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PREPARATION OF TRIS(TRIMETHYLSILYL)METHYL ("TRISYL") DERIVATIVES OF SILICON *

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Summary

Treatment of $(Me_3Si)_3CLi$ ("trisyl"lithium, TsiLi) with appropriate silicon halides has given a range of compounds of the type $(Me_3Si)_3CSiRR'X$; e.g., $TsiSiCl_3$, $TsiSiMeCl_2$, $TsiSiMe_2X$ (X = Cl, OMe), $TsiSiPh_2X$ (X = F, Cl, OMe), and TsiSiPhMeH. The trisyl group causes very large steric hindrance to nucleophilic displacements at the silicon to which it is attached, so that (unless one or more hydride ligands are present) most of the common displacements at silicon do not occur. However, halides can be reduced to hydrides by $LiAlH_4$, and the hydrides can be reconverted into halides in electrophilic displacements by halogens. The presence of even one hydride ligand markedly reduces the hindrance, so that, for example, TsiSiPhHI reacts with refluxing methanol to give TsiSiPhH(OMe).

Introduction

Work in this laboratory a few years ago showed that tris(trimethylsilyl)methane, $(Me_3Si)_3CH$, could be metallated by use of methyllithium in tetrahydrofuran/diethyl ether, and that the $(Me_3Si)_3CLi$ thus formed could be coupled with chlorotrimethylsilane to give $(Me_3Si)_4C$ [1]. (For other metallations, and reactions of the lithium derivative see ref. 2). We describe below the reaction of the $(Me_3Si)_3CLi$ with some silicon chlorides or fluorides to give a range of derivatives of the type $(Me_3Si)_3CSiRR'X$ and report some simple reactions of the latter. The products described have been used in studies which have revealed several highly unusual reactions [e.g. see refs. 3—5], and which will be described in later papers.

* Dedicated to Eugene G. Rochow on his 70th birthday. C.E. wishes to record his especial appreciation of the courtesy, kindness and encouragement which Professor Rochow extended to him during his early years in organosilicon chemistry.

For convenience, we refer to the $(Me_3Si)_3C$ group as the "trisyl" group, and denote it by Tsi [3—5].

Results and discussion

Treatment of TsiLi with $SiCl_4$ gives $TsiSiCl_3$ in good yield. Use of an excess of TsiLi and prolonged reaction times do not bring about introduction of more than one Tsi group, and, indeed, $TsiSiCl_3$ does not react with either PhMgBr or PhLi, illustrating the very large steric hindrance towards nucleophilic substitution at silicon caused by even one Tsi group. Reactions with a range of other silicon chlorides, e.g. $MeSiCl_3$, Me_2SiCl_2, Et_2SiCl_2, and $PhSiCl_3$, all give the expected products resulting from introduction of one Tsi group (Table 1). Steric effects are critical, and only an 8% yield of $TsiSiPh_2Cl$ was obtained from Ph_2SiCl_2, but use of Ph_2SiF_2 led to a good yield of $TsiSiPh_2F$. (The advantage of using silicon fluorides rather than chlorides for the attachment of bulky organic groups to silicon was clearly demonstrated almost 30 years ago [6] and recently rediscovered in the preparation of $t\text{-}Bu_3SiX$ species [7]). Additional examples of the use of silicon fluorides are included in Table 1.

With compounds of the type TsiSiRR'X (R and R' = alkyl or aryl) there is great steric hindrance to direct displacement of X by nucleophiles, and the range of simple substitutions is very limited. (More complex reactions resulting in loss of X, involving either fragmentations or rearrangements, have been briefly reported [3—5], and will be fully described in later papers.) With the compounds $TsiSiR_2X$ (R = Me or Ph; X = halogen), the only simple nucleophilic displacements we have observed are the reduction of halides by $LiAlH_4$, which involve introduction of the small hydrogen atom. The hydrides $TsiSiR_2H$ do, however, react with halogenating agents such as Cl_2, Br_2 and ICl (see Table 2); the formation of the iodides rather than the chlorides from ICl is noteworthy, and is commented on again below. It was observed that when more than one molar proportion of ICl was used, the iodide product was sometimes contaminated with chloride, $TsiSiR_2Cl$, and we confirmed that $TsiSiMe_2I$ reacts rapidly with ICl to give $TsiSiMe_2Cl$ in quantitative yield.

