Formation and Reactions of the First Diarylgermanone Stable in Solution

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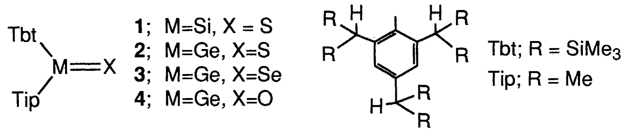
Treatment of an overcrowded diarylgermylene bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl and 2,4,6-triisopropylphenyl groups with tribenzylamine *N*-oxide gave the corresponding diarylgermanone **4**, the first example of a stable germanium–oxygen double-bond compound. Germanone **4** was stable in solution at room temperature for a short time and underwent [2+3]cycloaddition with mesitonitrile oxide, while in the absence of such a trapping reagent **4** gave two diastereomeric intramolecular cyclization products **8** and **9**.

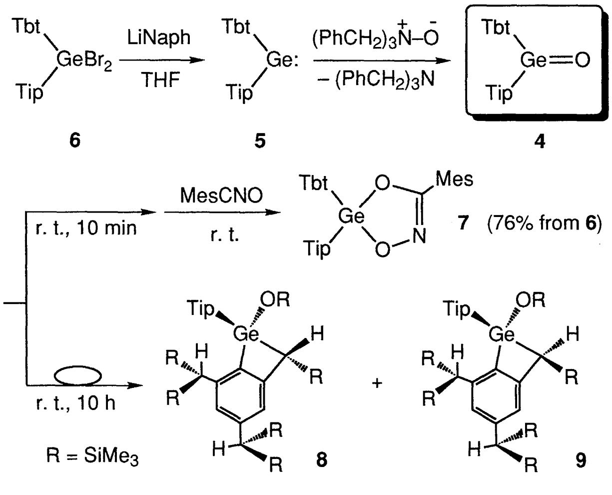
We have recently reported the syntheses and crystal structures of the first examples of silanethione **1**,[1] germanethione **2**,[2] and germaneselone **3**,[3] Tbt(Tip)M=X (**1**; M=Si, X=S, **2**; M=Ge, X=S, **3**; M=Ge, X=Se), the heavier congeners of carbonyl compounds kinetically stabilized by taking advantage of two steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,4,6-triisopropylphenyl (Tip).



By contrast, neither thermodynamically nor kinetically stabilized germanones, germanium–oxygen double-bond species, have been synthesized, though they have often been postulated as reactive intermediates.[4] In contrast to the successful isolation of stable germathiourea as a monomer by Veith *et al.* using a nitrogen-containing bicyclic ligand,[5] a recent approach to a thermodynamically stabilized germaurea using the same substituent resulted in the formation of a dioxadigermetane derivative, a head-to-tail dimer of the expected monomeric germaurea.[5a] This liability to dimerization is most likely due to the high polarity of the Ge=O bond, which has been predicted by ab initio calculation for dimethylgermanone.[6] Here, we wish to present the synthesis and reactions of kinetically stabilized germanone Tbt(Tip)Ge=O (**4**), a new member of a family of stable germanium–chalcogen double-bond compounds, *i. e.* germanium-containing "heavy ketones".

The germanone **4** was synthesized by the reaction of the corresponding overcrowded germylene Tbt(Tip)Ge: (**5**)[7] with tribenzylamine *N*-oxide as an oxygen source to the complete exclusion of any water because of the expected extremely high reactivity of a germanone toward water. Thus, a blue THF solution (8 ml) of the germylene **5**, prepared by the reductive debromination of Tbt(Tip)$GeBr_2$ (**6**; 242 mg, 0.222 mmol) with lithium naphthalenide (0.57 M in THF, 1.0 ml, 2.57 equiv.), was treated with tribenzylamine *N*-oxide (68.0 mg, 0.224 mmol) at room temperature and the solution was stirred for 10 min, during which time the blue color of the germylene **5** disappeared (Scheme 1).

