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

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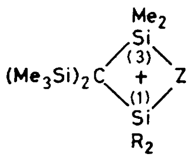
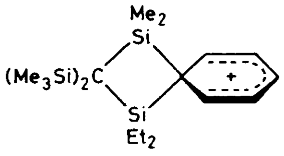
The reaction of $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2I)$ with $AgBF_4$ in Et_2O has been shown to give a *ca.* 2 : 3 ratio of the unrearranged $(Me_3Si)_2C(SiMe_2Ph)(SiEt_2F)$ and the rearranged $(Me_3Si)_2C(SiMe_2F)(SiEt_2Ph)$; the reaction is thought to proceed *via* a Ph-bridged cation (II).

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.

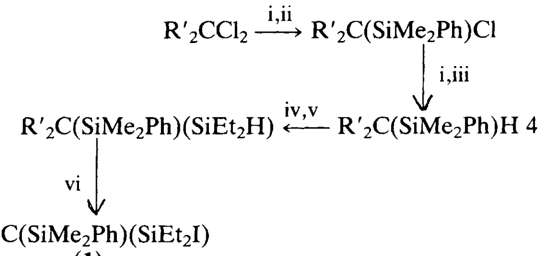


(I)



(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,



(**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.

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$SiEt_2F$)], 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]

We thank the S.E.R.C. for support, Dr. J. D. Smith for helpful discussions, the Royal Society for the award of a 1983 University Research Fellowship (to P. D. L.), Dr. A. G. Avent and Mr. B. D. Meadows for help with the n.m.r. spectra, Mr. A. M. Greenway and A. J. Adams for the mass spectra, and the Iraqi Ministry of Higher Education and the University of Basrah for the award of a postgraduate scholarship (to S. T. N.).

Received, 8th June 1987; Com. 783

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