The 1,3 migration of a methyl group in reactions of the trisyl iodide $(Me_3Si)_3CSi(CD_3)_2I$ and related iodides with silver salts in 2,2,2-trifluoroethanol. Refinement of the mechanism †

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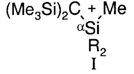
In the reactions of the isotopically labelled iodide $(Me_3Si)_3CSi(CD_3)_2I$ with silver salts AgX the mixtures of unrearranged $(Me_3Si)_3CSi(CD_3)_2X$ and rearranged $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2X$ are formed in lower yields in CF_3CH_2OH than in EtOH but the proportion of the rearranged isomer is markedly larger in the former alcohol, sometimes approaching 50%. The yields of the trifluoroethoxides $(Me_3Si)_3CSi(CD_3)_2OCH_2CF_3$ and $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2OCH_2CF_3$ are correspondingly smaller than those of the ethoxides in EtOH, but the percentage of the rearranged product is markedly higher, at 63 ± 5, the first observations of percentages of rearranged alkoxide products of > 50%. In some reactions in which not all the iodide has reacted that remaining contains significant amounts of the rearranged iodide $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2I$. Formation from this of $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2X$ and $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2OCH_2CF_3$ must contribute to the unusually high proportions of rearranged products in this medium. It is suggested that the initial reaction of the $(Me_3Si)_3CSi(CD_3)_2I$ with AgX produces an ion pair containing the Me-bridged cation $[(Me_3Si)_2Me_2Si\overline{CSi(CD_3)_2IM}e]^+$ and the argentate ion $[AgXI]^-$ and that attack on the cation by the solvent at either the α-Si or γ-Si ends of the bridge to give trifluoroethoxides competes with release of an X^- or an I^- ion from the argentate ion to the α-site and also with migration of the argentate ion to the γ-site. The cation in the new ion pair formed by this migration can then in turn be attacked by the solvent or abstract X^- or I^- from the argentate ion. Such migration of argentate ion is assumed to occur also in the corresponding reactions in inert and other hydroxylic media.

Reaction of $(Me_3Si)_3CSiEt_2I$ with AgO_3SMe in CF_3CH_2OH gives the expected $(Me_3Si)_3CSiEt_2OSO_2Me$, $(Me_3Si)_2(Et_2MeSi)CSiMe_2OSO_2Me$, $(Me_3Si)_3CSiEt_2OCH_2CF_3$, and $(Me_3Si)_2(Et_2MeSi)CSiMe_2OSO_2Me$, together with a little $(Me_3Si)_2(EtMe_2Si)CSiMeEtOCH_2CF_3$. The presence of this last product is attributed to the generation of some of the rearranged iodide $(Me_3Si)_2(Et_2MeSi)CSiMe_2I$ and formation from that of an Et-bridged cation. The iodide $(Me_3Si)_3CSi(CD_3)_2I$ also undergoes solvolysis slowly in refluxing CF_3CH_2OH alone to give the rearranged and unrearranged trifluoroethoxides, but only in roughly 1 : 4 ratio.

Introduction

Reactions of organosilicon iodides $(Me_3Si)_3CSiR_2I$ with silver salts AgX in inert solvents are known to give rearranged products $(Me_3Si)_2(R_2MeSi)CSiMe_2X$, sometimes virtually exclusively, *e.g.* R = Ph, and sometimes along with the unrearranged isomer $(Me_3Si)_3CSiR_2X$, *e.g.* R = Et.[1–3] This is attributed to the formation of a methyl-bridged cation of type **I**, which can capture an anion X^- either at the α-Si atom to give unrearranged product $(Me_3Si)_3CSiR_2X$ or at the γ-Si atom to give the rearranged $(Me_3Si)_2(R_2MeSi)CSiMe_2X$. When the reaction is carried out in an alcohol R′OH these same products are formed along with the unrearranged and rearranged alkoxides $(Me_3Si)_3CSiR_2OR'$ and $(Me_3Si)_2(R_2MeSi)CSiMe_2OR$. Where R is a simple organic group, such as alkyl, phenyl or vinyl, the relative ease of attack at the α-Si and γ-Si centres, and thus the extent of rearrangement, is mainly influenced by the relative degrees of steric hindrance to attack at those centres, although it also depends on the nature of X and the solvent.[1,2] Reactions with ICl likewise give rearranged chlorides, along with, in alcohols, alkoxides.[4] Solvolysis in trifluoroacetic acid alone gives a mixture of unrearranged and rearranged trifluoroacetates.[1]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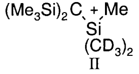
II

