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Synthesis and Crystal Structure of an Intermediate of the Germanium–Peterson Reaction

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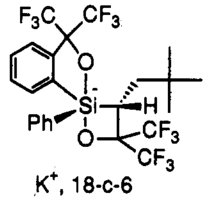
Peterson-type reactions, using β-hydroxy silanes, germanes, stannanes, and plumbanes, stereospecifically produce the corresponding olefins under acidic and neutral (or basic) conditions.[1] Recently, we achieved the syntheses of pentacoordinate 1,2-oxasiletanide **1**[2] and 1,2-oxastannetanide **2**,[3] intermediates of the Peterson and tin-Peterson reactions, respectively.



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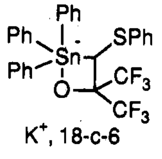

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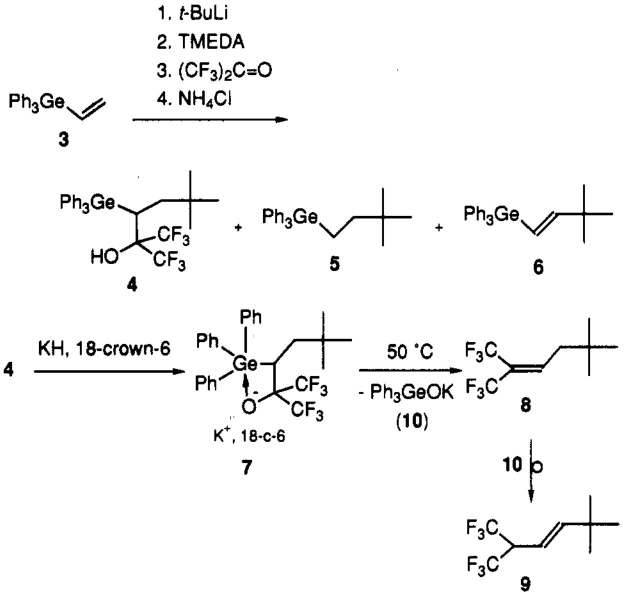
We now report the first synthesis and crystal structure of an intermediate of the germanium–Peterson reaction.

Sequential treatment of triphenylvinylgermane (**3**)[4] with 1.3 equiv of *t*-BuLi (THF, −72 °C, 1 h), 2 equiv of tetramethylethylenediamine (TMEDA), excess hexafluoroacetone (THF, −72 °C, 15 min), and aqueous NH_4Cl gave the corresponding β-hydroxy germane **4** (16%) along with a mixture of byproducts **5** and **6** (84%) (Scheme 1).

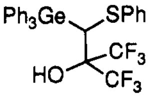
Deprotonation of **4** with KH in the presence of 18-crown-6 in THF was monitored by ^{19}F NMR spectroscopy and showed the quantitative formation of a new species **7** having a double quartet with centers of δ_F −68.73 ($^4J_{FF}$ = 8.3 Hz) and −74.49 ($^4J_{FF}$ = 8.3 Hz), which was stable from −50 °C to room temperature.[5] In the ^{13}C NMR spectrum, a downfield shift of the signals assigned to the α-carbon (δ_C 28.80 → 41.06) and the *ipso*-carbon of the phenyl groups of **4** (δ_C 138.18 → 143.75) was observed. This is characteristic of the structural change from a tetracoordinate to a pentacoordinate species as shown in the cases of 1,2-oxasiletanide **1**, 1,2-oxastannetanide **2**, and diorganotrifluorosilicate,[2,3,6] suggesting that **7** exists as a pentacoordinate 1,2-oxagermetanide in solution. The ^1H and ^{13}C NMR spectra showed only one set of signals for GePh, indicating the occurence of fast positional isomerization.

Scheme 1



It was determined by ^{19}F NMR spectroscopy that, upon heating (50 °C, CD_3CN, 1 h), **7** provided, quantitatively, the double-bond migrated olefin **9**, which was formed by base-catalyzed isomerization of a Peterson-type reaction product **8**, along with potassium triphenylgermyl oxide **10**. However, heating in $CDCl_3$ at 110 °C for 15 h gave olefin **8** in 20% yield, with recovery of **7** (80%). The lower reactivity and the absence of isomerization in the latter reaction are probably due to solvent effects on olefin formation and the lower basicity of **10** in $CDCl_3$ than CD_3CN, respectively. Similar treatment of β-hydroxy germane **11**, which was prepared as described for the tin analog,[2] did not give a stable intermediate, but afforded the corresponding olefin even at −20 °C, in sharp contrast to the cases of **7** and 1,2-oxastannetanide **2**.

