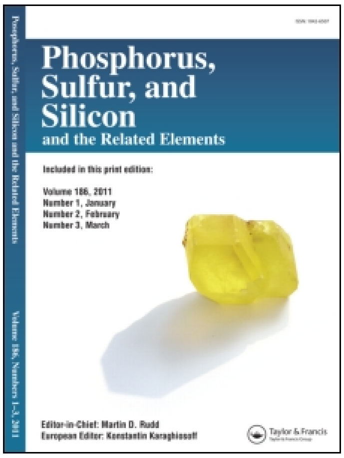

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Synthesis and Reactions of Hepta-*t*-Butylcyclotetragermane

MASAFUMI UNNO, RYOJI TANAKA, SOICHIRO KYUSHIN and HIDEYUKI MATSUMOTO

Department of Applied Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376–8515, JAPAN

Hepta-*t*-butylcyclotetragermane **1** was synthesized from 1,2-dichloro-1,1,2,2-tetra-*t*-butyldigermane. The generation of hepta-*t*-butylcyclotetragermanyllithium **2** was observed by NMR spectra, and also confirmed by the trapping reactions. Thermal reaction of **1** gave two isomers of hexa-*t*-butylcyclotetragermane, 2,4-*trans*-**3** and 2,4-*cis*-**3**. Chlorination reaction of **1** with carbon tetrachloride gave hepta-*t*-butylchlorocyclotetragermane **4**. The structure of **1**, 2,4-*cis*-**3**, and **4** was determined by X-ray crystallography.

Keywords: cyclotetragermane; germyllithium; thermal reaction; chlorination; crystal structure

INTRODUCTION

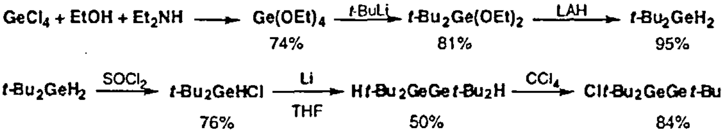
Recent years, polygermanes have been attracting interests because of their reactivity and physical properties.[1] The unique electronic properties of cyclopolygermanes are mostly arising from the σ-conjugation of the framework, and high electron donating ability. In addition, bonding energy of Ge–Ge is less than that of Si–Si bond, thus bond fission by thermal and photoreaction is observed relatively easier.[2] Here we will report the synthesis of hepta-*t*-butylcyclotetragermyllithium (**1**) from 1,2-di-*t*-butyltetrachlorodigermane, and the thermal and chlorination reactions from **1**.

RESULTS AND DISCUSSION

Synthesis and Structure of hepta-*t*-butylcyclotetragermane

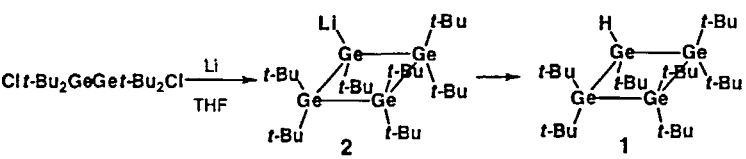
Weidenbruch et al. reported that the reductive coupling from di-*t*-butyldichlorogermane gave cyclotrigermane, and cyclotetragermane was not obtained.[3] If we use $R_2ClGeGeClR_2$ as a starting material, cyclotetragermane is the most probable product.

In order to synthesis octa-*t*-butylcyclotetragermane, we prepared 1,2-dichloro-1,1,2,2-tetra-*t*-butyldigermane, and reductive coupling was made. The preparation of di-*t*-butylgermane was reported,[4] and we followed their method. The synthesis of 1,2-dichloro-1,1,2,2-tetra-*t*-butyldigermane was effected by applying the known procedure.



Scheme 1

The reductive coupling of 1,2-dichloro-1,1,2,2-tetra-*t*-butyldigermane was effected with lithium dispersion in THF (Scheme 2). After 12 h, the dark brown solution was obtained; the color of the solution promptly faded with exposure to the air. The HPLC chromatogram (ODS, MeOH/THF=7/3) showed only single peak indicating the reaction