There was a puzzling feature in the reactions of the fluorides with $LiAlH_4$, namely that TsiSiPhMeF undergoes no reaction under conditions in which Tsi-

TABLE 1

FORMATION OF TRISYLSILICON COMPOUNDS FROM TsiLi IN THF/Et_2O

Substrate	Product and yield (%)	Substrate	Product and yield (%)
$SiCl_4$	$TsiSiCl_3$; 78	$PhSiCl_3$	$TsiSiPhCl_2$; 75
$Me_2SiCl(OMe)$	$TsiSiMe_2OMe$; 60	$PhSiHCl_2$	TsiSiPhHCl; 17
$Si(OPr\text{-}n)Cl_3$	$TsiSi(OPr\text{-}n)Cl_2$; 40	Ph_2SiCl_2	$TsiSiPh_2Cl$; 8
$MeSiCl_3$	$TsiSiMeCl_2$; 70	PhMeSiHCl	TsiSiPhMeH; 80
Me_2SiCl_2	$TsiMeSiMe_2Cl$; 82	Et_2SiF_2	$TsiSiEt_2F$; 40
$MeSiHCl_2$	TsiSiMeClH; 55	Ph_2SiF_2	$TsiSiPh_2F$; 76
Me_2SiHCl	$TsiSiMe_2H$; 40	$PhMeSiF_2$	TsiSiPhMeF; 74
Et_2SiCl_2	$TsiSiEt_2Cl$; 48	$Ph_2SiF(OMe)$	$TsiSiPh_2(OMe)$; 9
EtMeSiHCl	TsiSiEtMeH; 60		

TABLE 2

REACTION OF TRISYLSILICON COMPOUNDS $(Me_3Si)_3CZ$

Z	Reagent	Conditions	Product and yield (%)
$SiCl_3$	$LiAlH_4$	THF/Et_2O, reflux, 3 h	$TsiSiH_3$, 80
$SiMe_2Cl$	$LiAlH_4$	THF/Et_2O, reflux, 5 h	$TsiSiMe_2H$, 80
$SiEt_2Cl$	$LiAlH_4$	THF/Et_2O, reflux, 24 h	$TsiSiEt_2H$, 80
$SiPhCl_2$	$LiAlH_4$	THF/Et_2O, reflux, 5 h	$TsiSiPhH_2$, 72
$SiPh_2F$	$LiAlH_4$	THF, reflux, 20 h	$TsiSiPh_2H$, 70
$SiPh_2F$	$LiAlD_4$	THF, reflux, 24 h	$TsiSiPh_2D$, 77
SiPhMeF	$LiAlH_4$	THF, reflux, 20 h	No reaction
$SiMe_2I$	ICl	CCl_4, 20° C	$SiMe_2Cl$ [a]
SiH_3	ICl	CCl_4, 20° C	$TsiSiH_2I$, 93 [b]
SiMeClH	ICl	CCl_4, 20° C	TsiSiMeClI, 95
$SiPhH_2$	ICl	CCl_4, 20° C	TsiSiPhHI, 92
$SiPh_2H$	ICl	CCl_4, 20° C	$TsiSiPh_2I$, 95
$SiMe_2H$	ICl	CCl_4, 20° C	$TsiSiMe_2I$, 95
$SiMe_2EtH$	ICl	CCl_4, 20° C	TsiSiMeEtI, 83
$SiEt_2H$	ICl	CCl_4, 20° C	$TsiSiEt_2I$, 65 [c]
SiPhMeH	ICl	CCl_4, 20° C	TsiSiPhMeI, 96
$SiPh_2H$	I_2	CCl_4, reflux, 5 h	No reaction
$SiMe_2H$	Br_2	CCl_4, 20° C	$TsiSiMe_2Br$, 90
$SiPh_2H$	Br_2	CCl_4, 20° C	$TsiSiPh_2Br$, 98
SiH_2I	MeOH	20° C	$TsiSiH_2OMe$, 93
SiH_2I	AgOAc/AcOH	20° C	$TsiSiH_2OAc$, 95 [d]
SiPhHI	MeOH	Reflux, 3 min	TsiSiPhHOMe, 96
SiPhHI	AgOAc/AcOH	Reflux, 20 min	TsiSiPhH(OAc), 92

