Unusual Oxidation Reaction of an Overcrowded Thiagermacyclohexene Derivative

Norihiro Tokitoh,[*##] Ibrahim El-Tantawy El-Sayed,[†,††] and Renji Okazaki[*#]
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033
[†]*Chemistry Department, Faculty of Science, El-Menoufeia University, Shebin, El Kom, Egypt*

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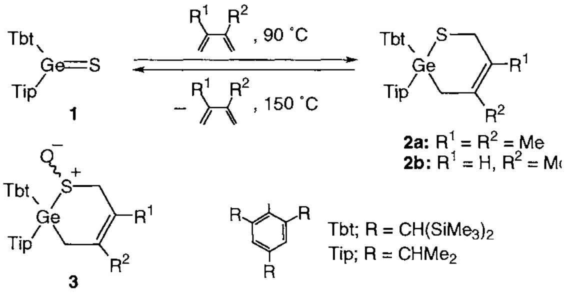
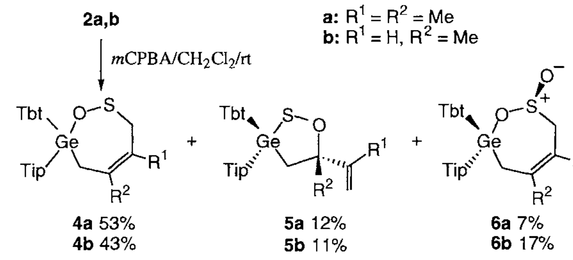
Oxidation of extremely overcrowded 1,2-thiagermacyclohex-4-ene derivatives with *m*-chloroperbenzoic acid resulted in competitive formation of the ring expanded 1,2,7-oxathiagermacyclohept-4-ene derivatives and the ring contracted 1,2,3-oxathiagermacyclopentane derivatives. The latter reaction products are found to isomerize into the former ones very slowly at room temperature not only in solution but also in the crystalline state.

Recently, we have succeeded in the synthesis and characterization of the first stable germanium–sulfur double bond compounds, *i. e.*, germanethione Tbt(Tip)Ge=S (**1**),[1] by taking advantage of an extremely bulky and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter).[2] During the course of our study on the reactions of this newly obtained germanethione **1**, we carried out a [2+4]-cycloaddition of **1** with 1,3-dienes to obtain the corresponding cycloadducts, 1,2-thiagermacyclohex-4-ene derivatives **2**, in high yields.[1,3]



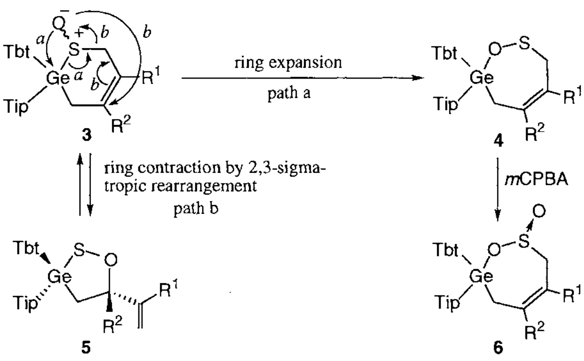
We have also found that cycloadducts **2** undergoes a facile thermal cycloreversion into the starting germanethione **1** and a diene.[3,4] These findings prompted us to examine the *S*-oxidation of **2**, which will provide us with a promising precursor for the unprecedented germasulfine, Tbt(Tip)Ge=S=O, via thermal cycloreversion. Interestingly, however, the oxidation of **2** with *m*-chloroperbenzoic acid (*m*CPBA) did not afford the expected *S*-oxide (**3**) but resulted in the formation of rearranged products. Here, we wish to present the outcome of the peracid oxidation of these overcrowded 1,2-thiagermacyclohex-4-ene derivatives **2** together with a unique crystalline-state isomerization of the resulting allyl-substituted 1,2,3-oxathiagermacyclopentane derivatives.

When the 4,5-dimethyl-1,2-thiagermacyclohex-4-ene **2a** (300 mg, 0.317 mmol) was treated with an equimolar amount of *m*CPBA (68.6 mg, 80% content, 0.317 mmol) in dichloromethane (20 ml) at room temperature for two days, not the expected *S*-oxide **3a** but 1,2,7-oxathiagermacyclohept-4-ene derivative **4a** was obtained as a major product (160 mg, 53%) together with small amounts of 1,2,3-oxathiagermolane derivative **5a** (36 mg, 12%) and cyclic germyl sulfinate **6a** (21 mg, 7%) after purification by GPLC with a recycling system and flash column chromatography (silica gel, hexane/CH_2Cl_2 = 15:1) (Scheme 1). In the oxidation of **2b**, *i. e.* the isoprene adduct of **1**, with *m*CPBA, similar reaction products, **4b**, **5b**, and **6b** were obtained in 43, 11, and 17%, respectively.[5] The molecular structures of **4a**, **5a**, and **6a** were definitively determined by X-ray crystallographic analysis, and the ORTEP drawings of **4a** and **5a** are shown in Figure 1.[6]



Scheme 1.