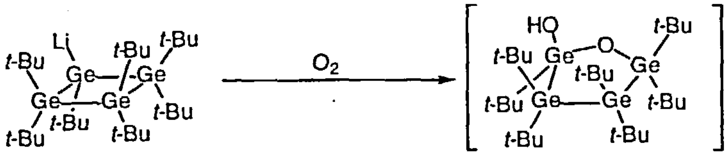


Scheme 2

was selective. Methanol was added to the solution and the salt was separated, then recrystallization of the crude product gave hepta-*t*-butylcyclotetragermane **1** in 60% yield. We concluded that the cyclotetragermanyllithium **2** generated from the following results: 1) The ^{7}Li NMR of the solution showed a peak at δ 0.10 ppm, and this peak disappeared when the solution was exposed to the air. 2) When the mixture was worked-up with MeOD, the deuterated product was obtained (69% yield, 88% *d*-content). The cyclic germyllithium **2** is stable under an inert atmosphere, and could be kept without decomposition at room temperature. So far, cyclic germyllithium has not been reported, and this case is the first example. The stability is explained by the effective steric protection of bulky *t*-butyl groups, in addition to the delocalization of the charge in the small ring.

The mechanism of the generation of germyllithium is not clear, however, in the case of silicon analogues, hepta-*t*-butylcyclotetrasilane and hexa-*t*-butylcyclotetrasilane were reported to generate in the reductive coupling of di-*t*-butyldichlorosilane.[5] Similar removal of the substituents was also observed in the coupling reaction of aminochlorosilanes.[6] When **1** was subjected to the reaction with lithium, no germyllithium was obtained, then we can conclude this germyllithium did not obtained from **1**. We postulate that the elimination occurred in the stage of ring closure, as the steric hindrance of open-chain compounds is no severe. We think excess lithium displaces *t*-butyl group, then ring-closure occurred. It is also possible that α-elimination of *t*-BuLi followed by ring-closure by insertion reaction.

When **2** was exposed to the air, colorless solution was obtained. Methanol was added to the solution, and separation with HPLC gave the compound $t\text{-Bu}_7\text{Ge}_4\text{O}_2\text{H}$ in 75% yield. The result of NMR, IR, and MS spectrum, and preliminary result of X-ray crystallography indicated the structure shown below.



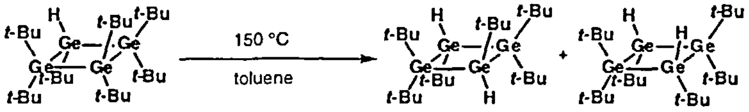
2

75%

Scheme 3

Thermal Reaction of hepta-*t*-butylcyclotetragermane (1)

When hepta-*t*-butylcyclotetragermane (1) was heated at 150 °C in toluene then the products were separated with recycle-type HPLC, two isomers of hexa-*t*-butylcyclotetragermane (2,4-*trans*- and 2,4-*cis*-3) were obtained.



1 2,4-*trans*-3 66% 2,4-*cis*-3 8%

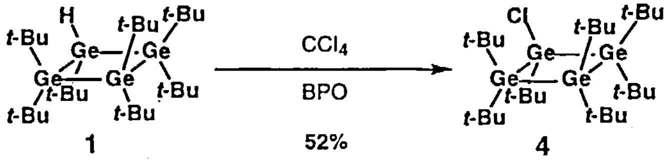
Scheme 4

The yield was 66% and 8%, respectively. The structure of 2,4-*trans*-3 was determined by the following NMR data: In ^{1}H and ^{13}C NMR, two kinds of *t*-Bu groups were observed (2:1 in ^{1}H NMR). Out of four isomers of hexa-*t*-butylcyclotetragermane, only 2,4-*trans* form shows this spectral feature and all the other isomers (3,4-*cis*, 3,4-*trans*, and 2,4-*cis* forms) should show three kinds of substituents. The structure of another product was determined by X-ray crystallography.

Similar thermal reaction was reported from hepta-*t*-butylcyclotetrasilane, but at higher temperature. Thus hepta-*t*-butylcyclotetrasilane gave 2,4-*trans*-hexa-*t*-butylcyclotetrasilane at 190 °C in decalin in 63% yield.[7] Unlike this case, hepta-*t*-butylcyclotetragermane gave two isomers. The driving force of the reaction is thought to be the steric hindrance of the substituents, and the product is the most stable isomer. Due to the longer length of Ge–Ge bonds than that of Si–Si bonds, the steric hindrance in hexa-*t*-butylcyclotetragermane is not severe, and this seems to be the reason of the generation of two isomers.

