Review

NOVEL PROPERTIES OF SOME HIGHLY STERICALLY HINDERED ORGANOSILICON COMPOUNDS *

COLIN EABORN

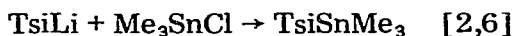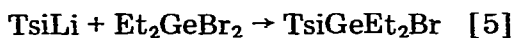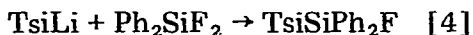*School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)*
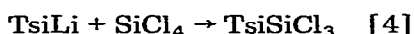
(Received in India December 8th, 1981; in Amsterdam May 25th, 1982)

Introduction

Recent studies of compounds containing the very bulky tris(trimethylsilyl)-methyl group (the 'trisyl' group, frequently denoted by the symbol Tsi) have revealed some highly novel organosilicon chemistry and produced some unusual compounds of other elements. Some of the main features of the results are outlined below.

Attachment of trisyl groups to metals and metalloids

The starting point for the trisyl-silicon and other trisyl-metal derivatives is tris(trimethylsilyl)methane, which is readily obtained from the reaction of Me_3SiCl in tetrahydrofuran with $CHCl_3$ and Li or CBr_4 and Mg [1]. Metallation of $(Me_3Si)_3CH$ (TsiH) with MeLi in Et_2O-THF gives TsiLi [2] (no other metallating agent has yet been found to be satisfactory, see, e.g., ref. 3), and this reacts with a variety of metal and metalloid halides ** : e.g.

$TsiLi + SiCl_4 \rightarrow TsiSiCl_3$ [4]

$TsiLi + Ph_2SiF_2 \rightarrow TsiSiPh_2F$ [4]

$TsiLi + Et_2GeBr_2 \rightarrow TsiGeEt_2Br$ [5]

$TsiLi + Me_3SnCl \rightarrow TsiSnMe_3$ [2,6]

$TsiLi + MCl_2 \rightarrow (Tsi)_2M$ (M = Zn, Cd, Hg) [7,8]

---

* Dedicated to Prof. R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).
** After the metallation it is sometimes advantageous to remove any residual MeLi by adding a little Me_3SiOMe, which does not react with TsiLi.

TsiLi + PCl$_3$ $\rightarrow$ TsiPCl$_2$ [9]

TsiLi + PPh$_2$Cl $\rightarrow$ TsiPPh$_2$ [10]
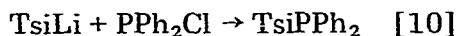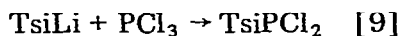
(A complication in the reaction of TsiLi with BF$_3$ in THF-Et$_2$O is noted at the end of this review.)
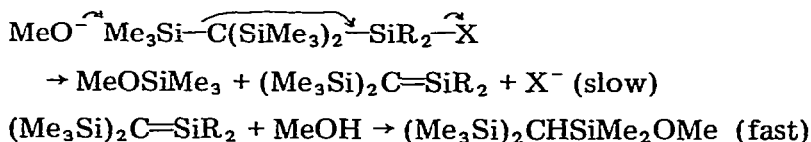
Tris(trimethylsilyl)methane

This compound is itself of considerable interest, in particular: (a) It is a fairly strong acid, as carbon acids go; thus measurement of rates of detritiation of (Me$_3$Si)$_3$C^{3}H in KOH-Me$_2$SO-H$_2$O shows that its kinetic acidity is higher than that of Ph$_3$CH [11]. This high acidity can be attributed to delocalization of the lone pair of the carbanion into the d-orbitals of the silicon atoms, though some doubts have been expressed about the importance of such delocalization (see, e.g. ref. 12). (b) The structure, as revealed by electron diffraction studies, shows a very marked deviation from the tetrahedral configuration about the central carbon atom, the Me$_3$SiCSiMe$_3$ angles being 117° [13]. This implies a degree of s-character in the C-SiMe$_3$ bonds which is unusually high for a nominally sp^3 carbon centre, and thus an unusually high degree of p-character in the unique C-H bond (a feature usually associated with a low acidity). In keeping with the low p-character the coupling constant $J(^{13}$C—^{1}H) for the bond is unusually low, viz. 100 Hz, but other factors may be important.

Inhibition of bimolecular nucleophilic substitution in trisyl-silicon compounds

The most important single feature of the effect of the trisyl group is the inhibition of direct attack of nucleophiles on the silicon atom to which the group is attached. Thus TsiSiCl$_3$ does not react with RLi, even MeLi, and is stable to prolonged boiling in MeOH, even in the presence of AgNO$_3$ [4]. Reaction with a dilute solution of NaOMe in refluxing MeOH does give TsiSi-(OMe)Cl$_2$, though fairly slowly, but substitution does not proceed further, and prolonged reaction with more concentrated base leads to fragmentation of the molecule [14,15]. Such fragmentation is effectively the sole reaction when TsiSiR$_2$Cl (R = Me or Ph) and related TsiSiR$_2$X species are boiled with 1—2 M NaOMe-MeOH:

(Me$_3$Si)$_3$CSiR$_2$X + MeOH + MeO$^-$

$\rightarrow$ (Me$_3$Si)$_2$CHSiR$_2$OMe + Me$_3$SiOMe + X$^-$
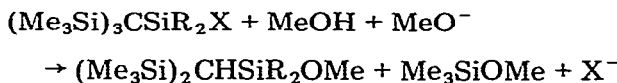
The features of this reaction are most simply interpreted in terms of the following mechanism, involving the formation of an unstable sila-olefin intermediate [15].

