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THE REACTIONS OF [TRIS(TRIMETHYLSILYL)METHYL]SILICON HALIDES AND HYDRIDES WITH ELECTROPHILIC REAGENTS *

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Summary

A study has been made of the reactions of compounds of the type $(Me_3Si)_3CSiR_2X$ (e.g. X = I, $R_2 = Me_2$, Ph_2, PhMe, Et_2, or EtMe; X = H, $R_2 = Me_2$, Et_2) with electrophilic reagents such as $AgNO_3$, AgOAc, AgO_2CCF_3, $Hg(NO_3)_2$, $Hg(OAc)_2$, $HgCl_2$ and $HgBr_2$, in alcohols, AcOH, CF_3CO_2H, or mixtures of these. Reactions of $(Me_3Si)_3CSiPh_2I$ take place exclusively with rearrangement, to give products of the type $(Me_3Si)_2C(SiMe_2Y)(SiPh_2Me)$ (e.g. with $AgNO_3$ — i-PrOH — MeOH, a mixture of products, with Y = NO_3, OMe or OPr-i is formed), while the compounds $TsiSiR_2I$ with $R_2 = Et_2$, PhMe, or EtMe give both rearranged products, $(Me_3Si)_2CH(SiMe_2Y)(SiR_2Me)$, and unrearranged products, $(Me_3Si)_3CSiR_2Y$. With $AgNO_3$ or $Hg(NO_3)_2$ in MeOH, added $NaNO_3$ does not increase the $SiONO_2$/SiOMe product ratio. The reactions of $(Me_3Si)_3CSiMe_2H$ and $(Me_3Si)_3CSiMe_2I$ with $Hg(NO_3)_2$ — AcOH — MeOH give virtually the same product distribution, as do those of $(Me_3Si)_3CSiMe_2I$ and $(Me_3Si)_3SiMe_2Br$ with $AgNO_3$ — MeOH. (The bromide reacts much more slowly than the iodide in the latter case, and no reaction was observed in the case of $(Me_3Si)_3CSiMe_2Cl$). The iodide $(Me_3Si)_3SCiMe_2I$ undergoes solvolysis slowly in CF_3CO_2H alone, and added NaO_2CCF_3 has no effect.

The results are interpreted in terms of the formation of a cationic intermediate by abstraction of X^- from $(Me_3Si)_3CSiR_2X$ by the electrophile. A structure involving a Me group bridging the 1- and 3-silicon atoms is favoured for this cation, with the nucleophile subsequently attacking at either of these atoms.

Introduction

We have previously noted that because of steric hindrance tris(trimethylsilyl)methyl-silicon compounds, $(Me_3Si)_3CSiRR'X$, (e.g. X = halogen) are

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* No reprints available.

extremely inert towards direct displacement of X by nucleophiles [1,2]. Thus their study seemed to offer a good prospect of observing reactions proceeding through siliconium ions *. The investigation described below of reactions of $(Me_3Si)_3CSiR_2X$ species with electrophilic reagents in protic media has shown that cationic species are indeed involved, and are associated with novel rearrangements, but these species may not be simple siliconium ions. (For a brief preliminary account see ref. 5). Some of the reactions described involve the production of organosilicon chlorides, bromides, nitrates, or acetates in alcoholic media or acetic acid; the novelty of this will be apparent to organosilicon chemists.

In the subsequent discussion we shall, as previously [1,2,5], frequently use the symbol Tsi (denoting the "trisyl" group) for $(Me_3Si)_3C$.

Results and discussion

Our first observation of interest was that none of the halides $TsiSiPh_2X$ or $TsiSiMe_2X$ (X = Cl, Br or I) undergo solvolysis in refluxing methanol. Thus these halides, even the iodides which have relatively weak Si—Hal bonds, show no tendency to react by a simple S_N1 type mechanism under conditions commonly associated with such reactions in the case of alkyl halides. Ionization might be expected to be especially favoured for $TsiSiPh_2X$ compounds, since (a) the ion $TsiSiPh_2^+$ should be stabilized to some extent by conjugation with the Ph groups and by hyperconjugative electron release from the Tsi group (compare the stabilization of the ion $Me_3SiCH_2CH_2^+$ [6], and (b) the ionization would be accompanied by considerable release of steric strain. However, steric hindrance to solvation would have some counter influence.

We next studied in detail the reactions of some $TsiSiR_2X$ compounds with silver or mercury(II) salts in alcohols or acetic acid, and the results are shown in Table 1, and discussed below.

The chloride $TsiSiMe_2Cl$ was found to undergo no reaction with silver nitrate in methanol during 20 h under reflux (Rct. 48), but the corresponding bromide underwent about 50% reaction under these conditions to give a mixture of the methoxide $TsiSiMe_2OMe$ and the nitrate $TsiSiMe_2ONO_2$ (Rct.49). However, the corresponding diphenyl derivative, $TsiSiPh_2Br$ underwent no significant reaction in 36 h (Rct. 14). The iodides $TsiSiPh_2I$ and $TsiSiMe_2I$ were very much more reactive in reactions with $AgNO_3$ — MeOH and a variety of other electrophilic reagents in protic solvents.

More restricted studies were made on the iodides $TsiSiEt_2I$ and TsiSiEtMeI, and on the hydrides $TsiSiMe_2H$ and $TsiSiEt_2H$, which were also found to react readily with electrophiles, and the results for these are also shown in Table 1.

We first examined the reactions of the dimethyl derivatives $TsiSiMe_2X$ (X = I or H). The participation of siliconium ion intermediates seemed to be indicated by the following features of the results.

(a) Mixtures of products resulting from reactions with solvent molecules and counter anions were commonly obtained, e.g. of (i) $TsiSiMe_2OMe$ and TsiSi-

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* By siliconium ions we mean ions such as H_3Si^+ and its derivatives. For a review of attempts to detect siliconium ions in solution see ref. 3, and for later leading references see ref. 4.

Me_2ONO_2 from $AgNO_3$ — MeOH (Rcts. 16 and 17); (ii) $TsiSiMe_2OAc$ and $TsiSiMe_2ONO_2$ from $Hg(NO_3)_2$ — AcOH (Rct. 31); (iii) $TsiSiMe_2OAc$ and $TsiSiMe_2Cl$ from $HgCl_2$ — AcOH (Rct. 45); and (iv) of $TsiSiMe_2OMe$, $TsiSiMe_2OAc$, and $TsiSiMe_2ONO_2$ from $AgNO_3$ in 1 : 1 MeOH — AcOH (Rct. 27).

(b) The proportion of nitrate product obtained with $AgNO_3$ or $Hg(NO_3)_2$ in MeOH or with $AgNO_3$ in i-PrOH was not significantly increased by the addition of an excess of nitrate ion (Rcts. 16—19; 21, 22; 28, 29) which argues strongly against simultaneous attack of the nucleophile at silicon and of the electrophile at iodine.