Chlorination Reaction of hepta-*t*-butylcyclotetragermane (1)

Chlorination of hepta-*t*-butylcyclotetragermane (1) could be effected in the reaction with carbon tetrachloride and benzoyl peroxide. After three hours of stirring, the starting material disappeared, then the product was purified with recycle-type HPLC. Hepta-*t*-butylchlorocyclotetragermane (4) was obtained in 52% yield. The structure of 4 was also determined by X-ray crystallography.

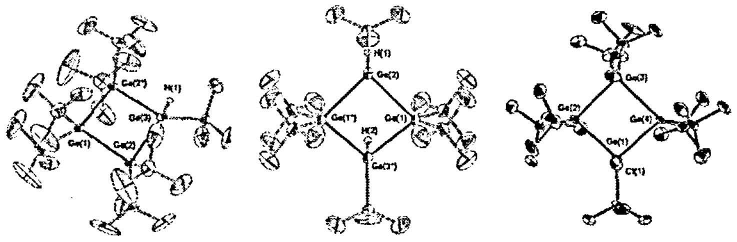


Scheme 5

The Structures of 1, 2,4-*cis*-3, and 4

The ORTEP drawings of **1**, 2,4-*cis*-**3**, and **4** are shown in Figure 1. Summary of crystal data, data collection, and refinement is shown in Table 1. Selected bond lengths and angles are shown in Table 2. For **1**, symmetry axis passes through Ge(1) and Ge(3), and thus a disorder was observed on Ge(3) atom. For 2,4-*cis*-**3**, symmetry axis also passed through Ge(2) and Ge(3*), and a disorder on Ge(3*) was observed similarly. In each case, one of the structures is shown in Figure 1. For **4**, space group was *P*21 and no symmetry elements existed. We tried a couple of other space groups, however, no space groups those are more symmetrical could be applied. Average Ge–Ge bond lengths were 2.518(1) Å for **1** and 2.521(2) Å for 2,4-*cis*-**3**, and these two values are similar within the errors. For **4**, average Ge–Ge bond length was 2.559(1) Å and this result shows the steric hindrance of **4** is much more than other two compounds, as expected. Bond angles around Ge atoms are basically in the normal range, however, sum of bond angles around Ge(3) atom in **1** (Ge(2)–Ge(3)–Ge(2*), Ge(2)–Ge(3)-C(8), and Ge(2*)–Ge(3)-C(8)) was 346.8°, and became closer to planar. Situation for 2,4-*cis*-**3** is similar, and sum of bond angles around Ge(2) was 341.6°, and distorted to planar structure. These features can be explained by the release of steric hindrance of bulky *t*-butyl groups.

The interesting feature of these compounds was dihedral angles of the four membered rings. The dihedral angles for **1** were 15.5° and 16.2°, on the other hand, those for 2,4-*cis*-**3** were 32.0° and 34.5°, and for **4**,



1 2,4-*cis*-3 4

Figure 1. Molecular structures of 1, 2,4-*cis*-3, and 4. Thermal Ellipsoids are drawn in the 30% probability level.

Table 1. Summary of Crystal Data, Collection, and Refinement

	t-Bu_7Ge_4H (1)	*t*-$Bu_6Ge_4H_2$ (*cis*-3)	*t*-Bu_7Ge_4Cl (4)
		Crystal Data	
Formula	$C_{28}H_{64}Ge_4$	$C_{24}H_{56}Ge_4$	$C_{28}H_{63}ClGe_4$
Mol wt	691.17	635.07	725.62
Cryst. descript	colorless prisms	colorless prisms	colorless prisms
Cryst. size/mm	0.6 x 0.5 x 0.5	0.2 x 0.2 x 0.2	0.3 x 0.3 x 0.3
Cryst. syst.	orthorhombic	monoclinic	monoclinic
Space group	*Cmcm*	*C* 2/*m*	*P* 2_1
a /Å	12.189(3)	16.776(3)	10.7988(7)
b /Å	18.133(3)	11.778(1)	15.5715(7)
c /Å	15.562(4)	8.6556(8)	11.5984(5)
β /deg		114.271(6)	116.973(3)
V /Å3	3439(1)	1559.0(3)	1738.2(2)
Z	4	2	2
		Data Collection	
Diffractometer	Rigaku AFC7S	Rigaku RAXIS-IV	Rigaku AFC7S