Since the relative yields of rearranged and unrearranged products appeared to be largely determined by the relative degrees of steric hindrance at the α- and γ-Si centres we had expected that reactions of the labelled iodide $(Me_3Si)_3CSi(CD_3)_2I$, **1**, would give essentially equal amounts of the isomeric products but we found that for a range of inert solvents this was far from the case. The percentage, P_R, of rearranged product in the mixture of $(Me_3Si)_3CSi(CD_3)_2X$, TX, and $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2X$, T′X, was usually significantly below 50 (in some cases < 10) and depended markedly on the silver salt AgX and the solvent.[4] However, for reactions with AgO_3SCF_3 (silver triflate, AgOTf) or AgO_2CCF_3 (AgOtfa) in CH_2Cl_2 values of P_R of between 50 and 80 were observed. (Reactions of **1** with ICl gave P_R values varying from 15 in $CHCl_3$ to 42 in

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† Electronic supplementary information (ESI) available: details of the methods used in the quantitative analysis of reaction products and the estimation of their reliability. See http://www.rsc.org/suppdata/p2/b2/b204130h/

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CH_2Cl_2.[5]) Moreover, in some cases in which reaction was not taken to completion the residual iodide was found to be partly rearranged, more than 80% so when the reaction with AgOTf in CH_2Cl_2 was *ca.* 90% complete.[4] Such rearrangement was tentatively attributed to occasional recapture by the bridged cation of I^- from a newly formed molecule of AgI before the latter left to become part of an inactive cluster or precipitate. We now have a much better explanation, which involves an important refinement of our picture of the reaction mechanism.

$(Me_3Si)_3CSi(CD_3)_2I$ **1** $(Me_3Si)_3CSiEt_2I$ **2**

$T = (Me_3Si)_3CSi(CD_3)_2$ $T' = (Me_3Si)_2[Me(CD_3)_2Si]CSiMe_2$

Results and discussion

When we previously examined the reactions of **1** with AgX in the alcohols R′OH, R′ = Me, Et, Pr^i, Bu^t, we found that the ratio of the combined yields of TX and T′X products to those of solvolysis products TOR′ and T′OR′ increased markedly with the bulk of the alcohol and that the P_R values for both sets of products were < 50, although some values for the alkoxides exceeded 40.[6] (Small amounts of hydroxides TOH and T′OH were also formed from traces of water.) We have now studied the reactions with silver salts in 2,2,2-trifluoroethanol (TFE) and observed some unexpected behaviour of important mechanistic significance. The results of the reactions of **1** with silver salts AgX, usually in 1 : 1 molar ratio, in refluxing TFE are shown in Table 1. (Reactions were also carried out at room temperature for longer times with essentially identical results.) For comparison, in Table 2 some of the results are shown along with those previously obtained for the same reactions in EtOH, an alcohol of similar steric requirements.[6] Data obtained under modified conditions, namely with an excess of **1** or in the presence of added water, MeOH or LiX are shown in Table 3. The main features of the results shown in three tables are as follows:

(i) In TFE the combined yields of unrearranged products $TsiSi(CD_3)_2X$ [Tsi = $(Me_3Si)_3C$], TX, and their rearranged isomers $(Me_3Si)_2[Me(CD_3)_2Si]CSiMe_2X$, T′X, vary from *ca.* 5 to *ca.* 27%. (The yield given for perchlorate products in EtOH is actually that of the hydroxides; this is partly because the $AgClO_4$ was used as the monohydrate and partly because the formed silicon perchlorates are very readily solvolysed, with an exceptionally high selectivity towards traces of water.[7] Hydrolysis is insignificant in TFE.) The yields are highest in the cases in which X is derived from the strongest acids HX, *viz.* those with X = BF_4, NO_3, ClO_4 and O_3SCF_3. (Note that $AgBF_4$ gives rise to fluoride products.) The combined yields of TX and T′X from AgX with X = NO_3, O_2CCF_3, and BF_4 (*ca.* 26, 7, and 27%), respectively, are substantially lower than those in EtOH (34, 26, and 47%). This was contrary to our expectation, since we thought that the more weakly nucleophilic TFE was likely to compete less effectively than EtOH with X^- in capture of the intermediate cation, but enhanced solvation of negative ions in the more acidic TFE could hinder the release of X^-.

(ii) The proportion of the rearranged $T'OSO_2Me$ (T′OMs) formed in the reaction with silver mesylate AgO_3SMe (AgOMs) in TFE was not significantly changed when an excess of LiOMs was present in the solution. The relatively small effect of added LiX in reaction with AgX was observed previously for reactions in MeOH.[1,4]

(iii) The values of P_R for the TX + T′X product mixtures are significantly higher for the reactions in TFE than for those in other alcohols, and in some cases are not far from that of 50 expected for trapping of a fully free cationic intermediate **II**.