(c) The composition of the product mixture from $TsiSiMe_2I$ is the same as that from $TsiSiMe_2H$ in the reaction with $Hg(OAc)_2$ — MeOH — AcOH (Rcts. 38, 52). Similarly, the composition of the product mixture from $TsiSiMe_2I$ is the same as that from the much less reactive $TsiSiMe_2Br$ in the reaction with $AgNO_3$ in MeOH (Rcts. 16, 49). This argues in favour of a common intermediate rather than concerted nucleophilic and electrophilic attack.

Study of the reactions of $TsiSiPh_2I$ (Rcts. 1—13) then revealed, however, that the reaction was more complex, since the products were shown unambiguously by their ^1H NMR spectra to be of the type $(Me_3Si)_2C(SiMe_2Y)(SiPh_2Me)$ rather than the expected $(Me_3Si)_3CSiPh_2Y$; that is, the nucleophile Y attaches at a silicon atom [denoted Si(3)] different from that [denoted Si(1)] from which X leaves, and there is a corresponding 3 → 1 migration of a methyl group.

We suggest that the methyl-bridged cationic species (I) is formed by movement of a Me group as X is removed by the electrophile in the rate-determining step of the reaction. The nucleophile Y can then attack, to break the bridge, either at Si(1) or Si(3), to give respectively, the unrearranged product $(Me_3Si)_3CSiR_2Y$ or the rearranged product $(Me_3Si)_2C(SiMe_2Y)(SiR_2Me)$. In these highly sterically hindered systems, the dominant (though not necessarily the only) factor determining the position of attack is likely to be the degree of hindrance at each centre, and thus for $R_2 = Ph_2$ the substantially greater hindrance at Si(1) would markedly favour formation of the rearranged product, and this is apparently exclusively produced *.

As the difference of the degree of hindrance at Si(1) and Si(3) becomes smaller, we should expect an increasing proportion of unrearranged product; in keeping with this, in reactions with $Hg(OAc)_2$ — AcOH, while $TsiSiPh_2I$ gives 100% of rearranged product (Rct. 13), TsiSiPhMeI gives a 78/22 ratio of rearranged to unrearranged product (Rct. 15), and $TsiSiEt_2I$ gives an approximately 50/50 ratio (Rct. 55). We have no direct evidence, in the absence of experiments with labelled compounds, that any rearrangement occurs in the case of $TsiSiMe_2X$ derivatives, but it seems safe to assume that it does.

We should note at this point that rearranged products could also be formed if, instead of the bridged ion I, an equilibrated mixture of the classical ions III and IV were formed, as in Equation 1, after removal of X^-. The nucleophile

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* In the reaction of $TsiSiPh_2I$ with $AgNO_3$-i-PrOH, along with $(Me_3Si)_2C(SiMe_2OPr\text{-}i)(SiPh_2Me)$ and $(Me_3Si)_2C(SiMe_2ONO_2)SiPh_2Me$, a second isoproxide is produced in small amount (Rct. 5). We previously described this as unrearranged $TsiSiPh_2OPr$-i [5] but reexamination of the ^1H NMR spectrum reveals that there is some doubt about his, and we are postponing consideration of this product until we have made it on a larger scale and identified it unambiguously.

(continued on p. 184)

TABLE 1

REACTIONS OF $(Me_3Si)_3SiR_2X$ COMPOUNDS WITH ELECTROPHILIC REAGENTS

Reaction	Substrate R_2X	Solvent [a]	Salt(s) and amount (mmol)	Time [b]	Products and proportion (%) [c]		Notes
					Y in $(Me_3Si)_2C(SiMe_2Y)(SiR_2Me)$	Y in $(Me_3Si)_3CSiR_2Y$	
1	Ph_2I, 0.10	MeOH	$AgNO_3$, 0.40	10 min	OMe, 87; ONO_2, 13		
2		AcOH	$AgNO_3$, 0.14	10 min	OAc, 90; ONO_2, 10		
3		MeOH	$AgNO_3$, 0.20; $NaNO_3$, 1.0	10 min	OMe, 85; ONO_2, 15		
4		i-PrOH	$AgNO_3$, 0.14	10 min	OPr-i, 28; ONO_2, 62	? OPr-i, 10	*d*
5		i-PrOH - MeOH	$AgNO_3$, 0.14	15 min	OPr-i, 22; OMe, 61; ONO_2, 17		
6		i-PrOH - MeOH (1/2)	$AgNO_3$, 0.14	15 min	OPr-i, 15; OMe, 73; ONO_2, 12		
7		MeOH - AcOH	$AgNO_3$, 0.14	5 min	OAc, 61; OMe, 30; ONO_2, 9		
8		i-PrOH - AcOH (1/2)	$AgNO_3$, 0.14	10 min	OAc, 82; OPr-i, 9; ONO_2, 9		
9		MeOH	AgOAc, 0.14	1.5 h	OAc, 94; OMe, 6		
10		AcOH	AgOAc, 0.14	7 min	OAc, 100		
11		MeOH - AcOH	AgOAc, 0.14	3 min	OAc, 55; OMe, 45		
12		AcOH	$Hg(NO_3)_2$, 0.30	3 min	OAc, 90; ONO_2, 10		
13		AcOH	$Hg(OAc)_2$, 0.31	3 min	OAc, 100		*e*
14	Ph_2Br, 0.15	MeOH	$AgNO_3$, 0.60	36 h	Br (SM), 100		
15	PhMeI, 0.10	AcOH	AgOAc, 0.14	0.5 h	OAc, 78	OAc, 22	*e*
16	Me_2I, 0.10	MeOH	$AgNO_3$, 0.12	0.5 h	OMe, 76; ONO_2, 24		
17		MeOH	$AgNO_3$, 0.24	0.5 h	OMe, 75; ONO_2, 25		
18		MeOH	$AgNO_3$, 0.18; $NaNO_3$, 1.0	0.5 h	OMe, 76; ONO_2, 24		
19		MeOH	$AgNO_3$, 0.18; $LiNO_3$, 1.0	0.5 h	OMe, 78; ONO_2, 22		
20		i-PrOH	$AgNO_3$, 0.12	0.5 h	OPr-i, 33; ONO_2, 67		
21		i-PrOH	$AgNO_3$, 0.24	0.5 h	OPr-i, 33, ONO_2, 67		*f*
22		i-PrOH	$AgNO_3$, 0.18; $NaNO_3$, 1.0	0.5 h	OPr-i, 34; ONO_2, 66		
23		t-BuOH	$AgNO_3$, 0.18	0.5 h	OBu-t, 34; ONO_2, 66		
24		AcOH	$AgNO_3$, 0.18	0.5 h	OAc, 91; ONO_2, 9		*e*
25		AcOH	$AgNO_3$, 0.18; $NaNO_3$, 1.0	0.5 h	OAc, 75; ONO_2, 25		*e*
26		i-PrOH - MeOH	$AgNO_3$, 0.18	0.5 h	OMe, 58; ONO_2, 42		
27		MeOH - AcOH	$AgNO_3$, 0.18	0.5 h	OAc. 45; OMe, 29; ONO_2, 26		
28		MeOH	$Hg(NO_3)_2$, 0.30	0.5 h	OMe, 75; ONO_2, 25		
29		MeOH	$Hg(NO_3)_2$, 0.30; $NaNO_3$, 1.0	0.5 h	OMe, 71; ONO_2, 29		
30		i-PrOH	$Hg(NO_3)_2$, 0.31	0.5 h	POr-i, 59; ONO_2, 41		
31		AcOH	$Hg(NO_3)_2$, 0.30	0.5 h	OAc, 78; ONO_2, 22		*e*
32		AcOH	$Hg(NO_3)_2$, 0.30; $NaNO_3$, 1.0	0.5 h	OAc, 66; ONO_2, 34		
33		t-BuOH	$Hg(NO_3)_2$, 0.31	1 h	OBu-t, 38; ONO_2, 62		
34		i-PrOH - MeOH	$Hg(NO_3)_2$, 0.31	0.5 h	OMe, 49; OPr-i 31; ONO_2, 20		
35		t-BuOH - MeOH	$Hg(NO_3)_2$, 0.31	0.5 h	OMe, 46; OBu-t, 20; ONO_2, 34		

