Predominance of Unrearranged Products in the Reactions of the Iodide $(Me_3Si)_3CSi(CD_3)_2I$ with Silver Salts, and its Mechanistic Implications

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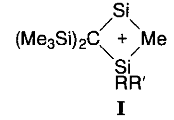
In the title reactions, unrearranged products $(Me_3Si)_3C[Si(CD_3)_2Y]$ usually predominate over their rearranged isomers $(Me_3Si)_2C[Si(CD_3)_2Me](SiMe_2Y)$, revealing the inadequacy of the simplest mechanistic picture in which the two bridged silicon centres in a methyl-bridged cationic intermediate are equally available for attachment of a nucleophile.

Reactions of organosilicon iodides $(Me_3Si)_3CSiRR'I$ with electrophiles such as silver salts, iodine monochloride or trifluoroacetic acid have been shown to give rearranged products of the type $(Me_3Si)_2C(SiRR'Me)(SiMe_2Y)$, sometimes virtually exclusively (*e.g.* when R = R′ = Ph) and sometimes together with the unrearranged isomer $(Me_3Si)_3CSiMe_2Y$ (*e.g.* when R = R′ = Et).[1] This was attributed to the formation of a methyl-bridged cation of type **I**, which could be attacked by a nucleophile either at the α-Si to give the unrearranged product or at the γ-Si to give the rearranged isomer.[1,2] Since the proportion of rearranged product increased within a range of related iodides $(Me_3Si)_3CSiRR'I$ in line with the increasing size of R and R′, it was suggested that within such a series the extent of rearrangement is determined largely by the relative degrees of steric hindrance at the α- and γ-Si centres in **I**, but it became clear later that this was not the only relevant factor.[3–6]†

In order to gain clear information about the effects of other factors on the proportion of rearranged products from various reactions, it is necessary to study a system in which the steric hindrance at the α- and γ-centres is identical. To this end we have synthesized the labelled iodide $(Me_3Si)_3CSi(CD_3)_2I$ **1** by the method shown in Scheme 1, and examined its reactions with silver salts in a range of non-hydroxylic solvents.

A mixture of **1** (10 mg, 0.024 mmol) and AgY (usually 10 mg, an excess) in the relevant solvent (2.0 ml) was stirred at room temperature for the time indicated in Table 1. The solution was decanted from the AgI and evaporated under reduced pressure and the residue taken up in $CDCl_3$ for the recording of the ^1H NMR spectrum (300 MHz). The percentage P_R of rearranged product was determined from the ratio of the carefully measured integral of the signal from the $SiMe_2$ protons to that from the $(Me_3Si)_3C$ protons. The possible proportional errors are large for small values of P_R (see Table 1), but any uncertainties do not affect the validity of the discussion below. The results, which were very surprising, are shown in Table 1, and the main features, with comments, are as follows.

(*a*) In very few cases did the value of P_R come close to the 50% expected on the simple picture in which a free bridged ion **I** is attacked by a free anion Y^-; in about two-thirds of the cases P_R was < 20%. On the other hand, in the reactions with AgO_3SCF_3 and AgO_2CCF_3 in CH_2Cl_2, values of P_R significantly > 50% were observed.



I

Scheme 1 *Reagents*: i, $LiAlH_4$ in Et_2O; ii, CD_3Li in Et_2O; iii, ICl in CCl_4

(*b*) The value of P_R for reaction of a given AgY was found to depend markedly on the solvent. In general it was substantially higher for reactions in CH_2Cl_2 than for those in other solvents, and was especially low in Et_2O. We had previously observed that the proportion of rearranged product in reactions of various iodides $(Me_3Si)_3CSiRR'I$ with $AgBF_4$ could be significantly different in CH_2Cl_2 and Et_2O, and had tentatively associated this with complexation of the liberated BF_3 in the latter,[6] but it is evidently a more general phenomenon; we cannot at present account for the relative effectiveness of CH_2Cl_2 in promoting rearrangement, but we note that Lambert and coworkers suggested that in this medium a silylium ion R_3Si^+ might be stabilized as a chloronium ion complex $R_3Si{-}Cl^+CH_2Cl$.[7] The fact that compounds of the type $(Me_3Si)_3CSi(CD_3)_2Y$ can be obtained with little contamination by the rearranged isomer when the reaction is carried out in Et_2O is important, since it means that such compounds become available for studies of the extent of rearrangement in their reactions, especially solvolysis.

