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The proportion of 1,3-migration of a methyl group in the reactions of the iodide $(Me_3Si)_3CSi(CD_3)_2I$ with silver salts in alcohols. Mechanistic implications

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In the reactions of the isotopically labelled $(Me_3Si)_3CSi(CD_3)_2I$, 1-D, with alcohols ROH (R = Me, Et, Pr^i or Bu^t) in the presence of silver salts AgX (X = ClO_4, O_3SCF_3, O_2CCF_3, NO_3 or BF_4) the ratio of the rearranged product $(Me_3Si)_2C[Si(CD_3)_2Me]SiMe_2OR$ to unrearranged $(Me_3Si)_3CSi(CD_3)_2OR$ always falls below the value of 1:1 expected for capture of an intermediate methyl-bridged cation $[(Me_3Si)_2\overline{CSiMe_2\text{-}Me\text{-}Si}(CD_3)_2]^+$, II, by nucleophilic attack of the alcohol at either end of the bridge. For example, in the reaction with $AgClO_4$ the percentages of rearranged product are 26, 22 and 37 (all values ±8) for R = Me, Et and Pr^i, respectively, at room temperature and the corresponding figures at the reflux temperature are 29, 40, 41 and 44 (all ±8) for Me, Et, Pr^i and Bu^t. Thus the reaction cannot proceed exclusively by direct formation of a fully free cation II as assumed in the simplest picture. It is concluded that *ad hoc* modification of this simple picture, for example, by postulating some pre-association of an alcohol molecule at the Si–I bond in 1-D, is preferable to possible alternative mechanisms, such as one involving initial formation of an unbridged cation $[(Me_3Si)_3CSi(CD_3)_2]^+$ which can sometimes be captured before conversion into II. The alkoxide products are accompanied by some $(Me_3Si)_3CSi(CD_3)_2X$ and $(Me_3Si)_2C[Si(CD_3)_2Me]SiMe_2X$ (from $AgBF_4$, X = F in both cases) and the corresponding hydroxides, the proportion of rearranged product always being significantly below 50%. In the reactions with $AgClO_4$ or AgO_3SCF_3 the silicon hydroxides are mainly produced by hydrolysis of initially formed perchlorates or trifluoromethanesulfonates by traces of water in the solvents, but for the other silver salts they arise virtually wholly by capture of the intermediate cation by the water.

The type of rearrangement with which this paper is concerned[1] was first observed when the iodide $TsiSiPh_2I$, where Tsi denotes the very bulky tris(trimethylsilyl)methyl ('trisyl') group, was treated with silver salts AgX or mercury(II) salts HgX_2 in MeOH and found to give mixtures of rearranged products $(Me_3Si)_2C(SiPh_2Me)SiMe_2X$ and $(Me_3Si)_2C(SiPh_2Me)SiMe_2$-OMe, an Me group having undergone 1,3-Si-to-Si migration.[2,3] Subsequent studies showed that some related iodides, TsiSiRR′I, under similar conditions gave mixtures of rearranged and unrearranged products.[3,4]

The same type of rearrangement, complete in the case of $TsiSiPh_2I$, was found to take place in the reactions with (i) silver salts in inert solvents such as CH_2Cl_2;[5] (ii) ICl in CCl_4 [*e.g.* $TsiSiEt_2I$ gave $TsiSiEt_2Cl$ and $(Me_3Si)_2C(SiEt_2Me)SiMe_2Cl$ in *ca.* 35:65 ratio[6]]; (iii) CF_3CO_2H;[3] (iv) (in the case of $TsiSiPh_2I$ and TsiSiPhMeI) MeOH or $PhNH_2$ under UV irradiation;[7] and (v) *m*-chloroperoxybenzoic acid in MeOH.[8] It was suggested that in each case the reaction involved rate-determining formation of a methyl-bridged cation of type **I**, which could be rapidly attacked by a nucleophile either at the α-site to give an unrearranged product or at the γ-site to give a rearranged product.[3,9] It was further suggested that in the absence of significant electronic effects of the substituents R′ and R″ the proportion of rearranged product would be determined by the relative degrees of steric hindrance at the α- and γ-sites in the cation towards nucleophilic attack, so that, as observed,[3] more than 50% of rearranged product would be expected from say TsiSiPhMeI, and very predominantly rearranged product from $TsiSiPh_2I$.[10] That the ratio of attack at the α- and γ-sites is not determined solely by steric effects was shown by the finding that in the reactions with ICl or silver salts the iodides TsiSiMeYI with Y = Cl or F, gave only rearranged products (although the F atom, in particular, should have a substantially smaller steric effect than an Me group) and TsiSiMe(OMe)I gave exclusively unrearranged products (although OMe would be expected to have a steric effect similar to or slightly larger than an Me group).[9] Furthermore the nature of the solvent was found to have a substantial influence on the extent of rearrangement; *e.g.*, the reaction of TsiSiPhHI or TsiSiMeHI with $AgBF_4$ gave only rearranged fluoride in Et_2O but a mixture of rearranged and unrearranged fluorides in CH_2Cl_2.[11,†]