[a] ^1H NMR showed complete conversion; see text. [b] Sample for analysis purified by sublimation. [c] Yield after sublimation. [d] Sample for analysis obtained by preparative GLC (SE30 on 80—100 mesh Chromosorb P).

$SiPh_2F$ gives a good yield of $TsiSiPh_2H$. The hydride TsiSiPhMeH was subsequently made from TsiLi and PhMeSiHCl.

The trichloride $TsiSiCl_3$ is more reactive in direct nucleophilic substitution, since although it is indefinitely stable to boiling methanol (alone or containing silver nitrate) it does react completely with 0.1 *M* NaOMe in MeOH during 90 minutes at reflux to give some $TsiSiCl_2OMe$, along with the major product $(Me_3Si)_2CHSi(OMe)_3$, the substitution and fragmentation products being formed in 1/2 ratio. The trichloride can be reduced to $TsiSiH_3$, and the latter, being much less sterically hindered, reacts readily with NaOMe/MeOH to give TsiH as the only trisyl product.

The compound $TsiSiH_3$ can be iodinated to give $TsiSiH_2I$, and the latter is much more reactive than $TsiSiMe_2I$; for example, it reacts rapidly with MeOH and with AcOH to give $TsiSiH_2OMe$ and $TsiSiH_2OAc$ respectively. Indeed, the presence of even one hydrogen substituent on the relevant silicon atom of the trisyl compounds suffices to raise the reactivity very markedly, so that TsiSiPhHI reacts with MeOH under reflux to give TsiSiPhHOMe.

The chlorides and bromides $TsiSiMe_2Cl$, $TsiSiPh_2Cl$ and $TsiSiPh_2Br$ do not react with boiling methanol even when silver nitrate is present *. The corresponding iodides react readily in the presence of silver or mercury(II) salts [4].

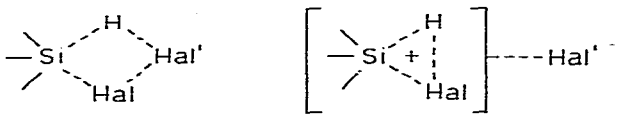
* The bromide $(Me_3Si)_3CSiMe_2Br$ was previously reported not to react with boiling methanolic silver nitrate [3], but we have now found that it does react slowly.

Mechanistic aspects

It is evident that a trisyl group causes great steric hindrance towards attack of nucleophiles at a silicon atom to which it is attached, and we have noted previously that $TsiSiMe_2Cl$ is less reactive than $t\text{-}Bu_3SiCl$ towards aqueous ethanolic alkali, and that most of the reaction which does occur in the case of $TsiSiMe_2Cl$ is not simple substitution but fragmentation, so that nucleophilic attack on the Si—Cl bond is markedly more hindered in $(Me_3Si)_3CSiMe_2Cl$ than in $t\text{-}Bu_3SiCl$ [3]. Because of this hindrance, the reactions are diverted away from simple substitution to fragmentations and rearrangements [3,4].