The isolated minor product **5a** was relatively labile and underwent slow isomerization at room temperature in solution giving the ring expansion product **4a** quantitatively after several days, while **4a** was stable even in a $CDCl_3$ solution at 150 °C (sealed tube) for a week.



Scheme 2.

The formation of the unexpected ring expansion product **4** and the ring contraction product **5** in the oxidation of **2** is most likely interpreted in terms of the high reactivity of initially formed *S*-oxide **3**. One of the possible isomers of **3** would most likely undergo ready ring expansion via Stevens-type rearrangement leading to **4** (Scheme 2, path a), while the other one would result in the ring contraction via 2,3-sigmatropic rearrangement to give **5** (Scheme 2, path b). The reaction path b is very similar to that of a well-known allyl sulfoxide–allyl sulfenate rearrangement.[7,8] Since this type of rearrangement is known to be reversible, the isomerization of **5** into **4** can also be explained in terms of the reverse process followed by the ring expansion reaction of the regenerated intermediary *S*-oxide **3**. Compound **6** probably results from the overoxidation of the ring expansion product **4**.

Furthermore, compound **5a** was found to undergo an in-

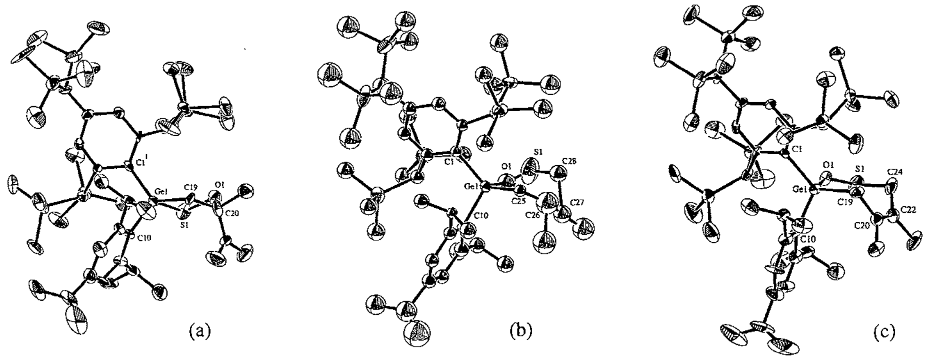
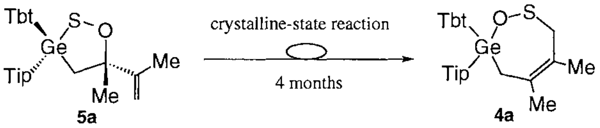


Figure 1. ORTEP drawings of (a) ring contraction product **5a**, (b) intermediary structure during the crystalline-state rearrangement of **5a** to **4a**, and (c) ring expansion product **4a**.

teresting isomerization into **4a** in the crystalline-state, the reaction rate of which was much slower than that in solution. Although the crystals left for 1 month at room temperature was found to contain both **5a** and **4a** (*ca.* 1:1) as judged by ^{1}H NMR, standing the crystals of **5a** for 4 months at room temperature resulted in the quantitative formation of **4a**.[9]



In order to confirm the progress of the isomerization from **5a** to **4a** in the crystalline-state, we examined the X-ray structural analysis of a single crystal of **5a** left for 1.5 month at room temperature.[10] It revealed that the single crystal still retained the crystallinity but showed a new lattice parameters fairly different from those of **5a**.[11] Structural analysis based on the intensity data collected at this stage indicated a severely disordered structure as depicted in Figure 1b,[11] which can be regarded as an intermediary structure on the way from **5a** to **4a**.

Although the complete monitoring of this crystalline-state reaction by crystallographic analysis failed due to the crystal crumbling, observations mentioned above suggest that the extreme steric bulkiness of the combination of Tbt and Tip groups on the germanium atom may provide a space large enough for the sequential rearrangement from the allyl sulfenate **5a** to the ring expansion product **4a** via unstable *S*-oxide **3a**.

Further investigation on the oxidation of these overcrowded 1,2-thiagermacyclohex-4-enes **2** using other oxidizing reagents is currently in progress.

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References and Notes

†† Postdoctoral Fellow of the Japan Society for the Promotion of Science (April, 1996–May, 1997) at the University of Tokyo.

\# Present address: Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University, 2-8-1 Mejirodai, Bunkyo-ku, Tokyo 112-8681.

\## Present address: Institute for Fundamental Research of Organic Chemistry, Kyushu Univesity, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581.

1 N. Tokitoh, T. Matsumoto, K. Manmaru, and R. Okazaki, *J. Am. Chem. Soc.*, **115**, 8855 (1993).

2 R. Okazaki, N. Tokitoh, and T. Matsumoto, in "Synthetic Methods of Organometallic and Inorganic Chemistry," ed by N. Auner and U. Klingebiel, Thieme, New York, (1996) Vol. 2, pp. 260-269.

