

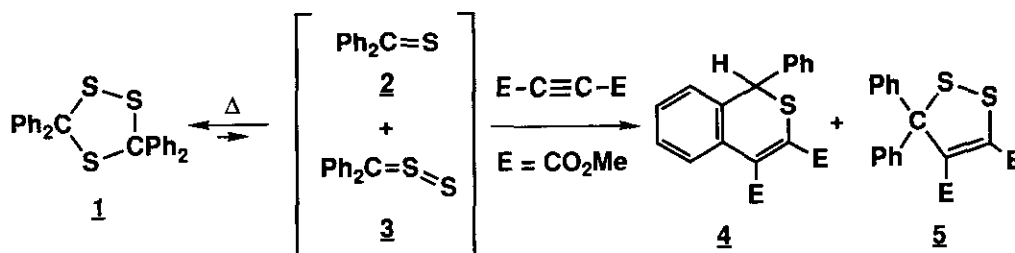
THERMAL RETROCYCLOADDITION OF 1,2,4,3-TRITHIAGERMOLANES:
A NEW METHOD FOR GENERATION OF GERMANETHIONES†

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Abstract— Thermolysis of 5,5-diphenyl-1,2,4,3-trithiagermolanes bearing bulky aromatic substituents on germanium atom resulted in the formation of novel germanium–sulfur double bond compounds, diarylgermanethiones, which were found to undergo ready [2+2] and [2+4] cycloaddition reactions with dimethyl acetylenedicarboxylate and 2,3-dimethyl-1,3-butadiene to give a new class of germanium-containing heterocycles.

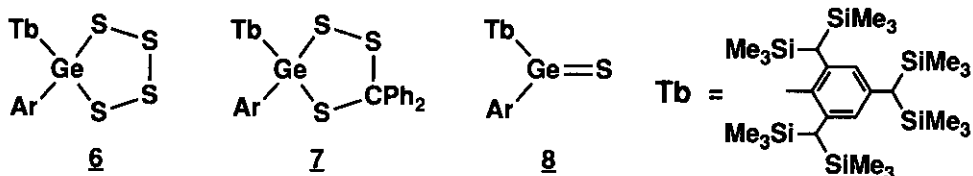
Recently, Huisgen *et al.* reported a thermal retrocycloaddition of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) into thiobenzophenone (**2**) and thioxothiobenzophenone (**3**), which were trapped by dimethyl acetylenedicarboxylate (DMAD) to give the corresponding cycloadducts (**4**) and (**5**), respectively.¹



In the meantime, we previously succeeded in the synthesis of novel 1,2,3,4,5-tetrathiaagermolanes Tb(Ar)GeS₄ (**6**)² and 1,2,4,3-trithiagermolanes Tb(Ar)GeS₃CPh₂ (**7**)³ [Ar = mesityl (Mes) or 2,4,6-triisopropyl-phenyl (Tip)], which are thought to be good precursors of germanium–sulfur double bond compounds, *i. e.* germanethiones Tb(Ar)Ge=S, by taking advantage of a new and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tb in this paper).⁴ Since the trithiagermolane (**7**) is considered to be a ger-

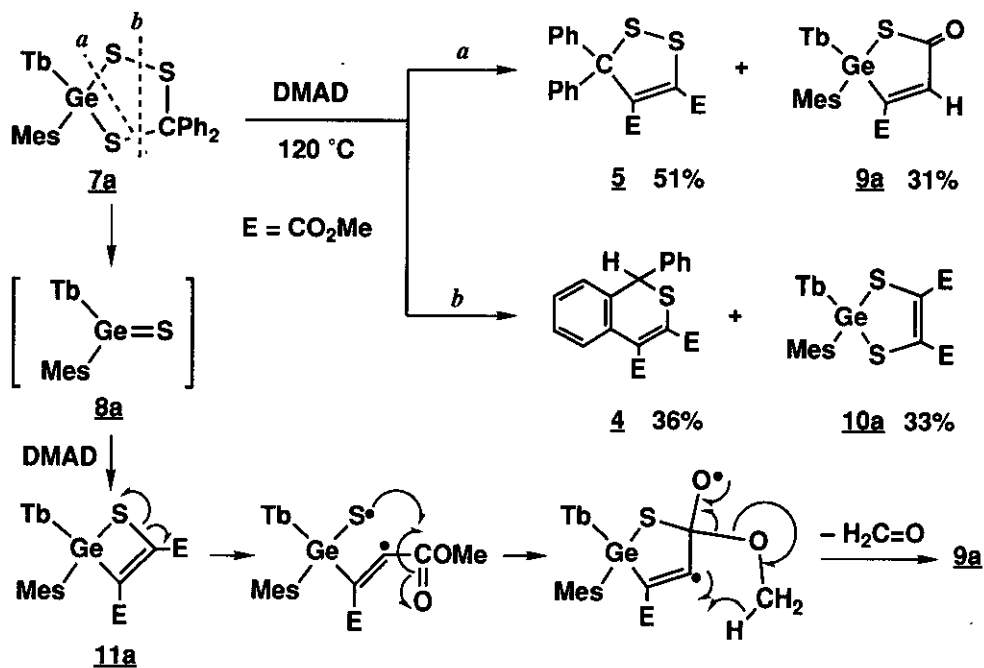
†Dedicated to Professor Rolf Huisgen of University of Munich on the occasion of his 75th birthday.