(iv) The values of P_R, 63 ± 5, for the alkoxide products $TOCH_2CF_3$ (TOtfe) and $T'OCH_2CF_3$ (T′Otfe) are unusually high, and markedly higher than those in EtOH. They are effectively independent of the nature of the silver salt used. We had never previously observed a P_R value of > 50 for the TOR′ and T′OR′ products in an alcohol R′OH.

Table 1 Yields (%)[a] and P_R values (uncertainty ±5) for products of reactions of $TsiSi(CD_3)_2I$ with AgX in refluxing trifluoroethanol

X	TX	T′X	P_R[b]	TOtfe	T′Otfe	P_R[c]	TOH[d]
ClO_4[e]	14	10	41	26	45	63	4
OTf	11	9	44	28	52	65	< 2
NO_3	16	10	39	27	47	64	< 2
OMs	8	4	33	33	53	62	< 2
OTs	10	5	35	30	54	64	< 2
Otfa	4	3	47	36	55	61	6
OAc	2	1	29	35	55	61	5
F	8	6	32	32	53	62	< 2[f]
BF_4[g]	15	12	46	26	47	64	< 2[g]

[a] The yields shown are subject to uncertainties of (i) ±1 (*e.g.* 2 ± 1; 4 ± 1) or (ii) ±10% of their values (*e.g* 20 ± 2; 50 ± 5), whichever is the greater. [b] Percentage of rearranged T′X in the TX + T′X mixture. [c] Percentage of T′Otfe in TOtfe + T′Otfe mixture. [d] The extent of rearrangement could not be determined. [e] The monohydrate was used. [f] An estimate based on results of reactions of $(Me_3Si)_3Si(CH_3)_2I$ under the same conditions. [g] The TX products were the fluorides.

Table 2 Yields (%) of products[a] and P_R[a] values for reactions of $TsiSi(CD_3)_2I$ with AgX in refluxing ethanol, with corresponding values for trifluoroethanol shown in parentheses[b]

X	TX	T′X	P_R	TOR	T′OR	P_R
ClO_4[c]	29 (14)	5 (10)	15 (44)	40 (28)	26 (52)	40 (65)
OTf	23 (11)	4 (9)	15 (45)	46 (28)	22 (52)	32 (65)
NO_3	41 (16)	3 (10)	7 (39)	38 (27)	17 (47)	31 (64)
OMs[d]	24 (8)	2 (4)	8 (33)	41 (33)	33 (53)	45 (62)
Otfa	18 (4)	4 (3)	18 (47)	57 (34)	21 (57)	27 (63)
BF_4[e]	38 (15)	9 (12)	19 (44)	35 (26)	17 (47)	32 (67)

[a] For uncertainties in the yields and P_R values see Table 1. [b] The ethanol data are from reference 6 unless otherwise specified. [c] In EtOH the initial product undergoes hydrolysis (without rearrangement) and the yield shown for TX is actually that of the hydroxide. [d] This work. [e] The TX products were the fluorides.

Table 3 Products of reactions of $TsiSi(CD_3)_2I$ with AgX under modified conditions[a]. Yields and (in parentheses) P_R values

X	$T_{tot}X$ (P_R)	$T_{tot}OR$ (P_R)	Other
OTf[b,c]	14 (43)	84 (41)	TI 50 (4)
OTf[d]	15 (45)	79 (62)	TOH 6
OMs[c,e]	11 (37)	82 (66)	TI 7 (11)
OMs[f]	9 (7)	63 (41)	TI 27 (4)
OTf[g]	20 (33)	31 (29)	TOMe 40 (36)

[a] Solvent is trifluoroethanol unless otherwise stated. For uncertainties in the yields and P_R values see Table 1. [b] [TI] : [AgOTf] = 1.5 : 1. The residual iodide was 4% rearranged. [c] Where similar proportions of residual iodide were found in other AgX reactions the proportion of T′I was also similar. [d] Water (1% v/v) added. The P_R of the TOH could not be determined. [e] LiOMs ≈ 10 × [AgOMs] added. [f] Solvent was MeOH. [g] Equimolar TFE–MeOH; other AgX under the same conditions gave similar methoxide–trifluoromethoxide ratios.

(v) Trifluoroethoxide and methoxide products are formed in 1 : 1.3 ratio in a 1 : 1 TFE–MeOH mixture. Since MeOH is much more nucleophilic than TFE the methoxides might have been expected to dominate, but strong hydrogen-bonding involving interaction of a proton of the TFE with the oxygen atom of MeOH markedly lowers the nucleophilicity of the latter alcohol and raises that of the former so that they become comparable.