36		MeOH - AcOH	$Hg(NO_3)_2$, 0.31	0.5 h	OMe, 18; OAc, 82		
37		AcOH	$Hg(OAc)_2$, 0.31	0.5 h	OAc, 100		
38		MeOH - AcOH	$Hg(OAc)_2$, 0.31	0.5 h	OMe, 32; OAc, 68		
39		MeOH	$HgSO_4$, 0.33	0.5 h	OMe, 100		g
40		MeOH	$HgCl_2$, 0.37	2 h	I(SM), 76; OMe, 24		
41		MeOH	$HgBr_2$, 0.28	2 h	I(SM), 100		
42		i-PrOH	$HgSO_4$, 0.33	2 h	I(SM), 100		g
43		t-BuOH	$HgSO_4$, 0.33	2 h	I(SM), 100		g
44		AcOH	$HgSO_4$, 0.33	2 h	OAc, 100		e
45		AcOH	$HgCl_2$, 0.37	2 h	I(SM), 43; OAc, 34; Cl, 22		e
46		AcOH	$HgBr_2$, 0.28	2 h	I(SM), 61; OAc, 19; Br, 20		e,g
47		AcOH	$Hg(OAc)_2$, 0.37; NaCl (excess)	2 h	I(SM), 33; OAc, 41; Cl, 26		h
48	Me_2Cl, 0.15	MeOH	$AgNO_3$, 0.60	20 h	Cl(SM), 100		
49	Me_2Br, 0.16	MeOH	$AgNO_3$, 0.60	20 h	Br(SM), 40; OMe, 45; ONO_2, 15		
50	Me_2H, 0.15	MeOH - AcOH	$AgNO_3$, 0.18	1.5 h	H(SM), 100		
51	Me_2H, 0.15	MeOH - AcOH	$Hg(NO_3)_2$, 0.31	2 h	OMe, 19; OAc, 81		
52		MeOH - AcOH	$Hg(OAc)_2$, 0.31	2 h	OMe, 34; OAc, 66		
53		i-PrOH - MeOH	$Hg(NO_3)_2$, 0.31	2 h	OMe, 45; OPr-i, 25; ONO_2, 30		
54		t-BuOH - MeOH	$Hg(NO_3)_2$, 0.31	2 h	OMe, 31; OBu-t, 20; ONO_2, 51		
55	Et_2I, 0.09	AcOH	AgOAc, 0.17	10 min	OAc, 50	OAc, 50	e,l
56	Me_2Cl, 0.15	CF_3CO_2H	None	17 h	Cl(SM), 100		
57	Me_2Br, 0.14	CF_3CH_2H	None	17 h	Br(SM), 100		
58	Me_2I, 0.10	CF_3CO_2H	None	18 h	I(SM), 54; O_2CCF_3, 46		
59		CF_3CO_2H	NaO_2CCF_3, 1.0	18 h	I(SM), 59; O_2CCF_3, 41		
60		CF_3CO_2H - AcOH	None	6 d	I(SM); O_2CCF_3; AOc		j
61		CF_3CO_2H	AgO_2CCF_3, 0.17	0.5 h	O_2CCF_3, 100		k
62		CF_3CO_2H - AcOH	Ag_2O, 0.20	5 min	O_2CCF_3, 82; OAc, 28		l
63	Me_2Cl, 0.15	CF_3CO_2H	AgO_2CCF_3, 0.20	0.5 h	O_2CCF_3, 100		
64	Me_2H, 0.15	CF_3CO_2H	AgO_2CCF_3, 0.20	1 h	H(SM), 50; O_2CCF_3, 50		
65	Et_2I, 0.10	CF_3CO_2H	None	7 d	O_2CCF_3, 44	O_2CCF_3, 56	
66		CF_3CO_2H	AgO_2CCF_3, 0.17	10 min	O_2CCF_3, 75	O_2CCF_3, 25	l,m,n
67	Et_2I, 0.16	CF_3CO_2H	AgO_2CCF_3, 0.17 + NaO_2CCF_3, 10	10 min	O_2CCF_3, 78	O_2CCF_3, 22	l,m
68	Et_2H, 0.10	CF_3CO_2H	AgO_2CCF_3, 0.26	5 h	O_2CCF_3, 40	O_2CCF_3, 60	
69	EtMeI, 0.10	CF_3CO_2H	None	4 d	O_2CCF_3, 36	O_2CCF_3, 64	
70		CF_3CO_2H	AgO_2CCF_3, 0.20	10 min	O_2CCF_3, 54	O_2CCF_3, 46	l

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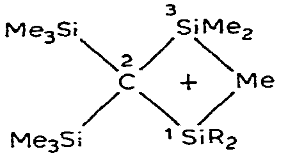
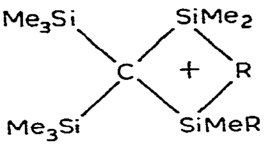
[a] 10 cm^3 of solvent was used. In mixed solvents the components were in 1/1 mole ratio unless otherwise indicated. [b] Reactions were at the reflux temperature unless otherwise indicated. [c] SM denotes unchanged starting material. From $TsiSiMe_2X$, the products $(Me_3Si)_2C(SiMe_2Y)(SiR_2Me)$ and $(Me_3Si)_3CSiR_2Y$ are identical. [d] A third component was present, and was isolated but not in pure form. Its ^1H NMR spectrum agreed with $(Me_3Si)_3CSiPh_2OPr$-i but additional peaks cast some doubt on this identification. (see Experimental section.) [e] Heated in bath at 90° C. [f] Only about half of the $NaNO_3$ dissolved. [g] Most or all of the mercury(II) salt removed undissolved. [h] Undissolved NaCl was present throughout. [i] The reaction appeared to be complete within a few seconds of mixing. [j] Very little reaction had occurred, but small peaks for $TsiSiMe_2O_2CCF_3$ and $TsiSiMe_2OAc$ were present in roughly 3/1 ratio. [k] Immediate precipitation of AgI occurred on mixing. [l] Reaction was slower than with $TsiSiMe_2Cl$. [m] At room temperature. [n] The product mixture gave ν(CO) bands at 1765 and 1725 cm^{-1}.

