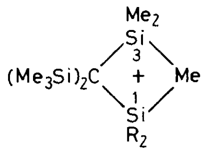
# 1,3-Methyl Migration from Germanium to Silicon in Reactions of $(Me_3Si)_2(Me_3Ge)C(SiMe_2Br)$ with Silver Salts

**Colin Eaborn* and Anil K. Saxena**

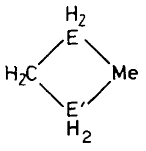
*School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.*

The germanium halide $(Me_3Si)_3C(GeMe_2Cl)$ reacts with silver salts AgY to give $(Me_3Si)_3C(GeMe_2Y)$, whereas the related silicon halide $(Me_3Si)_2(Me_3Ge)C(SiMe_2Br)$ gives a mixture of the rearranged and unrearranged products, $(Me_3Si)_3C(GeMe_2Y)$ and $(Me_3Si)_2(Me_3Ge)C(SiMe_2Y)$.

Various reactions of compounds of the type $(Me_3Si)_3C(SiR_2I)$, *e.g.* photolysis in MeOH,[1] reactions with electrophiles such as silver salts,[2] ICl,[3] and $CF_3CO_2H$,[2] and reactions with *m*-chloroperoxybenzoic acid in MeOH,[4] have been shown to give, wholly or partly, products of the type $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$ formed as a result of 1,3 Si to Si migration; *e.g.* reactions of $(Me_3Si)_3C(SiPh_2I)$ with silver salts AgY give exclusively the rearranged products $(Me_3Si)_2C(SiPh_2Me)(SiMe_2Y)$.[2] These reactions are thought to proceed through an Me-bridged cation of type (**1**), which can be attacked by a nucleophile at either Si(1) or the γ-centre Si(3) depending on the difference between the degrees of steric



(1)



(2)

hindrance at the two centres.[2] Calculations on model ions of type (**2**) indicate that such bridging is favourable for E = E′ = Si, but unfavourable for E = Si, E′ = C, and very unfavourable for E = E′ = C.[5] It seemed to us possible, however, that bridged species based on the skeleton shown in (**2**) might be accessible in cases in which E or E′ (or both) is a metal or metalloid other than Si, and so we examined the reactions of the germanium-containing species $(Me_3Si)_3C(GeMe_2Cl)$ and $(Me_3Si)_2(Me_3Ge)C(SiMe_2Br)$ with silver salts.

The germanium halide $(Me_3Si)_3C(GeMe_2Cl)$ was found to react with $AgBF_4$ in $CH_2Cl_2$ to give exclusively $(Me_3Si)_3C(GeMe_2F)$ [$\delta_H$ $(CDCl_3)$ 0.23 (27 H, s, $SiMe_3$) and 0.69 (6 H, d, GeMe); $\delta_F$ (in $CCl_4$ relative to $CFCl_3$) −176.1 p.p.m. (septet)]. Likewise, reactions with $AgO_2CCF_3$ in $CF_3CO_2H$ and $AgOSO_2CF_3$ in $CH_2Cl_2$ gave exclusively $(Me_3Si)_3C(GeMe_2O_2CCF_3)$ and $(Me_3Si)_3C(GeMe_2OSO_2CF_3)$, respectively.

In contrast, the silicon halide $(Me_3Si)_2(Me_3Ge)C(SiMe_2Br)$ was found to react with $AgBF_4$ in $CH_2Cl_2$ to give a 70:30 mixture of the unrearranged fluoride $(Me_3Si)_2(Me_3Ge)C(SiMe_2F)$ [$\delta_H$ $(CDCl_3)$ 0.21 (18 H, s, $SiMe_3$), 0.33 (6 H, d, $SiMe_2F$), and 0.41 (9 H, s, $GeMe_3$); $\delta_F$ ($CCl_4$, relative to $CFCl_3$) −144.4 p.p.m.] and the rearranged fluoride $(Me_3Si)_3C(GeMe_2F)$ [$\delta_H$ $(CDCl_3)$ 0.23 (27 H, s, $SiMe_3$) and 0.69 (6 H, d, $GeMe_2F$) (these two peaks were enhanced by the addition of an authentic sample); $\delta_F$ −176.1 p.p.m.]. Similarly, reactions with $AgO_2CCF_3$ in $CF_3CO_2H$ gave a product (with correct C and H analysis) which was shown by comparison of its n.m.r. spectrum with the spectra of authentic samples to be a *ca.* 65:35 mixture of $(Me_3Si)_3C(GeMe_2O_2CCF_3)$ and $(Me_3Si)_2(Me_3Ge)C(SiMe_2O_2CCF_3)$; linked g.l.c.–mass spectroscopy confirmed the presence of two components, in *ca.* 65:35 ratio, with very similar mass spectra, both showing the expected $[M - Me]^+$ ion at *m/z* 433. Reaction with $AgOSO_2CF_3$ gave the rearranged product $(Me_3Si)_3C(GeMe_2OSO_2CF_3)$ in >90% yield along with a small amount of the unrearranged $(Me_3Si)_2(Me_3Ge)C(SiMe_2OSO_2CF_3)$.

It seems likely that the reactions of the germanium halides with the silver salts do not involve cationic intermediates and so there is no assistance from Me-bridging. [The germanium halides $(Me_3Si)_3C(GeMe_2X)$ are much more reactive than the corresponding silicon halides; $(Me_3Si)_3C(SiMe_2Cl)$ does not react at all with silver salts under the conditions used.] In contrast, the reactions of the silicon halides require such assistance, and this can apparently be supplied by an Me group attached to a γ-Ge more readily than by one attached to a γ-Si atom. [The bromide $(Me_3Si)_3C(SiMe_2Br)$ reacts with silver salts only very slowly under the conditions used for $(Me_3Si)_2(Me_3Ge)C(SiMe_2Br)$.]

It is possible that 1,3-migration of alkyl and other groups between metal or metalloid centres within cationic intermediates in E–C–E′ systems will be found to be a fairly general phenomenon.

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