A P_R value of > 50 for the alkoxides TOR and T′OR might be generally expected if an alcohol ROH attacks the bridged cation before it is fully free, since the approach to the α-Si is likely to be hindered by the silver-containing entity near to that site, whereas there is no such obstruction at the γ-Si. (Such an outcome would be comparable to the predominant retention of configuration at carbon in an S_N1 reaction of an alkyl halide.) That such P_R values were not observed for reactions in the other alcohols used could be attributed to their higher nucleophilicity and so lower selectivity. However, a partial explanation of the high P_R value for the reactions in TFE derives from the observation that when the reaction with AgOTf was carried out with only 75% of the amount required for complete reaction the residual 25% of the iodide was *ca.* 4 (±1)% rearranged. Although this value is small, and the estimated uncertainty relatively large, there is no doubt that some rearranged iodide was formed, since the ^1H NMR signal from the $SiMe_2I$ group is easily identifiable, being sharp and well removed from other signals, and absent from the spectrum of the starting iodide **1**. We have noted previously that there is clear evidence for formation of the rearranged iodide in reactions in other media.[4] Any rearranged iodide formed will react further with the silver salt just as readily as the unrearranged iodide, and capture by the solvent of the bridged ion generated from it will give very predominantly (> 90%) rearranged T′Otfe. [This is mainly because only two CD_3 and one CH_3 group on the original α-Si are available for bridging, compared with six CH_3 groups in the other $SiMe_3$ groups, and capture by the solvent of the bridged cations formed by participation of any of the latter groups gives only rearranged trifluoroethoxide. Furthermore, (i) if the Me of $Si(CD_3)_2Me$ provides the bridge this should lead to approximately equal amounts of T′Otfe and TOtfe, and (ii) if a CD_3 on the original α-Si site provides the bridge this should lead to small, and approximately equal, quantities of TOtfe and $(Me_3Si)_2[(CD_3)Me_2Si]CSiMe(CD_3)Otfe$. The analytical method is such that this last product would not be observed but would appear in the analysis as though it were a mixture of equal amounts of TOtfe and T′Otfe. Thus if approximately equal amounts of TOtfe and T′Otfe were formed directly from **1**, the apparent yield of T′Otfe would be enhanced by an amount dependent on the amount of rearranged iodide formed during the course of the reaction. For example, if for simplicity the formation of small amounts of TX and Totfe from the rearranged cation–argentate ion pair is initially ignored, and the rate of formation of T′I is assumed to be 10% of that of the disappearance of TI, then 100 units of TI would give 10 units of T′I. The 90 units of products formed directly from TI would consist of *ca.* 20 units of TX + T′X and 70 of TOtfe + T′Otfe, *i.e. ca.* 35 of each. The 10 units of T′I would go to *ca.* 2.5 of T′X and 7.5 of TOtfe. Thus T′Otfe : TOtfe = 42.5 : 35, *i.e.* P_R = 55. (On the above assumptions the ratio T′I : TI would be expected to rise during the course of the reaction because for every 10 units of T′I that react one would be regenerated, but ultimately every 10 units thus recycled would go on to give *ca.* 2.5 of T′X + 7.5 of T′Otfe.) Allowance for the formation of TX and TOtfe from the rearranged ion pair reduces the calculated P_R to *ca.* 54. If T′I were formed at (a) 20% or (b) 30% of that of the disappearance of TI this figure would be raised to (a) 58 or (b) 62.

The previously reported high proportion of rearranged trifluoroacetates and triflates formed from the corresponding silver salts in CH_2Cl_2[4] can be accounted for in the same way. In the absence of competing reaction with the solvent, the rate of formation of T′I relative to that of the conversion of TI to TX and T′X could be substantially higher. If it were as high as, say, 30% then there would be a marked build-up of T′I during the course of the reaction. Such a build-up was clearly observed in the present work in the reaction of **1** with $AgO_3SC_6H_4Me$-*p* (silver tosylate, AgOTs) in CH_2Cl_2, in which the silver salt was only partly soluble (see Table 4). (Reactions with more soluble silver salts, *e.g.* AgOTf, are complete in 2 h or less.) However, it is difficult to reconcile the relatively small build-up in this case with our previous report of P_R values for the iodide of 80% in some of the reactions in CH_2Cl_2 and a systematic study of the rearrangement of the iodide under those conditions is desirable. There are some additional features of interest in the results in Table 4. First, the P_R value for the tosylates remains effectively constant, as would be expected for the proposed mechanism. Second, the disappearance of the TI appears to be roughly of zero order; we think that the solution is probably saturated throughout with the silver salt and so would expect the reaction to be of first order with respect to the iodide. Again further study seems to be required.