Treatment of this solution with mesitonitrile oxide[8] (45.0 mg, 0.28 mmol) at room temperature followed by separation using GPLC and silica gel column chromatography afforded the 1,3,4,2-dioxazagermole derivative **7** (170 mg, 76%), a [2+3]-cycloadduct of **4** with mesitonitrile oxide, clearly showing that the germanone **4** was formed by this reaction and stable in solution at ambient temperature.



Scheme 1.

Although the above trapping experiment demonstrates the existence of the germanone **4** as a monomer in solution at least for 10 min, on standing for a long time (10 h) in solution in the absence of mesitonitrile oxide there were formed two diastereomeric isomers of intramolecular cyclization products, benzogermacyclobutenes **8** and **9**, in the ratio of 1:1 (30 and 29%, respectively), indicating the occurrence of the rearrangement of a trimethylsilyl group on the *o*-benzyl carbon of the Tbt group onto the central germanium atom (Scheme 1). This is in sharp contrast to the fact that the corresponding germanethione **2** synthesized from the germylene **5** and $1/8S_8$ under similar conditions gave no rearranged product.[2]

All the reaction products **7**–**9** described here showed satisfactory spectral and analytical data,[9] and the relative configurations of diastereomers **8** and **9** was finally determined by the X-ray diffraction analysis of **9** (Figure 1),[10] which represents the first structural analysis of a germacyclobutene ring skeleton. The deformation from the normal sp^2 configuration is larger on C(1) atom than on C(2) atom judging from the bond angles of Ge(1)-C(1)-C(2) [88.5(6)°] and C(1)-C(2)-C(7) [110.5(8)°]. While C(7) is on the same plane as the aromatic ring, Ge(1) is slightly apart from this plane (0.40 Å). The germacyclobutene ring in **9** is slightly folded with the dihedral angle between planes C(1)-C(2)-C(7) and C(1)-Ge(1)-C(7) being 14.8°, while only slight change is observed in the aromatic ring despite the strain due to the condensation with the four membered ring.

As for the intramolecular cyclization of the germanone **4**, the predominant migration of a trimethylsilyl group over an *o*-benzyl hydrogen atom suggests that the Si–C bond cleavage and

Si–O bond formation in the silyl-migration are more advantageous than the C–H bond cleavage and O–H bond formation from a viewpoint of bond energies [360 (C–Si), 464 (O–Si), 435 (C–H), and 142 (O–H) kJ mol^{-1}].[11]

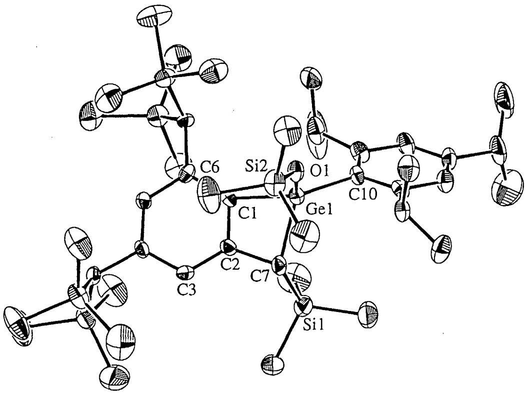
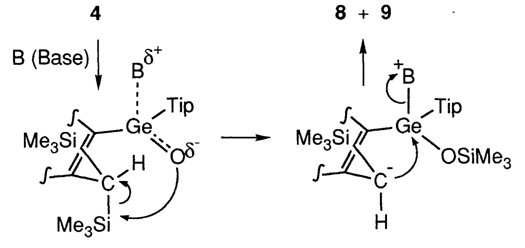


Figure 1. ORTEP drawing of **9** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (deg); Ge(1)-C(1) 1.980(8), Ge(1)-C(7) 1.987(8), Ge(1)-C(10) 1.967(8), Ge(1)-O(1) 1.772(5), C(1)-C(2) 1.40(1), C(2)-C(7) 1.52(1), C(7)-Si(1) 1.853(9), O(1)-Si(2) 1.633(6), C(1)-Ge(1)-C(7) 74.3(3), C(1)-Ge(1)-C(10) 134.7(4), C(1)-Ge(1)-O(1) 106.7(3), C(7)-Ge(1)-C(10) 119.1(3), C(7)-Ge(1)-O(1) 112.2(3), C(10)-Ge(1)-O(1) 106.4(3), Ge(1)-C(1)-C(2) 88.5(6), Ge(1)-C(1)-C(6) 148.7(7), C(2)-C(1)-C(6) 121.3(8), C(1)-C(2)-C(7) 110.5(8), C(1)-C(2)-C(3) 120.5(8), C(3)-C(2)-C(7) 128.9(8), Ge(1)-C(7)-C(2) 84.9(5), Ge(1)-C(7)-Si(1) 120.2(4), C(2)-C(7)-Si(1) 113.8(6), Ge(1)-O(1)-Si(2).

