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Synthesis and Structure of Organodiselenogermanes[1)]

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Diphenylselenogermanes are prepared for the first time in 32-89% yield by the reaction between sodium benzeneselenolate and dihalogermanes (halogen=Cl or Br). The X-ray structure of 1,1-diphenylseleno-1-germacyclopentane has been determined.

The essential concepts in conventional physical organic chemistry may sometimes fail to explain phenomena which emerge in the new area of "Heteroatom Chemistry". The germanium-selenium bond, which has been virtually unknown as a chemical bond incorporated in an organic substrate,[2)] may offer a unique opportunity to test their validity. In our research project directed toward the direct spectral observation of organogermylenes, we have chosen alkyl- or aryl-substituted diselenogermanes (**1**) as precursors. Literature survey has revealed that germanes having two selenium atoms directly bonded to germanium have not been described to date. We now report the first synthesis of **1** and the X-ray structure analysis of one of the crystalline examples of **1**.

Several approaches to **1** were considered, but the use of dihalogermanes (**2**) seemed to provide the easiest access to **1**. Since dihalogermanes (**2**) are not usually stable under aqueous or alcoholic conditions, we have employed standard anhydrous conditions according to Eq. 1. In the first step, sodium benzeneselenolate is prepared by the reaction of diphenyl diselenide and sodium metal in tetrahydrofuran(THF) at reflux temperature.[3)] Addition of a

$$\underset{\mathbf{2}}{R^1R^2GeX_2} + 2PhSeNa \xrightarrow[THF]{} \underset{\mathbf{1}}{R^1R^2Ge(SePh)_2} \quad (1)$$

dihalogermane (**2**) (halogen:X=Cl or Br)[4] to this mixture at -78 °C and subsequent stirring at -78 °C to room temperature for 10 to 15 h under argon atmosphere provided **1** in 31 to 89% yield after Kugel-rohr distillation followed by reverse-phase liquid chromatography(Table 1).[5] Compounds **1** were relatively air-stable at room temperature. However they decomposed completely upon aqueous workup or under chromatographic conditions on silica gel. It should be noted here that the selenium-germanium single bond, in which both elements fall in the same period in the periodic table, is stable under atmospheric conditions unlike the case of compounds containing Si-Se bond, which usually undergo decomposition by rapid reaction with atmospheric moisture.[3] The difference between germanium and silicon in the bond formation with selenium is apparent.

Table 1. Synthesis of Diselenogermanes (**1**)[a]

	2			**1**		Elemental analysis Found(Calcd)	
	R^1	R^2	X	Yield/%[b]	^{77}Se-NMR[c]	C %	H %
a	Me	Me	Cl	89	148.9	40.84(40.54)	3.98(3.89)
b	Et	Et	Br	88	98.1	43.22(43.40)	4.59(4.60)
c	n-Pr	n-Pr	Cl	60	111.2	45.61(45.91)	5.31(5.14)
d	n-Bu	n-Bu	Cl	61	109.5	48.21(48.14)	5.66(5.44)
e	Ph	Ph	Br	31	111.7	53.76(53.49)	3.82(3.74)
f	$-(CH_2)_4-$		Cl	45	117.1	44.85(44.89)	4.40(4.43)
g	$-(CH_2)_5-$		Cl	54	135.3	43.83(43.59)	4.24(4.12)