manium analogue of **1**, we have examined the thermolysis of **7** in a hope of developing a new synthetic route to germanethiones, the chemistry of which has been scarcely disclosed.



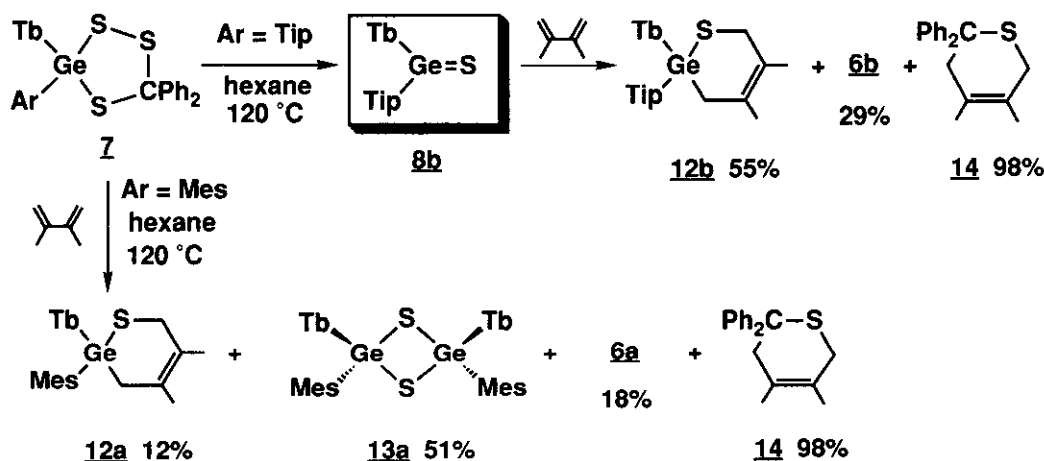
a: Ar = mesityl (Mes) **b**: Ar = 2,4,6-triisopropylphenyl (Tip)

When a mixture of mesityl-substituted 1,2,4,3-trithiagermanolane (**7a**) (100 mg, 0.099 mmol) and an excess amount of DMAD (0.08 ml, 1.0 mmol) dissolved in 0.8 ml of deuteriochloroform was heated in a sealed nmr tube at 120 °C for 6 h, disappearance of the starting material (**7a**) was confirmed by ¹H nmr spectroscopy and sequential separation and purification of the reaction mixture using gel permeation liquid chromatography and preparative thin layer chromatography (SiO₂/hexane:AcOEt = 10:1) afforded 1-thia-2-germacyclopent-3-en-5-one (**9a**; 28.3 mg, 31%) and 1,3-dithia-2-germacyclopent-4-ene (**10a**; 31.2 mg, 33%) as germanium-containing reaction products together with **5** (18.9 mg, 51%) and **4** (12.1 mg, 36%).⁵