Product **7** was recrystallized from dichloromethane–hexane to afford colorless plates that melted at 129–130 °C with decomposition. The X-ray crystallographic analysis of **7** indicated that it is not a pentacoordinate 1,2-oxagermetanide, but rather a β-germylalkoxide with a strong interaction between the germanium and oxygen atoms (bond distance Ge(1)–O(1) = 2.832 (8) Å) (Figure 1).[7] Selected bond lengths and angles are summarized in Table 1. Crystal data are shown in Table 2. This is the first example of an intermediate of the germanium–Peterson reaction.



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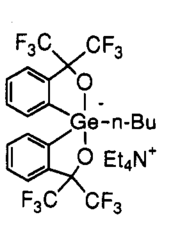

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[1] For recent reviews on the Peterson reaction, see: Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 58–73. Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 141–152. Ager, D. J. *Synthesis* **1984**, 384. Ager, D. J. *Org. React.* (*N.Y.*) **1990**, *38*, 1. For reviews on the Peterson-type reaction, see: Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410. Kauffmann, T. *Top. Curr. Chem.* **1980**, *92*, 109. For tin compounds, see: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987, pp 176–177.

[2] Kawashima, T.; Iwama, N.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 7598.

[3] Kawashima, T.; Iwama, N.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2507.

[4] Henry, M. C.; Noltes, J. G. *J. Am. Chem. Soc.* **1960**, *82*, 555.

[5] Except for **3** no signal was observed by ^{73}Ge NMR spectroscopy, because of difficulty of measurement mainly due to quadrupole relaxation.

[6] Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 182.

[7] The authors have deposited atomic coordinates for **7** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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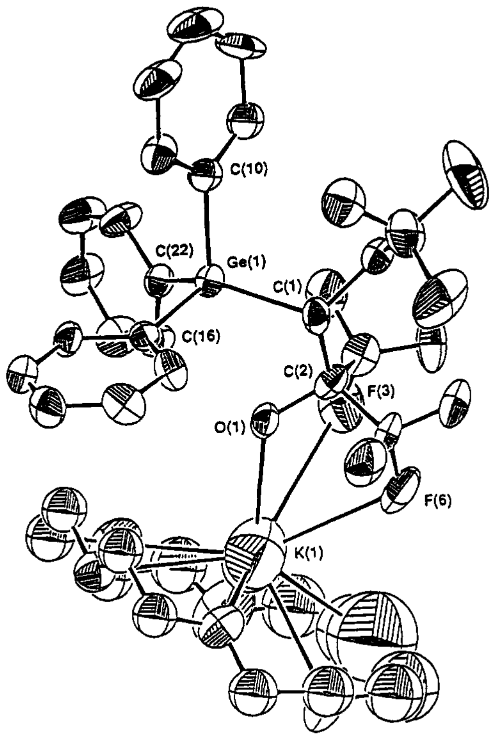

Figure 1. ORTEP drawing of 7.

Table 1. Selected Bond Lengths and Angles for 7

bond, Å		angle, deg	
Ge(1)–C(1)	2.04(1)	C(1)–Ge(1)–C(10)	109.2(5)
Ge(1)–C(10)	2.00(1)	C(1)–Ge(1)–C(16)	108.0(5)
Ge(1)–C(16)	1.96(1)	C(1)–Ge(1)–C(22)	122.7(5)
Ge(1)–C(22)	1.98(1)	C(10)–Ge(1)–C(16)	106.4(6)
C(1)–C(2)	1.53(2)	C(10)–Ge(1)–C(22)	102.3(5)
C(2)–O(1)	1.37(2)	C(16)–Ge(1)–C(22)	107.1(5)
K(1)–O(1)	2.67(1)	Ge(1)–C(1)–C(2)	110.1(8)
K(1)–F(3)	3.28(2)	O(1)–C(2)–C(1)	106(1)
K(1)–F(6)	3.01(1)	C(16)–Ge(1)–O(1)	85.8(4)
Ge(1)–O(1)	2.832(8)	C(10)–Ge(1)–O(1)	162.6(5)
		C(1)–Ge(1)–O(1)	54.1(4)

