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Shuttling Germanium Atoms into Branched Polysilanes

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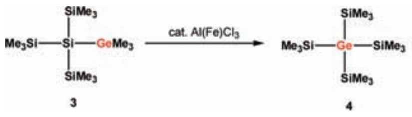
The Lewis acid-catalyzed rearrangement of oligosilanes, the silicon analogue of the well-known Wagner–Meerwein rearrangement of carbon chemistry, is a fundamentally important reaction in organosilicon chemistry.[1,2] The rearrangement is extensively used for the synthesis of highly branched open-chain,[1,2a] cyclic,[2b,3] and polycyclic[4] polysilanes from their linear isomers.[1–3] In a previous study, Blinka and West[3] reported that the introduction of a single ethyl group into an otherwise permethylated substrate leads to intra- and intermolecular scrambling of the ethyl substituent in the products. We have now investigated the fate of a germyl substituent in an otherwise methylated or silylated oligosilane substrate. We report that the germanium exhibits a surprising tendency to occupy central positions in the framework of the products and illustrate how the remarkable selectivity of this rearrangement, together with the oligosilyl potassium chemistry we have recently developed,[5] provides a rather unique and novel route to polygermanes.

The treatment of 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane with a catalytic amount of aluminum trichloride has been shown to give the branched isomer 1,1,3,3,4-pentakis(trimethylsilyl)pentamethylcyclopentasilane.[6] Surprisingly, treatment of the analogous substrate **1**, in which one trimethylsilyl substituent has been replaced with a trimethylgermyl substituent, cleanly yielded a 1:1 mixture of two compounds (**2a** and **2b**), both of which contain the same framework as the all-silicon isomerization product but feature the germanium atom at one of the two central nonmethylated positions (eq 1).

(1)

Lewis acid-catalyzed rearrangement reactions of silylgermanes are not without precedent. While we are not aware of a report detailing the pronounced shuttling of germanium to central positions, the 1,2-shift of a trimethylsilyl group was observed during the BCl$_3$-induced cleavage of a [tris(trimethylsilyl)germyl]methyl ether.[7] In a related reaction, Pannell and co-workers[8] found an AlCl$_3$-catalyzed 1,2-shift of the trimethylgermyl group in ClCH$_2$SiMe$_2$GeMe$_3$.

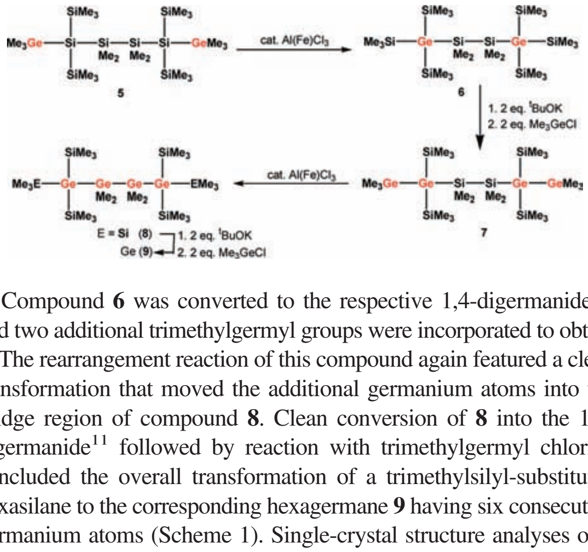
The unexpected move of the germanium atom in **1** to a central position was also observed when starting from **3**,[9] which cleanly proceeded to tetrakis(trimethylsilyl)germane (**4**),[10] a known precursor for the generation of tris(trimethylsilyl)germyl anions (eq 2).[11]



(2)

To demonstrate the synthetic complementarities of the rearrangement process and polygermyl anion formation, we devised and carried out the reaction sequence shown in Scheme 1. The terminally trimethylgermylated compound **5** was easily available utilizing recently reported chemistry.[12] Subjecting it to rearrangement conditions led cleanly to 1,2-bis[tris(trimethylsilyl)germyl]tetramethyldisilane (**6**)[11] (Scheme 1).