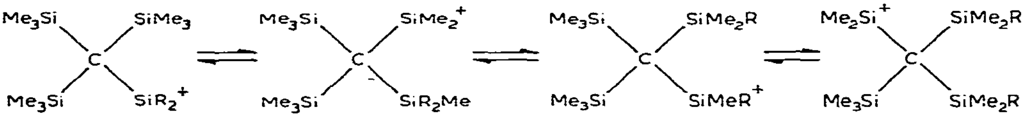


(I)



(II)

could then attack either the ion III to give unrearranged or the ion IV to give rearranged product. We cannot rule out this possibility, but we favour the bridged intermediate I, primarily on the basis of a consideration of the propor-



(1)

(III) (IV) (V) (VI)

tions of products. In a statistically determined equilibrium (i.e. any specific effects of the R groups being neglected), the ion IV would be nine times as likely as III, and so even in the absence of any steric favouring of attack at Si(3), 90% of rearranged and 10% of unrearranged product would be expected, whereas only 50% of rearrangement is formed with $TsiSiEt_2I$ in AgOAc — AcOH (Rct. 55). Even more significantly, if reversible migration of Me groups occurs rapidly, giving ions III and IV, similar migrations of the R groups would be expected, to give ions of the type V and VI and these would lead to products of the type $(Me_3Si)_2C(SiMeRY)(SiMe_2R)$ and $(Me_3Si)C(SiMe_2X)(SiMe_2R)_2$ which we have never observed; in fact, in a statistically-determined equilibrium the ions of the type V and VI would comprise 88% of the mixture, and such products would be expected to dominate *.

We cannot be sure that the Ph groups would migrate readily in the systems, though this would be expected in the light of their very facile migrations in carbonium ions and their high bridging ability in phenylaluminium compounds (see below) [7], and certainly no great difference would be expected between the migrating abilities of Me and Et groups.

We also favour the bridged intermediate because the system seems to have nothing to gain by going to the mixture of classical ions (though it might still do so incidentally), whereas formation of the bridged species I in an anchimerically-assisted process as X^- separates means that generation of an actual siliconium ion, which appears to be a highly disfavoured species, is avoided.

We should note that while the absence of marked increase in the proportion of $SiONO_2$ products on increasing the nitrate concentration in various media rules out formation of such products by concerted attack of separated nitrate ion at Si(1) or (with accompanying Me migration) at Si(3) as X^- is being abstracted, this observation does not, in itself, preclude such concerted attack involving the nucleophile and electrophile in association (either covalently

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* Observation of small amounts of rearranged products of this type would not preclude the intermediacy of bridged-ions, since it would not be surprising to find that the ions of type I could undergo some transformation into those of type II.

bonded, as in $Hg(NO_3)_2$, or electrostatistically linked in an ion pair, as with $AgNO_3$). However, not only would such processes be highly unlikely for steric and entropic reasons, but furthermore such reactions leading to entry of the nucleophile at Si(1) or Si(3) would have to be assumed to be in competition not only with one another but also with open systems involving concerted attack of the solvents as the nucleophile. This would present a highly complex picture, and many coincidences would have to be postulated to explain features of the product distributions which can be fairly interpreted in terms of a cationic intermediate.

There can be little doubt that in the media used, ion pairs must play important roles. In the reactions with silver salts, not only will $AgNO_3$, for example, be mainly present as ion pairs, but after the formation of AgX the nitrate ion can be expected largely to remain paired with the ion I, and become incorporated into the $SiONO_2$ product. Thus it is easy to understand why added nitrate ion has little, if any, effect on the $SiONO_2/SiOMe$ product ratio from $TsiSiPh_2I$ (Rcts. 1—3) or $TsiSiMe_2I$ (Rcts. 16—19) with $AgNO_3$ — MeOH. However, there might also be some separation of the initial ion pairs, and thus for $TsiSiMe_2I$ with $AgNO_3$ — AcOH added nitrate does increase the $SiONO_2/SiOAc$ ratio (Rcts. 24, 25), but the increases are markedly less than the increases in the concentration of metal nitrate. The situation is more complex with mercury(II) salts, HgY_2, since either Y^- or HgY_2X^- might form the counter anion, but, in fact, the effects of added nitrate ion on $Hg(NO_3)_2$ reactions in MeOH and AcOH are similar to those observed with $AgNO_3$ (Rcts. 28, 29; 30, 31).

Some additional features of interest in the results are as follows:

(1) The mercury(II) halides $HgCl_2$ and $HgBr_2$ are much less reactive than $Hg(NO_3)$, $Hg(OAc)_2$, and $HgSO_4$ (Rcts. 28, 31, 37, 38, 40, 41), which is in keeping with the generally lower electrophilic reactivity of the halides [8]. Not surprisingly, since Hg—Cl bonds must be formed, addition of an excess of NaCl to $Hg(OAc)_2$ — AcOH considerably reduces the rate, and leads to a SiOAc/SiCl product ratio similar to that from $HgCl_2$ — AcOH (Rcts. 45, 47). No silicon sulphate is obtained from $HgSO_4$ in MeOH or AcOH (Rcts. 39, 44), and $HgSO_4$ — MeOH is the only reagent system used which converts $TsiSiMe_2I$ exclusively into $TsiSiMe_2OMe$.