Table 4 Reaction of **1** with $AgO_3SC_6H_4Me$-*p* (AgOTs) in CH_2Cl_2.[a] Composition (%) of reaction mixture (with P_R values) at various times *t*

t/h	TI + T′I (P_R)	TOTs + T′OTs (P_R)	TOH[b]
0	100 (0)	0	0
24	91 (1.5)	9 (22)	< 2
48	72 (2)	22 (21)	5
96	59 (4.5)	38 (20)	3
192	13 (13)	73 (23)	14

[a] For uncertainties in the yields and P_R values see Table 1. [b] The proportion of rearranged product could not be determined.

Table 5 Yields[a] and P_R[a] values for products from reaction of TsiSiRR′I with AgOMs, in alcohols R″OH. $T_{tot}OMs$ denotes the combined yield of rearranged and unrearranged mesylates, and P_R the percentage rearranged. $T_{tot}OR''$ denotes the combined yield of the relevant alkoxides, and P_R the percentage rearranged

R″	R	R′	$T_{tot}OMs$	P_R	TOR″	P_R
Me	CD_3	CD_3	10	10	87	40
Et	CD_3	CD_3	26	8	74	44
CF_3CH_2	CD_3	CD_3	13	33	86	62
Me	Et	Et	6	23	94	56
Et	Et	Et	15	24	84	56
CF_3CH_2[b]	Et	Et	9	66	91	78
Me	Et	Me	8	17	91	42
Et	Et	Me	17	12	84	44
CF_3CH_2	Et	Me	12	50	88	66

[a] For uncertainties in the yields and P_R values see Table 1. [b] $(Me_3Si)_2(EtSiMe)CSiEtMe_2Otfe$ (5.5%) and a trace of $(Me_3Si)_2(EtSiMe)CsiEtMe_2OMs$ (0.2%) were formed in the reaction.

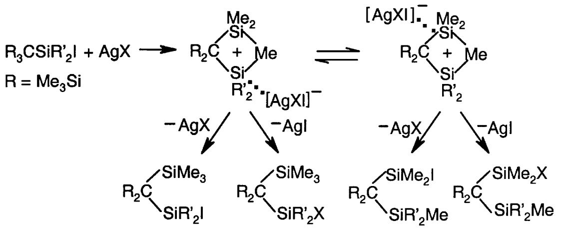
To provide additional evidence for iodide migration we examined the reaction of the iodide **2** with AgOMs in MeOH, EtOH, and TFE. Rearrangement of this substrate would give $(Me_3Si)_2(Et_2MeSi)CSiMe_2I$, and some of this would be expected to react through Et-bridging. In TFE this would generate some $(Me_3Si)_2(EtMe_2Si)CSiMeEtOtfe$, which would be readily detectable in the products because the ^1H NMR signals from the methylene hydrogens of an $SiMeEtOCH_2CF_3$ group are clearly separated from those of an $SiMe_2OCH_2CF_3$ or $SiEt_2OCH_2CF_3$ group. The results (see Table 5) reveal that some of the ‘scrambled’ product $(Me_3Si)_2(EtMe_2Si)CSiMeEtOCH_2CF_3$ is, indeed, formed.

The reaction of **2** with AgO_2CCH_3 (AgOAc) in CH_3CO_2H had previously been shown to give roughly equal amounts of unrearranged $(Me_3Si)_3CSiEt_2OAc$ and rearranged $(Me_3Si)_2(Et_2MeSi)CSiMe_2OAc$, while that with AgO_2CCF_3 (AgOtfa) in CF_3CO_2H gave the rearranged and unrearranged trifluoroacetates in 75 : 25 ratio, and solvolysis in CF_3CO_2H alone gave the same products in *ca.* 44 : 56 ratio.[1] The high proportion of rearranged product relative to those from reactions of **1** in inert media and ordinary alcohols was taken to reflect the greater steric hindrance at the $SiEt_2$ end of the Me bridge. In the reactions with AgOMs in MeOH and EtOH (Table 5) the yields of mesylate products were quite low, at *ca.* 6 and 15%, respectively, and, more surprisingly, in both solvents the P_R values, *ca.* 24, were well below 50, indicating that the steric hindrance at the $SiEt_2$ centre is not great enough to overcome the intrinsic favouring of attack at an α-Si centre. We had not previously recognised this because we studied reactions of **2** with silver salts only for AgOAc in acetic acid and for AgOtfa in trifluoroacetic acid, so that formation of the product direct from the silver salt could not be distinguished from that arising from attack of the solvent. The implication of the new observation is that the true P_R values for trapping of the initial intermediate cation by the solvent could be even higher than those mentioned above. (We note that the P_R values for the mesylates in reactions of **1** with silver mesylate in MeOH, EtOH and CF_3CH_2OH are reasonably consistent with the value of 25 observed for the chlorides formed from **2** and ICl in CCl_4.[5])