Radiation (λ, Å)	Cu Kα (1.5418)	Mo Kα(0.71070)	Cu Kα (1.5418)
Temperature/°C	20	-100	20
μ /mm^{-1}	4.105	3.83	4.78
2θ max/deg	120	55	120
Scan width/deg	$1.78+0.30\tan\theta$		$1.73+0.30\tan\theta$
No. of reflcns measd	1406	1522	3266
No. of obsd reflcns ($\vert F_o \vert \geq 3\sigma(F_o)$)	1357	1260	2666
		Refinement	
R	0.045	0.075	0.031
R_w	0.057	0.081	0.032
$(\Delta/\sigma)_{max}$	0.03	0.00	0.40
$((\Delta\rho)_{max}$/eÅ^{-3}	0.48	1.25	0.43
$(\Delta\rho)_{min}$/eÅ^{-3}	-0.54	-1.59	-0.42
No. of params	95	85	299

Table 2. Selected Bond Lengths (Å), and Angles (deg) for 1, *cis*-3, and 4

		Bond Lengths for **1**	
Ge(1)–Ge(2)	2.599(1)	Ge(2)–Ge(3)	2.478(1)
Ge(1)–C(1)	2.061(9)	Ge(2)–C(4)	2.044(6)
Ge(3)–C(8)	2.00(1)	Ge(3)–H(1)	1.430(6)
		Bond Angles for **1**	
Ge(2)–Ge(1)–Ge(2*)	88.97(5)	Ge(1)–Ge(2)–Ge(3)	87.10(4)
Ge(2)–Ge(3)–Ge(2*)	94.63(6)	Ge(2)–Ge(1)–C(1)	116.3(2)
Ge(1)–Ge(2)–C(4)	117.5(2)	Ge(3)–Ge(2)–C(4)	103.6(2)
Ge(2)–Ge(3)–C(8)	126.07(5)	Ge(2)–Ge(3)–H(1)	98(2)
		Bond Lengths for *cis*-**3**	
Ge(1)–Ge(2)	2.555(2)	Ge(1)–Ge(3*)	2.488(2)
Ge(1)–C(1)	2.009(9)	Ge(2)–C(5)	2.044(6)
Ge(2)–H(1)	1.59(9)	Ge(3*)–H(2)	1.57

Bond Angles for *cis*-3

Ge(2)-Ge(1)-Ge(2*)	89.80(7)	Ge(2)-Ge(1)-Ge(3*)	83.35(6)
Ge(1)-Ge(2*)-Ge(1*)	90.20(7)	Ge(2)-Ge(1)-C(1)	124.1(2)
Ge(3*)-Ge(1)-C(1)	125.0(2)	Ge(1)-Ge(2)-C(5)	125.7(2)
Ge(1)-Ge(3*)-C(5*)	126.0(2)	Ge(1)-Ge(2)-H(1)	113(1)
Ge(1)-Ge(3*)-H(2)	93.5		

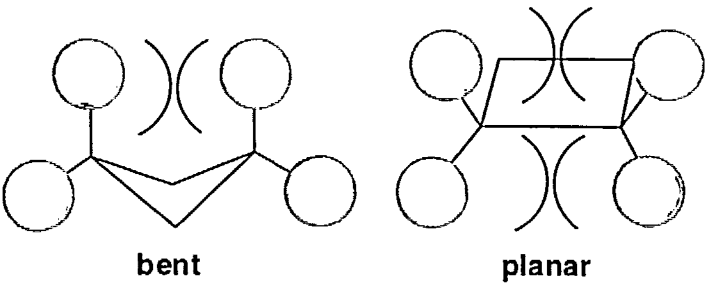
Bond Lengths for 4

Ge(1)-Ge(2)	2.508(1)	Ge(1)-Ge(4)	2.508(1)
Ge(2)-Ge(3)	2.602(1)	Ge(3)-Ge(4)	2.619(1)
Ge(1)-Cl(1)	2.226(2)	Ge(1)-C(1)	2.043(7)
Ge(2)-C(5)	2.032(8)	Ge(2)-C(9)	2.067(8)
Ge(3)-C(13)	2.034(8)	Ge(3)-C(17)	2.066(8)
Ge(4)-C(21)	2.074(9)	Ge(4)-C(25)	2.069(8)

