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Germanium(II) and Germanium(IV) Compounds from Elemental Germanium

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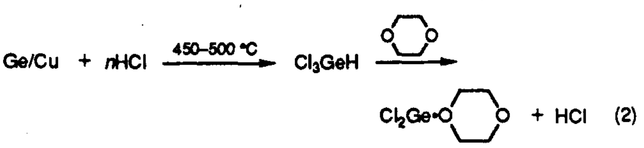
Summary: Divalent germanium derivatives (GeX_2 and RGeX) were generated by direct reaction between germanium powder and various mercury(II) halides. Difluorogermylene was isolated by means of sublimation, while other halogermylenes (GeX_2 and RGeX) were characterized by trapping cycloaddition or insertion reactions. Adducts and cycloadducts thus obtained have been either isolated or characterized by means of comparison (GC and NMR and mass spectroscopy) with authentic samples synthesized by other routes.

Among the different syntheses for divalent germanium halides (germylenes), the main synthesis from elemental germanium (direct synthesis) is the reaction of hydrogen halides with germanium at high temperatures:[1-6]

$$\mathrm{Ge} + 2\mathrm{HF} \xrightarrow{225\ ^\circ\mathrm{C}} \mathrm{F_2Ge} + \mathrm{H_2}\uparrow \qquad (1)$$



(2)

However, oxidation of Ge (eq 3)

$$\mathrm{Ge} + \mathrm{Hg}^{2+} \rightarrow \mathrm{Hg} + \mathrm{Ge}^{2+} \qquad (3)$$

should be possible according to the relative potentials of the corresponding elements[7] and to Brewer and Dennis,[8] whose results showed that the reaction of germanium with Hg_2Cl_2 at high temperature yields germanium tetrachloride:

$$\mathrm{Ge} + 2\mathrm{Hg_2Cl_2} \xrightarrow[\mathrm{N_2\ (15\ mmHg)}]{\text{heating}} 4\mathrm{Hg} + \mathrm{GeCl_4} \qquad (4)$$

The aim of this work was to investigate the possible reactions of elemental germanium with some mercury(II) halides in order to obtain germylenes and tetravalent halogermanes.

Reaction between Germanium Powder and Mercury(II) Chloride. We observed that germanium powder reduced mercury(II) chloride almost quantitatively in THF to elemental mercury[9] (Scheme I).

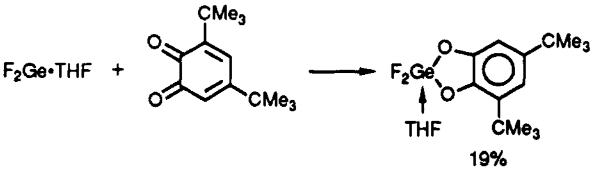
The reaction was very slow at room temperature, and some of the reaction products were detected only by mass spectrometry, but the conversion was more effective at higher temperatures and was achieved at 140 °C. Dichlorogermylene, which was generated during the reaction, was trapped by cycloaddition reactions with 2,3-dimethylbutadiene[5,10] or 3,5-di-*tert*-butyl-*o*-quinone[11] and also by insertion reactions into the carbon–halogen bond of chloromethyl methyl ether[5,10] and chloroethyl methyl ether (Scheme I).

The direct reaction of germanium powder with the trapping reagents used did not occur in the absence of mercury(II) chloride.

Characterization of the adducts, which usually were formed in low yield (Scheme I), was effected by spectroscopic analysis (GC and NMR and mass spectrometry) and by comparison with authentic samples.[9,11-13]

Reaction between Germanium Powder and Mercury(II) Fluoride. In a Carius tube, mercury(II) fluoride reacted with germanium powder without solvent, at 160 °C under reduced pressure (10^{-2} mmHg). The redox reaction was violent; GeF_2 sublimed on the upper walls of the Carius tube, and mercury condensed in the cold part of the tube. The GeF_2 formed was extracted with use of anhydrous THF and characterized by its reaction with 3,5-di-*tert*-butyl-*o*-quinone:[11,14]

$$\mathrm{Ge} + \mathrm{HgF_2} \xrightarrow{160\ ^\circ\mathrm{C}} \mathrm{Hg} + \mathrm{F_2Ge} \qquad (5)$$



(6)

When the Carius tube was sealed under argon (1 atm), the reaction started only at about 270 °C and led to GeF_2 (10–12%) and GeF_4, which was characterized as its eth-

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(1) Muetterties, E. L.; Castle, J. E. *J. Inorg. Nucl. Chem.* **1961**, *18*, 148.

(2) Rochow, E. G.; Abel, E. W. *The Chemistry of Germanium, Tin and Lead*; Pergamon Texts in Inorganic Chemistry 14; Pergamon: Oxford, U.K., 1975; p 26.

(3) Wiberg, E.; Amberger, E. *Hydrides of the Elements of Main Group I-IV*; Elsevier: Amsterdam, 1971; p 688.

(4) Lesbre, M.; Mazerolles, P.; Satgé, J. *The Organic Compounds of Germanium*; Wiley: London, 1971; p 223.

(5) Satgé, J.; Massol, M.; Rivière, P. *J. Organomet. Chem.* **1973**, *56*, 1.

(6) Bähr, G.; Kalinowski, H. O.; Pawlenko, S. In *Methoden der Organischen Chemie (Houben-Weyl)*; Thieme Verlag: Stuttgart, Germany, 1972; Metallorganische Verbindungen (Ge, Sn).

(7) Lourié, Y. Aide mémoire de chimie analytique. In *Analyse qualitative et quantitative*, 3rd ed.; Alexeiv, V., Ed.; Mir: Moscow, USSR, 1975; pp 346–367.

(8) Brewer, F. M.; Dennis, L. M. *J. Phys. Chem.* **1927**, *31*, 1527.

(9) The Ge powder (about 11.20 μm) used was obtained from Sogemet Neuilly (France). It was washed with THF and dried in vacuo before use. A typical procedure is as follows: a mixture of Ge metal (2 g, 28 mmol), $HgCl_2$ (5.5 g, 20 mmol), and $ClCH_2OCH_3$ (2.52 g, 31 mmol) was heated in a Carius tube (sealed under an argon atmosphere) at 130 °C for 72 h. A drop of Hg was formed. The upper liquid was syringed out and distilled under vacuum to give $Cl_3GeCH_2OCH_3$ (2.87 g; 62%). Crude Hg was washed with HCl (10%), alcohol, and ether and dried under vacuum to give 3.06 g (74%) of the product.

(10) Rivière, P.; Rivière-Baudet, M.; Satgé, J. Germanium. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Chapter 10.

(11) Rivière, P.; Castel, A.; Satgé, J.; Guyot, D. *J. Organomet. