CHEMISTRY LETTERS, pp. 1061-1064, 1994.

Formation of Strained Cyclic Azapolysila Compounds via N-(Azidosilyl)germanimines and Stannanimines

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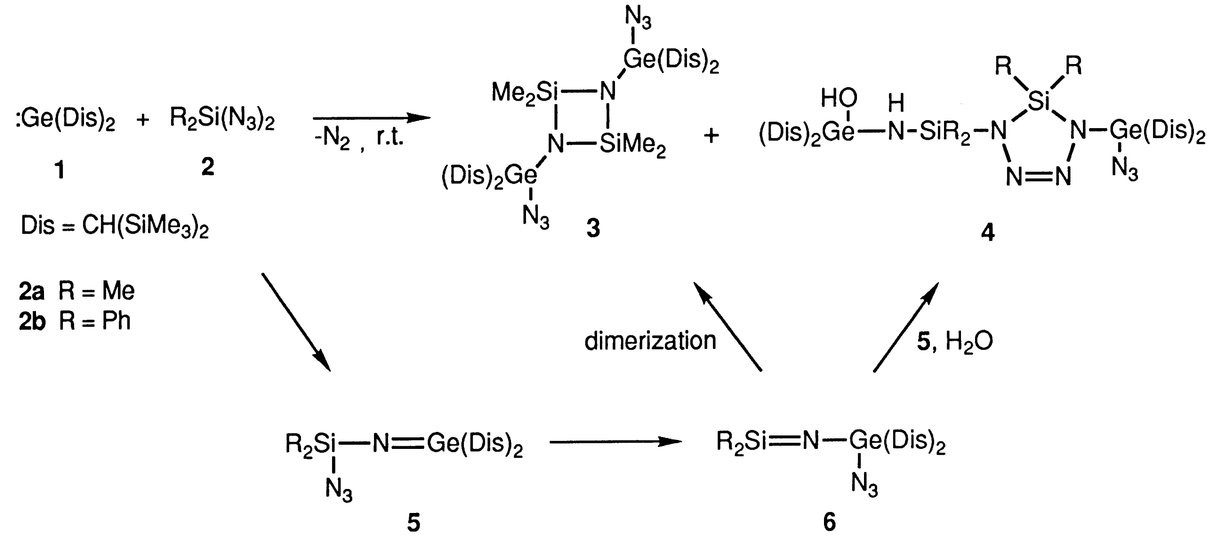
The reaction of bis[bis(trimethylsilyl)methyl]germylene (**1**) with 1,1-diazidosilanes gave siladihydrotetrazole derivative and cyclodisilazane. The structure of the latter has been confirmed by single-crystal X-ray diffraction. The similar reaction of **1** or bis[bis(trimethylsilyl)methyl]stannylene with 1,3-diazidohexamethyltrisilane furnished azatrisilacyclobutanes in quantitative yield respectively.

The chemistry of group 14 element-heteroatom double bonds is a currently intriguing subject. In particular, it is well known that germanimines (Ge=N) and stannanimines (Sn=N) are easily accessible by reactions of germylenes or stannylenes with azides.1) In a recent paper,2) we reported the synthesis of stable N-(azidosilyl)germanimines by the reaction of bis[bis(trimethylsilyl)methyl]germylene (**1**) with di-tert-butyl or dimesityldiazidosilane. Straightforwardly, reactions of methyl-substituted diazidomono-, di-, and trisilanes with **1** were studied. Herein, we report the remarkable migration ability of the azide group in N-(azidosilyl)germanimines and N-(azidosilyl)stannanimines, to give transient silanimine or cyclic azapolysila compounds.

Treatment of a deep yellow solution of **1** with 1 equiv. of dimethyldiazidosilane (**2a**) in hexane at room temperature resulted in rapid decolorization of the solution accompanied by evolution of nitrogen gas. After evaporation of the solvent, the residue was separated by preparative HPLC (gel permeation chromatography,



Scheme 1.