(2) With $AgNO_3$ — MeOH the $SiOR/SiONO_2$ product ratio from $TsiSiMe_2I$ is ca. 3/1 (Rct. 16), while with $AgNO_3$ — i-PrOH it is ca. 1/2 (Rct. 20), indicating (the different solvent molarities and solvation effects being neglected) that MeOH is ca. 6 times as effective a nucleophile towards the cationic intermediate as i-PrOH, but it is a little surprising that no significant amount of $TsiSiMe_2$-OPr-i is formed with $AgNO_3$ in 1/1 i-PrOH — MeOH (Rct. 26). There is qualitative but not quantitative correspondence between the results for separate and mixed solvents; thus, for $TsiSiMe_2I$ with $AgNO_3$ in MeOH, the $SiOMe/SiONO_2$ product ratio is ca. 3/1 (Rct. 16), while with $AgNO_3$ in AcOH the SiOAc/$SiONO_2$ ratio is ca. 10/1, and so on the simplest reasoning a SiOAc/SiOMe ratio of ca. 3/1 would be expected with $AgNO_3$ in 1/1 MeOH — AcOH, whereas the actual ratio is 1.6/1 (Rct. 27). With $Hg(NO_3)_2$ in 1/1 MeOH — i-PrOH a SiOMe/SiOPr-i ratio of ca. 1.7/1 would be expected from the results in the separate solvents (Rcts. 29, 30), while the actual ratio is 1.6/1 (Rct. 34). The high SiOAc/SiOMe ratio (ca. 3/1) obtained with $Hg(OAc)_2$ in 1/1 MeOH — AcOH

(Rct. 36) was expected, since the OAc group can be supplied by both the solvent and the salt, but the even higher SiOAc/SiOMe ratio (ca. 4/1) and the absence of $SiONO_2$ product obtained with $Hg(NO_3)_2$ in 1/1 AcOH — MeOH (Rct. 36) is most puzzling. Also surprising is that the SiOAc/SiOMe product ratio from $TsiSiPh_2I$ in 1/1 MeOH — AcOH is lower with AgOAc than with $AgNO_3$ (Rcts. 7, 11).

(3) The proportion of alkoxy product, SiOR, from $TsiSiMe_2I$ with $AgNO_3$ or $Hg(NO_3)_2$ in an alcohol ROH falls on going from MeOH to i-PrOH (Rcts. 17, 20; 28, 30) as would be expected on steric grounds, and in the case of $Hg(NO_3)_2$ there is a further fall on going to t-BuOH (Rct. 33), but with $AgNO_3$ the proportion of SiOBu-t (Rct. 23) is the same as that of SiOPr-i product (Rct. 22). It is surprising that the effects of steric hindrance on going to the branched alcohols, especially to t-BuOH, are not larger.

The fact that a substantial amount of $TsiSiMe_2OPr$-i is formed with $Hg(NO_3)_2$ in 1/1 i-PrOH — MeOH (Rct. 34) whereas none was detected with $AgNO_3$ in this medium (Rct. 26) is in keeping with the higher SiOPr-i/$SiONO_2$ ratio obtained with $Hg(NO_3)_2$ than with $AgNO_3$ in i-PrOH alone (Rcts. 20, 30). A substantial proportion of SiOBu-t product is also formed from $Hg(NO_3)_2$ in 1/1 t-BuOH — MeOH (Rct. 35).

(4) Roughly the same SiOR/SiOMe ratios (R = Ac, i-Pr, or t-Bu) are obtained from $TsiSiMe_2I$ and $TsiSiMe_2H$ with both $Hg(NO_3)_2$ and $Hg(OAc)_2$ in ROH — MeOH mixtures (Rcts. 34, 53; 36, 51; 35, 54; 38,52), as expected for formation of a common intermediate. The proportion of $SiONO_2$ product from $Hg(NO_3)_2$ is probably higher for $TsiSiMe_2H$ (Rct. 53) than for $TsiSiMe_2I$ in i-PrOH — MeOH (Rct. 34), and certainly so in t-BuOH — MeOH (Rcts. 35, 54). This does not represent an anomaly, however, since different counter anions, with different abilities to release nitrate ion, are produced by the initial electrophilic attack, viz. $HgI(NO_3)_2^-$ and (notionally) $HgH(NO_3)_2^-$. (The latter ion is most unlikely to exist for a significant length of time.)

(5) If the cationic intermediates I became fully separated before reaction with the nucleophiles, we should expect the product distributions from $TsiSiPh_2I$ to be similar to those from $TsiSiMe_2I$ under given conditions, since the silicon centre under attack would be very similar in the two cases. In fact the distributions differ, although the differences are not large if the experimental uncertainty in the values is kept in mind. However, with $TsiSiPh_2I$ the products result from attack at only Si(3), while with $TsiSiMe_2I$ they come from attack at both Si(1) and Si(3), and since these two centres may not become identical before the nucleophile attacks (the leaving group in association with the electrophile still being in the neighborhood of Si(1)), they could give rise to different product distributions.

(6) When a mixture of 0.10 mol each of $TsiSiPh_2I$ and $TsiSiMe_2I$ was treated with a deficiency (0.13 mol) of $AgNO_3$ in MeOH, $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$ and $TsiSiMe_2OMe$ were formed in a ratio of ca. 43/57, indicating that the dimethyl compound is the more reactive by a factor in the region of 1.6/1. If the bridged ion I is formed in the rate-determining step, as we postulate, then the factors which might be expected to favour formation of the ion $TsiSiPh_2^+$ compared with $TsiSiMe_2^+$ (viz. conjugation with the phenyl groups, and greater release of steric strain on ionization) would operate only to a limited extent, if at all.

(7) The nitrate $(Me_3Si)_3CSiMe_2ONO_2$ was obtained in excellent yield, free from other products, by treatment of $(Me_3Si)_3CSiMe_2I$ with $AgNO_3$ in the presence of $LiNO_3$ in glyme.

Reactions in trifluoroacetic acid

We turned to the use of trifluoroacetic acid because we reasoned that if the $TsiSiR_2X$ species can give cationic intermediates (whether bridged or not), reaction might be expected to occur with this solvent even without added salts, since it is known to promote very strongly the S_N1 reactions of alkyl halides and related species [9]. It will be seen from the results in Table 1 that $TsiSiMe_2I$, $TsiSiEt_2I$ and TsiSiEtMeI do react with the acid alone, though fairly slowly even at 90° C, and that the rearrangements we associate with cationic intermediates occur (Rcts. 58, 65, 69). The rearranged trifluoroacetate accounts for roughly 55% of the products from $TsiSiEt_2I$ and 44% from TsiSiEtMeI. The determination of product ratios by ^1H NMR spectroscopy is subject to a fairly large uncertainty in these systems (see Experimental section), and the apparent formation of slightly less rearranged than unrearranged product from TsiSiEtMeI may not be real.