Bond Angles for 4

Ge(2)-Ge(1)-Ge(4)	95.14(4)	Ge(1)-Ge(2)-Ge(3)	86.08(4)
Ge(2)-Ge(3)-Ge(4)	90.33(4)	Ge(1)-Ge(4)-Ge(3)	85.71(4)
Ge(2)-Ge(1)-Cl(1)	99.92(7)	Ge(4)-Ge(1)-Cl(1)	101.62(6)
Ge(2)-Ge(1)-C(1)	128.6(2)	Ge(4)-Ge(1)-C(1)	127.6(3)
Ge(1)-Ge(2)-C(5)	111.9(3)	Ge(3)-Ge(2)-C(5)	114.5(3)
Ge(1)-Ge(2)-C(9)	111.6(3)	Ge(3)-Ge(2)-C(9)	122.9(2)
Ge(2)-Ge(3)-C(13)	121.9(2)	Ge(2)-Ge(3)-C(17)	108.0(3)
Ge(4)-Ge(3)-C(13)	110.5(3)	Ge(4)-Ge(3)-C(17)	121.1(3)
Ge(1)-Ge(4)-C(21)	111.9(2)	Ge(1)-Ge(4)-C(25)	111.4(2)
Ge(3)-Ge(4)-C(21)	121.4(2)	Ge(3)-Ge(4)-C(25)	118.3(2)

17.2° and 18.2°. It is not easy to account for the relationship of dihedral angles and the substituents. So far as reported, octaisopropylcyclotetrasilane[8] had very large 37.1° of dihedral angle, meanwhile hepta-*t*-butylcyclotetrasilane was planar.[5] As a general rule, planar structure is advantageous when the bulky substituents occupy 1,3-*cis* because with larger dihedral angle, those two substituents come closer. When the large groups stay on 1,2-*cis* position, larger dihedral angles are favorable as the 1,2-substituents move from the eclipse conformation.



Scheme 6

These situations are depicted in Scheme 6. In addition, packing in the single crystal is one of the major factors of the dihedral angles.

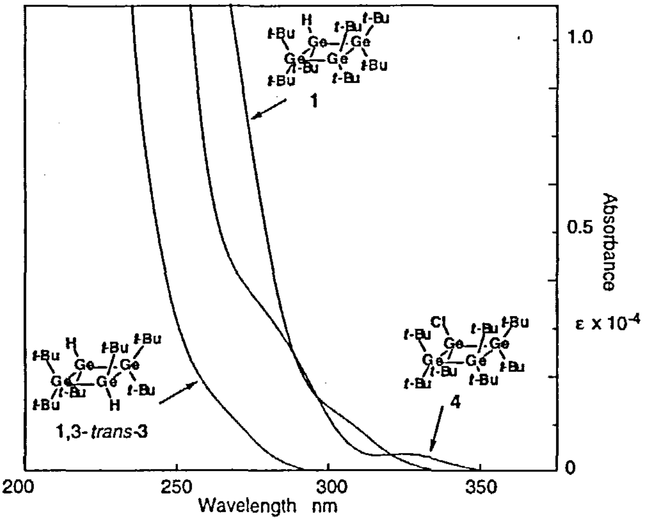


Figure 2. UV spectra in Hexane

UV-vis Spectra

All the compounds described herein possess bulky substituents, and their steric repulsion is expected to perturb the electronic property of cyclotetragermane ring. The UV-vis spectra of **1**, 2,4-*trans*-**3**, and **4** are shown in Figure 2. The absorption maximum of octaisopropylcyclotetragermane[9] and octaethylcyclotetragermane[10] was reported to be 280 and 285 nm, respectively, and **1** and 2,4-*trans*-**3** both showed bathochromic shift. In addition, **1** showed its absorption in longer wavelength than that of 2,4-*trans*-**3**, and this indicated that **1** has more strain than 2,4-*trans*-**3**. By introducing chlorine to the ring, more bathochromic shift was observed.

In summary, we prepared 1,2-dichloro-1,1,2,2-tetra-*t*-butyldigermane and reductive coupling was performed. Hepta-*t*-butylcyclotetragermane (**1**) was obtained via stable cyclic germyllithium. With thermal reaction, two isomers of hexa-*t*-butylcyclotetragermane (**3**) were obtained. Compound **1** also could be transferred to hepta-*t*-butylchlorocyclotetragermane (**4**) by the reaction with CCl_4/BPO. The structure of **1**, 2,4-*cis*-**3**, and **4** was determined by X-ray crystallography.

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