The presence of even one hydrogen atom on the silicon atom bearing the trisyl group permits simple nucleophilic substitution to occur fairly readily, and so we can assume that the steric compression in a transition state approximating in structure to a 5-coordinate species such as $[TsiSi(Ph)(H)(Hal)(OMe)]^-$, formed by attack of MeO^- on TsiSi(Ph)(H)Hal, is not prohibitive. Consequently it is understandable that TsiSiRR'Hal species can be reduced by $LiAlH_4$, since the transition state could approximate to the rather similar 5-coordinate species $[TsiSiRR'(Hal)(H)]^-$.

The relative ease of the halogenations of TsiSiRR'H species can also be attributed to the presence of the sterically-undemanding hydrogen substituent in the extra-coordinate transition state. The simple four-centre mechanism (I) was ruled out by Sommer for halogenation of hydrides because BrCl (which is polarized in the direction $Br^+ Cl^-$) would be expected to give the Si—Cl rather than the observed Si—Br product [8]. (Likewise, our reactions with ICl would be expected to give the chlorides not iodides.)



(I) (II)

Sommer proposed instead that a "3-centre intermediate" of type (II) (e.g. Hal = Br, Hal' = Cl) is formed in the slow step of the reaction, and while in the absence of any supporting evidence for species of type II this can be regarded as little more than a diagramatic rationalization of the experimental observations, the scheme does have the advantage from our point of view that the partial bonding between the leaving H and incoming halogen atoms (approximating to a three-membered ring, with a small HSiHal angle) would reduce the unfavourable steric interactions with the other ligands.

We defer discussion of the reaction of the iodides TsiSiRR'I with ICl, since we have indications that these occur with rearrangement, and thus are not direct displacements. We note, however, that some years ago, silicon hydrides, R_3SiH, were found to react with ICl to give chlorides, R_3SiCl, and iodine [9].

$$R_3SiH + ICl \rightarrow R_3SiI + HCl; \qquad R_3SiI + ICl \rightarrow R_3SiCl + I_2 \qquad (1)$$

$$R_3SiH + ICl \rightarrow R_3SiCl + HI; \qquad HI + ICl \rightarrow HCl + I_2 \qquad (2)$$

Since both R_3SiI and HCl were shown to react with ICl to give I_2, the alterna-

tive sequences (1) and (2) were considered. Sequence (2) was favoured, but the behaviour of the trisyl compounds, which give iodides initially, shows that (1) is the correct one.

The ready formation of TsiH from $TsiSiH_3$ and MeOH/MeONa is of interest. We cannot say whether any conversion of Si—H into Si—OMe bonds precedes cleavage of the Tsi—Si bond, but we suspect that if more than one Si—OMe bond were introduced then the cleavage would become substantially slower than is observed. It is quite likely that in the attack of MeO^- on $TsiSiH_3$, the relief of steric strain favours the loss of the $(Me_3Si)_3C$ group rather than the H atom, and the fairly high acidity of TsiH implies that the trisyl group would be a relatively good leaving group [10].

The failure of the chlorides $TsiSiCl_3$, $TsiSiMe_2Cl$, and $TsiSiPh_2Cl$, and the bromide $TsiSiPh_2Br$ to react with boiling methanol even in the presence of silver salts is an impressive illustration of the reluctance of organosilicon compounds to form silico-cations. With $TsiSiPh_2Br$ in particular, there are obvious factors in favour of ionization (especially with assistance by silver ion to compensate for the relatively large dissociation energy of Si—Br bonds), viz. considerable release of steric strain on going from tetrahedral to trigonal silicon, and stabilization of the cationic centre by hyperconjugation from the β-Me_3-Si—C bonds and conjugation with the aromatic rings. The iodide $TsiSiPh_2I$ reacts readily with methanolic silver nitrate, but the solvolysis is accompanied by a rearrangement in which the silicocation is apparently avoided [4].

Experimental

General

NMR spectra were recorded with solutions in CCl_4 containing $CHCl_3$ or CH_2Cl_2 as internal standard.

IR spectra of solids were recorded with Nujol mulls.