MeO$^-$ Me$_3$Si—C(SiMe$_3$)$_2$—SiR$_2$—X

$\rightarrow$ MeOSiMe$_3$ + (Me$_3$Si)$_2$C=SiR$_2$ + X$^-$ (slow)

(Me$_3$Si)$_2$C=SiR$_2$ + MeOH $\rightarrow$ (Me$_3$Si)$_2$CHSiMe$_2$OMe (fast)

The first, rate-determining, step of the reaction is an $E2$ process, closely analogous to $E2$ elimination reactions of alkyl halides. This provides a clear example of the uncovering of a previously unobserved mechanism of reaction at a silicon centre which is normally not accessible because of the much faster direct S_N2 substitution.

The only reactions which seem to involve direct displacement of a group X from $TsiSiR_2X$ compounds (R = Me or Ph) by an incoming group Y without prior dissociation of the Si—X bond (to ions or radicals, as considered below) is when either X or Y is hydrogen *. Thus the $TsiSiR_2X$ compounds with X = Cl or F are reduced to the hydrides $TsiSiR_2H$ by $LiAlH_4$ in Et_2O, while these hydrides $TsiSiR_2H$ react with I_2 or, much more rapidly, with (1 mol of) ICl to give the iodides $TsiSiR_2I$ [4].

$$TsiSiR_2X + LiAlH_4 \rightarrow TsiSiR_2H$$

$$TsiSiR_2H + ICl \rightarrow TsiSiR_2I$$

The reactions of the hydrides with halogens present a mechanistic problem. The reaction with ICl would have been predicted to produce not $TsiSiR_2I$ but $TsiSiR_2Cl$ on the basis of the bond polarizations Si^+H^- and I^+Cl^-, and the larger size of the iodine than of the chlorine atom should additionally favour Si—Cl bond formation in the trisyl systems. However Sommer [16] had previously noted that reactions of ordinary organosilicon hydrides with BrCl gave predominantly silyl bromide products, and, reasonably taking this to rule out the four-centre process (I), suggested the rate-determining formation of a "three-centre immediate" (II) (X = Br); in keeping with this proposal, substituent effects in the reactions of silicon hydrides with halogens indicated the formation of a significant degree of positive charge at silicon in the transition state [16,17]. While this mechanism is little more than a diagramatic representation of the observations, it does have the advantage, in accounting for the reactivity of the $TsiSiR_2H$ compounds towards halogens, that the partial bonding between the leaving H and the incoming X atom (approximating to a three-membered ring with a small HSiX angle) would tend to lower the unfavourable steric interactions with and between the other ligands on silicon.
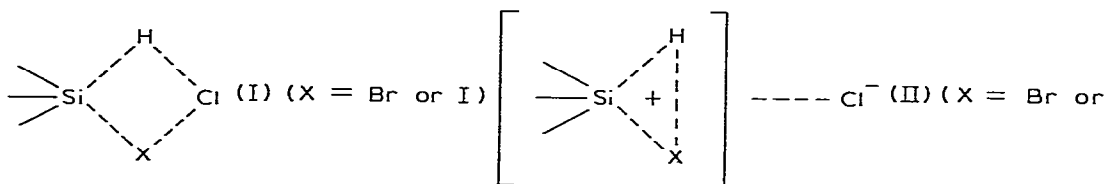

The reactions just mentioned are important in the synthesis of trisyl-silicon derivatives. For example, TsiLi does not give an acceptable yield of $TsiSiPh_2Cl$ when treated with Ph_2SiCl_2, but the corresponding fluoride $TsiSiPh_2F$ is formed satisfactorily from the difluoride Ph_2SiF_2 [4]. The $TsiSiPh_2F$ can then be reduced to $TsiSiPh_2H$, and this with ICl gives the iodide $TsiSiPh_2I$, which is

---

* *Note added in proof.* $TsiSiMe_2I$ is now thought to react with NaN_3 in MeOH by an S_N2 process. For another possible example of such a process see R. Damrauer, J. Organometal. Chem., 216 (1982) C1.

reactive towards electrophiles (see below) and can be converted into a wide range of derivatives.
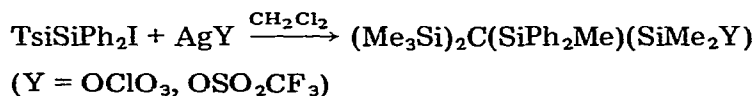
Reactions of iodides and hydrides with electrophiles. 1,3-Methyl migrations