The most likely mechanism is shown in Scheme 2. Since the solution of the germanone **4** prepared in the present study necessarily contains tribenzylamine, it coordinates to the germanium atom to enhance the anionic character of the oxygen atom of the Ge=O group. The oxygen anion then undergoes a nucleophilic attack on the trimethylsilyl group of the Tbt group to give a relatively stable benzyl anion, which slowly cyclizes to afford compounds **8** and **9** in the ratio of approximately 1:1. When **8** and **9** were allowed to stand overnight in the presence of tribenzylamine in THF at room temperature, the starting materials were quantitatively recovered, indicating the absence of an equilibrium between the two diastereomers.



Scheme 2.

Thus, the germanone **4** here generated has shown reactivities different from those of the corresponding germanethione **2** and germaneselone **3** most likely owing to the large polarity of the Ge=O bond and the high affinity of an oxygen atom toward a silicon atom.

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8 All the isolated heavy ketones **1–3** afforded the corresponding [2+3]-cycloadducts with mesitonitrile oxide at room temperature in very high yields. See Refs. 1–3.

9 The spectral and analytical data for **7** were described as a representative as follows. Compound **7**:white crystals, mp 219-220 °C (CH_2Cl_2/EtOH), ^1H NMR ($CDCl_3$, 500 MHz, 340 K) δ -0.03 (s, 18H), 0.09 (s, 18H), 0.12 (s, 18H), 1.19 (d, *J*=6.9 Hz, 6H), 1.23 (d, *J*=6.9 Hz, 6H), 1.30 (d, *J*=6.9 Hz, 6H), 1.41 (s, 1H), 2.09 (s, 6H), 2.23 (s, 3H), 2.25 (br s, 2H), 2.87 (sept, *J*=6.9 Hz, 1H), 3.41 (br s, 2H), 6.48 (br s, 2H), 6.76 (s, 2H), 7.06 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, 340 K) δ 1.04 (q), 1.12 (q), 1.60 (q), 20.94 (q), 20.97(q), 23.78 (q), 23.81 (q), 25.40 (d), 26.69 (q), 29.30 (d), 29.38 (d), 31.34 (d), 34.43 (d), 34.56 (d), 122.81 (d), 123.87 (d), 126.44 (s), 128.60 (d), 129.08 (d), 129.57 (s), 134.16 (s), 137.99 (s×2), 138.36 (s), 146.59 (s), 150.97 (s×2), 152.01 (s), 153.79 (s). Found: C, 61.57; H, 9.12; N, 1.72%. Calcd for $C_{52}H_{93}GeNO_2Si_6 \bullet 0.5H_2O$: C, 61.56; H, 9.34; N, 1.38%. High-resolution FAB-MS: observed m/z 1006.5090 ($[M+H]^+$); calcd for $C_{52}H_{94}{}^{74}GeNO_2Si_6$ 1006.5112.

10 Crystal data for **9**: $C_{42}H_{82}GeOSi_6$; *MW* = 844.21; *monoclinic*; space group $P2_1/a$; a = 17.718(4), b = 14.243(3), c = 21.917(4) Å; β = 105.84(2)°; V = 5321(2) Å^3; Z = 4; D_c = 1.054 g cm^{-3}; μ(Mo Kα) = 7.25 cm^{-1}. $R(R_w)$ = 0.053(0.048). The intensity data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å), and the structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located in calculated positions. The final cycles of least-square refinement was based on 3026 observed reflections [$I > 3\sigma(I)$] and 451 variable parameters.

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