Scheme 1. Construction of a Linear Hexagermane by Repeated Introduction of Trimethylgermyl Groups Followed by Rearrangement



Compound **6** was converted to the respective 1,4-digermanide,[11] and two additional trimethylgermyl groups were incorporated to obtain **7**. The rearrangement reaction of this compound again featured a clean transformation that moved the additional germanium atoms into the bridge region of compound **8**. Clean conversion of **8** into the 1,4-digermanide[11] followed by reaction with trimethylgermyl chloride concluded the overall transformation of a trimethylsilyl-substituted hexasilane to the corresponding hexagermane **9** having six consecutive germanium atoms (Scheme 1). Single-crystal structure analyses of **6** and **8** (Figure 1 and Figure S-1 in the Supporting Information) showed that they are structurally closely related to 1,2-bis[tris(trimethylsilyl)silyl]tetramethyldisilane.[13]

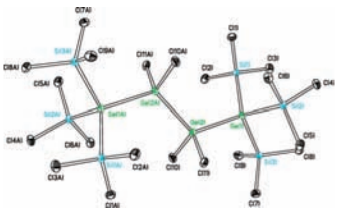


Figure 1. Thermal ellipsoid plot of **8** drawn at the 30% probability level.

Further insights into this intriguing rearrangement chemistry were obtained from quantum-mechanical computations of the transformation **3** → **4**, which is exothermic by 75.9 kJ mol^{-1} according to density functional theory computations[14] at the B3LYP/6-311+G(d,p) level. Similarly, it was found that the 1,2-digermatetrasilane (Me$_3$Ge)(Me$_3$Si)$_2$GeSiMe$_2$SiMe$_3$ (**10**) is less stable than its 2,3-digerma isomer (Me$_3$Si)$_3$GeGeMe$_2$SiMe$_3$ (**11**) by 30.1 kJ mol^{-1}. The latter result explains the thermodynamic preference for

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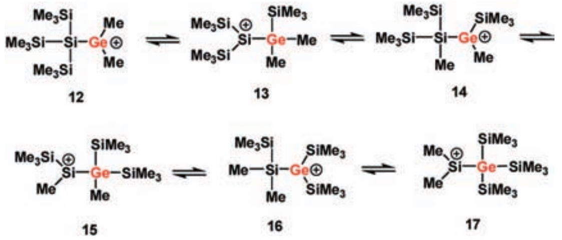
tetragermane **8** over its isomer **7**. The results of the computations suggest a considerable thermodynamic drive for the germanium atom to occupy the nonmethylated positions in germaoligosilanes, which is in agreement with previous qualitative considerations based on bond increments.[8] A plausible mechanistic scenario for the reaction **3** → **4** starts with the heterolytic bond cleavage of a relatively weak Ge−C bond at the periphery of germapolysilane **3** and formation of the germyl cation **12** along with methyltrichloroaluminate, $[MeAlCl_3]^-$. Germylium ion **12** is the starting point of a reaction cascade along which the isomeric cations **13**−**17** are formed in subsequent 1,2-trimethylsilyl and 1,2-methyl shifts (Scheme 2).[15] The product-forming step is methyl transfer from the aluminate to silyl cation **17**, which yields tetrasilylgermane **4**. A more detailed theoretical investigation revealed that the overall isomerization of germyl cation **12** to give silyl cation **17** is an exothermic process ($\Delta E = -44.0$ kJ mol^{-1}), although several steps of the reaction sequence are endothermic (Figure 2). The calculated barriers involved in this reaction cascade are all below 40 kJ mol^{-1}, and the highest point along the reaction coordinate is 47.1 kJ mol^{-1} above germylium ion **12**. Inspection of the G^{298} reaction coordinate (Figure 2), which includes entropy and thermal effects, reveals a similar situation, with the highest point being 50.1 kJ mol^{-1} above cation **12**. These relatively small activation barriers are in qualitative agreement with the fact that the reaction proceeds at 80 °C.

