CHEMISTRY LETTERS, pp. 1697-1700, 1992.

Synthesis of Cyclotetragermanes of the Type of $[R(Ph)Ge]_4$ and Conversion to $[R(Cl)Ge]_4$. The First Functionalized Cyclotetragermanes

Akira SEKIGUCHI, Tetsuo YATABE, Hiroyoshi NAITO, Chizuko KABUTO, and Hideki SAKURAI
Department of Chemistry and Organosilicon Research Laboratory,
Faculty of Science, Tohoku University, Sendai, Aoba-ku, 980

Condensations of $R(Ph)GeCl_2$ (R = t-Bu and R = CEt_2Me) with $Mg/MgBr_2$ in THF produced cyclotetragermanes $[R(Ph)Ge]_4$, which were converted to $[R(Cl)Ge]_4$ by treatment with $HCl/AlCl_3$ or with CF_3SO_3H followed by CH_3COCl. The crystal structure of $[t\text{-}Bu(Cl)Ge]_4$ was established by X-ray diffraction. Unusual configurational behavior of cyclotetragermanes is also described.

The chemistry of three and four membered ring systems consisting of Group 14 elements is one of the subjects of considerable interest.1) Very recently, we have reported hexagermaprismane2) and octagermacubane3) as polyhedral polygermanes as well as polycyclopolygermane.4) Halogenated cyclopolygermanes should be the logical synthetic intermediates for these polycyclopolygermanes. However, the most of the extensive works on cyclopolygermanes of three and four membered rings has been limited to the types of $(R_2Ge)_3$ and $(R_2Ge)_4$.5) No example of the type of $[R(X)Ge]_3$ and $[R(X)Ge]_4$, where X stands for halogens and other negative groups, has been reported yet so far. We report here the synthesis of cyclotetragermanes containing four chlorines and its crystal structure determined by the X-ray diffraction method along with the configurational studies.

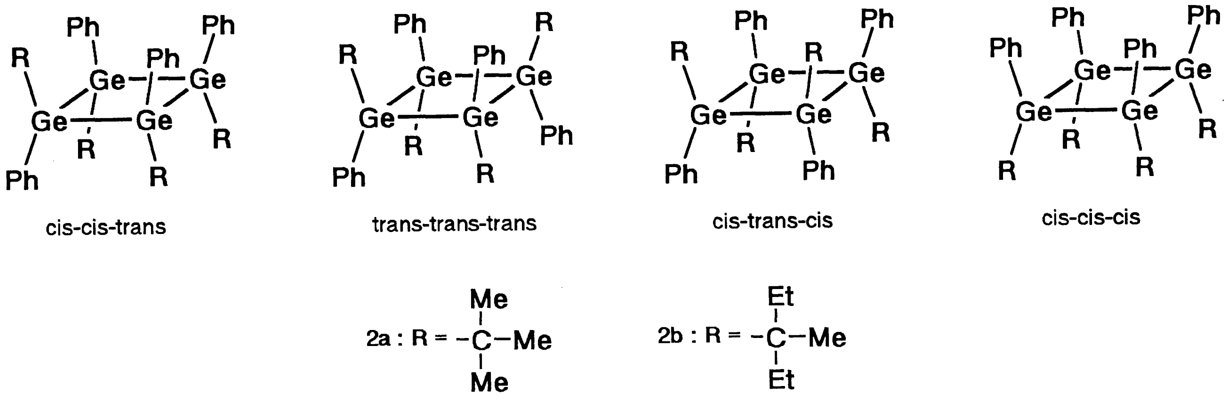
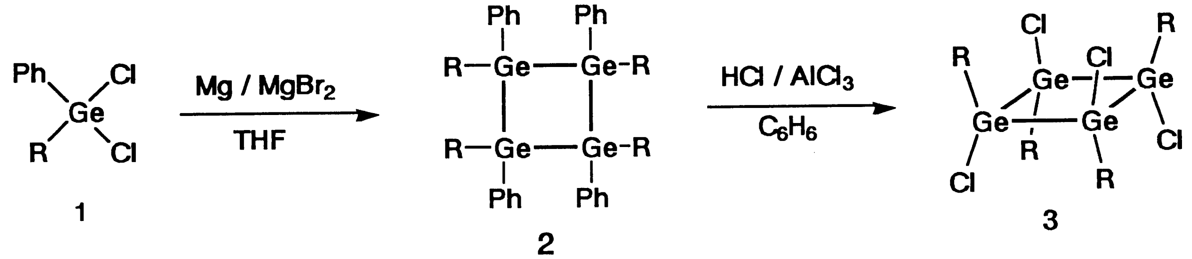


Fig. 1. Possible stereoisomers of **2**.