Table 2. Crystal Data of 7

formula	$C_{39}H_{51}GeF_6O_7K$
formula weight	857.51
crystal color	colorless
crystal dimensions (mm)	0.500 × 0.400 × 0.050
crystal system	triclinic
space group	$P\bar{1}$
Z	2
a (Å)	13.567(6)
b (Å)	14.554(3)
c (Å)	13.176(3)
V (Å^3)	2124(1)
d (calcd) (g/cm^3)	1.340
α (deg)	96.66(2)
β (deg)	116.77(2)
γ(deg)	66.54(1)
F(000)	892
μ (cm^{-1})	8.76
2θ max (deg)	55.1
no. of data	7723
no. of data used	3211
no. variables	413
R	0.084
Rw	0.109

The distance between Ge(1) and O(1) is shorter than the sum of the van der Waals radii (3.62 Å), but longer than the bond lengths of O(1)–K(1) (2.67 (1) Å) and Ge–O (1.984 (5) or 1.994 (5) Å) of 12.[8] The bond length Ge(1)–C(10) (2.00 (1) Å) is slightly longer than those of Ge(1)–C(16) (1.96 (1) Å) and Ge(1)–C(22) (1.98 (1) Å). The largest and smallest bond angles are those of C(1)–Ge(1)–C(22) (122.7(5)°) and of C(16)–Ge(1)–C(22) (102.3(5)°), respectively, deviant from a typical tetrahedral angle. The Ge atom is not in the plane of the three carbon ligands [C(1), C(16), and C(22)], but lies 0.548 Å above it, toward the side of the C(10) atom. The torsion angle Ge(1)–C(1)–C(2)–O(1) is −33 (1)°, indicating that the four-membered ring is significantly puckered. The potassium atom is not located in the plane of the crown ether and interacts with O(1) and one fluorine atom of each trifluoromethyl group. These results strongly suggest that 7 is an intermediary structure between a β-germylalkoxide and a 1,2-oxagermetanide.

Taking into account the present results and structural features of 1 and 2 it can be reasonably concluded that whether or not intermediates of Peterson-type reactions have a pentacoordinate structure in the solid state is dependent on the central atom and its substituents.

Experimental Section

Tetrahydrofuran (THF) was distilled from benzophenone ketyl under argon atmosphere prior to use, and other solvents were purified by the usual procedures. Alkyllithiums (Tosoh-Akzo), hexafluoroacetone trihydrate (Central Glass), and germanium tetrachloride (ASAI Germanium Institute) were used as received. ^1H and ^{13}C NMR spectra were measured with a Bruker AM-500 spectrometer using tetramethylsilane (TMS) as internal standard. ^{19}F NMR spectra were taken with a JEOL FX-90Q spectrometer using fleon as external standard. All NMR chemical shifts are reported by δ values based on those of standard compounds. Mass spectra were recorded with a JEOL JMX-SX102 mass spectrometer operating in the electron impact (EI) mode. Melting points were determined on a Yanaco micro melting point apparatus. Dry column chromatography (dry CC) was carried out with ICN silica DCC 60A. Elemental analyses were determined on a Perkin-Elmer micro analyzer.

Michael Addition Reaction of *t*-BuLi with Triphenylvinylgermane (3). To a solution of triphenylvinylgermane (3)[4] (193 mg, 0.58 mmol), which was prepared from bromotriphenylgermane,[9] in dry THF (5 mL) was added a pentane solution of *t*-BuLi (0.55 mL, 0.88 mmol) at −72 °C under argon atmosphere. The resulting solution was stirred at −72 °C for 45 min and then quenched with aqueous NH_4Cl. After the usual workup, the residue was subjected to dry CC (hexane) to give (3,3-dimethylbutyl)triphenylgermane (5) (212 mg, 93%): colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (s, 9 H), 1.39–1.51 (m, 4 H), 7.33–7.39 (m, 9 H), 7.46–7.50 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.49, 28.81, 31.47, 38.71, 128.15, 128.80, 134.95, 137.27; HRMS *m/z* calcd for $C_{24}H_{28}{}^{74}Ge$ 390.1379, found 390.1403.

