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SYNTHESIS OF GERMATHIIRANES

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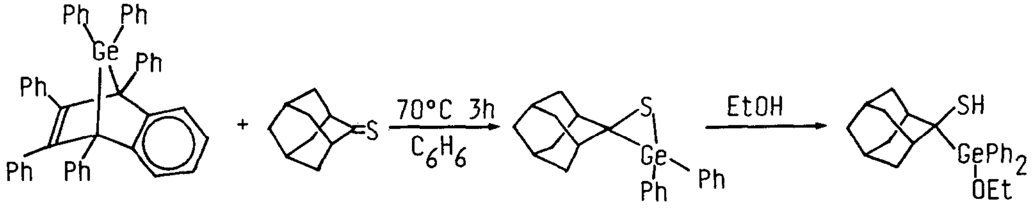
Summary: Thermolysis of 7,7-diphenyl-7-germanorbornadiene with adamantanethione produced germathiirane which reacted with ethanol to give germylmercaptan 3. Dimesitylgermylene induced photochemically reacted with adamantanethione to give a crystalline germathiirane 5 characterized by spectrum data. Digermathiirane 6 and digermaepiselenide 7 were also synthesized by the photolysis of hexamesitylcyclotrigermane with S_8 and Se.

There has been a considerable interest in the chemistry of small ring compounds because of high reactivities resulting from the strain energy. Many three membered cyclosilanes have been synthesized so far[1] and synthesis of strained small ring silanes is one of the current topics in silicon chemistry. In contrast to this situation only a few three membered cyclogermanes have been synthesized[2] and their chemical properties are not well known.

We previously reported that germathiirane was obtained only as intermediate in the reaction of germylene with thioketone.[3] Now we report here the first synthesis of a stable germathiirane.

Diphenylgermylene generated by the thermolysis of 7,7-diphenyl-7-germanorbornadiene 1[4] (0.6 mmol) reacted smoothly with adamantanethione (2 mmol), and after treatment by ethanol at room temperature germylmercaptan 3[5] (50%) was obtained (Scheme 1).

Scheme 1

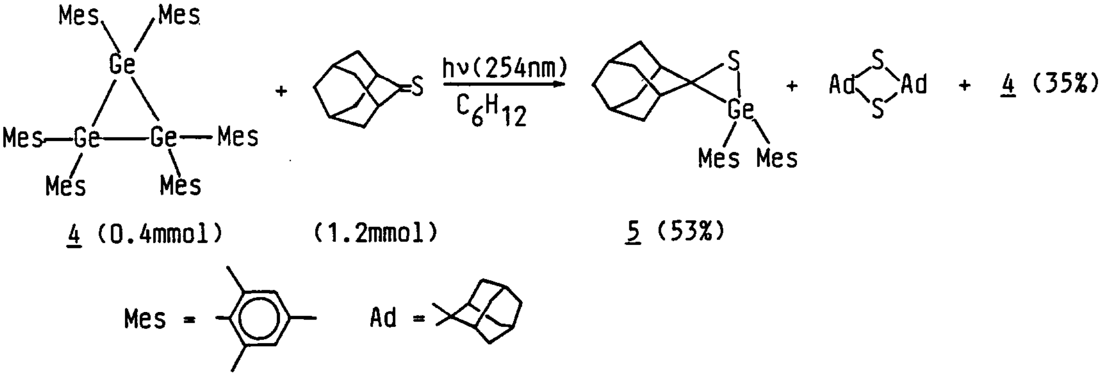


1 (0.6mmol) (2mmol) 2 3 (50%)

This result suggested that compound 2 is probably stable at room temperature in solution.