The coupling reaction of t-butyldichloro(phenyl)germane **1a** with a mixture of Mg and $MgBr_2$ in

THF produced 1,2,3,4-tetra-*t*-butyl-1,2,3,4-tetraphenylcyclotetragermane **2a** as a mixture of stereoisomers in 71% yield in the following manner. A solution of 1,2-dibromoethane (67.6 g, 0.36 mol) in THF (100 ml) was added to magnesium (31.6 g, 1.30 mol) in THF (200 ml) to prepare magnesium bromide. To the resulting mixture of Mg and $MgBr_2$ was added dropwise a solution of **1a** (100 g, 0.36 mol) in THF (700 ml). The exothermic reaction took place and the color of the mixture turned to dark-brown. The mixture was stirred for 12 h, and then the usual work-up afforded white solids of **2a** (52.9 g).[6)]

Although four stereoisomers are possible in **2a** as depicted in Fig. 1, three stereoisomers are formed in an approximate ratio of 70 : 20 : 10. One major isomer was obtained as a pure form after recrystallization; ^1H NMR (300 MHz, $CDCl_3$, δ) 0.85 (s, 9H), 1.13 (s, 9H), 1.46 (s, 18H), 6.79 - 7.92 (m, 20H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 29.01 ($\underline{C}Me_3$), 30.33 ($C\underline{Me}_3$), 30.69 ($C\underline{Me}_3$), 31.99 ($C\underline{Me}_3$), 32.48 ($\underline{C}Me_3$), 32.67 ($\underline{C}Me_3$), 126.69, 127.11, 127.13, 127.25, 127.64, 127.83, 137.33 (ortho C), 137.74 (ortho C), 138.07 (ortho C), 140.25 (ipso C), 140.32 (ipso C), 141.51 (ipso C); Mass (FAB) 818 - 836 (M^+ cluster). The ^1H and ^{13}C NMR spectra of the major isomer of **2a** showed existence of the t-butyl in a ratio of 1: 1: 2 in accordance with the configuration of cis-cis-trans. Thus the most abundant one was reasonably assigned to cis-cis-trans, the other two being tentatively assigned to all-trans and cis-trans-cis, respectively. The formation of the all-cis isomer may be disfavored by the steric reason. ^1H NMR chemical shifts of t-butyl groups for other isomers are assigned as follows: 1.10 ppm for the all-trans and 1.51 ppm for the cis-trans-cis.



The four phenyl groups of **2a** were readily replaced to chlorine without cleavage of the Ge-Ge linkage by the action of hydrogen chloride in the presence of $AlCl_3$. Thus, into a stirred mixture of the cyclotetragermane **2a** (20.0 g, 24.2 mmol), anhydrous $AlCl_3$ (0.65 g, 4.9 mmol), and benzene (20 ml) was passed dry hydrogen chloride for 1 h to yield 1,2,3,4-tetra-t-butyl-1,2,3,4-tetrachlorocyclotetragermane **3a** (13.8 g, 86%).

Interestingly, among the four possible stereoisomers of **3a**, only one isomer was produced; mp. 189 - 190 °C; ^1H NMR (300 MHz, $CDCl_3$, δ) 1.41 (s, 36H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ) 28.5, 41.6; Anal. Calcd for $C_{16}H_{36}Ge_4Cl_4$: C, 29.09, H, 5.49; found: C, 29.09, H, 5.33. The mass spectrum (DEI) revealed the M^+ cluster ion in the range of 652 - 670 in agreement with the formula of $C_{16}H_{36}Ge_4Cl_4$.

The all-trans configuration of **3a** was established unequivocally by X-ray diffraction as shown in Fig. 2.[7)] The cyclotetragermane ring is puckered with the dihedral angle of 21° for Ge(1)-Ge(3)-Ge(2)/Ge(1)-Ge(3')-Ge(2). The chlorine atoms and the t-butyl groups occupy the pseudo-axial and the less hindered pseudo-equatorial positions, respectively. The Ge-Ge-Ge bond angles constructing the four-membered ring are in the range of 88.8 - 89.5° (av. 89.1°) and the Ge-Ge bond lengths are 2.455 - 2.471 Å. The Ge-Ge-C bond angles (125°) are largely expanded due to the steric repulsion, whereas Ge-Ge-Cl bond angles (105°) are contracted.