In terms of the simplest picture of the mechanism of the rearrangement, involving formation of a bridged cation of type **I** that is fully free before being captured by a nucleophile, then in the case of $TsiSiMe_2I$, **1**, there should be equal amounts of rearranged and unrearranged products. In order to confirm this we prepared the labelled iodide $TsiSi(CD_3)_2I$, **1-D**, and first examined its reactions with silver salts AgX in a range of aprotic solvents, which we assume involve intermediate formation of cation **II**.[12] To our surprise the percentage, P_R, of rearranged product $(Me_3Si)_2C[Si(CD_3)_2Me]SiMe_2X$, formed along with the unrearranged $TsiSi(CD_3)_2X$, was in most cases significantly below the expected value of 50, and sometimes below 10, and varied markedly with the solvent.‡ These findings were tentatively attributed to preferential attack at the α-site by

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† In the reaction of a wide range of compounds TsiSiR′R″I with $AgBF_4$, the proportion of rearranged fluoride has been shown to vary widely with the nature of the solvent and the electronic effects of R and R′ (S. M. Whittaker, PhD Thesis, University of Salford, 1993; P. D. Lickiss, personal communication).

‡ Values of $P_R > 50$ were observed in the reactions with AgO_3SCF_3 and AgO_2CCF_3 in CH_2Cl_2, perhaps because of some return of I^- to the γ-site of the bridged cation (as well as to the α-site) before complete separation of AgI.

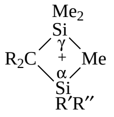
Table 1 Yields of products TX, TOH and TOR from reactions of $Tsi(CD_3)_2I$, **1-D**, with alcohols ROH in the presence of AgX, at room temperature or under reflux, and proportion, P_R (%), of rearranged product, with estimated uncertainty (±) denoted by the subscript.[a] Where there is no entry for P_R the value could not be even approximately determined.

	Room temperature						Under reflux					
X	TX	P_R	TOH	P_R	TOR	P_R	TX	P_R	TOH	P_R	TOR	P_R
In MeOH												
ClO_4	3	14_8	11	16_8	86	26_8	<2		8	18_8	92	29_8
Otf[b]	6	17_8	6	9_5	88	22_5	5	21_8	7	18_8	87	38_8
NO_3	14	8_3	1		85	22_5	27	9_3	<2		73	33_8
Otfa[c]	7	10_3	2		91	28_5	7	10_3	<2		92	31_5
BF_4	11	15_8	11		77	21_5	14	25_8	7		79	35_8
In EtOH												
ClO_4	1–7	14_8	35–40	10_5	52	22_8	<2		34	15_5	66	40
Otf[b]	3–30	12_5	12–35	7_3	60	16_5	27	14_5	4		68	33_8
NO_3	36	5_3	<2		64	22_5	44	6_5	<2		55	30_5
Otfa[c]	21	6_3	2		76	20_5	21	17_3	2		77	27_5
BF_4	52	5_3	3		45	29_5	46	19_8	3		51	33_8
In Pr^iOH												
ClO_4	0		75	12_5	25	37_8	<2		70–80	13_5	20–30	41_8
Otf[b]	39	4_3	42	6_3	19	25_5	28	14_5	32	11	40	36_8
NO_3	78	2_3	5	12_3	17	23_5	64	7_3	4		32	30_5
Otfa[c]	46	5_3	4		50		39	8_3	4		57	
BF_4	81	5_3	3		16	40_8	70	17_8	3		27	44_8
In Bu^tOH												
ClO_4	<2		97	7_3	3		0–20	20_5	70–95	18_5	8	44_8
Otf[b]	10	<2	87	$<2_3$	2		47	18_5	35	17_5	14	48_8
NO_3	62	2_3	33	<2	5		79	7_3	6		15	22_8
Otfa[c]	25	$<2_3$	71	$<2_3$	7		42	17_5	22	13_5	36	30_8
BF_4	83	5_3	17	<2	<2		77	20_8	17	24_8	6	

[a] TY (Y = X, OH or OR) denotes the mixture of $(Me_3Si)_3CSi(CD_3)_2Y$ and $(Me_3Si)_2C[Si(CD_3)_2Me)]SiMe_2Y$. [b] Otf = O_2CCF_3. [c] Otfa = O_3SCF_3.

X^- liberated from an ion-pair $[Ag^+ \cdots X^-]$ near that site by formation of AgI. Subsequently reaction of **1-D** with ICl in aprotic solvents was found to give less than 50% of rearranged chloride, and this was correspondingly attributed to preferential transfer of Cl^- to the α-silicon centre in the cation from the formed I_2Cl^- before it diffused away from that site.[13] However a P_R value of only 16 was found for the methoxides formed alongside the chlorides in the corresponding reaction in MeOH, and that presented a greater problem, consideration of which was deferred until presentation of the results of the study described below involving reactions of **1-D** with silver salts in alcohols.

$(Me_3Si)_3CSiMe_2I$ **1** $(Me_3Si)_3CSi(CD_3)_2I$ **1-D**



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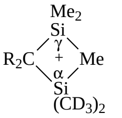

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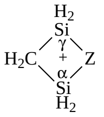