While the $TsiSiPh_2X$ and TsiSiPhRX compounds melted normally, most of the other trisyl derivatives prepared sublimed very readily, and melting points could be obtained only by sealing the samples in small capillary tubes which allowed little dead space above the solid. In some cases the samples were so volatile that the tubes could not be satisfactorily sealed.

Reactions of TsiLi with silicon halides

TsiH was metallated with MeLi in THF/Et_2O for 6 h at reflux temperature as previously described [1], the MeLi usually being prepared at or below room temperature from MeI and lithium shot.

In most cases obvious reaction occurred on mixing the TsiLi with the silicon halide (usually in 1/1 mol ratio) in THF/Et_2O, but the mixture was usually refluxed for 1—3 h. It was then usually cooled and saturated aqueous ammonium chloride was added. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated. Usually washing of the residue with cold methanol (mainly to remove TsiH) was sufficient to give a good sample, but samples for analysis and spectroscopy were prepared by recrystallization from ethanol and/or by sublimation.

Sometimes a different work-up was used. This involved stripping the solvent

TABLE 3

PHYSICAL PROPERTIES AND ELEMENTAL ANALYSES OF TRISYLSILICON COMPOUNDS [a]

Compound	M.p. (°C)	^{1}H NMR (δ in ppm) [b]	γ(SiH) (cm^{-1})	Analysis (Found (calcd.)(%))	
				C	H
$TsiSiCl_3$	>360 [a]	0.38 (s, Tsi)		33.0 (32.8)	7.4 (7.4)
$TsiSiCl_2(OPr\text{-}n)$	210–212	0.25 (s, Tsi); 3.8, 1.6, 1.0 (OPr)		40.3 (40.1)	8.3 (8.8)
$TsiSiCl_2OMe$		0.32 (s, Tsi); 3.60 (s, OMe)		36.5 (36.5)	8.3 (8.4)
$TsiSiPhCl_2$	178	0.40 (s, Tsi); 7.3–8.1 (m, Ph)		47.1 (47.2)	8.0 (7.9)
$TsiSiH_3$	254 c	0.16 (s, Tsi); 3.65 (s, SiH)	2120	45.4 (45.7)	11.5 (11.5)
$TsiSiH_2I$	273 [c]	0.26 (s, Tsi); 4.38 (s, SiH)	2150	31.1 (30.9)	7.6 (7.5)
$TsiSiH_2OMe$	228 [c]	0.15 (s, Tsi); 3.46 (s, OMe); 4.55 (s, SiH)	2100	44.8 (45.2)	11.1 (10.95)
$TsiSiH_2OAc$ [d]	128	0.22 (s, Tsi); 2.03 (s, OAc); 4.78 (s, SiH)	2160	44.6 (45.0)	9.9 (10.0)
$TsiSiMeCl_2$		0.38 (s, Tsi); 1.20 (s, Me)		38.6 (38.2)	8.9 (8.7)
$TsiSiMe_2Cl$	>360 [c]	0.22 (s, Tsi); 0.62 (s, $SiMe_2$)		44.4 (44.4)	9.9 (10.2)