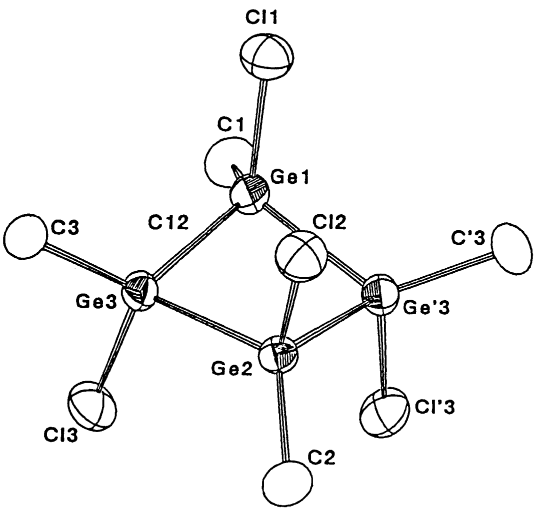
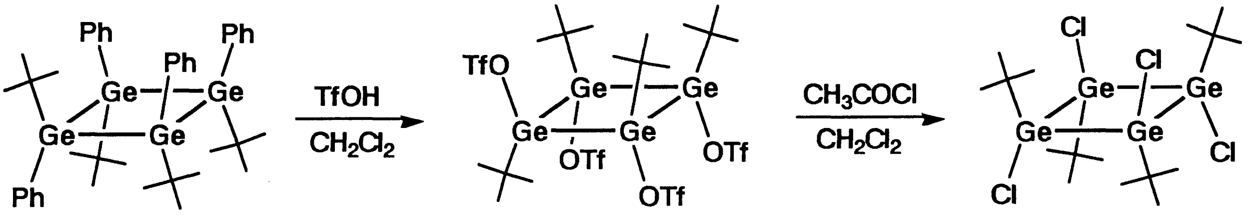


Fig. 2. ORTEP drawing of **3a** (methyl groups were omitted for the clarity). Selected bond lengths (Å): Ge1–Ge3 2.471(2), Ge2–Ge3 2.455(2). Selected bond angles (deg): Ge3–Ge1–Ge3' 88.8(0), Ge3–Ge2–Ge3' 89.5(0), Ge1–Ge3–Ge2 89.0(0), Ge1–Ge3–C3 125.3(3), Ge2–Ge3–C3 125.3(3), Ge1–Ge3–Cl3 104.9(1), Ge2–Ge3–Cl3 104.5(1).

The formation of the all–trans isomer **3a** indicates that stereochemical isomerization occurred during the reaction probably because of configurational instability of the chlorogermanes. To clarify this point, the cyclotetragermane **2a** was reacted with 4 equivalent of trifluoromethane sulfonic acid in dichloromethane-d_2. The ^{1}H NMR spectrum of the reaction mixture showed the three set of t-butyl signals at 1.64 (18H), 1.55 (9H), and 1.36 (9H) together with the resonance attributable to benzene. This indicates the complete replacement of the four phenyl groups by the triflate substituents with the cis–cis–trans configuration.8) The resulting germyl triflate **4a** was converted to all–trans isomer **3a** with acetyl chloride. The isomerization probably proceeded via either a penta–coordinate germanium intermediate or a germanium cation to produce thermodynamically stable **3a** with the configuration of all–trans.



2a (cis-cis-trans)

4a (cis-cis-trans)

Tf = $-SO_2CF_3$

3a (trans-trans-trans)

The cyclotetragermane **3b** (R = CEt_2Me) with configuration of all–trans was prepared in a similar way. Thus, the cyclotetragermane **2b**9) (main configuration: cis–cis–trans) was allowed to react with trifluoromethane sulfonic acid followed by acetyl chloride to afford all–trans isomer of **3b** (41%).10)

These results indicate that one should be careful for the stereochemical outcome in the functionalization of polygermanes. Nevertheless, the formation of all–trans $(RXGe)_4$ is important as precursors of the cage compounds, the properties of which should be extremely interesting.

We are grateful for the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 02102004). A. S. is grateful to The Kurata Research Grant. We also thank ASAI Germanium Research Institute for the gift of chlorogermanes.

References

1) H. Bock, *Angew. Chem., Int. Ed. Engl.*, **28**, 1627 (1989); T. Tsumuraya, S. A. Batcheller, and S. Masamune, *ibid.*, **30**, 902 (1991); S. Nagase, *Polyhedron*, **10**, 1299 (1991); A. Sekiguchi and H. Sakurai, "The Chemistry of Inorganic Ring Systems," ed by R. Steudel, Chapt. 7, Elsevier (1992).

2) A. Sekiguchi, C. Kabuto, and H. Sakurai, *Angew. Chem., Int. Ed. Engl.*, **28**, 55 (1989).

3) A. Sekiguchi, T. Yatabe, H. Kamatani, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **114**, 6260 (1992).

4) A. Sekiguchi, H. Naito, H. Nameki, K. Ebata, C. Kabuto, and H. Sakurai, *J. Organomet. Chem.*, **368**, C1 (1989).