Preparation of [3,3-Dimethyl-1-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]butyl]triphenylgermane (4). To a solution of 3 (540 mg, 1.63 mmol) in dry THF (10 mL) was added a pentane solution of *t*-BuLi (1.3 mL, 2.12 mmol) at −72 °C under argon atmosphere. After the resulting orange solution was stirred at −72 °C for 1 h, tetramethylethylenediamine (0.5 mL, 3.26 mmol) and excess hexafluoroacetone, which was freshly prepared by adding its trihydrate (1.11 mL, 8.15 mmol) into concentrated H_2SO_4 (30 mL) at 150–200 °C, were added sequentially. The solution turned colorless, and stirring was continued at −72 °C for an additional 15 min. After the usual workup, the residue was subjected to dry CC (hexane–CH_2Cl_2 (2:1)) to give β-hydroxy germane 4 (166 mg, 16%) and a mixture of 5 and *trans*-(3,3-dimethyl-1-butenyl)triphenylgermane (6) in 84% yield. Further separation of 5 and 6 was not done. 4: colorless crystals; mp 169–171 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.56 (s, 9 H), 1.78 (d, ^2J = 16 Hz, 1 H), 2.09 (dd, ^2J = 16 Hz,

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[8] Denmark, S. E.; Jacobs, R. T.; Dai-Ho, G.; Wilson, S. *Organometallics* **1990**, *9*, 3015.

[9] Johnson, O. H.; Nebergall, W. H.; Harris, D. M. *Inorg. Synth.* **1957**, *5*, 76.

^3J = 7 Hz, 1 H), 3.06–3.11 (m, 1 H), 3.12 (s, 1 H), 7.32–7.40 (m, 9 H), 7.57–7.59 (m, 6 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 28.8, 29.56, 31.48, 35.66, 80.88 (sept, $^2J_{CF}$ = 28 Hz), 123.69 (q, $^1J_{CF}$ = 289 Hz), 124.22 (q, $^1J_{CF}$ = 290 Hz), 128.36, 129.15, 136.34, 138.28; ^{19}F NMR ($CDCl_3$) δ –68.79 (q, J_{FF} = 8.1 Hz), –74.94 (q, J_{FF} = 8.1 Hz). Anal. Calcd for $C_{27}H_{28}GeF_6O$: C, 58.42; H, 5.08. Found: C, 58.22; H, 4.93. **6** (a mixture with **5**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (s, 9 H), 6.07 (d, ^3J = 19 Hz, 1 H), 6.17 (d, ^3J = 19 Hz, 1 H), 7.34–7.39 (m, 9 H), 7.47–7.49 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.10, 35.72, 116.74, 128.13, 128.86, 135.07, 137.01, 161.00; HRMS *m/z* calcd for $C_{24}H_{26}{}^{74}Ge$ 388.1246, found 388.1227.

Synthesis of an Intermediate of the Germanium–Peterson Reaction, Potassium (18-crown-6) 4,4-Dimethyl-1,1-bis(trifluoromethyl)-2-(triphenylgermyl)pentoxide (7). To a solution of **4** (203 mg, 0.37 mmol) and 18-crown-6 (96 mg, 0.37 mmol) in dry THF (4 mL) was added a THF suspension of excess of KH at –72 °C. The mixture was stirred at –72 °C for 10 min and 0 °C for 30 min, and the solvent was evaporated to give a tarry oil. The oil was recrystallized from hexane–CH_2Cl_2 to give potassium (18-crown-6) 4,4-dimethyl-1,1-bis(trifluoromethyl)-2-(triphenylgermyl)pentoxide (**7**) (317 mg, 92%) as colorless crystals: mp 129–130 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.53 (s, 9 H), 1.80 (d, ^2J = 15 Hz, 1 H), 2.06 (dd, ^2J = 15 Hz, ^3J = 7 Hz, 1 H), 3.13 (d, ^3J = 7 Hz, 1 H), 3.62 (s, 24 H), 7.28–7.31 (m, 9 H), 7.59–7.61 (m, 6 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 29.79, 31.29, 36.37, 41.06, 70.33, 84.03 (sept, $^2J_{CF}$ = 24 Hz), 127.21, 127.39, 127.80 (q, $^1J_{CF}$ = 298 Hz), 128.39 (q, $^1J_{CF}$ = 299 Hz), 137.12, 143.75; ^{19}F NMR ($CDCl_3$) δ –68.73, –74.49 (A_3B_3, $^4J_{FF}$ = 8.3 Hz). Anal. Calcd for $C_{39}H_{51}F_6GeO_7K\cdot 2/3CH_2Cl_2$: C, 52.12; H, 5.77. Found: C, 52.11; H, 5.98.