III

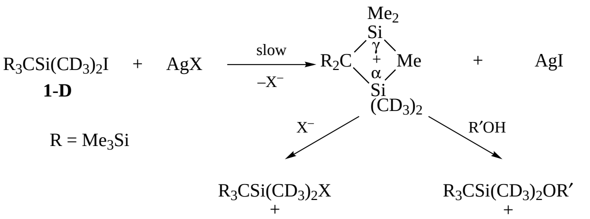
R = Me_3Si

In alcohols, not only should the good solvating ability of the medium be more likely to enable the intermediate to become fully free before taking up the nucleophile but, furthermore, in the formation of alkoxide products the relevant nucleophile, the solvent, should be equally available at the α- and γ-sites, giving rise to values of P_R of 50. We thus determined the values of P_R for formation of the alkoxide [and also for formation of $TsiSi(CD_3)_2Y$ and its isomer where Y = X or OH] from a variety of silver salts AgX in MeOH, EtOH, Pr^iOH and Bu^tOH (all dried by standard methods but evidently containing traces of water). The results are shown in Table 1. In this table and in the discussion below, for convenience the symbol TY, where Y = X, OH or OR, is used to denote the mixture of unrearranged and rearranged products, $TsiSi(CD_3)_2Y$ and $(Me_3Si)_2C[Si(CD_3)_2Me]SiMe_2Y$. It should also be noted that the products TX formed from $AgBF_4$ are always actually the fluorides.

As discussed in the Experimental section, the reliability of the P_R value for a particular product depends on the proportion of that product and sometimes also on the degree of separation of the relevant ^1H NMR signals. In some cases the estimated uncertainties, shown as subscripts to the P_R values in the Tables, are comparable with the values of P_R themselves, but in no case are they such as to cast doubt on the validity of the discussion below.

Results and discussion

We first focus on the results of the reactions in MeOH, initially considering the results in terms of the simple mechanism shown in Scheme 1. The main features with comments, are as follows.



Scheme 1 Simplest representation of the reaction of **1-D** with AgX in an alcohol R′OH used as the basis of the discussion, where its inadequacies and possible modifications are considered

(*a*) Some TOH is formed in every case. For the reactions with AgX where X = NO_3, O_2CCF_3 or BF_4, the TOH could not have come from hydrolysis of the initially formed products TX, which are inert under the conditions used, and can be assumed to arise from reaction of the intermediate cation with water. Unfortunately, reliable values of P_R for TOH could not be

Table 2 Yields of products TX, TOH and TOMe from reactions of $TsiSi(CD_3)_2X$, **1-D**, with AgX in MeOH, with or without added H_2O, at room temperature, rt, or under reflux, rf, and proportion, P_R (%), of rearranged product, with estimated uncertainty (±) denoted by the subscript

X	T	H_2O^a	TX^b	P_R	TOH^b	P_R	$TOMe^b$	P_R
ClO_4	rt	0	3	14_5	11	16_5	86	26_5
	rf	0	0		8	18_5	92	29_5
	rt	1.0	0		30	11_5	70	24_5
	rf	31^c	0		50	23_5	50	30_5
O_3SCF_3	rt	0	6	17_5	6	9_5	88	22_5
	rf	1.0	0		27	10_5	73	21_5

[a] Added water, vol%. [b] Refers to the mixture of rearranged and unrearranged products (see footnote to Table 1). [c] *ca.* 50 mol% H_2O.

obtained in these cases because of overlap of the relevant ^1H NMR signals.

For the reactions with $AgClO_4$ and AgO_3SCF_3 however, much of the TOH is likely to come from initially-formed TX, since the compounds $TsiSiMe_2X$ in which X is a very good leaving group, *viz.* $OClO_3$, OSO_2CF_3 or OCN, select water very efficiently from MeOH (the selectivity factors being *ca.* 500 and 5700 for OSO_2CF_3 and OCN, respectively, in molar terms).[14]

The effects of added water on the outcome of the reaction with $AgClO_4$ (see Table 2) are revealing in this connection. With 1 vol% of added water (*i.e. ca.* 2.2 mol%) at room temperature the proportion of TOH is raised from 11 to 30%, but on going to 31 vol% of water (50 mol%) the proportion (under reflux) is further raised only to 50%; that is, under these conditions water and methanol compete on roughly equal terms. The results are consistent with the view that the TOH is formed by two distinct processes, the first the hydrolysis of $TOClO_3$, which is highly selective towards water, and the second the direct reaction of water with cation **II** which, being highly reactive does not discriminate strongly between water and methanol. At the very low water concentrations the value of P_R observed for TOH would be expected to be effectively the same as that for $TOClO_3$ (and so relatively low), since the solvolysis of $TsiSi(CD_3)_2OClO_3$ proceeds without rearrangement, as was confirmed during the present work, giving unrearranged $TsiSi(CD_3)_2OH$ and $TsiSi(CD_3)_2OMe$ in *ca.* 50:50 ratio in the 'anhydrous' MeOH and solely unrearranged $TsiSi(CD_3)_2OH$ in an equimolar H_2O–MeOH mixture. [The methanolysis of $TsiSi(CD_3)_2OCN$,[15] the hydrolysis of **1-D**,[15] and the hydrolysis and methanolysis of $TsiSiPh_2I$ and $TsiSiEt_2I$,[16] are known not to involve rearrangement.] On the other hand, the P_R value for the TOH formed directly from the cation would be expected to be comparable with that observed for TOMe, and the value for TOH formed in 1:1 H_2O–MeOH under reflux, *viz.* 23, is seen to lie between that observed in the 'anhydrous' MeOH, *i.e.* 18, and that for TOMe, *i.e.* 30.