As expected, the presence of silver trifluoroacetate generally increases the rate of reaction (Rcts. 66, 70). Even the chloride $TsiSiMe_2Cl$ reacts readily (Rcts. 56), but in competition for a deficiency of AgO_2CCF_3 between $TsiSiMe_2I$ and $TsiSiMe_2Cl$ only the iodide reacted. With $TsiSiEt_2I$ the proportion of rearranged product is greater with $AgO_2CCF_3 - CF_3CO_2H$ than with CF_3CO_2H alone (Rcts. 65, 66). A possible explanation of this is that the nucleophilic attack by trifluoroacetate ion or trifluoroacetic acid takes place while the Si(1) silicon centre is still shielded by the formed AgI, which may taken a significant time to diffuse away. The proportion of rearranged product obtained from $TsiSiEt_2I$ with $AgO_2CCF_3 - CF_3CO_2H$ is not changed by the addition of NaO_2CCF_3 (Rcts. 66, 67). Interestingly, in the reaction of $TsiSiEt_2H$ with $AgO_2CCF_3 - CF_3CO_2H$ (Rct. 68), the unrearranged product predominates, and this represents the only case in which it is clearly so. It is conceivable that the forming AgH interacts with the solvent as it separates, and generates additional trifluoroacetate ion in the neighbourhood of Si(1), but we have previously noted that the presence of only one Si—H bond in trisylsilicon systems, by markedly reducing the steric crowding, permits direct displacement to occur [1], and there might be some contribution from a process involving nucleophilic attachment of trifluoroacetate at Si(1) as the Si—H bond breaks, with either an open or cyclic transition state.

It is noteworthy that the reaction of $TsiSiMe_2I$ with CF_3CO_2H alone is not accelerated by the presence of sodium trifluoroacetate (Rcts. 58, 59), suggesting that nucleophilic attack plays no significant part in the rate-determining step, as we have assumed above. Trifluoroacetic acid (while a very weak nucleophile [10]) is, of course, a quite powerful electrophile, and can be assumed to form a covalent bond to the iodine (to give HI) in the halogen abstraction.

It is in keeping with our mechanistic proposals that while $TsiSiMe_2I$ does not react with AcOH alone, both $TsiSiMe_2OAc$ and $TsiSiMe_2O_2CCF_3$ are produced, in ca. 1/3 ratio, in the very slow reaction which occurs in 1/1 $AcOH - CF_3CO_2H$ at 90° (Rct. 60). A similar ratio, actually 28/82, is produced in the rapid reaction which takes place at room temperature with 1/1 AcOH — CF_3CO_2H in which silver oxide has been dissolved (Rct. 62).

The nature of the methyl-bridged cation

The formation of the bridged cation I might seem highly improbable in the light of the lack of any comparable structure in the very extensive chemistry of carbonium ions, or even, as far as we are aware, of any example of 1,3-methyl migration within a carbonium ion. However, the cation I becomes plausible when the close analogy to methyl bridging in aluminium compounds is considered. Thus the relevant bridged portion of the electron-deficient silicon species I is actually iso-electronic with the corresponding section of Al_2Me_6, and we can assume that the detail of the bonding in the bridge of I is closely similar to that in Al_2Me_6.

Even if cation I has no real existence, the observed methyl migration would still have to be accounted for in terms of a transition state close to I in structure, and the analogy with bonding in Al_2Me_6 would still apply. Models show that in $(Me_3Si)_3CSiR_2X$ compounds, some Me groups are held in very close to the silicon atom of the SiR_2 entity, so that as X^- leaves very little movement of a Me group would be needed to form the bridge in cation I, and there would be relatively little entropy loss.

Concluding Remarks

Our mechanistic proposals satisfactorily account for the great majority of our observations, but several anomalies, which have been pointed out, remain. The reactions we describe are wholly unprecedented, and full definition of the details of the mechanism(s) involved will require much more extensive studies, probably including kinetic investigations. It is relevant to note that the (evidently very complex) mechanisms of solvolyses of alkyl halides catalysed by silver or mercury salts are still very imperfectly understood in spite of the large number of kinetic studies extending back some 70 years [11].

Experimental

Starting materials

The preparation of the $TsiSiR_2X$ compounds used as reactants have been described previously [2].

Preparative scale reactions

Details of some typical procedures used in reactions leading to isolated products or recovery of unchanged starting material are as follows.

(i) Reaction of $TsiSiPh_2Cl$ with $AgNO_3$ — MeOH. A solution of $TsiSiPh_2Cl$ (0.20 g, 0.44 mmol) and $AgNO_3$ (0.10 g, 0.58 mmol) in MeOH (15 cm^3) was refluxed for 2 h then added to water. Extraction with hexane, followed by separation, drying ($MgSO_4$), and evaporation of the organic layer, left a solid which was shown by its ^1H NMR spectrum to be unchanged $TsiSiPh_2Cl$.

(ii) Reaction of $TsiSiPh_2I$ with $AgNO_3$ — AcOH. A solution of $TsiSiPh_2I$ (0.20 g, 0.44 mmol) and $AgNO_3$ (0.10 g, 0.58 mmol) in MeOH (15 cm^3) was refluxed for 10 min. Hexane was added, and the solution was decanted from

TABLE 2

NMR SPECTRA OF $(Me_3Si)_3CSiMe_2X$ AND $(Me_3Si)_2C(SiMe_2X)(SiPh_2Me)$ COMPOUNDS

Compound	δ [a] (ccpm)q	Notes
$TsiSiMe_2OAc$	0.27 (s, 27H, $SiMe_3$); 0.52 (s, 6h, $SiMe_2$); 2.00 (s, 3H, COMe)	b
$TsiSiMe_2O_2CCF_3$	0.28 (s, 27H, $SiMe_3$); 0.62 (s, 6H, $SiMe_2$)	c
$TsiSiMe_2ONO_2$	0.30 (s, 27H, $SiMe_3$); 0.63 (s, 6H, $SiMe_2$)	
$TsiSiMe_2OMe$	0.23 (s, 27H, $SiMe_3$); 0.27 (s, 6H, $SiMe_2$); 3.33 (s, 3H, OMe)	
$TsiSiMe_2OPr$-i	0.18 (s, 27H, $SiMe_3$); 0.22 (s, 6H, $SiMe_2$); 1.18 (d, 6H, CMe_2); 3.44 (m, 1H, OCH)	
$TsiSiMe_2OBu$-t	0.22 (s, 33H, $SiMe_3$ + $SiMe_2$); 1.32 (s, 9H, CMe_3)	
$TsiSiPh_2Cl$	0.32 (s, 27H, $SiMe_3$); 7.2 — 8.1 (m, 10H, Ph)	d
TsiSiPhMeOAc	0.34 (s, 27H, $SiMe_3$); 0.90 (s, 3H, SiMe); 2.19 (s, 3H, COMe); 7.1—7.9 (m, 5H, Ph)	
$(Me_3Si)_2C(SiMe_2OAc)(SiPh_2Me)$	0.25 (s, 18H, $SiMe_3$); 0.38 (s, 6H, $SiMe_2$); 0.95 (s, 3H, SiMe); 2.2 (s, 3H, COMe); 7.0—8.0 (m, 10H, Ph)	
$(Me_3Si)_2C(SiMe_2ONO_2)(SiPh_2Me)$	0.40 (s, 18H, $SiMe_3$); 0.47 (s, 6H, $SiMe_2$): 1.1 (s, 3H, SiMe); 7.2—8.2 (m, 10H, Ph)	
$(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Me)$	0.02 (s, 6H, $SiMe_2$); 0.20 (s, 18H, $SiMe_3$); 0.96 (s, 3H, SiMe); 3.55 (s, 3H, OMe); 7.1—8.1 (m, 10H, Ph)	
$(Me_3Si)_2C(SiMe_2OPr$-i$)(SiPh_2Me)$	0.37 (s, 18H, $SiMe_3$); 0.43 (s, 6H, $SiMe_2$); 1.07 (s, 3H, SiMe); 1.5 (d, 6H, CMe_2); 4.32 (m, 1H, OCH) 7.2—8.3 (m, 10H, Ph)	
$(Me_3Si)_2C(SiMe_2OAc)(SiPhMe)$	0.34 (s, 18H, $SiMe_3$); 0.45 (s, 6H, $Si\mathit{Me}_2Ph$); 0.66 (s, $Si\mathit{Me}_2OAc$); 7.1—7.9 (m, 5H, Ph)	