$TsiSiMe_2Br$		0.30 (s, Tsi); 0.78 (s, $SiMe_2$)		39.0 (39.0)	9.1 (9.0)
TsiSiMeClH		0.35 (s, Tsi); 0.73 (d, Me); 4.98 (s, SiH)	2140	43.1 (42.5)	10.2 (10.2)
$TsiSiMe_2I$	>360 [c]	0.33 (s, Tsi); 1.03 (s, SiMe2)		34.6 (34.6)	8.0 (8.0)
$TsiSiMe_2H$	312 [c]	0.13 (s, Tsi); 0.21 (d, Me); 4.07 (m, SiH)	2095	49.8 (49.65)	11.2 (11.6)
TsiSiEtMeI	~370 [c]	0.30 (s, Tsi); 0.94 (s, Me); 1.10 (m, Et)		36.6 (36.25)	8.2 (8.2)
$TsiSiEt_2I$	~360 [c]	0.32 (s, Tsi); 1.08 (m, Et)		37.5 (37.8)	8.1 (8.4)
$TsiSiEt_2Cl$	275–280 [c]	0.25 (s, Tsi); 1.05 (m, Et)		47.4 (47.6)	10.2 (10.6)
TsiSiMeClI	>365 [c]	0.34 (s, Tsi); 1.37 (s, Me)		30.2 (30.2)	6.8 (6.9)
$TsiSiEt_2H$	258–265 [c]	0.18 (s, Tsi); 0.78–1.28 (m, Et); 3.78 (m, SiH)	2080	52.2 (52.7)	12.0 (12.0)
TsiSiEtMeH	280–285 [c]	0.20 (s, Tsi); 0.26 (s, Me); 0.90 (m, Et); 3.93 (m, SiH)	2080	50.9 (51.2)	11.6 (11.9)
$TsiSiPh_2F$	140	0.31 (s, Tsi); 7.2–8.0 (m, Ph)		61.1 (61.1)	8.6 (8.6)
$TsiSiPh_2Cl$	135	0.28 (s, Tsi); 7.2–8.0 (m, Ph)		58.9 (58.9)	8.3 (8.3)
$TsiSiPh_2Br$	153	0.31 (s, Tsi); 7.2–8.1 (m, Ph)		54.2 (53.5)	7.5 (7.5)
$TsiSiPh_2I$	227	0.38 (s, Tsi); 7.2–8.1 (m, Ph)		48.9 (48.9)	7.0 (6.85)
TsiSiPhHCl	90–92	0.20 (s, Tsi); 5.3 (SiH); 7–8(m, Ph)	2130	51.3 (51.5)	8.7 (8.9)
TsiSiPhMeI	246	0.31 (s, Tsi); 1.38 (s, Me); 7.2–8.0 (m, Ph)		42.7 (42.7)	7.3 (7.3)
TsiSiPhHI	133	0.33 (s, Tsi); 5.08 (s, SiH); 7.2–7.8 (m, Ph)	2140	41.6 (41.4)	7.3 (7.1)
$TsiSiPhH_2$	46	0.25 (s, Tsi); 4.56 (s, SiH); 7.2–7.9 (m, Ph)	2120	56.5 (56.8)	10.3 (10.1)
$TsiSiPh_2H$	132	0.31 (s, Tsi); 5.21 (s, SiH); 7.2–7.8 (m, Ph)	2100	63.8 (63.8)	8.9 (9.2)
$TsiSiPh_2OMe$	170	0.21 (s, Tsi); 3.43 (s, OMe); 7.1–7.9 (m, Ph)		62.3 (62.2)	9.0 (9.0)
TsiSiPhMe(OMe)	148	0.01 (d, Tsi); 0.45 (s, SiMe); 3.28 (s, OMe); 7.2–7.6 (m, Ph)		56.7 (56.5)	10.0 (9.9)
TsiSiPhMeF	98	0.24 (s, Tsi); 0.56 (d, OMe); 7.2–7.8 (m, Ph)		55.2 (55.1)	9.5 (9.5)
TsiSiPhMeH	68	0.21 (s, Tsi); 0.50 (d, OMe); 4.63 (SiH); 7.1–7.7(m, Ph)	2100	57.9 (57.95)	10.2 (10.2)
TsiSiPhH(OMe)	107	0.23 (s, Tsi); 3.28 (s, OMe); 5.10 (s, SiH); 7.2–7.8 (m, Ph)	2100	55.1 (55.4)	9.6 (9.8)
TsiSiPhH(OAc) [d]	96	0.31 (s, Tsi); 2.00 (s, OAc); 5.50 (s, SiH); 7.2–7.7 (m, Ph)	2160	54.7 (54.5)	9.3 (9.1)
$TsiSiEt_2F$		0.17 (s, Tsi); 0.96 (m, Et)		49.8 (49.9)	10.7 (11.1)