In the light of the above results the P_R value of 63 (±5) for mesylate products from **2** in TFE is remarkably high. A little of the rearranged mesylate must come from rearranged iodide (see below), formation of which seems to be favoured in TFE, and since the total yield of mesylates is so small the proportion formed in this way could be high enough to raise the P_R value towards that observed.

A significant observation is that the approximate P_R value for the trifluoroethoxides, 77 ± 5, is substantially higher than that for methoxide or ethoxide products, 56 in both cases. This result is in keeping with the high value of 63 ± 5 observed for the trifluoroethoxides from **1** in the fluorinated alcohol and attributed in part to some initial migration of the iodide ligand.

We turn now to the question of how rearranged iodides might be formed from iodides $(Me_3Si)_3CSiR_2I$. We suggest that the initial species formed in the reaction of a silver salt AgX with the iodide is a Me-bridged cation **I** ion-paired at the α-position with an argentate ion $[AgXI]^-$. In an inert solvent the argentate ion will usually give up X^- or I^- to the α-Si to give $(Me_3Si)_3CSiR_2Y$ or regenerate $(Me_3Si)_3CSiR_2I$, but occasionally it will slip over the surface of the cation to the very close γ-site and there give up X^- or I^-, to form rearranged $(Me_3Si)_2(R_2MeSi)CSiMe_2X$ or $(Me_3Si)_2(R_2MeSi)CSiMe_2I$. (See Scheme 1 for the reaction in inert media.) In support of this suggestion we note that calculations indicate that in a model Me-bridged cation the bridged α- and γ-Si atoms are only 2.55 Å apart,[8] and those in the actual H- and Ph-bridged cations are respectively 2.49 and 2.62 Å apart.[9]



Scheme 1 Proposed mechanism of reaction of $R_3CSiR'_2I$ with AgX in an inert solvent.

It is reasonable to assume that more weakly coordinated ions such as ClO_4^-, $O_3SCF_3^-$, NO_3^- and BF_4^- would be released most readily from the argentate ion and so give higher proportions of both $(Me_3Si)_3CSiR_2X$ and $(Me_3Si)_2(R_2MeSi)CSiMe_2X$. The formation of an argentate ion would be directly analogous to those of the ate ions $[HgX_2I]^-$ and I_2Cl^- that we have always assumed to be the initial products in reactions with HgX_2 and ICl, respectively.[1–3,5] We now suggest that in these cases, also, the formation of rearranged products follows migration of the ate anions to the γ-site of the bridged cation. This concept of formation of rearranged products only after migration of the argentate ion accounts nicely for the observation that the presence of LiX salts in reactions with AgX has little effect on the yields or P_R values of X-substituted products (such as TX or T′X).

In reactions in alcohols the solvent can attack at the α-Si either before or after the argentate ion has migrated to the γ-site or attack at the latter site before or after migration of that ion. Release at the α-site of an alcohol molecule initially solvating the AgX could favour attack at that position to give unrearranged TOR as could the availability of one or more molecules of alcohol pre-associated with the Si–I bond.‡ However, ROH from the bulk solvent could also attack at that site or at the γ-site either before or after migration of the argentate ion. We had not in the past observed formation of rearranged iodide in reactions with silver salts in MeOH, EtOH or Bu^tOH but we had not specifically looked for it. We have now found that in a reaction of **1** with AgOMs in MeOH that was allowed to go to only 73% completion the residual iodide was *ca.* 4% rearranged and the mesylate and methoxide products constituted 9 and 63%, respectively, of the mixture and were respectively *ca.* 7 and 41% rearranged. However, no detectable amounts of $(Me_3Si)_2(EtMe_2Si)CSiEtMeOR$ were formed in the reaction of **2** with AgOMs in either MeOH or EtOH. This suggests that iodide migration may occur less readily in these solvents than in TFE, possibly because their higher nucleophilicity means that there is less time for migration of the argentate ion before it reacts with the bridged cation.