Some of the most interesting features of the chemistry of trisyl-silicon compounds, the 1,3-migrations of Me groups from one silicon atom to another, and the probability of the existence of bridged silico-cations, emerged from a study of the reactions of the iodide TsiSiPh$_2$I with electrophiles, in particular Ag^I and Hg^{II} salts [18,19]. For example, TsiSiPh$_2$I reacted readily with AgNO$_3$ in MeOH, to give a mixture of a silyl methoxide (87%) and a silyl nitrate (13%), but these were found to have not the expected structure TsiSiPh$_2$Y (Y = ONO$_2$ or OMe) but the rearranged structure III (Y = OMe or ONO$_2$). The formation


(III)   (IV)
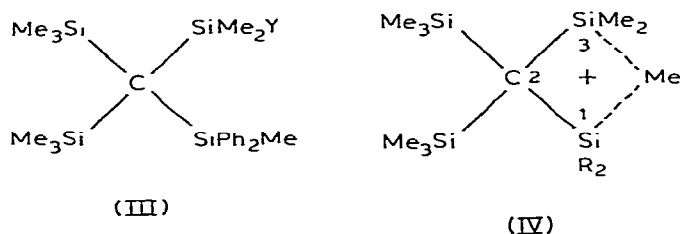
of these products involves a previously unobserved 1,3-methyl migration, and is best interpreted in terms of the existence of the methyl-bridged cationic intermediate IV (R = Ph) [18,19]. The attack of the nucleophile Y$^-$ on this cation can, in principle, occur at either Si(1) or Si(3), but when R = Ph the attack is virtually exclusively at the much less sterically hindered Si(3) centre. In keeping with this explanation, whereas TsiSiPh$_2$I gives exclusively the rearranged acetate III (Y = OAc) on treatment with AgOAc in AcOH, the closely related TsiSiPhMeI, which would give a cation IV (R$_2$ = Ph, Me) in which there is a smaller difference between the steric hindrance at Si(1) and Si(3), gives 78% of rearranged acetate III (Y = OAc) and 22% of the unrearranged TsiSiPh$_2$OAc. TsiSiEt$_2$I gives almost equal amounts of the unrearranged and rearranged acetate on treatment with AgOAc in AcOH. The corresponding hydride TsiSiEt$_2$H similarly reacts with AgO$_2$CCF$_3$ in CF$_3$CO$_2$H to give ca. 60% of the unrearranged trifluoroacetate TsiSiEt$_2$(O$_2$CCF$_3$) and ca. 40% of the rearranged trifluoroacetate (Me$_3$Si)$_2$C(SiEt$_2$Me)(SiMe$_2$O$_2$CCF$_3$).

The rearrangement also takes place when the iodide TsiSiPh$_2$I is treated with appropriate silver salts in aprotic media: e.g., [20,21],

$$\text{TsiSiPh}_2\text{I} + \text{AgY} \xrightarrow{\text{CH}_2\text{Cl}_2} (\text{Me}_3\text{Si})_2\text{C(SiPh}_2\text{Me)(SiMe}_2\text{Y)}$$

(Y = OClO$_3$, OSO$_2$CF$_3$)

The presence of electrophilic metal salts is not essential for these rearrangements. Thus the iodides TsiSiR$_2$I (R = Me or Et) undergo solvolysis in the electrophilic solvent CF$_3$CO$_2$H, and with R = Et comparable amounts of rearranged and unrearranged trifluoroacetate products are formed [19]. Moreover, halogens can act as the electrophiles; thus TsiSiPh$_2$I reacts with ICl to give

exclusively the rearranged chloride:

TsiSiPh$_2$I + ICl → IV (R = Ph) + I$_2$Cl$^-$ → (Me$_3$Si)$_2$C(SiPh$_2$Me)(SiMe$_2$Cl) + I$_2$
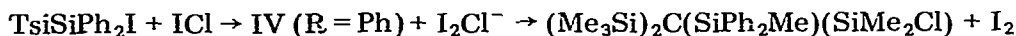
If the reaction of TsiSiMe$_2$I with ICl is carried out in methanol, the product is mainly the methoxide TsiSiMe$_2$OMe, along with some of the chloride TsiSiMe$_2$-Cl [23]; the methoxide is presumably produced by trapping of the cation IV (R = Me) by MeOH, since TsiSiMe$_2$Cl does not react with MeOH under these conditions *. The solvolysis of the iodide TsiSiMe$_2$I in methanol is also catalysed by iodine [23]:

TsiSiMe$_2$I + I$_2$ → IV (R = Me) + I$_3^-$

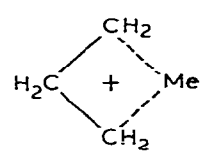IV (R = Me) + MeOH → TsiSiMe$_2$OMe + H$^+$
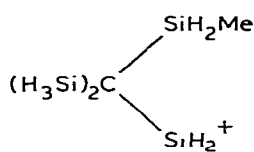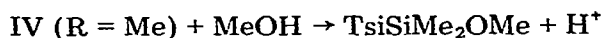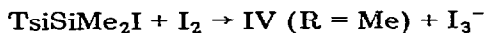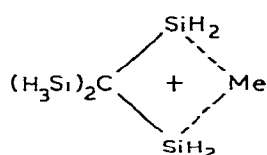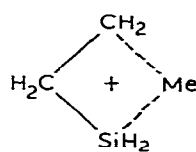
(V)   (VI)   (VII)   (VIII)