(*c*) In reactions in which some of the iodide remained after the allotted time it was found to be partly rearranged. It is likely that values of P_R of > 50% noted for the reactions with AgO_3SCF_3 and AgO_2CCF_3 arise by formation of some of the products from the rearranged iodide. We tentatively suggest that the ion **I** can sometimes recapture I^- from the newly formed molecule of AgI

Table 1 Percentage, P_R of rearranged product $(Me_3Si)_2C[Si(CD_3)_2Me](SiMe_2Y)$[a] formed in the reactions of **1** with AgY at room temperature in various solvents.[b] The estimated uncertainty in P_R varies from ±3 at P_R = 5 to *ca.* ±7 at P_R = 50

	Y									
	ClO_4		O_3SCF_3		NO_3		BF_4		O_2CCF_3[c]	
Solvent	*t*/h	P_R	*t*/h	P_R	*t*/h	P_R	*t*/h	P_R	*t*/h	P_R
Et_2O	2	5	2	6	420	3	0.5	5	2	8
CH_2Cl_2	1.5	28	0.5[d]	50–60	3[e]	20–30	0.5	32–47	2	66–80
n-C_5H_{12}	30	16	2	30	20	5	1	17	3	28
C_6H_6	30	11	18	9	30	5	18	35	2	32
MeCN	30	11	24	14	18	2	18	7	18[f]	14
$CHCl_3$	1.5	12	1.5	22	1.5	8	1.5	20	1.5	31
CCl_4	2[g]	8	2	31	2	7	2	12	2	40

[a] From $AgBF_4$ the products were $(Me_3Si)_3CSi(CD_3)_2F$ and $(Me_3Si)_2C[Si(CD_3)_2Me](SiMe_2F)$. [b] In most cases, small amounts of hydroxides (total *ca.* 5–8%) were formed; slightly larger amounts were formed from $AgClO_4$ because this was used as the hydrate. [c] Rearranged and unrearranged fluorides (total 10–25%) also formed. [d] In two reactions stopped at 90% completion, residual iodide was > 80% rearranged. [e] Reaction only 20–25% complete; residual iodide *ca.* 15–20% rearranged. [f] Reaction 85% complete; residual iodide 12% rearranged. [f] Some 70% of iodide remained, *ca.* 15–20% of it rearranged. [g] Reaction 70% complete; residual iodide *ca.* 10% rearranged.

before the latter leaves to become part of an inactive cluster or precipitate. No rearrangement of **1** occurred when its solution in CH_2Cl_2 was stirred for 2 h over newly precipitated AgI.

(*d*) The reactions of AgO_2CCF_3 showed another surprising feature, namely the formation of significant amounts of the fluoride $(Me_3Si)_3CSi(CD_3)_2F$ and its rearranged isomer. It seems that the intermediate cation can abstract F^- from $CF_3CO_2^-$, reflecting the great affinity of silicon for fluorine.

(*e*) In the reactions of **1** in Et_2O, significant amounts of the ethoxides $(Me_3Si)_3C[Si(CD_3)_2OEt]$ and $(Me_3Si)_2C[Si(CD_3)_2Me](SiMe_2OEt)$ were formed; the combined yield was usually *ca.* 3–8%, but in the reaction with AgO_2CCF_3 it was *ca.* 35% and the ratio of unrearranged to rearranged ethoxides was *ca.* 65 : 35. It seems that the intermediate cation can cleave the Et_2O, presumably by initial formation of an oxonium ion species analogous to the ion $[Me_3SiOEt_2]^+$ recently observed by Sakurai *et al.*[8]

It is evident that in the reactions of **1** with silver salts there is usually a clear preference for formation of unrearranged products. If, as we have previously assumed, the bridged ion **I** with $R = R' = CD_3$ is formed directly from **1**, the preference for attachment of Y^- at the α-Si centre could be attributed to the presence near that centre of Y^- released from an attacking $[Ag^+\cdots Y^-]$ ion pair (or an ion cluster). [It is significant that in the reaction with AgO_2CCF_3 in Et_2O the value of P_R for the trifluoroacetate (8%) is much lower than that for the ethoxide (35%), which is formed from solvent molecules freely available at both reaction sites.] There is, however, a possibility that an unbridged cation is initially formed and is sometimes captured by Y^- before undergoing conversion into the more stable bridged ion. (Such a route seems unlikely, however, when better bridging groups such as Ph,[9] $CH_2{=}CH$,[10] or OMe[11] are involved, since these are known to provide anchimeric assistance in a range of reactions, implying that the bridged ion is formed directly.) In view of the way in which the initially simple concept of the S_N1 reactions of alkyl halides [to which reactions of compounds $(Me_3Si)_3CSiRR'I$ and related species show some remarkably close analogies[12]] had to be progessively modified to include multistep sequences involving several intermediates,[13] it would not be surprising if the simple picture that seemed fairly satisfactory for reactions of $(Me_3Si)_3CSiRR'I$ and related species proved to be similarly inadequate as more information is accumulated. With this in mind we are examining further reactions of **1** and other $(Me_3Si)_3CSi(CD_3)_2X$ compounds.

We thank the SERC for support (*via* C. E.) and the King Saud University, Saudi Arabia, for the grant of sabbatical leave to A. I. A.

Received, 15th December 1994; Com. 4/07635D

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† In reactions of a range of compounds $(Me_3Si)_3CSiRR'I$ with $AgBF_4$ the proportion of rearranged fluoride varies widely with the electronic effects of R and R′ and with the solvent (S. M. Whittaker, PhD Thesis, University of Salford, 1993, and P. D. Lickiss, personal communication).

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