[a] In CCl_4, with CH_2Cl_2 as internal standard. [b] ν(CO) (Nujol), 1720 cm^{-1}. [c] ν(CO) (Nujol), 1765 cm^{-1}.
[d] A slightly different δ value for the $SiMe_3$ singlet was given previously [2].

the silver iodide then added to water. The organic layer was washed several times with water, dried ($MgSO_4$), and evaporated, to leave a solid. This was recrystallized from methanol to give $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Me)$ (0.14 g, 87%), m.p. 162°C. (Found: C, 62.2; H, 9.0. Calcd. for $C_{23}H_{40}OSi_4$: C, 62.2; H, 9.0%). The ^1H NMR spectral data are given in Table 2.

(iii) Reaction of $TsiSiPh_2I$ with AgOAc — AcOH. A solution of $TsiSiPh_2I$ (0.20 g, 0.37 mmol) and AgOAc (0.085 g, 0.50 mmol) in AcOH (15 cm^3) was refluxed for 10 min. Work-up as described under (ii) left a sticky residue, which was sublimed (150—160°C/0.2 mmHg) to give $(Me_3Si)_2C(SiMe_2OAc)(SiPh_2Me)$ (0.16 g, 93%), m.p. 118°C; IR, ν(CO), 1720 and 1230 cm^{-1} (Found: C, 61.1; H, 8.5. Calcd. for $C_{24}H_{40}O_2Si_4$: C, 61.0; H, 8.5%). The ^1H NMR spectral data are given in Table 2.

(iv) Reaction of $TsiSiPh_2I$ with $Hg(OAc)_2$ — AcOH. A mixture of $TsiSiPh_2I$ (0.50 g, 0.90 mmol), $Hg(OAc)_2$ (0.60 g, 2.7 mmol), and AcOH (20 cm^3) was refluxed for 20 min. Work-up as under (ii), culminating in sublimation, gave $(Me_3Si)_2C(SiMe_2OAc)(SiPh_2Me)$ (0.40 g, 92%), with physical properties identical with those given above.

(v) Reaction of $TsiSiPh_2I$ with $AgNO_3$ — i-PrOH. A solution of $TsiSiPh_2I$ (1.0 g, 0.18 mmol) and $AgNO_3$ (0.40 g, 0.23 mmol) in i-PrOH (40 cm^3) was refluxed for 15 min. Work-up as under (ii) gave a solid residue, which was separated by preparative TLC (SiO_2, hexane) into three components, (a) $(Me_3Si)_2C(SiMe_2ONO_2)(SiPh_2Me)$ (0.20 g, 23%), m.p. 158°C; IR, $\nu(ONO_2)$, 1590 and 1285 cm^{-1} (Found: C, 55.6; H, 7.8; N, 2.9. Calcd. for $C_{22}H_{37}NO_3Si_4$: C, 55.5; H, 7.7; N, 2.9%). For ^1H NMR spectral data see Table 2. (b) $(Me_3Si)_2C$-

$(SiMe_2OPr$-i$)(SiPh_2Me)$ (0.40 g, 47%), m.p. 112° C. (Found: C, 63.6; H, 9.4. Calcd. for $C_{25}H_{44}OSi_4$: C, 63.5, H, 9.3%). For ^1H NMR spectral data see Table 2. (c) A solid (0.031 g, ca. 4%) m.p. 250—258° C, the ^1H NMR spectrum of which showed resonances consistent with the formula $(Me_3Si)_3CSiPh_2OPr$-i, viz. δ 0.30 (s, 27H, $SiMe_3$), 1.06 (d, 6H, CMe_2), 4.14 (sept, 1H, CH), 7—8 ppm (m, 10H, aryl H), but with two additional peaks at δ 0.44 ppm (s, 3H) and 0.33 (s, ca. 6H) which could not be assigned, and which could be due to impurities. (Found: C, 62.7; H, 9.3. Calcd. for $C_{25}H_{44}OSi$: C, 63.5; H, 9.3%).

(vi) Reaction of $TsiSiPh_2I$ with $AgNO_3$ — t-BuOH. A solution of $TsiSiPh_2I$ (0.50 g, 0.92 mmol) and $AgNO_3$ (0.23 g, 1.3 mmol) in t-BuOH (25 cm^3) was refluxed for 15 min. Work-up as under (ii) left a solid residue, which was resolved by preparative TLC (SiO_2, hexane) into two components: (a) $(Me_3Si)_2C(SiMe_2ONO_2)(SiPh_2Me)$ (0.18 g, 41%), with physical constants as described under (iv); (b) an additional solid (0.20 g) which was shown by GLC (1% OV_1 on 100—120 mesh Chromosorb G at 275° C) to contain at least 3 components, none of which seemed from the ^1H NMR spectrum of the mixture to be the expected $(Me_3Si)_2C(SiMe_2OBu^t)(SiPh_2Me)$.

(vii) Reaction of $TsiSiMe_2I$ with $Hg(OAc)_2$ — AcOH. A mixture of $TsiSiMe_2I$ (42 mg, 0.10 mmol), yellow HgO (70 mg, 3.2 mmol) and AcOH (5 cm^3) was refluxed for 2 h. Work-up as in (ii) left a solid (which sublimed without melting), which was shown by its ^1H NMR spectrum (Table 2) and analysis (Found: 48.2; H, 10.4. Calcd. for $C_{14}H_{36}O_2Si_4$: C, 48.2; H, 10.4%) to be $(Me_3Si)_3SiMe_2OAc$.