Monitoring of Olefin Formation from 7 by ^{19}F NMR. A mixture of **7** and CD_3CN was placed in an NMR tube, degassed, and sealed. After heating at 50 °C for 30 min, ^{19}F NMR showed quantitative formation of (*E*)-1,1,1-trifluoro-5,5-dimethyl-2-(trifluoromethyl)-3-hexene (**9**) instead of 1,1,1-trifluoro-5,5-dimethyl-2-(trifluoromethyl)-2-hexene (**8**). **9**: ^{1}H NMR (500 MHz, CD_3CN) δ 1.05 (s, 9 H), 3.84–3.94 (m, 1 H), 5.32 (dd, ^3J = 16 Hz, ^3J = 10 Hz, 1 H), 6.09 (d, ^3J = 16 Hz, 1 H); ^{19}F NMR (CD_3CN) δ –68.59 (d, $^3J_{HF}$ = 8.3 Hz, 6 F).

Preparation of Triphenyl[(phenylthio)methyl]germane (13). To a solution of bromotriphenylgermane (1.12 g, 2.89 mmol) in dry THF (10 mL) was added a solution of [(phenylthio)methyl]lithium (3.48 mmol) in dry THF (10 mL) at –72 °C. The mixture was allowed to warm to 0 °C immediately and stirred at 0 °C for 2 h, and then quenched with aqueous NH_4Cl. After the usual workup, recrystallization of the mixture from hexane–CH_2Cl_2 gave triphenyl[(phenylthio)methyl]germane (**13**) (952 mg, 77%), and the filtrate was subjected to dry CC (hexane) to give **13** (197 mg, 16%). Total yield was 93%. **13**: colorless crystals; mp 126–127.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.06 (s, 2 H), 7.09–7.12 (m, 1 H), 7.24–7.32 (m, 4 H), 7.37–7.44 (m, 9 H), 7.56–7.58 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.86, 124.88, 126.24, 128.33, 128.67, 129.42, 134.92, 135.29, 140.21. Anal. Calcd for $C_{25}H_{22}GeS$: C, 70.30; H, 5.19. Found: C, 70.10; H, 5.20.

Preparation of Triphenyl[3,3,3-trifluoro-2-hydroxy-1-(phenylthio)-2-(trifluoromethyl)propyl]germane (11). To a solution of **10** (714 mg, 1.67 mmol) in dry THF (10 mL) was added a solution of LDA (5.02 mmol) in dry THF (5 mL) at –72 °C. The mixture was allowed to warm to –10 °C over 2 h and cooled to –72 °C. Then, hexamethylphosphoric triamide (HMPA) (1.45 mL, 8.36 mmol) and hexafluoroacetone were added to the mixture, sequentially. The resulting solution was stirred at –72 °C for 15 min and then quenched with aqueous NH_4Cl. After the usual workup, the residue was subjected to dry CC (hexane–CH_2Cl_2 (2:1)) to give triphenyl[3,3,3-trifluoro-2-hydroxy-1-(phenylthio)-2-(trifluoromethyl)propyl]germane (**11**) (118 mg, 12%) as colorless crystals: mp 113–115 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 1 H), 4.27 (s, 1 H), 7.02–7.03 (m, 2 H), 7.12–7.17 (m, 3 H), 7.31–7.40 (m, 9 H), 7.59–7.61 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.07, 77.54 (sept, $^2J_{CF}$ = 29 Hz), 122.74 (q, $^1J_{CF}$ = 288 Hz), 122.82 (q, $^1J_{CF}$ = 288 Hz), 127.48, 128.19, 128.99, 129.48, 130.21, 134.96, 135.54, 136.34; ^{19}F NMR ($CDCl_3$) δ –72.74, –74.06 (A_3B_3, $^4J_{FF}$ = 8.3 Hz). Anal. Calcd for $C_{28}H_{22}GeF_6OS$: C, 56.70; H, 3.74. Found: C, 56.68; H, 3.83.

Reaction of β-Hydroxy Germane 11 with KH. A solution of **11** (20 mg, 0.03 mmol) and 18-crown-6 (9 mg, 0.03 mmol) in dry THF was placed in an NMR tube. A THF suspension of excess of KH was added at –72 °C. Measurement of ^{19}F NMR was carried out over the range from –50 to –20 °C. At –50 °C broad complicated signals were observed, and the signal due to olefin appeared when the temperature became –20 °C.

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