The postulation of the existence of the bridged species IV has received strong support from MNDO calculations on the model cations V—VIII [24]; these indicate that the bridged species VI is slightly more stable than the open species V (while in the corresponding systems with H atoms in place of H$_3$Si groups on the central carbon the open is slightly more stable than the cyclic cation), and it is possible that the steric effects in the cations of type IV would, by favouring the formation of the 4-membered ring (with SiCSi angles of ca. 90°), to relieve the interaction between the Me$_3$Si groups, lead to greater stabilization of the bridged compared with the unbridged cation. Significantly, the bridged species VII and VIII, containing one or two carbon atoms in the 4-membered rings in place of silicon, are significantly less and much less stable, respectively, than the corresponding open cations [24], in accord with the fact that no 1,3-methyl migrations are known within carbocations.

It is perhaps relevant to note at this point that while the 1,3-methyl migration has no precedent in carbocation ion systems, the Si—Me—Si bridge in IV shows a close analogy to the well established Al—Me—Al bridge in Al$_2$Me$_6$, Si$^+$ being isoelectronic with Al.

Unimolecular solvolysis of trisylsilicon iodides, perchlorates and triflates

Since direct nucleophilic attack on the silicon of TsiSiR$_2$X species is sterically inhibited, it was reasonable to expect that if reactions at Si—X bonds could ever involve rate-determining ionization (a mechanism which had long been

---

* Readers very familiar with organosilicon chemistry will appreciate the novelty of being able to make organosilicon halides, nitrates, etc. (normally highly reactive towards hydroxylic media) in methanol.

sought without success) it would be in TsiSiR$_2$X compounds containing a sufficiently good leaving group *. Thus the perchlorate TsiSiMe$_2$OClO$_3$ was examined, and its methanolysis was indeed found to be of the S_N1 type [25,26]:

$$TsiSiMe_2OClO_3 \rightarrow TsiSiMe_2^+ + ClO_4^- \quad (slow)$$

$$TsiSiMe_2^+ + MeOH \rightarrow TsiSiMe_2OMe + H^+ \quad (fast)$$
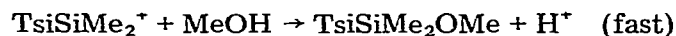
The main items of evidence were: (a) the smallness of the rate increase caused by added NaOMe, indicating that the latter exerted only a salt effect, and (b) the diversion of a substantial proportion of the product from the solvolysis product TsiSiMe$_2$OMe to the nitrate TsiSiMe$_2$ONO$_2$ in the presence of LiNO$_3$. It was later shown that the triflate TsiSiMe$_2$OSO$_2$CF$_3$ also undergoes methanolysis by the S_N1 mechanism, somewhat more slowly than the corresponding perchlorate [21]. Rather unexpectedly (since it seemed likely that the high reactivity associated with the presence of a hydride ligand on silicon was to be attributed to the much smaller hindrance to direct nucleophilic attack of the S_N2 type), the rapid methanolyses of the iodides TsiSiPhHI and TsiSiMeHI were also shown to be of the S_N1 type, but, interestingly, the methanolyses of the corresponding bromide TsiSiPhHBr and nitrate TsiSiPhH(ONO$_2$) were found to be greatly accelerated by NaOMe, indicating that the reaction in the presence of base was of the S_N2 type, and that in the neutral solvent probably so [26]. Yet later the iodide TsiSiMe$_2$I was also found to react by an S_N1 mechanism with MeOH, though slowly even at 50°C, but the corresponding diphenyl compound TsiSiPh$_2$I showed no reaction even after 4 days in refluxing MeOH [27]. It will be appreciated that the effect of substituents on the formation of the cation are very different from those observed with carbocations, which are formed much more readily from tertiary than from secondary or primary alkyl halides, and in which the presence of phenyl groups on the potentially cationic centre greatly increases the ease of S_N1 hydrolysis. Presumably this difference arises mainly from the fact that stabilization of the positive ion by conjugation or hyperconjugation, which involves $(p—p)_\pi$ bonding, is much less effective with silicon [36]. The dominant effect of the Me and Ph groups on a positive silicon centre is thus steric inhibition of solvation.
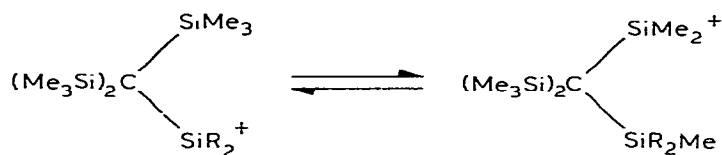
There is at present no means of assessing the extent to which the ease of ionization of the TsiSiRHX and TsiSiR$_2$X species studied depends on the presence of the trisyl group, and is attributable to (a) anchimeric assistance associated with formation of bridged ions of type IV (see below), and (b) relief of strain on separation of the leaving group. Orginary silicon iodides, such as Me$_3$SiI and Me$_2$HSiI, are very much more reactive towards alcohols, and it is impossible to estimate how rapidly they would react by an S_N1 mechanism if the much faster bimolecular process were not available.
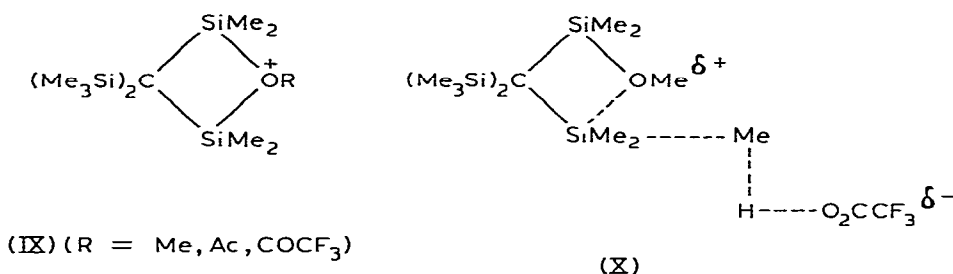