(*b*) Except for the reaction with $AgNO_3$ under reflux (for which it seems anomalously large, at 27%) the proportion of TX formed is seen to be <15% even if it is assumed that most of the TOH product in the case of $X = OClO_3$ or OSO_2CF_3 is formed *via* TX. The P_R values for TX vary between 8 and 17 at room temperature and 9 and *ca.* 25 under reflux. These values fall in the range observed for the reaction with the silver salts in non-hydroxylic solvents,[12] and the same explanation could apply, namely that cation **II** is preferentially attacked at the α-site by the X^- liberated near that site within an ion pair [**II** $\cdots X^-$] as AgI is formed. However, it seems appropriate to wonder whether if the cation **II** ever became fully free it would be expected to react to a significant extent with $[Ag^+ \cdots X^-]$ or X^-, especially in the case of the very weakly nucleophilic ClO_4^- or $CF_3SO_3^-$ ions, rather than with the MeOH molecules present in much larger concentration and presumably providing solvation at the α- and γ-Si sites. In the four-membered ring of cation **II** these sites would be held close together (calculations on the model bridged ion **III** with Z = Me gives the separation as 2.55 Å[17]) and it would require very little movement of X^- over the periphery of the cation within the ion-pair to bring it near to the γ-site, where it could attack. If such a migration occurs in the reactions in MeOH then it could be assumed, of course, to occur also for those in the non-hydroxylic media, and, indeed, would be even more likely there. Whether or not there is such migration of liberated X^-, it is perhaps somewhat surprising that the yield of TX (when account is taken of subsequent conversion of some of it into TOH for $X = OClO_3$ and OSO_2CF_3) shows no obvious dependence on the relative nucleophilicities of X^-.

(*c*) The presence of LiX for $X = NO_3$ or O_2CCF_3 leads to significant increases in the product ratio TX:TOMe but these increases are much smaller than would be expected in terms of simple direct competition between X^- and MeOH for the intermediate cation. The concentration of AgX in the reaction medium was *ca.* 0.025 mol cm^{-3}, and so for direct competition the product ratio TX:TOMe for the reaction involving only $AgNO_3$, *viz.* 1:6 (15:85), should rise to *ca.* 3.5:1 (300:85) and 7:1 (600:85) in the presence of 0.050 and 0.10 mol cm^{-3} $LiNO_3$, respectively, compared with the observed ratios of 1:2.6 and 1:1.8. That the observed effects of added X^- are so small can be rationalized in terms of the modification of Scheme 1 suggested above, involving initial attack of the ion pair $[Ag^+ \cdots X^-]$, since it can be reasonably assumed that the proportion of such ion pairs, already high, will not be much raised as the concentration of X^- is increased.

(*d*) The P_R values for TX are mostly raised only by a factor of *ca.* 1.3 in the presence of 0.050 mol cm^{-3} LiX, and further only by a similar factor on going to 0.10 mol cm^{-3} LiX. To the extent that the rearranged TX is formed by internal transfer of X^- to the γ-site within the ion pair [**II** $\cdots X^-$] the presence of additional X^- should not affect the proportion of attack at the γ-site, and the small rise in P_R could be attributed to the relatively minor proportion of direct attack of X^- at that site.

(*e*) The values of P_R for TOMe are mostly substantially below 50, especially in the case of reactions at room temperature. For $X = ClO_4$ or O_3SCCF_3 some of the TOMe could arise by solvolysis of initially formed TX, leading to low values of P_R of <50, but this could not be the case for formation of TOMe from the other TX compounds, which gives similar P_R values. In terms of the assumed mechanism this implies that the cation **II** is not, or not always, fully-free (*i.e.* solvent-separated from other species involved in the reaction) before the attack by the MeOH, but is in some way rendered unsymmetrical. This asymmetry, while very significant in showing unambiguously that the mechanism of the solvolysis cannot be as simple as that depicted in Scheme 1, is not large; a P_R of 25 means that attack at the α-site takes place three times as readily as that at the γ-site, and for a P_R of 40 the factor is 1.5.

As one possible explanation of the asymmetry we suggest that there is some preassociation of an alcohol molecule by hydrogen-bonding to the I atom of the Si–I bond and that as the I atom leaves this molecule is released in a favourable position to attach to the α-site of the bridged cation. This suggestion has the attraction that the currently favoured explanation of remarkable observations on the solvolysis of the highly reactive compounds $TsiSiMe_2X$ with $X = OClO_3$, OCN, OSO_2CF_3 also involves assumption of similar preassociation,[14] and if it is relevant in those reactions it could be expected to be so for reactions of the iodide **1-D** when Ag^+ ions are present to assist the departure of I^-, although the extent of the hydrogen bonding is likely to be smaller with the I atom than with the O-bonded ligands. Such preassociation would also account for the low values of $P_\mathbf{R}$ in the reactions of **1-D** with ICl in MeOH.§

Another tentative alternative explanation of the low $P_\mathbf{R}$ values is that some TOR is produced from the cation before the X^- released from $[Ag^+ \cdots X^-]$ has fully separated, and that solvent molecules engaged in solvation of X^-, *e.g.* as $[ROH \cdots X]^-$, carrying a small negative charge, are slightly more nucleophilic than the bulk solvent molecules near the γ-site. Since at higher temperatures that solvated X^- ions would diffuse away from the α-site more rapidly the values of $P_\mathbf{R}$ for TOR formation would be higher, as observed.

(*f*) When account is taken of the uncertainties in the values of $P_\mathbf{R}$, for reactions at room temperature there is no significant variation in the values as X in AgX is varied, which is as would be expected if the intermediate cation becomes free from X before reaction with the MeOH. The values appear to be generally higher for reactions under reflux, but again there is no significant variation within them.