(viii) Reaction of $TsiSiMe_2I$ with $AgNO_3$ — $LiNO_3$ — $MeOCH_2CH_2OMe$. A mixture of $TsiSiMe_2I$ (0.20 g), $AgNO_3$ (0.10 g), $LiNO_3$ (0.20 mg) and glyme (10 cm^3) was refluxed for 1 h. Work-up as in (ii) gave a residue, which was triturated with a little MeOH and then dried, to give $TsiSiMe_2ONO_2$ (0.16 g, 94%), m.p. 286—288° C (Found: C, 41.2; H, 9.5. Calcd. for $C_{12}H_{33}O_3NSi_4$: C, 41.0; H, 9.5%). The ^1H NMR spectrum was as shown in Table 2.

(ix) Reaction of $TsiSiMe_2I$ with trifluoroacetic acid. Trifluoroacetic acid (10 cm^3) was added to a mixture of $TsiSiMe_2I$ (40 mg) and Ag_2O (40 mg), and the solution was heated under reflux. Silver iodide was precipitated very rapidly, but the mixture was heated under reflux for 1 h. The usual hexane extraction and work-up (without any purification procedure) gave $TsiSiMe_2O_2CCF_3$, m.p. 280°C, ν(CO) 1765 cm^{-1} (Found: C, 41.8; H, 8.1. Calcd. for $C_{14}H_{33}O_2F_3Si_4$: C, 41.75; H, 8.3%). The ^1H NMR spectral data are shown in Table 2.

(x) Reaction of $TsiSiEt_2I$ with AgO_2CCF_3 — CF_3CO_2H. A mixture of silver oxide (40 mg) and $TsiSiEt_2I$ (40 mg) was dissolved in CF_3CO_2H (5 ml) at room temperature with stirring. After 5 min hexane was added, and the usual work-up gave a solid residue which was identified from its ^1H NMR spectrum as a mixture of $(Me_3Si)_2C(SiMe_2O_2CCF_3)(SiEt_2Me)$ and $TsiSiEt_2O_2CCF_3$ in 3/1 ratio [Found (for mixture): C, 44.6; H, 8.7. Calcd. for $C_{16}H_{37}O_2F_3Si_4$: C, 44.6; H, 8.7%].

Determination of Product Composition by ^1H NMR Spectroscopy

The results listed in Table 1 were obtained in the following way.

The $TsiSiR_2X$ compound and any salt(s), in the amounts specified in Table 1, were placed in a 25 cm^3 flask fitted with a magnetic stirrer and 10 cm^3 of the appropriate solvent was added. A reflux condenser was attached, the flask was placed in a bath preheated to a suitable temperature, and stirring was begun. The reactions involving $TsiSiPh_2I$ were all carried out at the reflux temperature, while the others were conducted with heating in a bath maintained at 90°C. [This means that in some cases the reaction was at this temperature (e.g. with AcOH as solvent) while on others (e.g. in MeOH or CF_3CO_2H) it was at the boiling point.] After the specified time, the contents of the flask were cooled, hexane was added, and the solution was decanted from any precipitated salts (and filtered if necessary), combined with the hexane washings of the precipitate, and shaken several times with water. The organic layer was dried ($MgSO_4$), and the solvent evaporated off. The residual solid was then dissolved in the minimum amount of CCl_4 containing 5% CH_2Cl_2, and the ^1H NMR spectrum was recorded.

Suitable sets of peaks were then chosen for comparison of peak heights or integration ratios. (In a set of 10 typical analyses no significant difference was found between product ratios derived from integrations and those from peak heights.) As far as possible analogous peaks were compared; e.g., $SiOMe$ with $SiOCHMe_2$, $SiOCMe_3$, or SiO_2CMe, and $SiMe_2ONO_2$ with $SiMe_2OMe$. In some cases comparisons of several peaks were made and the ratios averaged.

For the reaction of $TsiSiEt_2I$ with AgOAc — AcOH, the appearance of two clearly resolved SiO_2CMe peaks (at ca. δ 2.0 ppm) of equal heights showed that the rearranged and unrearranged products had been formed in approximately equal amounts. For the reaction of TsiSiPhMeI with AgOAc — AcOH, the 25/91 intensity ratio for $SiMe_2OAc$ protons (δ 0.66 ppm) compared with total $SiMe_3$ protons (δ 0.34 ppm) indicated a rearranged/unrearranged product ratio of 76/24. Thus the larger SiO_2CMe peak could be attributed to $SiMe_2OAc$ (δ 2.14 ppm) and the smaller to SiPhMeOAc (δ 2.19 ppm), and the heights of these peaks were in the ratio 78/22.

Estimation of the relative amounts of rearranged and unrearranged trifluoroacetates from $TsiSiEt_2I$ and $TsiSiEt_2H$ was more complex and less accurate. The $SiMe_2O_2CCF_3$ peak (δ ca. 0.62 ppm) was identified and its intensity, $6x$, noted. The total intensity of all the SiMe signals of $(Me_3Si)_2C(SiMe_2O_2CCF_3)(SiEt_2Me)$ was then taken to be $21x$, the total intensity, y, of all SiMe signals from the product mixture was noted, and the contribution, z, from the unrearranged product calculated as $y - 21x$. The proportion of rearranged product was then given by $x/[x + (z/27)]$. The analogous procedure was used for TsiSiEtMeI reactions. The product proportions determined in this way are subject to a rather large uncertainty, and the values for Rcts. 66—71 in Table 1 should be regarded as reliable only to within about ±10.

The $Hg(OAc)_2$ — AcOH and AgO_2CCF_3 — CF_3CO_2H were made by dissolving HgO or Ag_2O in the appropriate acid, a little water thus being introduced.

Relative reactivities of $TsiSiMe_2I$ and $TsiSiPh_2I$

(a) The appropriate silicon iodide (0.10 mmol) was dissolved in MeOH (15 cm^3), and methanol (5 cm^3) containing $AgNO_3$ (0.12 mmol) was added at room temperature (ca. 21°C) with rapid stirring. After 2 min the mixture was added to water.

Hexane extraction, followed by washing and drying of the extract, and evaporation of the solvent left a residue, which was shown by ^{1}H NMR spectroscopy to contain the methoxide $TsiSiR_2OMe$ and starting material $TsiSiR_2I$ in 20/80 ratio for R = Me and 16/84 ratio for R = Ph. (b) To a refluxing solution of $TsiSiPh_2I$ (0.10 mmol) and $TsiSiMe_2I$ (0.10 mmol) in MeOH (10 cm^3) was added finely ground $AgNO_3$ (0.13 mmol). After 10 min the mixture was added to water, and the usual work-up and analysis by ^{1}H NMR spectroscopy showed that $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$ and $TsiSiMe_2OMe$ had been produced in a ratio of ca. 43/57.

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