Anchimeric assistance

The results considered above are most satisfactorily interpreted in terms of formation of a bridged cation of type IV, with the bridging stabilising the ion, so that an Me group on Si(3) provides anchimeric assistance to the leaving of X from Si(1), but the possibility cannot be excluded that there is an equilibrium involving open cations:

$$(Me_3Si)_2C \begin{array}{c} SiMe_3 \\ \diagup \\ \diagdown \\ SiR_2^+ \end{array} \quad \underset{\longleftarrow}{\overset{\longrightarrow}{}} \quad (Me_3Si)_2C \begin{array}{c} SiMe_2^+ \\ \diagup \\ \diagdown \\ SiR_2Me \end{array}$$

However, there seems clear evidence for powerful anchimeric assistance by MeO, CH_3CO_2, and CF_3CO_2 groups, which could be expected to bridge more effectively than the Me group.

The first indication of anchimeric assistance by such groups came when the compound TsiSiMeClI was treated with $Hg(OAc)_2$ in AcOH and the product was found to be $(Me_3Si)_2C(SiMe_2OAc)_2$ [28]. While $TsiSiMe_2I$ reacts with this reagent, $TsiSiMe_2Cl$ does not, and so it is evident that the Si—Cl bond in the initially formed $(Me_3Si)_2C(SiMe_2OAc)(SiMe_2Cl)$ is unusually reactive. Then the $(Me_3Si)_2C(SiMe_2OAc)_2$ was found to react with CF_3CO_2H to give $(Me_3Si)_2$-$C(SiMe_2O_2CCF_3)_2$ under conditions in which $TsiSiMe_2OAc$ is inert. Originally, anchimeric assistance involving interaction of the carbonyl oxygen with the silicon of the breaking Si—X bond was proposed [28], but it is now thought more likely that it is the ether-type oxygen which is involved (to form a cation of the type IX), as in the much more effective assistance by the OMe group.

$$(Me_3Si)_2C \begin{array}{c} SiMe_2 \\ \diagup \quad \diagdown \\ \quad \quad \overset{+}{OR} \\ \diagdown \quad \diagup \\ SiMe_2 \end{array} \qquad\qquad (Me_3Si)_2C \begin{array}{c} SiMe_2 \\ \diagup \quad \diagdown \\ \quad \quad OMe^{\delta+} \\ \diagdown \quad \diagup \\ SiMe_2 ------ Me \\ | \\ | \\ H----O_2CCF_3{}^{\delta-} \end{array}$$

(IX) (R = Me, Ac, COCF₃)

(X)

The very effective anchimeric assistance by the OMe group shows up, for example, in the methanolysis of $(Me_3Si)_2C(SiMe_2Cl)(SiMe_2OSO_2CF_3)$. The triflate group is rapidly lost (more quickly than from $TsiSiMe_2OSO_2CF_3$, suggesting anchimeric assistance by the Cl atom), as expected, and the loss of the Cl occurs at the same rate, the product being $(Me_3Si)_2C(SiMe_2OMe)_2$ [21]. It seems that once the triflate group is replaced by an OMe group, the Cl leaves very readily, so that no significant concentration of the intermediate $(Me_3Si)_2$-$C(SiMe_2Cl)(SiMe_2OMe)$ builds up:

$(Me_3Si)_2C(SiMe_2Cl)(SiMe_2OSO_2CF_3)$ + MeOH

$\rightarrow (Me_3Si)_2C(SiMe_2Cl)(SiMe_2OMe)$

$(Me_3Si)_2C(SiMe_2Cl)(SiMe_2OMe) + MeOH$

$$\rightarrow (Me_3Si)_2C(SiMe_2OMe)_2 \qquad (fast)$$
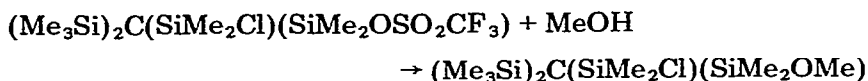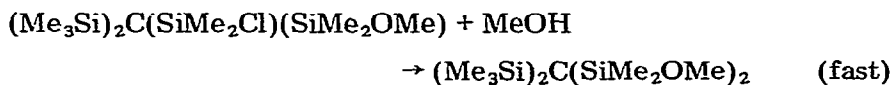
An even more striking example of assistance by the OMe group is provided by the reaction of TsiSiMe$_2$OMe with CF_3CO_2H to give $(Me_3Si)_2C[SiMe_2$-$(O_2CCF_3)]_2$, i.e. with loss of a Me group from a silicon atom [29]. It can be assumed that this remarkable cleavage of an Si—Me bond is assisted by the neighbouring OMe group, as in X, and the loss of the OMe group from the product is then assisted by the neighbouring O_2CCF_3 group.