5) For $(Ar_2Ge)_3$ (Ar = 2,6–dimethylphenyl): a) S. Masamune, Y. Hanzawa, and D. J. Williams, *J. Am. Chem. Soc.*, **104**, 6136 (1982). For $(Ar_2Ge)_3$ (Ar = 2,6–diethylphenyl): b) J. T. Snow, S. Murakami, S. Masamune, and D. J. Williams, *Tetrahedron Lett.*, **25**, 4191 (1984). For $[Mes(t\text{–}Bu)Ge]_3$: c) W. Ando and T. Tsumuraya, *J. Chem. Soc., Chem. Commun.*, **1987**, 1514. For $(t\text{–}Bu_2Ge)_3$: d) M. Weidenbruch, F. –T. Grimm, M. Herrndorf, and A. Schäfer, *J. Organomet. Chem.*, **341**, 335 (1988). For $(Me_2Ge)_4$: e) H. Sakurai, K. Sakamoto, and M. Kira, *Chem. Lett.*, **1984**, 1379. For $(Et_2Ge)_4$: f) P. Riviere, A. Castel, J. Satgé, and D. Guyot, *J. Organomet. Chem.*, **264**, 193 (1984). For $(Ph_2Ge)_4$: g) W. P. Neumann and K. Kühlein, *Tetrahedron Lett.*, **1963**, 1541; h) L. Ross and M. Dräger, *J. Organomet. Chem.*, **199**, 195 (1980). For $(p\text{–}Tol_2Ge)_4$: i) M. Richter and W. P. Neumann, *ibid.*, **20**, 81 (1969). For $(i\text{–}Pr_2Ge)_4$ and $[(Me_3SiCH_2)_2Ge]_4$: see Ref. 5c.

6) The ring size of the products formed in this process largely depends on the steric bulk of the substituents on germanium. Reactions with dihalogenogermanes bearing bulky substitents afforded cyclotrigermanes, whereas less hindered dihalogenogermanes gave cyclotetragermanes. See Ref. 5c.

7) Crystal data of **3a**: M. F. = $C_{16}H_{36}Cl_4Ge_4$, M. W. = 660.7, a = 13.835 (2), b = 14.955 (2), c = 13.366 (2) Å, $\alpha = \beta = \gamma = 90°$, V = 2642.4(6) Å^3, orthorhombic, space group P_{bcm}, Z = 4, Dc = 1.59 g/cm^3, R = 0.0532 (Rw = 0.0545).

8) It is precedent that the four phenyl groups of octaphenylcyclotetrasilane were removed and replaced by the trifrates. M. Cypryk, Y. Gupta, and K. Matyjaszewski, *J. Am. Chem. Soc.*, **113**, 1046 (1991).

9) Compound **2b** (cis–cis–trans): ^1H NMR ($CDCl_3$, δ) 0.57 (t, 12H, J = 7.5 Hz, $CCH_2C\underline{H}_3$), 0.80 (s, 3H, CMe), 0.94 (t, 6H, J = 7.8Hz, $CCH_2C\underline{H}_3$), 0.96 (t, 6H, J = 7.8Hz, $CCH_2C\underline{H}_3$), 1.14 (s, 3H, CMe), 1.47 (s, 6H, CMe), 1.26 – 1.52 (m, 4H, CCH_2), 1.65 – 1.80 (m, 4H, CCH_2), 1.84 – 1.97 (m, 8H, CCH_2), 6.69 – 7.94 (m, 20H, ArH); ^{13}C NMR ($CDCl_3$, δ) 9.53 $C\underline{Me}$), 9.84 ($C\underline{Me}$), 10.23 ($C\underline{Me}$), 20.77 ($CCH_2\underline{C}H_3$), 22.77 ($CCH_2\underline{C}H_3$), 24.28 ($CCH_2\underline{C}H_3$), 31.40 ($C\underline{C}H_2CH_3$), 31.71 ($C\underline{C}H_2CH_3$), 32.22 ($C\underline{C}H_2CH_3$), 32.53 ($C\underline{C}H_2CH_3$), 36.50 (C_q), 42.62 (C_q), 42.93 (C_q), 126.40, 126.79, 126.95, 127.10, 127.56, 137.61 (ortho C), 137.88 (ortho C), 138.17 (ortho C), 141.01 (ipso C), 141.74 (ipso C), 143.44 (ipso C); MS (FAB) m/e 930 – 948 (M^+ cluster).

10) Compound **3b**: Mp 148 – 150 °C; ^1H NMR ($CDCl_3$, δ) 0.97 (t, 24H, J = 7.5Hz), 1.40 (s, 12H), 1.73 – 2.00 (m, 32H); ^{13}C NMR ($CDCl_3$, δ) 9.52, 23.0, 29.8, 53.7; MS (FAB) m/e 762 – 784 (M^+ cluster). As a matter of possibility, **3b** can have either all–cis or cis–trans–cis configuration judging from the NMR results. However, the fact that only the all–trans isomer was obtained for **3a** may exclude the possibility for **3b** with much bulkier substituents.

(Received June 25, 1992)