The formation of **4**, **5**, and **10a** can be interpreted in terms of the direct cycloaddition of the intermediates formed

via the possible two modes of retrocycloaddition reaction (paths *a* and *b*), while that of thiagermacyclopentenone (**9a**) can be rationalized by the initial formation of 1,2-thiagermete (**11a**), an expected [2+2] cycloadduct of germanethione (**8a**). Since the thiagermete (**11a**) is considered to be highly strained, it would undergo ready ring opening reaction to give **9a** under the reaction conditions. Thermolysis of Tip-substituted trithiagermolane (**7b**) in the presence of DMAD under the similar reaction conditions resulted in the formation of the four types of reaction products as in the case of **7a**, *i. e.* thiagermacyclopentenone (**9b**) (18%), dithiagermacyclopentene (**10b**) (5%), **4** (31%), and **5** (27%). The intermediacy of **11** is strongly supported by the fact that we have already succeeded in the isolation of the analogous overcrowded 1,2-chalcogenastannetes as stable compounds in the thermolysis of the corresponding 1,2,4,3-trichalcogenastannolanes, Tb(Tip)SnY₃CPh₂ (Y=S, Se), in the presence of DMAD under the reaction conditions similar to those for **7a**.⁶ It is reasonably considered that the 1,2-thiagermete (**11**) is less stable than the 1,2-thiastannete because of a ring strain caused by shorter Ge–C and Ge–S bond lengths, thus undergoing homolytic cleavage to give **9** as the final product.



An attempt at trapping of the intermediary germanethione (**8a**) with 2,3-dimethyl-1,3-butadiene in the thermolysis of **7a** in hexane at 120 °C (in a sealed tube) gave the expected [4+2] cycloadduct (**12a**) (12%) and 1,3,2,4-dithiadigermetane (**13a**) (51%), *i. e.* the self-dimerization product of **8a**, along with tetrathiagermolane (**6a**) (18%) and the butadiene adduct of thiobenzophenone (**14**) (98%). Furthermore, thermolysis of Tip-substituted trithiagermolane (**7b**) in the presence of 2,3-dimethyl-1,3-butadiene gave an expected thiagermacyclohexene (**12b**) (55%), tetrathiagermolane (**6b**) (29%), and **14** (98%) without any dimerization products, indicating the higher stability of the germanethione (**8b**) than less hindered **8a**.⁷

It is noteworthy that the kinetically stabilized germanethiones (**8a**) and (**8b**) thus generated survived under such

severe reaction conditions and were capable of undergoing [2+2] and [2+4] cycloaddition reactions leading to a new class of germanium-containing heterocyclic compounds.

ACKNOWLEDGMENT

This work was supported by Grants-in-Aid for Scientific Research (No. 04403005 and 05804047) from the Ministry of Education, Science and Culture, Japan. We are grateful to ASAI Germanium Research Institute, Shinetsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd. for the generous gift of tetrachlorogermane, chlorosilanes, and alkyllithiums, respectively.

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5. All the products described in this paper gave satisfactory spectral and analytical data. The physical properties for compound (**9a**) are listed as representatives as follows: **9a**; white crystals, mp 219–220 °C (CH₂Cl₂-EtOH); ¹H nmr(CDCl₃, 500 MHz) δ -0.053(br s, 9H), -0.041(br s, 18H), -0.026(br s, 9H), 0.043(s, 9H), 0.046(s, 9H), 1.36(s, 1H), 1.98(br s, 1H), 2.10(br s, 1H), 2.24(s, 3H), 2.49(s, 6H), 3.79(s, 3H), 6.34(br s, 1H), 6.48(br s, 1H), 6.83(s, 2H), 7.18(s, 1H); ¹³C nmr(CDCl₃, 125 MHz) δ 0.61(q), 0.71(q), 0.82(q), 0.86(q), 0.91(q), 1.13(q), 20.95(q), 25.16(q), 28.68(d), 28.99(d), 31.08(d), 51.74(q), 121.86(d), 123.19(d), 126.19(s), 128.16(d), 129.84(d), 136.11(s), 141.08(s), 141.24(s), 144.79(s), 147.64(s), 151.54(s), 151.77(s), 165.65(s), 166.46(s);
Anal. Calcd for C₄₁H₇₄O₃GeSSi₆•H₂O C, 54.34; H, 8.45; S, 3.54. Found C, 54.03; H, 8.08; S, 3.78.
6. N. Tokitoh, Y. Matsuhashi, and R. Okazaki, *J. Chem. Soc., Chem. Commun.*, 1993, 407.
7. Very recently, we have succeeded in the isolation of the germanethione (**8b**) as a stable crystalline compound by desulfurization of the tetrathiagermolane (**6b**) with triphenylphosphine; N. Tokitoh, T. Matsumoto, K. Manmaru, and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 8855.

Received, 21st April, 1994