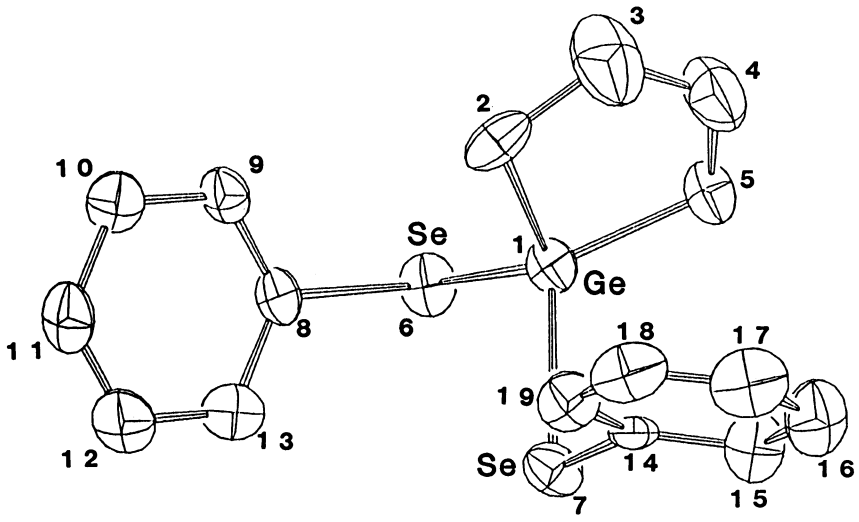
a)See text for experimental details. b)Isolated yield. c)In $CDCl_3$ using Me_2Se as external standard.

Spectroscopic properties of **1** (IR, ^{1}H, ^{13}C, and ^{77}Se NMR, and MS) as well as elemental analysis were consistent with the expected structures. For example, the NMR spectrum of dimethyldiphenylselenogermane (**1a**) showed protons at $\delta(CDCl_3/Me_4Si)$ 0.77(s, 2 x Me) and 7.10-7.70(m, 2 x Ph), five carbon peaks at $\delta(CDCl_3/Me_4Si)$ 5.0(q, Me), 125.5(s, Ph), 127.2(d, Ph), 128.8 (d, Ph) and 136.3(d, Ph) and a single selenium peak at $\delta(CDCl_3/Me_2Se)$ 148.9. The low chemical shift value of ^{77}Se NMR for **1a** (δ 148.9) clearly showed that the selenium atom is directly bonded to the germanium.[6] All compounds (**1**) except for 1,1-diphenylseleno-1-germacyclopentane (**1f**) (mp 75 °C,

recrystallized from acetonitrile) were light yellow oil.

In order to obtain the structure parameters for diselenogermanes **1**, we have carried out an X-ray diffraction analysis for 1,1-diphenylseleno-1-germacyclopentane (**1f**), which was readily recrystallized from acetonitrile. The crystallographic data are as follows: $C_{16}H_{18}GeSe_2$, M=441.5, monoclinic, space group $P2_1/n$, a=22.04(1), b=8.507(4), c=8.900(4) Å, β=96.03°(3), Z=4, Mo-K_α radiation λ=0.7107 Å. Intensities were measured on a Philips fourcircle diffractometer and the number of the independent reflections was 2298. The structure was solved by the direct method and refined by the block-diagonal least squares calculations which converged at R=0.107. The molecular structure thus obtained is shown in Fig. 1.

The mean value of the Se-Ge bond length for **1f** is 2.362(5) Å. This is slightly longer than the corresponding value for inorganic compounds containing Se-Ge bond (mean value=2.135 Å).[7] The germacyclopentane ring is significantly distorted from normal alicyclic 5-membered ring because of the long C-Ge bonds(mean value=1.965 Å). The conformation of the five membered ring of the germacyclopentane (**1f**) causes the C(2)-Ge(1)-C(5) bond angle deviation(95.7°) from normal tetrahedral geometry on the germanium atom.



Bond distance(Å)

Ge(1)-Se(6)	2.360
Ge(1)-Se(7)	2.365
Ge(1)-C(5)	1.966
Ge(1)-C(2)	1.964
Se(6)-C(8)	1.942
Se(7)-C(14)	1.907

Bond Angle(°)

Se(6)-Ge(1)-Se(7)	101.7
C(2)-Ge(1)-C(5)	95.7
Ge(1)-C(2)-C(3)	102.3
Ge(1)-C(5)-C(4)	99.4
C(2)-C(3)-C(4)	117.3
C(3)-C(4)-C(5)	122.8
Ge(1)-Se(6)-C(8)	94.8
Ge(1)-Se(7)-C(14)	95.7

Fig. 1. A perspective view of 1,1-diphenylseleno-1-germacyclopentane (**1f**) (Hydrogen atoms are omitted), drawn by ORTEP program(see Ref.8). Atoms are shown by 30% probability ellipsoids.

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