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Thermolysis of Cyclotrigermane: Simple Preparation of Digermetanes containing a Germanium–Germanium Bond

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Thermolysis of hexamesitylcyclotrigermane in the presence of paraformaldehyde, thiobenzophenone, and phenylacetylene at 80 °C produces the corresponding adducts with tetramesityldigermene.

In recent years the chemistry of small-ring systems involving a germanium–germanium bond has been the subject of considerable interest, and several papers that deal with the preparation and the chemistry of these compounds have been reported.^{1—8} We recently prepared digermirane and its heterocyclic analogues using the reactions of digermene (Ge=Ge), demonstrating that this method was useful for the preparation of such molecules.^{5,6} We report here a convenient synthesis of 1,2,3-oxa- and -thia-digermetanes and 1,2-digermetene by the reactions of digermene generated thermally

from cyclotrigermane¹⁻³ with formaldehyde, thiobenzophenone, and phenylacetylene.[†]

During thermolysis of a cyclohexane solution of hexamesitylcyclotrigermane $(1)^2$ [mesityl (Mes) = 2,4,6-trimethylphenyl] without any trapping reagents at 80 °C under argon,

[†] Very recently, a 1,2,3-oxadigermetane and a 1,2-digermetene were prepared by Masamune *et al.* from the direct reaction of a ketone or an acetylene with an isolable digermene, tetrakis(2,6-diethylphenyl)digermene; see ref. 7.





the solution turned yellow[‡] and had an absorption with a maximum at 410 nm. This absorption band is identical to that obtained from the photolysis of (1) giving tetramesityldigermene (2),⁹ so this yellow species is ascribed to (2). When a benzene solution of (1) (0.3 mmol) and 2,3-dimethylbuta-1,3diene (10 mmol) was heated to reflux for 10 h, 1.2-digermacyclohex-4-ene (4) and germacyclopent-3-ene $(5)^{10}$ were obtained in 77 and 80% yields, respectively.§ Compounds (4) and (5) appear to have derived from the cycloaddition of 2,3-dimethylbuta-1,3-diene with tetramesityldigermene (2) and dimesitylgermylene (3), which were generated thermally from cyclotrigermane (1) (Scheme 1). In the absence of trapping reagents, cyclotrigermane (1) was recovered almost quantitatively, suggesting that the decomposition of (1) into digermene (2) and germylene (germanediyl) (3) may be a reversible reaction. In the case of hexakis(2,6-diethylphenyl)cyclotrigermane,^{1,2} more vigorous conditions are required for the thermolysis. Refluxing in toluene effected



decomposition of the cyclotrigermane. Although generation of germylenes and digermenes from the photolysis of cyclotrigermanes is well known, 1,5,6,11 thermal generation has no precedent.

To prepare four-membered cyclogermanes containing a germanium-germanium bond using thermally generated digermene, we attempted thermal decomposition of cyclotrigermane (1) in the presence of unsaturated compounds, for example carbonyl and thiocarbonyl compounds and an acetylene. Thermolysis of a benzene solution of cyclotrigermane (1) (0.1 mmol) and paraformaldehyde (10 mmol) at 80 °C for 15 h produced mainly 1,2,3-oxadigermetane (6) in 30% yield (Scheme 2). Spectral data and elemental analysis of (6) supported the proposed structure [¹H n.m.r. (CDCl₃) δ 2.16 (s, 12H), 2.21 (s, 24H), 5.11 (s, 2H), 6.71 (s, 4H), and 6.75 (s, 4H); ¹³C n.m.r. (CDCl₃) δ 20.99 (q), 21.03 (q), 22.53 (q), 23.79 (q), 74.32 (t), 128.65 (d), 137.17 (s), 138.49 (s), 138.74 (s), 138.93 (s), 142.47 (s), and 142.95 (s); m/z (relative intensity) 622 (34, M⁺-CH₂O), 431 (100, Mes₃Ge), and 312 (15, Mes₂Ge)]. 1,2,3-Oxadigermetane (6) is stable in air and moisture, and does not decompose even when heated to its melting point (m.p. 253-255 °C). Compound (6) is presumably formed by the direct reaction of tetramesityldigermene (2) with formaldehyde, although at the moment we cannot exclude another possible mechanism; a stepwise insertion of dimesitylgermylene (3) into formaldehyde.

Similarly, in the presence of thiobenzophenone or phenylacetylene, thermolysis of cyclotrigermane (1) gave 1,2,3thiadigermetane (7) or 1,2-digermetene (8) in 75 and 32% yields, respectively. In the reaction with thiobenzophenone 1,3,2-dithiagermolane (9) was obtained in 73% yield (Scheme 3). Compound (9) may be derived from the addition of thiobenzophenone to the initially formed germathiocarbonyl ylide (10), or thiagermirane (11) as shown in Scheme 3.^{4,11} Unlike 1,2-digermetenes which have been reported earlier,⁸ compound (8) does not react with atmospheric oxygen, since it is sterically protected by the bulky groups on germanium.

These results indicate that cyclotrigermanes are also good thermal precursors of bulky group substituted germylenes and digermenes.** Since this method can avoid the photolysis of

[‡] The colour disappeared when the solution was cooled.