toluene) to afford cyclodisilazane **3** (23%) and siladihydrotetrazole derivative **4a** (27%) as major products.3) The structures were assigned on the basis of NMR spectroscopic data, in particular, the structure of **3** was confirmed by single-crystal X-ray diffraction (Fig. 1).4) The cyclodisilazane moiety is planar, and the Si-N bond distances of 1.755 and 1.769 Å are comparable to those of other cyclodisilazanes. Nevertheless, the Si-N-Si bond angle of 91.1° and the wide N-Si-N bond angle of 88.9° shorten the Si•••Si distance of 2.516 Å in ring system.5) The formation of **3** and **4** suggests a rearrangement of N-(azidosilyl)germanimine (**5**) to N-(azidogermyl)silaimine (**6**). It is undoubted that compound **3** arose from a dimerization of compound **6**, while the formation of **4a** was delivered from a [3+2] cycloaddition of **5** to **6** followed by subsequent hydrolysis in air. Similar rearrangements between group 14-heteroatom double bonds are rare. However, Wiberg and co-workers reported a germanimine-silanimine rearrangement with phenyl group as migration moiety.6) Interestingly, when **1** was allowed to react with diphenyldiazidosilane (**2b**) instead of **2a**, the only isolated product was **4b**,3) and neither the cyclodisilazane derivatives nor product derived from phenyl group migration could be observed. This result clearly demonstrates that the azide group has a higher migration ability than the phenyl group in the germanimine-silanimine rearrangement.

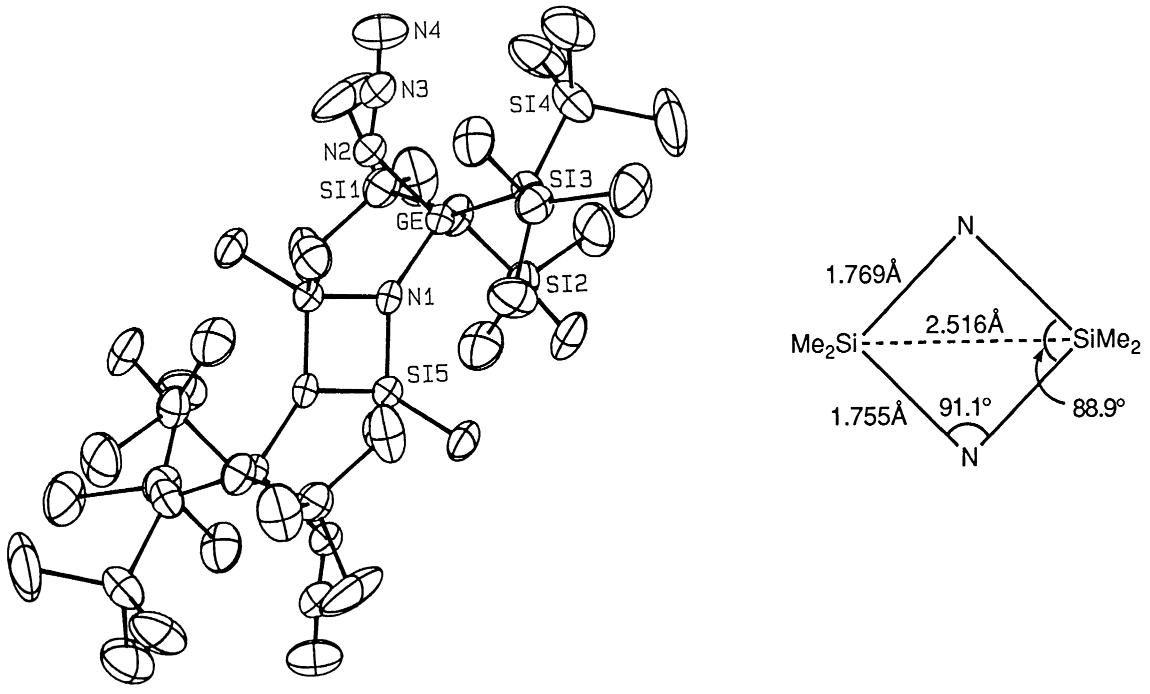
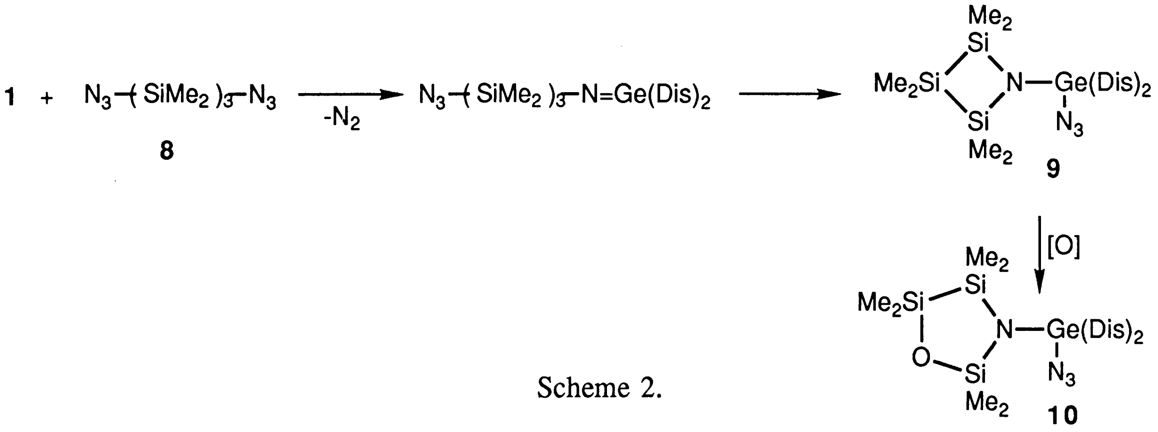


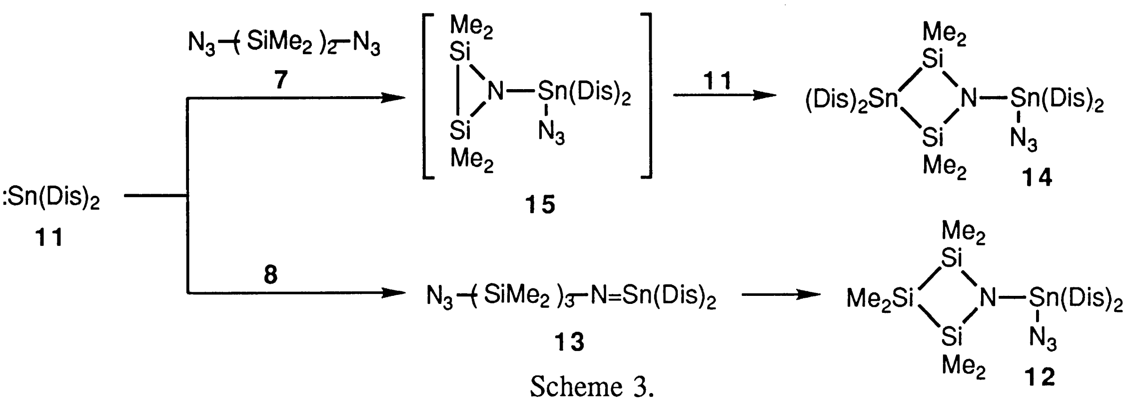
Fig. 1. Molecular structure of **3**.

To study the limit of aptitude for migration of azide group, compound **1** was treated with 1,2-diazidotetramethyldisilane (**7**). In appearance, decolorization with evolution of nitrogen gas is much the same as the reaction of **1** with **2**, however, NMR and HPLC method could not observe major products. In contrast, when **1** was allowed to react with 1,3-diazidohexamethyltrisilane (**8**),7) azatrisilacyclobutane (**9**) which is easily oxidized to siloxane **10** was obtained quantitatively (Scheme 2).8) In this connection it is noteworthy that highly strained azatrisilacyclobutane is easily prepared under mild conditions.



Scheme 2.

Moreover, bis[bis(trimethylsilyl)methyl]stannylene (**11**) as a higher homologue of **1** was treated with **8**. As expected, azatrisilacyclobutane (**12**) which arose from migration of an azide group in compound **13** was obtained quantitatively. However, the reaction of this stannylene with **7** gave four membered ring compound **14** (50%).[9] By employing 2 equiv. of the stannylene the yield of **14** increased to 90%. A reasonable first step of the pathway where **14** is produced is the formation of azadisilacyclopropane (**15**) by azide group migration. Assuming this intermediate, compound **14** is formed by an insertion of the stannylene into compound **15** (Scheme 3).



Scheme 3.

Thus, the azide group in (N-azidosilyl)germanimines and stannanimines exhibited a high migration ability, thereby transforming the unstable double bonds to highly strained ring systems.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan. We are grateful to Asai Germanium Research Institute for their gifts of chlorogermanes.