Pyrolysis of TsiSiPh$_2$X compounds

The compound TsiSiPh$_2$F was found to lose Me$_3$SiF under reflux, or on brief passage through a tube at 450°C, to give the three cyclized products XI, XII and XIII in approximately 20:20:60 ratio [30].


(XI)   (XII)   (XIII)
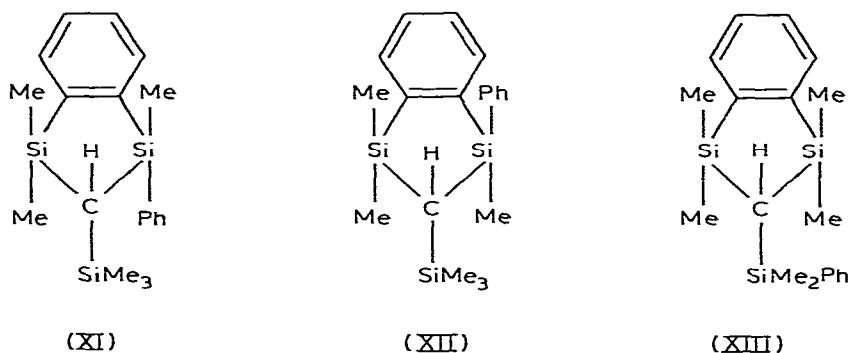
It was postulated that the sila-olefin $(Me_3Si)_2C=SiPh_2$ is first formed, and that this rapidly comes into equilibrium with the isomeric olefins by shifts of Me or Ph groups:
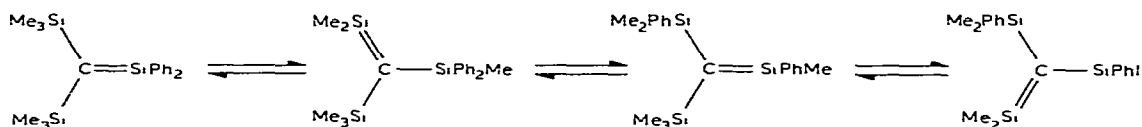
The cyclizations then in effect involve addition of a Ph—H bond across an adjacent Si=C bond.

The corresponding chloride and bromide TsiSiPh$_2$Cl and TsiSiPh$_2$Br do not undergo pyrolysis at the temperatures used, but the iodide TsiSiPh$_2$I readily decomposes on heating, but by loss of HI not Me$_3$SiI. Again cyclized products, XIV and XV, are formed (though some cleavage of the Si—Ph bonds in the products by HI then takes place). The reaction is thought to occur by initial homolytic dissociation of the Si—I bond, followed by radical rearrangements and then ring closure involving a free radical aromatic substitution process [31].
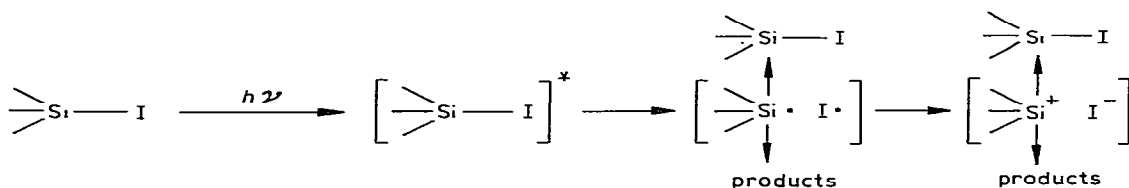
Me$_2$Si S$_i$Me$_3$ SiMePh

C

SiMe$_3$

(XIV)

Me$_2$Si S$_i$Me$_3$ SiMe$_2$

C

SiMe$_2$Ph

(XV)
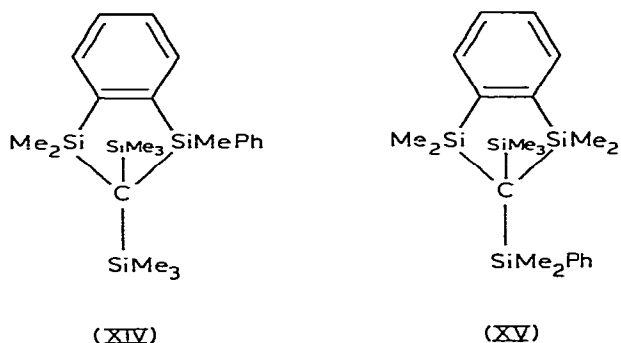
Photo-induced reactions

The iodide TsiSiPh$_2$I, which is virtually inert towards MeOH under prolonged reflux, readily undergoes methanolysis under UV irradiation, to give predominantly the rearranged methoxide (Me$_3$Si)$_2$C(SiPh$_2$Me)(SiMe$_2$OMe) [32,33]. If LiNO$_3$ is present, some of the rearranged nitrate (Me$_3$Si)$_2$C(SiPh$_2$Me)(SiMe$_2$ONO$_2$) is formed. All the evidence points to photo-induced generation of the bridged cation IV (R = Ph). (In contrast to the results in the reactions assisted by silver salts, some unrearranged methoxide TsiSiPh$_2$OMe, is also produced in the photo-induced process, presumably because a highly energetic, less selective, cation is formed.) Correspondingly, irradiation of the iodide in aniline gives the rearranged anilide (Me$_3$Si)$_2$C(SiPh$_2$Me)(SiMe$_2$NHPh) [33].

