Oxidation and Thermolysis of a Stable Germaketenedithioacetal Derivative

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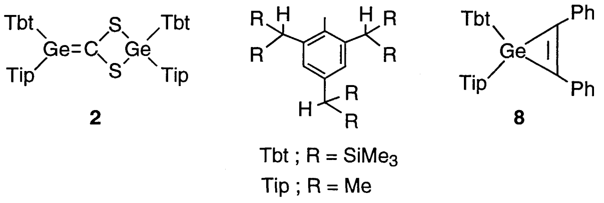
The reaction of germaketenedithioacetal **2** with oxygen gave 1,3,2-dithiagermetan-4-one **4** and dihydroxygermane **6**, suggesting the initial formation of a 1,2,3-dioxagermetane intermediate **3** followed by its dissociation into **4** and germanone **5**. Compound **2** underwent ready thermal dissociation into carbon disulfide and the corresponding germylene **1**, the efficient formation of which was evidenced by a trapping experiment with 2,3-dimethyl-1,3-butadiene.

Recently, much attention has been paid to the chemistry of multiple–bond compounds of heavier typical elements, and double–bond compounds between a heavier group 14 element and carbon such as silene[1] and germenes,[2] i. e. the heavy congeners of an alkene, are of current interest because of their unusual structure and reactivity. Since the first isolation of a silene by Brook et al.,[3] many examples of stable silenes have been synthesized and their structure and reactivity have been extensively explored. By contrast, the chemistry of their germanium analogues, i. e. germenes, has not been fully disclosed yet though some stable germenes[4] have already been synthesized and characterized. For example, there have been no detailed description on the reaction mechanism and products in the oxidation of a germene with oxygen in contrast to the reactions of silenes with oxygen which have been extensively studied.[3b]

Meanwhile, we have recently reported that treatment of overcrowded diarylgermylene[5] Tbt(Tip)Ge: (**1**; Tbt = 2,4,6-tri-[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl) with carbon disulfide afforded the first stable germaketenedithioacetal derivative **2**, one of a novel class of germanium–carbon double-bond systems.[6]



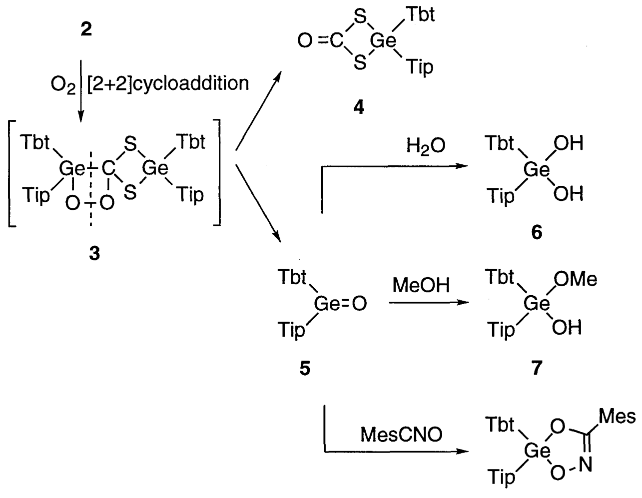
Scheme 1.

The germaketenedithioacetal **2** can survive even in the presence of excess amount of methanol in refluxing benzene, since it is effectively protected by the closely surrounding four bulky aryl groups, as indicated by crystallographic structure analysis. But, **2** showed a high reactivity toward oxygen, which is a smaller and more reactive reagent than methanol. Here, we wish to present our new findings on the oxidation and thermolysis of **2** which reveal the new reactivity of a germanium–carbon double bond.

When oxygen gas was bubbled into a THF solution (4.5 ml) of **2** (77.7 mg, 0.0449 mmol) in the presence of methanol (0.18 ml, 100eq.), the characteristic orange color of **2** disappeared, suggesting the reaction of **2** with oxygen. After the chromatographic separation, 1,3,2-dithiagermetan-4-one **4** (19.9 mg, 48%)[7] and dihydroxygermane **6** (8.4 mg, 22%) were obtained together with hydroxymethoxygermane **7** (11.4mg, 30%). Similarly, **2** obtained from the reaction (60 °C, 15 h in benzene-d_6) of carbon disulfide and germylene **1** generated in situ[5b] by the thermolysis of 2,3-diphenylgermirene **8** also gave **4** (22%)[8] and **6** (15%)[8] upon exposure to the open air.

The formation of the reaction products **4**, **6** and **7** from **2** can be interpreted in terms of an initial [2+2]cycloaddition of molecular oxygen with the germene unit of **2** leading to an intermediary spiro compound **3**, followed by the fission of the dioxagermetane ring of **3** into dithiagermetanone **4** and germanone **5**.[9] Although the germanone **5** is kinetically stabilized by Tbt and Tip groups, it is too reactive to be isolated, undergoing ready hydrolysis or methanolysis to give the final product **6** or **7** (Scheme 2).