(*g*) In the other alcohols, for reactions of AgX with X = NO_3, O_2CCF_3 or BF_4, the yield of TX rises, as expected, as the increasing bulk of the alcohol leads to increasing inhibition of attack of the alcohol to give TOR. This is almost certainly also the case for reactions involving $AgClO_4$ and AgO_3SCF_3, but the formed $TOClO_3$ and $TOSO_2CF_3$ are mainly converted into TOH. (In all the media the ratio of TOR : TX for X = $OCOCF_3$, is relatively high, especially in relation to that for X = ONO_2; this would not have been predicted since $CF_3CO_2^-$ would be expected to be rather more nucleophilic than NO_3^-.) The values of $P_\mathbf{R}$ for TOR could, other things being equal, also be expected to be higher in the bulkier alcohol because the increased steric hindrance to nucleophilic attack allows more time for the formation of the free cation; there is some indication that this is the case for the reactions in Pr^iOH and Bu^tOH, but the effect is rather small, perhaps because the greater bulk of the molecules also leads to lower rates of diffusion of X^- from the reaction site. For each alcohol values of $P_\mathbf{R}$ for TOR within the set at room temperature or within that under reflux remain reasonably constant within the uncertainty; some seeming possible deviations from this generalization are likely to be unreal; *e.g.* the value of 16 ± 5 for TOEt formed in the reaction with AgO_3SCF_3 seems rather low, but is probably simply an extreme reflection of the experimental error, since there is no such anomaly for the reaction under reflux or for reactions in the other alcohols.

Possible alternative mechanisms

We are not wholly satisfied with our suggested rationalizations of the experimental observations, especially of the fact that the $P_\mathbf{R}$ values for TOR are always <50, but possible alternative explanations, as considered below, seem to be even less satisfactory.

One obvious, and rather attractive, explanation is that the $SiMe_2$ and $Si(CD_3)_2$ sites in cation **II** are not equally prone to nucleophilic attack. Since the C−D bond is shorter than the C−H bond, the CD_3 group in **II** could be significantly smaller than the CH_3 group, the difference possibly being sufficiently large in this very crowded species to make attack at the α-site significantly easier than that at the γ-site (compare ref. 19). That this may indeed be the case was suggested by our finding that in the reaction of **1-D** with KSCN in MeCN, which involves unambiguous nucleophilic substitution at the α-site, the rate for $TsiSiMe_2I$ was *ca.* 25% lower than that for $TsiSi(CD_3)_2I$. It is impossible to estimate how large such an effect might be for attack of ROH on **II**; for a given nucleophile the steric effect could be expected to be markedly smaller than that at the silicon atom bearing a large I atom in $TsiSiMe_2I$, but against that the hindrance would be larger for attack by the MeOH molecule than by the small linear SCN^- ion. Our view is that the effect, while significant, is most unlikely to cause the attack at the γ-site in **II** to be *ca.* 3 times as slow as that at the α-site as it would have to be to account for $P_\mathbf{R}$ values of *ca.* 25%, and that major reason for such values must be sought elsewhere.

A further possible explanation of the fact that the values of $P_\mathbf{R}$ for TOR are always <50 is that the TOR products are formed by two distinct processes, one involving attack only at the α-site. Thus formation of an unbridged cation, $TsiCSi(CD_3)_2^+$, could precede that of the bridged ion **II**. Trapping of the unbridged ion by ROH would give unrearranged product, corresponding to $P_\mathbf{R} = 0$, while that of the fully-free bridged ion would give equal amounts of rearranged and unrearranged products, corresponding to $P_\mathbf{R} = 50$, and so any value of $P_\mathbf{R}$ up to 50 could be observed. (Similar considerations would apply, of course, to trapping by X^- or water.) Logically it would have to be assumed that the unbridged cation is also initially formed in reactions of **1-D** with AgX in inert solvents or with ICl in methanol or aprotic solvents.

Such a mechanism, which we refer to below as the two-stage ionization mechanism, can be ruled out for related reactions involving much better bridging groups, as in reactions of the compounds $(Me_3Si)_2(ZSiMe_2)CSiMe_2Y$ with, *e.g.* Z = Ph, CH=CH_2 or OMe, since in these cases there is clear anchimeric assistance, showing that the bridging is concerted with the departure of Y^-,[20] but there is no direct evidence for such assistance in the case of bridging Me. Furthermore calculations on the model bridged ion **III** with Z = Me (in contrast to those for **III** with Z = Ph) indicate that there is little difference in energy between the bridged and unbridged species.[17] Nevertheless we disfavour this mechanism for the following reasons.

(i) There is compelling evidence from high-level calculations that sterically-unhindered silylium ions R_3Si^+ must always be solvated in solution, strongly so even in alkanes, and significantly so in an argon matrix,[17] and even when account is taken of the considerable steric hindrance in a free cation $(Me_3Si)_3CSi(CD_3)_2^+$ it seems unlikely that this ion would be formed unsolvated in MeOH, or that the solvated ion once formed would fail to collapse to the methoxide rather than undergoing conversion to the bridged ion. In contrast, direct formation of the bridged cation keeps both the α- and γ-silicon atoms four-coordinate, greatly reducing the need for solvation at those centres.[17]

(ii) Although steric hindrance to nucleophilic attack appears to be rather similar at the functional centres in Bu^t_3SiI and $TsiSiMe_2I$, as indicated by their fairly similar reactivities towards KSCN in MeCN, $TsiSiMe_2I$ is much the more reactive towards electrophiles, *e.g.* silver salts or ICl, and this can reasonably be attributed to anchimeric assistance by a bridging Me group.[21] It is difficult to envisage any other acceptable explanation of the much greater ease of ionization of $(Me_3Si)_3CSiMe_2I$; there could be some stabilization of the $(Me_3Si)_3CSiMe_2^+$ ion by hyperconjugative electron-release from the Me_3Si−C bonds (analogous to stabilization of carbocations by β-Me_3Si groups) but it seems unlikely that this effect (which in valence bond terms requires double-bond character in the C−$SiMe_2$ bond) would be substantially larger than stabilization of the $Bu^t_3Si^+$ ion by the three alkyl groups.

