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

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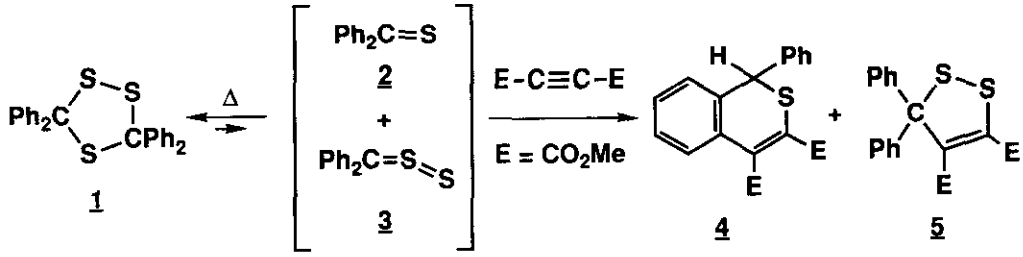
Abstract– Thermolysis of 5,5-diphenyl-1,2,4,3-trithiagermolanes bearing bulky aromatic substituents on germanium atom resulted in the formation of novel germanium–sulfur double bond compounds, diarylgermanethiones, which were found to undergo ready [2+2] and [2+4] cycloaddition reactions with dimethyl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

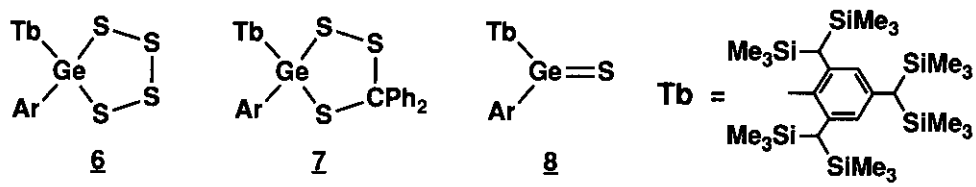
Recently, Huisgen *et al.* reported a thermal retrocycloaddition of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) into thiobenzophenone (**2**) and thioxothiobenzophenone (**3**), which were trapped by dimethyl acetylenedicarboxylate (DMAD) to give the corresponding cycloadducts (**4**) and (**5**),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



In the meantime, we previously succeeded in the synthesis of novel 1,2,3,4,5-tetrathiagermolanes Tb(Ar)GeS_4 (**6**)[2] and 1,2,4,3-trithiagermolanes Tb(Ar)GeS_3CPh_2 (**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.

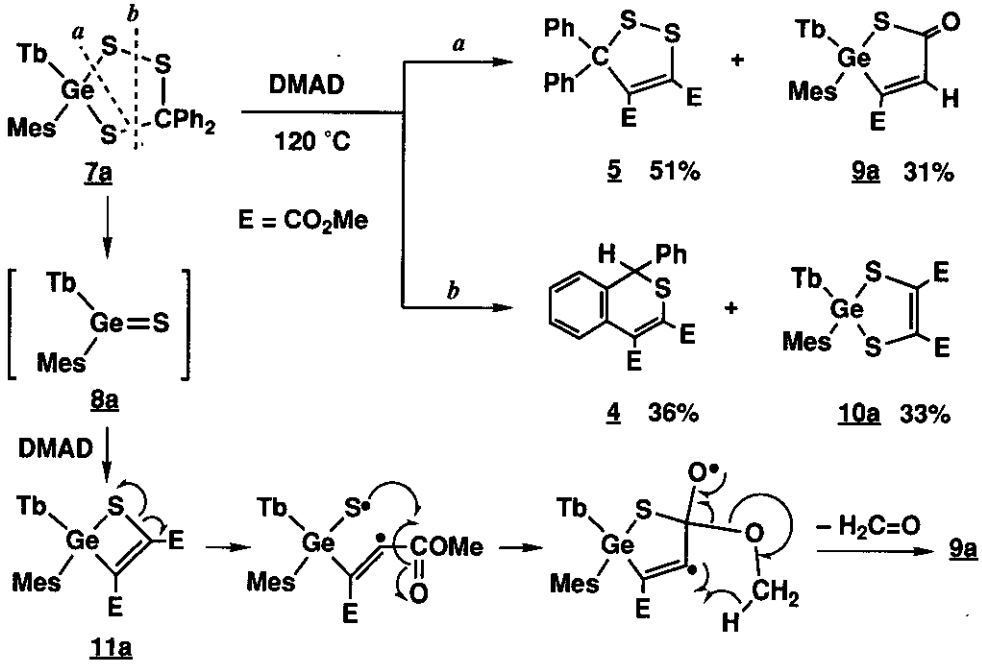
manium analogue of **1**, we have examined the thermolysis of **7** in a hope of developing a new synthetic route to germanethiones, the chemistry of which has been scarcely disclosed.



6 **7** **8**

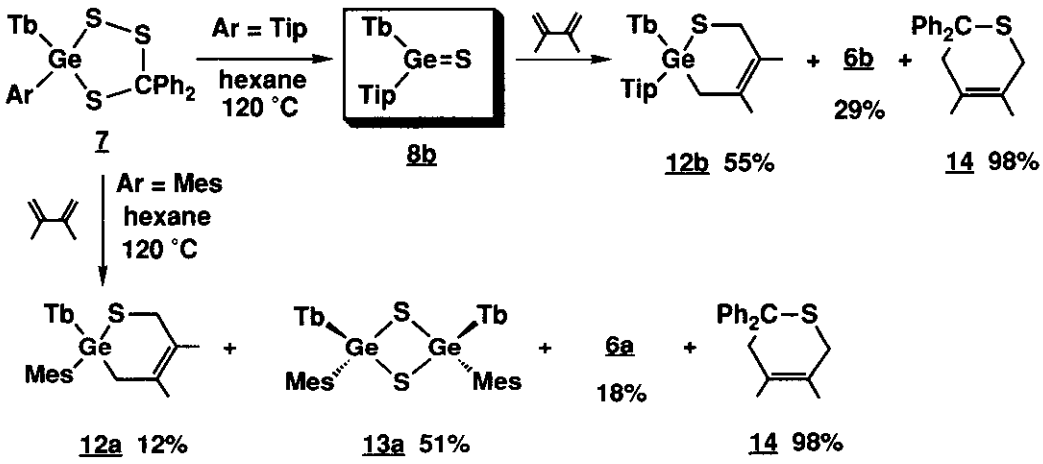
a: Ar = mesityl (Mes) b: Ar = 2,4,6-triisopropylphenyl (Tip)

When a mixture of mesityl-substituted 1,2,4,3-trithiagemolane (**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 ^{1}H nmr spectroscopy and sequential separation and purification of the reaction mixture using gel permiation liquid chromatography and preparative thin layer chromatography (SiO_2/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 thiagemacyclopentenone (**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, $Tb(Tip)SnY_3CPh_2$ (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

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4. R. Okazaki, M. Unno, and N. Inamoto, *Chem. Lett.*, 1987, 2293; R. Okazaki, M. Unno, N. Inamoto, and G. Yamamoto, *ibid.*, 1989, 493; R. Okazaki, M. Unno, and N. Inamoto, *ibid.*, 1989, 791; N. Tokitoh, T. Matsumoto, H. Suzuki, and R. Okazaki, *Tetrahedron Lett.*, 1991, **32**, 2049.
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 (CH_2Cl_2-EtOH); ^1H nmr($CDCl_3$, 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); ^{13}C nmr($CDCl_3$, 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 $C_{41}H_{74}O_3GeSSi_6 \cdot H_2O$ 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.

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