[§] Satisfactory elemental analyses were obtained for the compounds described. Selected spectral data: (4): m.p. 193-195 °C; ¹H n.m.r. (CDCl₃) & 1.58 (s, 4H), 1.96 (s, 6H), 2.18 (s, 12H), 2.21 (s, 24H), and 6.68 (s, 8H); m/z (relative intensity) 622 (2, $M^+ - C_6 H_{10}$), 503 (4, $M^+-C_6H_{10}-Mes$, 431 (100, Mes₃Ge), 312 (14, Mes₂Ge), and 193 (21, MesGe). (7): m.p. 189–190 °C; ¹H n.m.r. (CDCl₃) δ 2.02 (s, 12H), 2.15 (s, 6H), 2.18 (s, 6H), 2.31 (s, 12H), 6.62 (s, 8H), and 6.7-7.4 (m, 10H); m/z (relative intensity) 622 (10, M⁺-Ph₂CS), 431 (64, Mes₃Ge), 312 (60, Mes₂Ge), and 193 (100, MesGe). (8): m.p. 127-129 °C; ¹H n.m.r. (CDCl₃) δ 2.05 (s, 12H), 2.19 (s, 12H), 2.22 (s, 12H), 6.67 (s, 4H), 6.69 (s, 4H), 7.13 (s, 5H), and 7.84 (s, 1H); m/z (relative intensity) 724 (17, M⁺), 622 (36, M⁺-PhC₂H), 431 (100, Mes₃Ge), and 312 (11, Mes₂Ge). (9): m.p. 238-239 °C (decomp.); ¹H n.m.r. (CDCl₃) δ 2.20 (s, 6H), 2.47 (s, 12H), and 6.6-7.5 (m, 22H); m/z (relative intensity) 510 (3, M^+ -Ph₂CS), 344 (5, Mes₂Ge=S), 312 (15, Mes₂Ge), and 198 (100, Ph₂CS).

[¶] In the presence of 2,3-dimethylbuta-1,3-diene, thermolysis of hexakis(2,6-diethylphenyl)cyclotrigermane gave a yellow colour with the formation of a trapping product of the germylene, germa-cyclopent-3-ene. In this reaction no product from the digermene was obtained, probably due to steric factors.

^{||} When the preformed digermene, tetrakis(2,6-diethylphenyl)-digermene (see ref. 1) was treated with paraformaldehyde under the same conditions, a similar product, 2,2,3,3-tetrakis(2,6-diethylphenyl)-1,2,3-oxadigermetane (m.p. 148—150 °C) was obtained in 27% yield. ** Preparation of 3-alkylidenethiagermirane from thermally generated dimesitylgermylene under these conditions will be published elsewhere; W. Ando and T. Tsumuraya, *Organometallics*, in press.

co-reagents or products, it can be adopted in the various types of the reaction of germylene and digermene.

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References

- S. Masamune, Y. Hanzawa, and D. J. Williams, J. Am. Chem. Soc., 1982, 104, 6136; J. T. Snow, S. Murakami, S. Masamune, and D. J. Williams, *Tetrahedron Lett.*, 1984, 25, 4191; S. Collins, S. Murakami, J. T. Snow, and S. Masamune, *ibid.*, 1985, 26, 1281.
- 2 W. Ando and T. Tsumuraya, J. Chem. Soc., Chem. Commun., 1987, 1514.
- 3 M. Weidenbruch, F. -T. Grimm, M. Herrndorf, A. Schafer, K. Peters, and G. Schnering, J. Organomet. Chem., 1988, 341, 1514.

- 4 W. Ando, T. Tsumuraya, and A. Sekiguchi, *Tetrahedron Lett.*, 1985, **26**, 4523; W. Ando, T. Tsumuraya, and M. Goto, *ibid.*, 1986, **27**, 5105.
- 5 W. Ando and T. Tsumuraya, *Tetrahedron Lett.*, 1986, **27**, 3251; T. Tsumuraya, S. Sato, and W. Ando, *Organometallics*, 1988, **7**, 2015.
- 6 W. Ando and T. Tsumuraya, Organometallics, 1988, 7, 1882.
- 7 S. A. Batcheller and S. Masamune, Tetrahedron Lett., 1988, 29, 3383.
- 8 A. A. Espenbetov, Yu. Y. Struchkov, S. P. Kolesnikov, and O. M. Nefedov, J. Organomet. Chem., 1984, 275, 33; O. M. Nefedov, M. P. Egorov, A. M. Gal'minas, S. P. Kolesnikov, A. Krebs, and J. Berndt, *ibid.*, 1986, 301, C21.
- 9 W. Ando, T. Tsumuraya, and A. Sekiguchi, *Chem. Lett.*, 1987, 317; W. Ando, H. Itoh, T. Tsumuraya, and H. Yoshida, *Organometallics*, 1988, **7**, 1880.
- 10 P. Riviere, A. Castel, and J. Satge, J. Organomet. Chem., 1982, 232, 123.
- 11 T. Tsumuraya, S. Sato, and W. Ando, Organometallics, 1989, 8, 161.