However, radical processes can also be induced by the irradiation; thus irradiation of TsiSiPh$_2$I in CCl$_4$ gives the unrearranged chloride TsiSiPh$_2$Cl, the absence of rearrangement indicating that the cation is not involved in this case [32,33]. Irradiation in pentane causes rearrangement of the iodide to the isomeric (Me$_3$Si)$_2$C(SiPh$_2$Me)(SiMe$_2$I), while prolonged irradiation in anisole gives the cyclized compound XIV, which is also formed by pyrolysis, as noted above.

Overall the results show a remarkable similarity to those obtained by Kropp and his colleagues in the photo-induced reactions of alkyl iodides [34], though there are the expected differences (arising, for example, from the greater ease of abstraction of Cl atoms from C—Cl bonds by silicon- than by carbon-centred radicals, and the much smaller probability of forming Si=C than C=C double bonds). It seems likely that the type of mechanism proposed for the alkyl iodides [34] applies also to the silicon iodides; this involves initial dissociation to a radical pair, which can be trapped by suitable reagents or can, by internal electron transfer, give an ion pair, as in Scheme 1.

SCHEME 1

$$\text{Si}—\text{I} \xrightarrow{h\nu} \left[\text{Si}—\text{I}\right]^* \longrightarrow \left[\text{Si}\cdot\ \text{I}\cdot\right] \longrightarrow \left[\text{Si}^+\ \text{I}^-\right]$$

products   products

The related iodide TsiSiPhMeI also undergoes methanolysis readily under irradiation, while TsiSiMe$_2$I reacts more slowly, though much faster than in the absence of irradiation. It is likely that the absorption of light by the aryl group is important in the reactions of the compounds containing Si—Ph bonds.

Trisyl derivatives of other elements

Since the presence of a trisyl ligand bestows such unusual properties on a silicon centre to which it is attached, it was reasonable to expect that compounds containing the ligand attached to other metals or metalloids would also show unusual properties. The most striking realization of this expectation is provided by the observation that the dialkylzinc compound (Tsi)$_2$Zn is not only stable in the air, and towards reagents such as Br$_2$ and CH$_3$COCl, but can actually be steam-distilled unchanged [7]! The corresponding mercury and cadmium compounds also show high chemical and thermal stability, decomposing only above about 300°C; the high thermal stability of the mercurial (Tsi)$_2$Hg has important implications for the mechanism of thermal decomposition of organomercurials in general.

The phosphorus derivative TsiPCl$_2$ is unusual for an organodichlorophosphine in that it can be recrystallized unchanged from hot methanol, but it fairly readily loses Me$_3$SiCl on heating to give (Me$_3$Si)$_2$C=PCl and then Me$_3$SiC≡P [9]. The triorganophosphine TsiPPh$_2$, while stable to heat, undergoes a fairly ready cleavage reaction in methanol to give (Me$_3$Si)$_2$CHPPh$_2$, and the remaining Me$_3$Si groups come off in subsequent similar but slower reactions, ultimately to give CH$_3$PPh$_2$ [10].

(Me$_3$Si)$_3$CPPh$_2$ + MeOH → (Me$_3$Si)$_2$CHPPh$_2$ + Me$_3$SiOMe
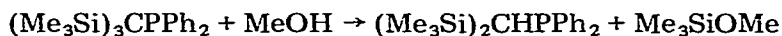
The mechanism of this cleavage presents an interesting problem, which is being studied.

The trisyl derivatives of germanium [2,5,35] and tin [2,6] so far examined, containing only one trisyl group attached to the metal, have not shown the exceptionally unusual behaviour observed for the silicon analogues. However, it should be possible to attach two trisyl groups to tin, and then novel properties can be expected, including possibly the stabilization of the Sn^{II} state.

The chemistry of trisyl derivatives of boron is remarkable in that the reaction of TsiLi with BF$_3$ in THF—Et$_2$O gives not TsiBF$_2$ but compound XVI, in which a chain from tetrahydrofuran has been incorporated [10].
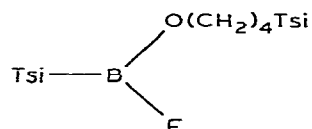
(XVI)

The steric hindrance to direct substitution in XVI appears to be much lower than that in trisyl-silicon compounds, no doubt because only four groups surround boron in the transition state for the bimolecular substitution, compared with the five groups around silicon. Thus PhLi reacts with XVI to give TsiB(Ph)-

[O(CH$_2$)$_4$Tsi] [10]. However, novel properties can be expected for trisyl-boron compounds, and these are being explored, as are the reactions of trisyl derivatives of a wide range of other elements.