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3) **3**: Colorless crystals, mp 205-206 °C (hexane); ^{1}H NMR (400 MHz, C_6D_6) δ 0.38 (s, 36H), 0.41 (s, 36H), 0.48 (s, 4H), 0.80 (s, 12H); Anal. Found: C, 37.65; H, 8.61; N, 11.04%. Calcd for $C_{32}H_{88}N_8Si_{10}Ge_2$: C, 38.01; H, 8.77; N, 11.08%. **4a**: White solid, mp 128-130°C; ^{1}H NMR (400 MHz, C_6D_6) δ 0.01 (s, 2H), 0.31 (s, 36H), 0.36 (s, 18H), 0.41 (s, 18H), 0.47 (s, 6H), 0.51 (s, 2H), 0.54 (s, 6H), 1.40 (s, 1H, NH), 2.92 (s, 1H, OH); Anal. Found: C, 38.23; H, 8.93; N, 11.01%. Calcd for $C_{32}H_{90}N_8OSi_{10}Ge_2$: C, 37.37; H, 8.75; N, 10.89%. **4b**: White solid, mp 163-164 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 0.20 (s, 18H), 0.27 (s, 18H), 0.29 (s, 2H), 0.35 (s, 2H), 0.40 (s, 18H), 0.42 (s, 18H), 2.16 (s, 1H, NH), 2.73 (s, 1H, OH), 7.02-7.16 (m, 12H), 7.57-7.71 (m, 8H). X-ray analysis of **4b** has confirmed connections of atoms, however, a final good quality structure is not yet obtained.

4) Crystallograhic data for **3**: $C_{32}H_{88}N_8Si_{10}Ge_2$, triclinic, space group $P\bar{1}$, a=9.242(1)Å, b=11.020(2)Å, c=15.744(2)Å, α=109.68(1)°, β=93.72(1), γ=109.71(1), V=1392.2Å^3, ρcalcd=1.21g/cm^3, μ=13.1cm^{-1}, Z=2. The structure was solved from 2334 collected independent reflections ($2\theta<50°$, $|Fo^2|>3\sigma|Fo^2|$) measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω-2θ scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically to R=0.057 and Rw=0.070.

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7) Compounds **7** and **8** were synthesized from the corresponding chlorosilanes and NaN_3. **7**: Colorless oil, bp 75-78 °C / 20 mmHg; ^{1}H NMR (60MHz, $CDCl_3$) δ 0.08 (s, 12H). **8**: Colorless oil, bp 80-84 °C / 1 mmHg; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.32 (s, 6H), 0.45 (s, 12H).

8) **9**: White solid, decomp pt. 155 °C; ^{1}H NMR (400 MHz C_6D_6) δ 0.36 (s, 18H), 0.37 (s,6H), 0.41 (s, 18H), 0.43 (s, 2H), 0.62 (s, 12H); ^{13}C NMR (100 MHz C_6D_6) δ -7.80 (q), 4.67 (q), 4.79 (q), 5.67 (q), 15.97 (d); ^{29}Si NMR (79.5 MHz C_6D_6) δ -31.2, 0.3, 1.2, 9.9; Anal. Found: C, 38.94; H, 9.35; N, 8.13%. Calcd for $C_{20}H_{56}N_4Si_7Ge$: C, 38.63; H, 9.08; N, 9.01%. **10**: White solid, mp 98-100 °C; ^{1}H NMR (400 MHz C_6D_6) δ 0.32 (s, 1H), 0.34 (s, 18H), 0.37 (s, 6H), 0.38 (s, 9H), 0.41 (s, 9H), 0.42 (s, 1H), 0.50 (s, 3H), 0.52 (s, 3H), 0.53 (s, 3H), 0.55 (s, 3H); Anal. Found: C, 38.37; H, 8.97; N, 7.94%. Calcd for $C_{20}H_{56}N_4OSi_7Ge$: C, 37.68; H, 8.79; N, 8.79%.

9) **12**: White solid; ^{1}H NMR (400 MHz C_6D_6) δ 0.32 (s, 18H), 0.33 (s, 2H), 0.39 (s, 18H), 0.40 (s, 6H), 0.61 (s, 12H); Anal. Found: C, 36.16; H, 8.67; N, 8.46%. Calcd for $C_{20}H_{56}N_4Si_7Sn$: C,35.96; H, 8.45; N, 8.39%. **14**: Colorless crystals, ^{1}H NMR (400 MHz C_6D_6) δ 0.07 (s, 2H), 0.33 (s, 18H), 0.36 (s, 36H), 0.41 (s, 18H), 0.44 (s, 2H), 0.84 (s, 12H); Anal. Found: C, 36.60; H, 8.50; N, 5.32%. Calcd for $C_{32}H_{88}N_4Si_{10}Sn_2$: C,36.71; H, 8.41; N, 5.35%.

(Received March 3, 1994)