(iii) It seems unlikely that the competition between attack on the unbridged ion and that on the bridged ion, which could give rise to a value of zero at one extreme and 50 at the other, would not more often fall near one or other of these extremes for

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§ The low $P_\mathbf{R}$ values observed in formation of TX in alcohols could likewise be attributed to preassociation of X^- (perhaps as an ion pair $[Ag^+ \cdots X^-]$) by a weak nucleophilic interaction at the Si atom of the Si–I bond, and it is noteworthy that the formation of tertiary alkyl azides accompanying solvolysis of simple tertiary alkyl halides in the presence of azide ion is now thought to arise by preassociation of that ion with the starting halide.[18]

formation of TX products in reactions with AgX in inert or protic solvents or of TOR products in reactions with AgX in various alcohols, or reactions with ICl in MeOH or inert solvents.

Another possible reaction scheme involves competition between two unrelated processes. In this picture a bridged-ion is formed, and perhaps attacked equally at α- and γ-sites, but this reaction is accompanied by a competing one at the α-site involving nucleophilic attack by X^- or ROH concerted with abstraction of I^-. This cannot be ruled out, but it seems even more improbable than for the two-stage ionization mechanism that the balance between the two processes, as indicated by P_R for TOR, would vary so little for the reactions of the iodide over the range of AgX in alcohols and ICl in MeOH. In particular one would expect that the rate of the reaction involving attack of ROH at the α-site synchronous with leaving of X^- would be greatly reduced on going to the bulkier alcohols, with the rate of the ionization much less affected, giving rise (on the assumption that the cation becomes fully free) to P_R values of 50.

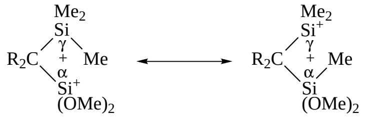
In summary it seems to us that although the fact that the P_R values for formation of the alkoxides TOR all fall below 50 shows that the bridged cation is not always fully free before capture by the alcohols, the discrepancy is not so large as to favour one of the more complex dual processes, especially that of the second type outlined above involving two wholly unrelated reactions, one ionization and the other nucleophilic attack synchronous with leaving of I^-. Our suggestions of pre-association of ROH at the I atom of the Si–I bond or of preferential reaction of the intermediate with an alcohol molecule solvating X^- liberated near the α-site provide plausible rationalizations, but others may suggest themselves as more evidence accumulates.

We hope to be able to throw further light on the mechanism of reactions of **1-D** in due course by synthesizing and studying the reactions of the related compound $(Me_3Si)_2C(SiPhMe_2)$-$Si(CD_3)_2I$, for which there would be no doubt that there is anchimeric assistance by the Ph group and so direct formation of the phenyl-bridged cation.

Conclusion

Although the simplest mechanistic picture, as shown in Scheme 1, can be reconciled with the experimental data only by making several *ad hoc* modifications, it seems to be substantially more satisfactory than the possible alternatives that we can suggest. Whatever the mechanism, it is clear that there is a definite preference for substitution at the α-site, and this is especially marked for formation of TX products in both alcoholic and aprotic media. This must be taken into account when the effects of substituents at the α- and γ-sites are considered. Thus in the case of the compound TsiSiMeEtI with $AgBF_4$ in CH_2Cl_2 the small additional steric effect at the α-site seems just to offset the inherent favouring of attack at that site, with *ca.* 50% of the fluoride product being rearranged.[22] compared with 32–47% in the case of **1-D**. However, even in the case of TsiSiMeEtI only *ca.* 10% of rearranged fluoride is formed in the reaction with $AgBF_4$ in Et_2O,[22] compared with 5 ± 3 in the case of **1-D**, and the remarkable effect of this solvent in inhibiting rearrangement still awaits satisfactory explanation, although we suspect that it may be associated with strong stabilization of, *e.g.* the ion $TsiSiMe_2^+$ by co-ordinated Et_2O (*cf.* the strong stabilization calculated[17] for $[Me_3Si{\cdot}OH_2]^+$).