Acknowledgement

I take this opportunity of acknowledging the important part played over the years in my researches on organosilicon and related compounds by workers who came to me from Prof. Mehrotra's laboratories.

References

1 R.L. Merker and M.J. Scott, J. Amer. Chem. Soc., 85 (1963) 2243; J. Organometal. Chem., 4 (1965) 98.
2 M.A. Cook, C. Eaborn, A.E. Jukes and D.R.M. Walton, J. Organometal. Chem., 24 (1970) 529.
3 O.W. Steward and J.J. Johnson, J. Organometal. Chem., 55 (1973) 209.
4 S.S. Dua, C. Eaborn, D.A.R. Happer, S.P. Hopper, K.D. Safa and D.R.M. Walton, J. Organometal. Chem., 178 (1979) 75.
5 C. Eaborn and N. Siew, J. Organometal. Chem., 202 (1980) 157.
6 F. Glockling, P. Harriott and W.K. Ng, J. Chem. Research, (1979) (S) 12; (M) 275; F. Glockling and W.K. Ng, ibid., (1980) (S) 230; (M) 3128.
7 C. Eaborn, N. Retta and J.D. Smith, J. Organometal. Chem., 190 (1980) 101.
8 F. Glockling, N.S. Hosmane, V.B. Mahale, J.J. Swindall, L. Magos and T. King, J. Chem. Res., (1977) (S) 116; (M) 1198.
9 K. Issleib, H. Schmidt and C. Wirkner, Z. Chem., 20 (1980) 153 and 419; Z. Anorg. Allgm. Chem., 473 (1981) 85.
10 C. Eaborn, N. Retta and J.D. Smith, Unpublished results.
11 C. Eaborn, R. Eidenschink, P.M. Jackson and D.R.M. Walton, J. Organometal. Chem., 101 (1975) C40.
12 A.C. Hopkinson and M.H. Lien, J. Organometal. Chem., 206 (1981) 287.
13 B. Beagley, R.G. Pritchard, C. Eaborn and S.S. Washburne, J. Chem. Soc., Chem. Commun., (1981) 710.
14 C. Eaborn, D.A.R. Happer, K.D. Safa and D.R.M. Walton, J. Organometal. Chem., 157 (1978) C50.
15 C. Eaborn, D.A.R. Happer and K.D. Safa, J. Organometal. Chem., 191 (1980) 355.
16 L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965, pp. 107—109.
17 D.R. Deans and C. Eaborn, J. Chem. Soc., (1954) 3169.
18 C. Eaborn, D.A.R. Happer, S.P. Hopper and K.D. Safa, J. Organometal. Chem., 170 (1979) C9.
19 C. Eaborn, D.A.R. Happer, S.P. Hopper and K.D. Safa, J. Organometal. Chem., 188 (1980) 179.
20 S.S. Dua and C. Eaborn, J. Organometal. Chem., 204 (1980) 21.
21 D.E. Reed, personal communication.
22 C. Eaborn and S.P. Hopper, J. Organometal. Chem., 192 (1980) 27.
23 A.I. Mansour, personal communication.
24 Dr. A. Kos, personal communication.
25 S.S. Dua, C. Eaborn and F.M.S. Mahmoud, J. Organometal. Chem., 192 (1980) 293.
26 C. Eaborn and F.M.S. Mahmoud, J. Chem. Soc. Perkin Trans II, (1981) 1309.
27 S.A.I. Al-Shali, C. Eaborn and F.M.S. Mahmoud, J. Organometal. Chem., 232 (1982) 215.
28 C. Eaborn and S.P. Hopper, J. Organometal. Chem., 170 (1979) C51.
29 P. Lickiss, personal communication.
30 C. Eaborn, D.A.R. Happer, P.B. Hitchcock, S.P. Hopper, K.D. Safa, S.S. Washburne and D.R.M. Walton, J. Organometal. Chem., 186 (1980) 309.
31 C. Eaborn and K.D. Safa, J. Organometal. Chem., 204 (1981) 169.
32 C. Eaborn, K.D. Safa, A. Ritter and W. Binder, J. Chem. Soc. Chem. Commun., (1981) 175.
33 C. Eaborn, K.D. Safa, A. Ritter and W. Binder, J. Chem. Soc. Perkin 2, in press.
34 P.J. Kropp, T.H. Jones and G.S. Poindexter, J. Amer. Chem. Soc., 95 (1973) 5420; G.S. Poindexter and P.J. Kropp, ibid., 98 (1976) 4319; P.J. Kropp, G.S. Poindexter, N.J. Peenta and D.C. Hamilton, ibid., 98 (1976) 8135.
35 I.V. Borisova, N.N. Zemlyanskii, N.D. Kolosova, Yu.A. Ustynuk and I.P. Beletskaya, Bull. Akad. Sci., U.S.S.R., 28 (1979) 2222.
36 C. Eaborn, Organosilicon Compounds, Butterworths, London, 1960, p. 115.