Furthermore, solvation of the argentate ion is likely to be stronger in the more acidic TFE, again allowing more time for its migration. It seems likely that migration of the iodide ligand of **1** will be most marked in cases in which high P_R values are observed for TX + T′X products. We have noted many times that P_R values for these are especially high in CH_2Cl_2, and it is in this inert solvent that iodide rearrangement also seems especially significant.[4]

The iodides **1** and **2** were also found to undergo slow solvolysis in TFE in the absence of silver salts. After 60 h under reflux *ca.* 20% of **1** was consumed to give 11% of TOtfe and 4% of T′Otfe; no rearranged iodide was observed. Under the same conditions 25% of **2** was consumed to give (along with small amounts of unidentified products) *ca.* 11% of $TsiSiEt_2Otfe$ and 14% of $(Me_3Si)_2[Et_2MeSi]CSiMe_2Otfe$. The P_R value of 56 for these products is the same as that observed for the products of solvolysis in CF_3CO_2H. Under the same conditions TsiSiEtMeI also underwent 25% reaction to give 14% of TsiSiEtMeOtfe and 8% of $(Me_3Si)_2(EtMe_2Si)CSiMe_2Otfe$, the presence of only one Et group at the reaction centre evidently not providing sufficient steric hindrance to overcome the inherent tendency for dominant attack at the α-site. (It was impossible with these Et-containing iodides to establish with certainty whether any rearranged iodide was formed because of the complexity of the ^1H NMR spectra of the product mixtures.) Since some rearranged product is formed it is clear that the solvolysis also proceeds partly, if not exclusively, through a bridged cation. We assume that during such a reaction a Me-bridged cation is paired with an iodide ion complexed with CF_3CH_2OH. Whether this ion can slip over to the γ-Si centre and release the iodide back to the cation cannot be decided from the limited evidence available. That the proportion of the rearranged T′Otfe in the products from the uncatalysed trifluoroethanolysis is much smaller than in those from the reaction in the presence of silver salts can be attributed to lower steric hindrance at the α-site by a leaving iodide ion than by a leaving argentate ion. To the extent that the uncatalysed solvolysis occurs through an alkyl-bridged cation the rates of reaction of the three iodides studied should be fairly similar since the immediate reaction centre is the same in each case and only a significant difference between the anchimeric assistance by Et and Me groups would result in appreciably different rates. The much faster solvolysis in the much more acidic trifluoroacetic

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‡ It is likely that one or more alcohol molecules would interact with the polar centre, that is the Si–I bond, in the large molecule that otherwise presents an essentially hydrocarbon surface (*cf.* reference 7).

acid does produce rearranged iodide, the amount increasing with the extent of reaction.[9]

Experimental

General

The preparations of **1**,[4] **2**[1] and TsiSiEtMeI[1] have been described previously. Methanol and ethanol were dried by distillation from magnesium methoxide and magnesium ethoxide, respectively. The TFE was dried over anhydrous calcium sulfate and distilled. All of the silver salts used were commercial products except for silver mesylate, which was prepared from silver carbonate and methanesulfonic acid. The ^1H NMR spectra were recorded with Varian Unity 300 MHz or Varian Inova 500 MHz spectrometers.

Reactions of 1 with silver salts in 2,2,2-trifluoroethanol

The iodide **1** (8 mg, *ca.* 0.02 mmol) and the silver salt AgX (usually 0.025 mmol) were weighed into a 100 mm × 10 mm test-tube, and TFE (1 cm^3) was added. The tube was fitted with a condenser and the mixture heated under reflux until the precipitate of AgI had coagulated (normally 15–30 min, depending on the solubility of the silver salt). The solution was allowed to cool, and extracted with pentane (1 cm^3). The extract was washed with water (4 × 5 cm^3), separated, and dried over a little anhydrous sodium sulfate, and the solvent removed under vacuum. The residue was taken up in $CDCl_3$ and the ^1H NMR spectrum recorded.

The major products were the isomeric trifluoroethoxides TOtfe and T′Otfe, together with smaller amounts of TX and T′X. In most reactions small amounts (< 3%) of silanol were present, and occasionally, residual iodide. Normally these six accounted for > 95% of the total material isolated. The relative yields of the various types of compounds present, *i.e.* the combined yield (T_{tot}TOtfe) of TOtfe and T′Otfe, the combined yield (T_{tot}TX) of TX and T′X, and the yields of hydroxides TOH, and iodide TI (if any) were determined by integration of appropriate peaks in the NMR spectra. The reliability of each analysis was estimated as ±1 (*e.g.* 2 ± 1; 4 ± 1) or ±10% of its value (*e.g.* 20 ± 2; 50 ± 5), whichever was greater.