The intermediacy of the germanone **5**[9] was also suggested by the fact that the treatment of a THF solution (5 ml) of **2** (54.8 mg, 0.0316 mmol) with oxygen gas followed by the addition of mesitonitrileoxide (25.3 mg, 5 eq.) resulted in the formation of an expected [2+3]cycloaddition product **9** (5.2 mg, 16%) together with **4** (22.4 mg, 77%) and **6** (13.2 mg, 49%).

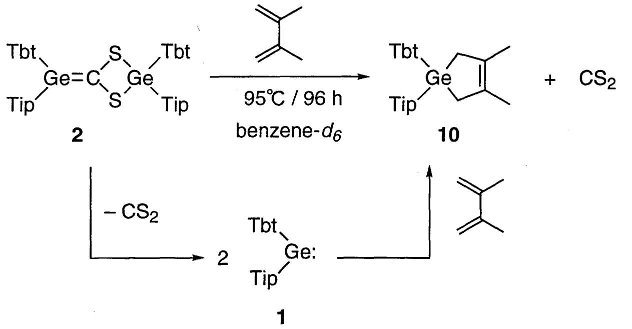


Scheme 2.

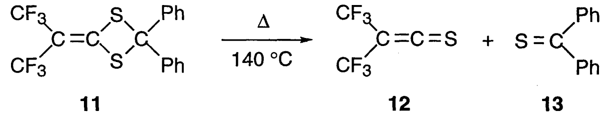
Similar oxidation of a silene (silicon-carbon double bond) with oxygen has already been reported by Brook et al.[3b] In this case an intermediary silanone, which arises from the ring fission of the initially formed 1,2,3-dioxasiletane species, undergoes a ready trimerization to afford the corresponding cyclic siloxane.[3b] The lack of such a polymerization product for **5** here described suggests the effectiveness of our steric protection system.[10]

We have also found that the germaketenedithioacetal **2** undergoes an interesting thermal decomposition. Thus, heating of a benzene-d_6 solution (0.6 ml) of **2** (88.6 mg, 0.0512 mmol) in a sealed tube at 95 °C for 96 h in the presence of 2,3-dimethyl-1,3-butadiene (0.06 ml, 10 eq.) [11] gave germacyclopentene **10** (85.3 mg, 0.0937 mmol) in 183% yield, which indicates the formation of two moles of germylene **1** in the thermolysis of **2** as shown in Scheme **3**.[12] The formation of carbon disulfide was substantiated by ^{13}C-NMR spectroscopy which showed a signal at 192.6 ppm due to CS_2.[13]

These results are worthy of noting as a new reaction mode of a germene and in sharp contrast to that in the thermolysis of a carbon analogue **11** having a similar skeleton which reportedly dissociates into the corresponding thioketene **12** and thioketone **13** (Scheme 4).[14]



Scheme 3.



Scheme 4.

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References and Notes

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7 The spectral and analytical data for **4** were described as a representative as follows. Compound **4**:white crystals, mp142-145°C (CH_2Cl_2/EtOH), ^{1}H NMR ($CDCl_3$, 500MHz, 300K) δ -0.04 (s, 18H), 0.05 (s, 18H), 0.06 (s, 18H), 1.16 (br s, 12H), 1.22 (d, J = 6.9 Hz, 6H), 1.34 (s, 1H), 2.37 (s, 1H), 2.87 (sept, J = 6.9 Hz, 1H), 2.97 (s, 1H), 3.07 (sept, J = 6.5 Hz, 2H), 6.34 (s, 1H), 6.52 (s, 1H), 7.06 (s, 2H); ^{13}C NMR ($CDCl_3$, 125MHz, 300K) δ 0.90 (q), 1.52 (q), 1.61 (q), 23.10 (q), 23.82 (q), 28.13 (q), 28.39 (q), 30.86 (d), 34.35 (d), 39.02 (d), 123.10 (d), 123.89 (d), 127.82 (s), 129.14 (d), 136.03 (s), 146.46 (s), 151.37 (s), 151.47 (s), 151.99 (s), 152.04 (s), 178.96 (s). Found: C, 56.05; H, 9.01; S; 6.58%. Calcd for $C_{43}H_{82}GeOS_2Si_6$: C, 56.10; H, 8.98; S; 6.99%.

8 The yields of **4** and **6** are based on the starting material **8**.

9 We have recently reported formation and reaction of the first stable germanone in solution derived from a kinetically stabilized germylene. N. Tokitoh, T. Matsumoto, and R. Okazaki, *Chem. Lett.*, **1995**, 1087.

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11 It was reported that stable germenes readily reacted with 2,3-dimethyl-1,3-butadiene to afford a [2+4]cycloadduct, germacyclohexene. This type of compound was not obtained in the reaction of **2** with 2,3-dimethyl-1,3-butadiene probably because the germene unit was closely surrounded by four bulky steric protection groups.

12 We have already reported that the reaction of diarylgermylene Tbt(Tip)Ge: with 2,3-dimethyl-1,3-butadiene gave the germacyclopentene **10**. See ref 5.

13 The chemical shift of CS_2 in benzene-d_6 was found to be δ_C = 192.6 by a separate experiment.

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