[a] For the following compounds, molecular weights were determined osmometrically in benzene, and found to be within 2% of the calculated value: $TsiSiCl_3$, $TsiSiMeCl_2$, $TsiSiMe_2Cl$, TsiSiPhHCl; $TsiSiPh_2Cl$, $TsiSiPhCl_2$, $TsiSiMe_2H$. [b] Integrations were correct in all cases. [c] In sealed tube. [d] ν(C = O), 1730 and 1230 cm^{-1}.

from the reaction mixture in a rotary evaporator, addition of light petroleum (b.p. 60—80° C) followed by water, separation of the organic layer, washing, drying, evaporation, and recrystallization of the solid obtained. This method was used for $TsiSiCl_3$, $TsiSi(OPr\text{-}n)Cl_2$, $TsiSiMe_2Cl$, $TsiSiMe_2OMe$, $TsiSiMe_2H$, and $TsiSiMe_3$, but there is no reason to believe that the other method would have given poorer results.

Reductions with $LiAlH_4$

The trisylsilicon halides were refluxed with $LiAlH_4$ in THF (usually one mol of $LiAlH_4$ was used for each Si—Hal bond to be reduced). The excess of the $LiAlH_4$ was cautiously destroyed with moist ether followed by cold saturated aqueous NH_4Cl, and ether extraction was followed by washing, drying, and evaporation of the extract to leave a solid, which was recrystallized (ethanol) and/or sublimed if necessary.

In the reduction of $TsiSiCl_3$, a 5/1 molar ratio of $LiAlH_4/TsiSiCl_3$ was used, and the final purification was by sublimation.

Halogenations of silicon hydrides

The hydride was treated with one mol of Cl_2, Br_2 or ICl in CCl_4 at room temperature, and after a few minutes the solvent was evaporated off. The product was usually fairly pure, but for analysis and spectroscopy samples were recrystallized from ethanol and/or sublimed. With TsiSiPhHI and $TsiSiH_2I$ recrystallization from ethanolic solvents is not practicable, and sublimation was used.

Reaction of $TsiSiMe_2I$ with ICl

The $TsiSiMe_2I$ (42 mg, 0.10 mmol) was placed in an NMR tube, and CCl_4 (0.4 cm^3) containing ICl (0.10 mmol) was added. The tube was capped, and shaken for 1 min, then the ^1H NMR spectrum was recorded and found to be identical with that of $TsiSiMe_2Cl$; the peaks at δ 1.03 and 0.33 ppm associated with the $TsiSiMe_2I$ were completely absent, and had been replaced by the corresponding peaks at δ 0.62 (s, 6 H) and 0.22 ppm (s, 27 H).

Reaction of $TsiSiCl_3$ with NaOMe/MeOH

$TsiSiCl_3$ (1.0 g, 2.7 mmol) was heated under reflux with 0.1 *M* NaOMe in MeOH (150 cm^3). After 90 min the solvent was evaporated off rapidly under reduced pressure, light petroleum was added, followed by water, and the organic layer was washed, dried, and evaporated. The ^1H NMR spectrum of the residue indicated that the product consisted of $TsiSiCl_2OMe$ and $(Me_3Si)_2CHSi(OMe)_3$ in ca. 1/2 ratio. Washing with methanol followed by sublimation of the solid residue gave pure $TsiSiCl_2(OMe)$.

The reaction was repeated but with $TsiSiCl_3$ (200 mg), 0.1 *M* NaOMe in MeOH (25 cm^3), and heating for 2 h. The reaction mixture was added to acidified aqueous silver nitrate, and the silver chloride was filtered off, washed, dried, and weighed; 0.181 g was obtained, corresponding to loss of ca. 77% of the chlorine of the $TsiSiCl_3$.

When the reaction was carried out with 2 *M* NaOMe in MeOH for 3 h, the AgCl corresponded to removal of 95% of the chlorine of the $TsiSiCl_3$, and a mixture of products, of which $(Me_3Si)_2CHSi(OMe)_3$ was a major component, was obtained.

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