Since germathiirane can be stabilized by the protection of the bulky substituents around the ring system, the reaction of bulkier substituted germylene with thioketone was carried out. A cyclohexane solution of hexamesitylcyclotrigermane 4[6] (0.4 mmol) and adamantanethione (1.2 mmol) in a quartz tube was irradiated at room temperature with a low pressure mercury lamp for 2.5 hrs. The resulting reaction mixture was concentrated, and the residue was subjected to separation by HPLC (JAIGel column) to give colorless crystal of germathiirane 5 (53%) along with adamantanethione dimer and unreacted 4 (35%) (Scheme 2).[7]

Scheme 2

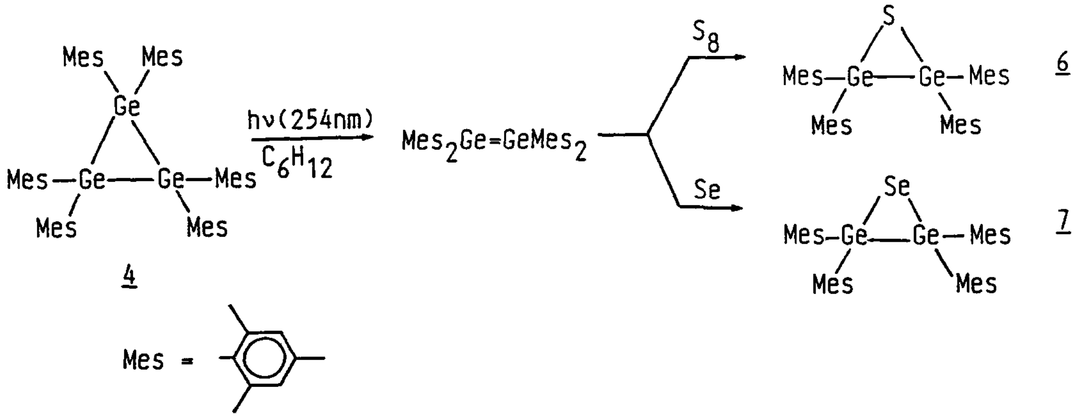


4 (0.4mmol) (1.2mmol) 5 (53%)

Germathiirane 5 is stable in atmosphere of oxygen or moisture, and does not decompose to its melting point (mp. 208-209°C). ^1H-NMR spectrum ($CDCl_3$, δ) shows broad peaks of adamantyl group at 1.54-2.47(m,14H), two singlet peaks attributed to methyl protons of mesityl groups, para 2.23(s,6H) and ortho 2.60 (s,12H), and aromatic protons, 6.87(s,4H); ^{13}C-NMR($CDCl_3$, δ) 20.90(q), 24.54(q) (CH_3 of mesityl groups), 27.07(d), 28.00(d), 35.64(t), 38.22(t), 39.10(d), 39.10(t)(adamantyl C), 56.30(s,-Ge-C-S), 128.75(d), 132.51(s), 139.14(s), 143.14(s)(aromatic C); Mass m/e 478(M^+). Elemental analysis also supports its structure, Calcd for $C_{28}H_{36}GeS$: C,70.46; H,7.60. Found: C,70.67; H,7.77. It is noted that 56.30ppm attributed to the ring carbon is similar to 53.60ppm of that of silathiirane.[1h] Germathiirane 5 was probably formed by the direct reaction of thioketone and germylene generated from cyclotrigermane 4.[8]

As related compounds, digermathiirane 6 and digermaepiselenide 7 were also synthesized (Scheme 3). A mixture of 4 (0.4 mmol) and elemental sulfur (0.8 mmol) in cyclohexane was irradiated with a low pressure mercury lamp. Evaporation of the solvent and separation by HPLC (JAIGel column) followed by recrystallization from hexane gave a white crystalline solid identified as 6 in 26% yield.[7] (mp. 205-209°C. ^{1}H-NMR($CDCl_3$,δ) 2.21(s,12H), 2.37(s,24H), 6.80 (s,8H), Mass m/e 656(M^+). Elemental analysis; Calcd for $C_{36}H_{44}Ge_2S$: C,66.11, H,6.78. Found: C,66.12, H,6.86.) Photochemically generated tetramesityldigermene[8] probably reacted with elemental sulfur to give digermathiirane 6. Photolysis of 4 (0.3 mmol) in solution with selenium (1.2 mmol) yielded digermaepiselenide 7 in 66% yield.[7] (mp. 217-219°C. ^{1}H-NMR($CDCl_3$,δ) 2.20(s,12H) 2.37(s,24H), 6.82(s,8H). Mass m/e 704(M^+). Elemental analysis; Calcd for $C_{36}H_{44}Ge_2Se$: C,61.69, H,6.32. Found: C,61.83, H,6.37.) Both 6 and 7 are stable in atmosphere of oxygen or moisture.