Scheme 2. Suggested Isomerization Cascade of Germylium Ion **12** to Silylium Ion **17**



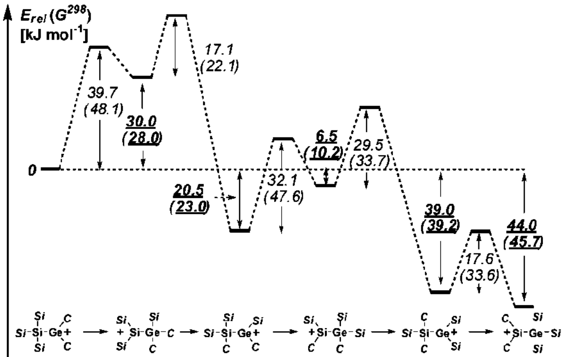


Figure 2. Reaction diagram for the isomerization **12** → **17** computed at the B3LYP/6-311+G(d,p) level. Ground-state energies, *E*, and Gibbs free energies at 298.15 K, G^{298} (in parentheses), relative to cation **12** are given in bold italic print and underlined, while activation energies $\Delta E^{\ddagger}$ and free energies $\Delta G^{\ddagger,298}$ for the forward reaction are given in italics. In the structures, *Si* stands for $SiMe_3$ and *C* for CH_3.

The thermodynamic driving force for the rearrangement **12** → **17** is the result of a subtle interplay between several factors that determine the relative thermodynamic stability of cations **12**−**17**: (i) There is a general energetic preference for germylium ions over silylium ions with the same substitution pattern. For example, Me_3Ge^+ is more stable than Me_3Si^+ by 38.8 kJ mol^{-1} at the B3LYP/6-311+G(d,p) level. (ii) An important contribution results from the different strengths (D_E) of the bonds, which are changed during the rearrangement steps (see Table S-4 in the Supporting Information). For example, purely on the basis of the different D_E values, the replacement of a Si−Si bond (D_E = 294 kJ mol^{-1}) in **12** by a Si−Ge bond (D_E = 281 kJ mol^{-1}) in **13** is connected with an energy loss of 13 kJ mol^{-1}, and the trading of a Ge−C bond (D_E = 305 kJ mol^{-1}) in cation **13** for a strong Si−C bond (D_E = 347 kJ mol^{-1}) in compound **14** results in an energy gain of 42 kJ mol^{-1}. (iii) Electronic effects, such as α-silyl, α-germyl, and in particular *β*-silyl effects, might be decisive for the relative stability order of cations **12**−**17**. The computed reaction energies of isodesmic methyl transfer reactions (eqs S1 and S2 in the Supporting Information) indicate that silylium ions are markedly stabilized by α-$SiMe_3$ and α-$GeMe_3$ groups compared with methyl groups (α-$SiMe_3$, 39.0 kJ mol^{-1}; α-$GeMe_3$, 36.5 kJ mol^{-1} (Table S-5, entries 1, 3)). For germylium ions, these α-effects are marginally larger (α-$SiMe_3$, 44.3 kJ mol^{-1}; α-$GeMe_3$, 43.9 kJ mol^{-1} (Table S-5, entries 2, 4)). More significant is the *β*-silyl effect, with computed substituent effects on the stability of silylium or germylium cations for the Si_2Me_5 group compared with the methyl group of 63.7 and 65.0 kJ mol^{-1} (Table S-5, entries 5, 6). These substituent effects are decisive, for example, in the rearrangement **16** → **17**. In this case, the stabilizing *β*-effect of three *β*-silyl groups in cation **17** overrules the effects (i) and (ii), which actually destabilize silylium ion **17** compared with germylium ion **16**.

The described rearrangement process that shuttles germanium atoms from trimethylgermyl groups to the core positions of silylgermanes offers unique possibilities for the straightforward synthesis of silylated and methylated polygermanes.

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Supporting Information Available: Experimental details; a CIF file; a technical description of the computations, including tables of the molecular structures at all determined stationary points, absolute energies, and calculated reaction energies of isodesmic reactions; and complete ref 14 (as SI ref 12). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) All computations were done using the *Gaussian 03* package: Frisch, M. J.; et al. *Gaussian 03*, revision D.01; Gaussian, Inc.: Pittsburgh, PA, 2003. For details, see the Supporting Information.
(15) The results of calculations (ref 14 on p S-30 in the Supporting Information) suggest that 1,3-methyl-bridged compounds do not play a significant role in this rearrangement.

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