the height of the SiH resonances after 0.5 h, and a substantial amount of the starting material was still present after 2.5 h. This was confirmed by recording the IR spectrum.

(In the reaction of TsiSiPhHI with ICl (above) the SiH bonds disappeared within 0.5 h.)

### *Reaction of TsiSiMeClI with ICl*

A solution of TsiSiMeClI (200 mg, 0.46 mmol) and ICl (0.46 mmol) in $CCl_4$ (2.8 $cm^3$) was set aside at room temperature. After 2 days the $^1$H NMR spectrum indicated that some (<10%) starting material still remained, but this had disappeared after 10 days. The solvent and traces of iodine were then removed by rotary evaporation followed by exposure of the warmed residue (50°C) to a low vacuum for 1 h. The white solid which remained was identified as $(Me_3Si)_2C(SiMe_2Cl)_2$ (102 mg, 64%); $^1$H NMR, $\delta$ 0.36 (s, 18 H, $Me_3Si$) and 0.69 ppm (s, 12 H, $Me_2Si$); $^{13}$C NMR. $\delta$ (upfield from internal $CDCl_3$) 68.2 (s) and 72.1 (s) ppm; $m/e$, $(M - Me)^+$ at 329 (base peak), $(M - Me_3SiCl)^+$ at 326 (Found: C, 37.7; H, 8.4. $C_{11}H_{30}Cl_2Si_4$ calcd.: C, 38.2; H, 8.75%).

### *Treatment of TsiSiPh$_2$I with Br$_2$ or I$_2$*

A solution of $TsiSiPh_2I$ (0.10 mmol) and either $Br_2$ (0.10 mmol) or $I_2$ (0.10 mmol) in $CCl_4$ (0.5 $cm^3$) was kept at room temperature for 1 h. The $^1$H NMR spectrum indicated that no reaction had occurred, and evaporation gave unchanged starting material.

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