Scheme 3



Further studies on the chemical properties and X-ray crystal analysis of germathiiranes are in progress.

References and Notes

(1)(a) R. L. Lambert, Jr. and D. Seyferth, J. Am. Chem. Soc., 1972, 94, 9246.
(b) R. T. Conlin and P. P. Gaspar, J. Am. Chem. Soc., 1976, 98, 3715.
(c) M. Baudler and H. Jongebloed, Z. Anorg. Allg. Chem., 1979, 458, 9.
(d) J. Hluchy and U. Klingebiel, Angew. Chem. Int. Ed. Engl., 1982, 21, 301.
(e) S. Masamune, Y. Hanzawa, S. Murakami, T. Bally and J. F. Blount, J. Am. Chem. Soc., 1982, 104, 1150.
(f) M. Ishikawa, H. Sugisawa, M. Kumada, T. Higuchi, K. Matsui, K. Hirotsu and J. Iyoda, Organometallics, 1983, 2, 174.
(g) W. Ando, Y. Hamada, A. Sekiguchi and K. Ueno, Tetrahedron Lett., 1982, 23, 5323.
(h) W. Ando, Y. Hamada, A. Sekiguchi and K. Ueno, Tetrahedron Lett., 1983, 24, 4033.
(i) M. J. Michalczyk, R. West and J. Michl, J. Chem. Soc., Chem. Commun.,

1984, 1525.

(j) R. West, Science, 1984, 225, 1109.

(2)(a) M. Baudler, Pure & Appl. Chem., 1980, 52, 755.

(b) S. Masamune, Y. Hanzawa and D. J. Williams, J. Am. Chem. Soc., 1982, 104, 6136.

(c) A. Krebs and J. Berndt, Tetrahedron Lett., 1983, 24, 4083.

(3) W. Ando, T. Tsumuraya and A. Sekiguchi, Tetrahedron Lett., 1985, 26, 4523.

(4) 1 was synthesized by the reaction of 1,1-diphenyl-2,3,4,5-tetraphenylgermole and benzyne generated by $Pb(OAc)_4$ and 1-aminobenzotriazole. (50% yield.

(5) mp. 151-152°C. ^{1}H-NMR($CDCl_3$,δ) 1.14(t,3H), 1.30-3.16(m,14H), 1.40(s,1H), 3.60(q,2H), 7.56-8.30(m,10H). ^{13}C-NMR($CDCl_3$,δ) 19.1(q), 27.1(d), 27.9(d), 32.4(t), 35.9(t), 37.1(d), 39.2(t), 52.0(s), 61.4(t), 128.0(d), 131.2(d), 134.5(s), 135.4(d). Mass m/e 394 (M^+-EtOH). Elemental analysis; Calcd for $C_{24}H_{30}OSGe$: C,65.64, H,6.88. Found: C,65.42, H,6.98.

(6) 4 was synthesized by the reaction of Mes_2GeCl_2 and Mg($MgBr_2$) in THF in 54% yield as the method described for the synthesis of $(Ph_2Si)_4$ (C. L. Smith and R. Gooden, J. Organomet. Chem., 1974, 81, 33.). 4; ^{1}H-NMR($CDCl_3$,δ) 1.92(s,36H), 2.13(s,18H), 6.60(s,12H). ^{13}C-NMR($CDCl_3$,δ) 20.78(q), 24.94(q), 128.11(d), 137.09(s), 142.43(s), 142.96(s). UV(c-Hexane)λmax 268nm(logε= 4.69), 310nm(shoulder). Elemental analysis; Calcd for $C_{54}H_{66}Ge_3$: C,69.52, H,7.13. Found: C,69.60, H,7.29.

(7) Yields are based on moles of cyclotrigermane 4.

(8) S. Collins, S. Murakami, J. T. Snow and S. Masamune, Tetrahedron Lett., 1985, 26, 1281.

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