Reaction of 2 with silver salts in 2,2,2-trifluoroethanol

The iodide **2** reacted equally readily with silver salts when subjected to the general procedure described above, but determination of the product yields was less straightforward. In compounds of the type $TsiSiEt_2Z$ the methylene hydrogens of the ethyl groups are diastereotopic, and appear as two broad multiplets. The associated methyl peaks are triplets and partly overlap with the methylenes. The spectra of the rearranged products are even more complex and tend to overlap with the others. Consequently analysis by the approach used for **1** was not possible. The relative yields of the rearranged and unrearranged trifluoroethoxides were determined by comparison of the areas under the methylene quartets of their trifluoroethoxy groups, which did not overlap. TX yields could only be determined when X contained a suitable hydrogen. For this reason investigations were restricted to X = OMs, OTs and OAc. There was no satisfactory way of determining the yields of hydroxide or residual iodide, but both must have been small because a mass balance (using an internal standard) showed that $(Me_3Si)_3CSiEt_2Y$ and $(Me_3Si)_2(Et_2MeSi)CSiMe_2Y$ (Y = Otfe or X) were the greatly dominant products in all cases.

Reaction of $(Me_3Si)_3CSiEtMeI$ with silver salts in 2,2,2-trifluoroethanol

Reaction of $(Me_3Si)_3CSiEtMeI$ with silver salts AgX in CF_3CH_2OH gave a mixture of two trifluoroethoxides and two products containing X. As in the case of **2**, the presence of the Et group complicated the determination of overall yields, and the same approach was adopted for the analysis.

Reactions in other alcohols

Samples of **1**, **2** and $(Me_3Si)_3CSiEtMeI$ were treated with AgOMs in MeOH or EtOH under the conditions used for trifluoroethanol. The products were isolated and their NMR spectra analysed in the usual way.

Trifluoroethanolysis of 1, 2, and TsiSiEtMeI

A solution of each iodide in trifluoroethanol was heated under reflux for 60 h. The products were isolated and analysed in the usual way. Each underwent about 20–25% solvolysis in this time to give a mixture of trifluoroethoxides. Iodide **1** gave a small amount of hydroxide. It was not possible to determine the proportion of rearranged trifluoroethoxide from the reaction of **1** because the $(Me_3Si)_3C$ peak for the iodide is very broad and the $SiMe_2Otfe$ peak appeared as a small peak at its shoulder. (By extending the reaction time to 7 days an approximate analysis was possible and indicated that the trifluoroethoxide was roughly 28% rearranged.) In both the $TsiSiEt_2I$ and TsiSiEtMeI reactions, the main products were the two expected isomeric trifluoroethoxides, formed in approximately equal amounts. Both $TsiSi(CD_3)_2I$ and $TsiSiEt_2I$ also gave a small amount of an additional unidentified product containing a trifluoroethoxy group (different in the two cases).

Reaction of 1 with silver toluene-*p*-sulfonate in dichloromethane

The iodide **1** (15 mg, 0.04 mmol) and AgOTs (15 mg, 0.05 mmol) were weighed into a reacti-vial and dichloromethane (5 cm^3) was added. The vial was wrapped in foil and stirred at room temperature. Aliquots (1 cm^3) were removed after 24, 48, 96, and 192 h, added to pentane (2 cm^3), and worked up and analysed in the usual way.

Note: Further details of the methods used in the quantitative analysis of reaction products and the estimation of their reliability are available as Electronic Supplementary Information.†

References

1 C. Eaborn, D. A. R. Happer, S. P. Hopper and K. D. Safa, *J. Organomet. Chem.*, 1980, **188**, 179–192.
2 C. Eaborn, *J. Chem. Soc., Dalton Trans.*, 2001, 3397.
3 C. Eaborn and S. P. Hopper, *J. Organomet. Chem.*, 1980, **192**, 27–32.
4 A. I. Almansour, J. R. Black, C. Eaborn, P. M. Garrity and D. A. R. Happer, *J. Chem. Soc., Chem. Commun.*, 1995, 705–706. (Readers should note that in this paper it was wrongly stated that Otf denoted O_2CCF_3 and Otfa denoted O_3SCF_3, whereas the reverse was the case.)
5 A. I. Almansour, H. A. Abubishait and C. Eaborn, *J. Organomet. Chem.*, 1997, **531**, 171–174.
6 J. R. Black, C. Eaborn, P. M. Garrity and D. A. R. Happer, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1623.
7 Y. Y. El-Kaddar, C. Eaborn, P. D. Lickiss and D. E. Reed, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1753–1759.
8 C. Maerker, J. Kapp and P. v. R. Schleyer, in *Organosilicon Chemistry II*, ed. N. Auner and J. Weiss, VCH, Weinheim, 1996, pp. 353–355.
9 P. D. Lickiss, *personal communication*, 2002.