Some other effects of substituents in reactions of the compounds TsiSiR′R″I can be interpreted mainly in terms of electronic effects on the distribution of the formal positive charge in a cation of type **I**. Thus in the case of $TsiSi(OMe)_2I$ and TsiSIMe(OMe)I the fact that only unrearranged products are formed in the reaction with silver salts in CH_2CL_2[11] or with ICl in CCl_4[12] can be attributed to greater interaction of the OMe than of the Me groups with the positive charge at the α- and γ-sites, respectively (compare the greater stabilization calculated for SiH_3^+ on introduction of an OH than of a Me substituent[17]). This will lead to a higher proportion of the cationic charge lying at the α- than at the γ-site [or, in resonance terms a greater contribution by, for example, the canonical form **IV** than by **V**], and so to a higher proportion of nucleophilic attack at the α-site. On the other hand, the fact that only rearranged product is formed in the reaction of TsiSiMeFI with $AgOSO_2CF_3$ in CH_2Cl_2 or with ICl in CCl_4[10] even though F should have a smaller steric effect than a Me substituent, can be attributed to substantial lowering of the proportion of the charge at the α-site in the bridged cation, calculations having indicated that $FSiH_2^+$ is considerably less stable than $MeSiH_2^+$.[17]



IV **V**

In continuing to favour the mechanism shown in Scheme 1, with *ad hoc* modifications, in spite of the problems this presents, we note that the simple concept of S_N1 reactions of alkyl halides and related species had to be progressively modified and refined in terms of multi-stage processes as more and more detailed information became available, and that it has taken studies by several research groups over more than 50 years even to allow a reasonably firm conclusion that solvolysis of secondary alkyl substrates involves an S_N1 process (with capture of a nucleophile at various stages of separation of the initially formed ions) rather than competing S_N1 and S_N2 processes.[23] Furthermore, even the question of whether the solvolysis of simple tertiary alkyl halides proceeds by an S_N1 mechanism is still a matter for investigation[18] some 60 years after it was first suggested that it does so.

Experimental

Syntheses

$TsiSi(CD_3)_2H$. A 0.50 mol dm^{-3} solution (50 cm^3) of CD_3Li in diethyl ether was added in one portion to solid $TsiSiH_3$ (2 g, 8 mmol) in a small flask. The mixture was stirred under nitrogen for 24 h, then treated dropwise with wet diethyl ether (20 cm^3) followed by water. When gas evolution had ceased, concentrated hydrochloric acid (10 cm^3) was added, and the ethereal layer was separated, washed with water and then aqueous $NaHCO_3$ and dried ($MgSO_4$). The diethyl ether was evaporated to leave a mixture of $TsiSI(CD_3)_2H$ and TsiH in *ca.* 2 : 1 ratio and the TsiH was removed by pumping under vacuum at 60 °C for *ca.* 1 h.

$TsiSi(CD_3)_2I$. [This procedure was performed several times on a 0.05–0.1 mmol scale as initial experiments showed that larger scale reactions often gave some $TsiSi(CD_3)_2Cl$ as a by-product.] A 0.10 mol dm^{-3} solution of ICl in Cl_4 was added dropwise to a rapidly stirred solution of $TsiSi(CD_3)_2H$ (*ca.* 50 mg, 0.5 mol) in CCl_4 (10 cm^3). The progress of the reaction could be monitored by ^1H NMR spectroscopy, but it was found with experience that it was possible to detect when an equivalent of ICl had been added by the appearance of a reddish tinge in the solution. At that point the solution was washed, first with 10 cm^3 of 0.05 mol dm^{-3} aqueous sodium bisulfite to remove any iodine, and then with water, and the organic layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure to leave the solid product, the purity of which was checked by ^1H NMR spectroscopy. It was normally pure enough to be used without further purification, but if necessary contaminants were removed by chromatography on silica gel with light petroleum as eluent.

Other $TsiSi(CD_3)_2X$ derivatives. These were prepared as needed by treating $TsiSi(CD_3)_2I$ with an excess of the appropriate silver salt in anhydrous diethyl ether. The products obtained in this way contained up to 5% of $(Me_3Si)_2CSi[(CD_3)_2Me]$-$SiMe_2X$, together with traces of $TsiSi(CD_3)_2OEt$ and $TsiSi$-$(CD_3)_2OH$. Since the samples of $TsiSi(CD_3)_2X$ were required only for solvolysis studies the presence of these other species was acceptable once the exact composition of the mixture had been established by ^1H NMR spectroscopy.

Other reagents. The alcohols used were treated by the best available standard methods to remove water but still contained traces of it. The silver salts were supplied (Aldrich) and 'anhydrous', except for $AgClO_4$ which was supplied as the monohydrate and used as such.

Analysis of product mixtures

Compounds were identified, and the composition of mixtures determined, by ^1H NMR spectrometry with a Varian Unity 300 MHz spectrometer. For the identification of products the ^1H NMR spectra were compared with those of authentic (non-deuterated) samples and the yields were determined by integration.

The extent of rearrangement accompanying the formation of products was calculated by use of eqn. (1) where *r* is the ratio of

$$\%\ \text{rearrangement}\ (P_\mathbf{R}) = 450/(r + 1) \qquad (1)$$

the area of the peak from all other SiMe groups to that of the peak from the $SiMe_2Y$ group. This formula is based on the assumption that the only species contributing to these peaks are $(Me_3Si)_3CSi(CD_3)_2Y$ and $(Me_3Si)_2C[SiMe(CD_3)_2]SiMe_2Y$.

