1,3-Migration of a Phenyl Group *via* a Silicocation

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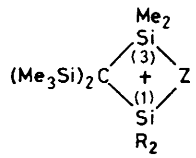
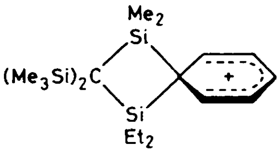
The reaction of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$ with $AgBF_4$ in Et_2O has been shown to give a *ca.* 2:3 ratio of the unrearranged $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$ and the rearranged $(Me_3Si)_2C(SiMe_2F)(SiEt_2Ph)$; the reaction is thought to proceed *via* a Ph-bridged cation (II).

Reactions of compounds of the type $(Me_3Si)_3CSiR_2I$ with various electrophiles, such as Ag^{I} or Hg^{II} salts, ICl, and CF_3CO_2H, are thought to involve rate-determining formation of cations of type (I, Z = Me), which can be attacked by a nucleophile Y^- at either the Si(1) or Si(3) centre, so that rearranged products $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$ can be formed either exclusively or along with unrearranged $(Me_3Si)_3CSiR_2Y$.[1,2]

Recently it was shown that similar migration of the vinyl group can occur in the reactions of $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiEt_2I)$ with silver salts, apparently *via* the cation (I, Z = $CH_2{=}CH_2$, R = Et).[3] The bridging in cations of type (I) bears some analogy both to that in the dimers $(AlMe_2Z)_2$[4] and to 1,2-bridging in carbocations.[5] 1,3-Migration of Me groups between carbon centres in carbocations is unknown, but that of vinyl groups was recently observed[6] following the demonstration of the related migration between silicon centres. The phenyl group bridges effectively in the dimer $(AlMe_2Ph)_2$),[4] but although it readily takes part in 1,2-bridging (and rearrangements) within carbocations, no corresponding 1,3-bridging (or rearrangement) is known. It was thus of interest to see whether bridged ions of type (I, Z = Ph) could be formed.

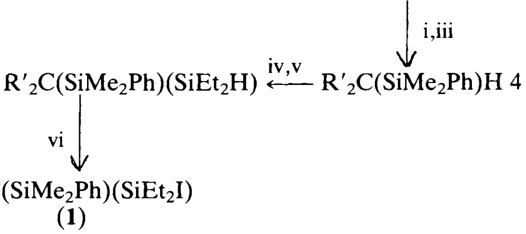


(I)



(II)

The compound $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$ (**1**) was made by the route shown in Scheme 1. A mixture of (**1**) (0.8 mmol), $AgBF_4$ (1.0 mmol), and Et_2O (20 cm^3) was stirred for 5 min at room temperature and the solvent was then evaporated and the residue extracted with pentane. The extract was filtered and evaporated, and the residue sublimed (110 °C at 0.02 Torr). Linked g.l.c.–mass spectrometry (OV-17 on Gas-chrome Q, 150—250 °C at 8 °C min^{-1}) revealed the presence of two components in a *ca.* 3:2 ratio, with the mass spectra of the components virtually identical and both consistent with the formulation $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$ (**2**), or an isomer of this, such as $(Me_3Si)_2C(SiMe_2F)(SiEt_2Ph)$ (**3**). The ^{19}F n.m.r. spectrum of the mixture in CCl_4–$CDCl_3$ showed a heptet (*J* 7.8 Hz) at −138.9 p.p.m. (relative to external $CFCl_3$), which was assigned to the Me_2FSi group of the rearranged product (**3**) [*cf.* δ_F − 143.0 p.p.m. for $(Me_3Si)_3CSiMe_2F$], and a quintet at −156.2 p.p.m., a shift identical with that for an authentic sample of (**2**) made by treatment of $(Me_3Si)_2C(SiMe_2Ph)(Li)$ with Et_2SiF_2. The ^{29}Si n.m.r. spectrum (in $CDCl_3$, relative to $SiMe_4$) showed the signals from (**2**) [δ −6.87 ($SiMe_2Ph$), −2.85 ($SiMe_3$), 26.59 (*J* 295 Hz,



$$\begin{tikzcd}
 & R'_2CCl_2 \arrow[r, "i,ii"] & R'_2C(SiMe_2Ph)Cl \arrow[d, "i,iii"] \\
 R'_2C(SiMe_2Ph)(SiEt_2H) \arrow[d, "vi"'] & & R'_2C(SiMe_2Ph)H\ 4 \arrow[ll, "iv,v"'] \\
 R'_2C(SiMe_2Ph)(SiEt_2I) & &
\end{tikzcd}$$

(**1**)

Scheme 1. R′ denotes Me_3Si throughout. *Reagents and conditions:* i, BuLi in tetrahydrofuran–Et_2O–hexane–pentane at −120 °C; ii, $Me_2PhSiCl$ at −110 °C, then allowed to warm to room temperature; iii, MeOH; iv, MeLi in tetrahydrofuran under reflux; v, Et_2SiHCl, reflux; vi, I_2 in CCl_4.

$SiEt_2F$)], along with those attributable to (**3**) [δ −2.92 ($SiMe_3$), −0.79 ($SiEt_2Ph$), 27.25 (*J* 285 Hz, $SiMe_2F$)].

The ^1H n.m.r. spectrum showed the following signals with the approximate integration ratios and assignments in parentheses: δ 0.20 (d, *J* 7.7 Hz) (1.9, $SiMe_2F$), 0.26 (s) (6.9, $SiMe_3$), 0.58 (s) (1.0, $Si\mathit{Me}_2Ph$), 0.60—1.44 (m) (5.2, $SiEt_2$); and 7.32—7.75 (m) (2.2, Ph); these are consistent with the presence of (**2**) and (**3**) in *ca.* 2:3 ratio. [The signals assigned to (**2**) were identical with those from the authentic sample.] An important feature of the spectrum is the integration ratio of *ca.* 2.2:1 for the signals from the protons of the Ph groups and those from the Me groups of $SiMe_2Ph$, since the ratio would be 5:6 if no migration of Ph groups took place. Expansion of the spectrum showed the ratio of the integrated signals from $Si\mathit{Me}_2Ph$ and $Si\mathit{Me}_2F$ to be *ca.* 1:4.4, reasonably consistent with 3:2 ratio of (**3**) to (**2**). The formation of more (**3**) than (**2**) is consistent with the somewhat greater steric hindrance at Si(1) than at Si(2) in the cation (I, Z = Ph, R = Et).[1]

Since 1,3-migration of a vinyl group from carbon to carbon *via* a carbocation has been observed[6] (following the demonstration of migration from silicon to silicon *via* a silicocation), it seems likely that 1,3-migration of a Ph group between carbon centres in a carbocation will also be observable for suitable substrates bearing bulky substituents at C(2). The magnitude of the anchimeric assistance that can be provided by a Ph group in the formation of the cations (I, Z = Ph, R = Me) is under investigation. The reactivity of the iodide $(PhMe_2Si)_3CSiMe_2I$ was judged to be consistent with assistance by a Ph group but not to provide unambiguous evidence for it.[7]

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