3 T. Matsumoto, Ph. D. Thesis, The University of Tokyo, Tokyo, 1994.

4 N. Tokitoh and R. Okazaki, *Main Group Chemistry News,* 3, 4 (1995).

5 All the products here obtained showed satisfactory spectral and analytical data. Although the crude samples of both **5a** and **5b** were found to contain trace amounts of impurities most likely assignable to the corresponding diastereomers concerning the stereochemistry of their allyl substituents, they are too small to be identified. The reason why **5a** and **5b** were obtained predominantly over their diastereomers is not clear at present. The data for compound **4a** is listed as a representative as follows.
4a: white crystals (CH_2Cl_2/EtOH); mp: 210-213 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ - 0.36 (br s, 9H), -0.01 (br s, 18H), 0.06 (s, 9H), 0.21 (br s, 9H), 0.24 (br s, 9H), 0.78 (br s, 3H), 1.177 (d, J = 7.02 Hz, 6H), 1.182 (d, J = 7.02 Hz, 6H), 1.20 (br s, 3H), 1.25 (s, 1H), 1.77 (br s, 3H+1H), 2.05 (br s, 1H), 2.52 (br s, 1H), 2.68 (br s, 1H), 2.79 (sept, J = 7.02 Hz, 1H), 3.60 (br s, 1H), 3.87 (br s, 1H), 3.91 (br s, 1H), 5.10 (br s, 1H), 6.13-6.45 (br m, 2H), 6.87 (s, 1H), 7.05 (s, 1H). ^{13}C NMR ($CDCl_3$, 67.70 MHz): δ 0.94 (q), 1.13 (q) , 2.00 (q), 20.10 (q), 22.16 (q), 23.78 (q), 23.85 (q), 25.27 (q), 25.45 (q), 27.47 (d), 30.51 (d), 32.31 (d), 33.98 (d), 34.16 (d), 36.23 (t), 47.32 (t), 122.39 (s), 123.09 (s), 123.47 (d), 124.05 (d), 127.68 (d), 128.47 (d), 129.03 (s), 135.21 (s), 135.28 (s), 143.87 (s), 150.04 (s), 152.70 (s), 153.31 (s), 155.24 (s). FAB-MS: Calcd for [M-H]; 957.4432. observed; 957.4584. Anal. Found; C 59.57; H 9.57; S 3.40%. Calcd for $C_{48}H_{92}GeOSi_6S$. C, 60.15; H, 9.68; S, 3.35%.

6 Crystallographic data for **4a**:$FW = 958.42$, triclinic, space group P-1(#2), $a = 13.962(6)$, $b = 17.606(6)$, $c = 12.355\ (5)$ Å, $\alpha = 101.48(3)$, $\beta = 97.78(3)$, $\gamma = 88.84(3)°$, $V = 2948(1)$ Å^3, $Z = 2$, $D_c = 1.079$ gcm^{-3}, $R(R_w) = 0.065(0.046)$ for 2354 reflections [$I>3\sigma(I)$]. **5a**: $FW = 958.42$, monoclinic, space group $P2_1/n$ (#14), $a = 13.888(7)$, $b = 9.95(1)$, $c = 42.401(10)$ Å, $\beta = 92.57(4)°$, $V = 5855(5)$ Å^3, $Z = 4$, $D_c = 1.087$ gcm^{-3}, $R(R_w) = 0.059(0.043)$ for 2565 reflections [$I>3\sigma(I)$]. Details of the structural analysis of **6a** will be described eleswhere.

7 R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **92**, 2100 (1970).

8 B. F. Bonini, M. C. Franchini, G. Mazzanti, J.-W. Slief, M. A. Wegman, and B. Zwanenburg, *Chem. Commun.*, **1997**, 1011.

9 Recently, West *et al.* have also reported an interesting isomerization of an overcrowded 1,2-dioxadisiletane derivative to the corresponding 1,3-dioxadisiletane isomer in the crystalline state, the process of which was partially monitored by X-ray diffraction technique and solid-state NMR. K. L. McKillop, G. R. Gillette, D. R. Powell, and R. West, *J. Am. Chem. Soc.*, **114**, 5203 (1992).

10 Quite recently, we have described a very unique crystalline-state oxidation reaction of an overcrowded distibene (Tbt-Sb=Sb-Tbt) with molecular oxygen, which can be monitored by taking advantage of X-ray crystallographic analysis with imaging-plate techniques. See, N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa, and Y. Ohashi, *J. Am. Chem. Soc.*, **120**, 433 (1998). On the other hand, the isomerization of **5a** into **4a** was so slow that we can monitor the reaction with normal four-circle X-ray diffractometer system.

11 Crystallographic data for the crystal of **5a** left for 1.5 month at r. t.: $FW = 958.42$, monoclinic, space group $P2_1/n$ (#14), $a = 13.895(10)$, $b = 10.152(9)$, $c = 42.450(6)$ Å, $\beta = 91.48(3)°$, $V = 5986(5)$ Å^3, $Z = 4$, $D_c = 1.063$ gcm^{-3}, $R(R_w) = 0.085(0.092)$ for 1477 reflections [$I>3\sigma(I)$].