The reliability of the $P_\mathbf{R}$ values derived in this way depends on how accurately the peak areas can be determined, and on the yield of the product under consideration. The reactions were fairly clean, and the species TX, TOR and TOH together constituted >95% of the product mixture. Any other products gave rise only to signals with chemical shifts <0.20 ppm, thus causing no significant interference. Most analysis problems arose from partial overlap of product peaks, the shifts for which were as follows. (*a*) For $Me_3Si + Me(CD_3)_2$ protons: (X =) I, 0.34; ClO_4, 0.29; O_3SCF_3, 0.30; NO_3, 0.28; O_2CCF_3, 0.28; F, 0.24; OH, 0.24; OMe, 0.21; OEt, 0.22; OPr^i, 0.23; OBu^t, 0.23. (*b*) For Me_2Si protons: (X =) I, 1.06; ClO_4, 0.72; O_3SCF_3, 0.72; NO_3, 0.63; O_2CCF_3, 0.63; F, 0.38; OH, 0.33; OMe, 0.25; OEt, 0.26; OPr^i, 0.27; OBu^t, 0.35.

The most serious overlap problems involved the $SiMe_2$ peaks of the silyl alkoxides, which lie in the region where the much larger Tsi peaks of other products (especially that of the silanol) usually appear; the Tsi peaks tended to be broad and as a result the signals from the $SiMe_2$ groups in the ethers often appeared as shoulders on them. This made electronic integration unreliable and in such cases areas were normally determined by cutting and weighing. In two cases overlap was so extensive that direct analysis was not possible. One was for TF in the $AgBF_4$ reactions, where the peak for the $Me_3Si + Me$ protons extensively overlapped that for $TsiSi(CD_3)_2OH$, a significant product in these reactions; the best that could be done was to derive estimates for $P_\mathbf{R}$ by partitioning the combined Tsi + Me peak in terms of the relative yields of the fluoride and silanol obtained for the reaction of $TsiSiMe_2I$ with $AgBF_4$ under the same conditions. The other was for the reaction with AgOtfa in Pr^iOH, where overlap between the peak for the $Me_3Si + Me$ protons of the TOtfa and that for the $SiMe_2OPr^i$ was so complete as to rule out even a rough estimate of $P_\mathbf{R}$. The yields and $P_\mathbf{R}$ values for $TOBu^t$ must be treated with particular caution, since $TsiSiMe_2OBu^t$ has never been isolated, and the assigned shifts are only tentative. Furthermore, the assigned Tsi peak for this derivative lies close to that for the silanol. As a result, the $P_\mathbf{R}$ values for $TOBu^t$ in reactions in which the yield of silanol was high are especially uncertain. Our estimates of the reliability of $P_\mathbf{R}$ values shown in the tables are based on the observed reproducibility and on analysis of a few standard mixtures. The least reliable values are those where the yield of product was small or overlap of peaks was extensive. In spite of the problems we believe that at no point do the uncertainties in the $P_\mathbf{R}$ values cast doubt on the validity of the conclusions drawn.

Reactions of $TsiSi(CD_3)_2I$ with Ag salts

For reactions carried out at room temperature $TsiSi(CD_3)_2I$ (8 mg, *ca.* 0.02 mmol) was added to a solution of the silver salt (8 mg) (and where relevant LiX) in the alcohol (2 cm^3) contained in a reacti-vial. The vial was filled with dry argon and capped to exclude air and the mixture was stirred until reaction was complete, as indicated by ^1H NMR spectroscopic monitoring. The time required varied with the alcohol, from 30–60 min for MeOH to 24 h for Pr^iOH and Bu^tOH. The product solution was worked up by adding it to pentane (3 cm), shaking the organic layer with water to remove the alcohol and any excess of silver salt, drying it over anhydrous sodium sulfate and evaporating the pentane under reduced pressure. The residual solid was dissolved in $CDCl_3$ for recording of the NMR spectrum. Checks showed that neither $TsiSiMe_2OClO_3$ nor $TsiSiMe_2O_3SCF_3$ underwent significant hydrolysis during such work-up.

For reactions performed under reflux conditions, the experiments were carried out under argon in a 10 mm diameter test-tube fitted with a condenser. Reactions were complete in 15–30 min. The scale and the method of work-up were as described for the room temperature reactions. Separate experiments showed that the compounds $TsiSiMe_2X$ with X = F, $OCOCF_3$, or ONO_2, underwent no appreciable reaction under the conditions used.

Solvolysis of $TsiSi(CD_3)_2X$ (X = $OClO_3$ or OSO_2CF_3)

The relevant compound {*ca.* 8 mg, containing up to 5% of $(Me_3Si)_2CSi[(CD_3)_2Me]SiMe_2X$, together with a little $TsiSi(CD_3)_2OEt$ and $TsiSi(CD_3)_2OH$ as noted above} was dissolved in MeOH under dry argon and the solution was kept at room temperature or under reflux under argon until reaction was judged to be complete. Work-up and analysis were then as described for the reactions in the presence of silver salts, appropriate allowance being made for the presence of the impurities in the starting material.

Reaction of $TsiSi(CH_3)_2I$ and $TsiSi(CD_3)_2I$ with KSCN in MeCN

A solution of the iodide (0.01 mol dm^{-3}) and KSCN (0.10 mol dm^{-3}) in anhydrous MeCN was kept under dry argon in a vessel immersed in a thermostat held at 35.0 ± 0.05 °C. Samples were removed at appropriate intervals and rapidly cooled, and the solvent was then evaporated off under vacuum. The organic component of the residue was extracted into $CDCl_3$ for determination of the ^1H NMR spectrum. The relative integrals of the signals from the $(Me_3Si)_3C$ groups in the reactant and product indicated the extent of reaction. Good first order kinetics were observed, giving rate constants of 11.10 ± 0.04 and 8.80 ± 0.04 s^{-1}, respectively.

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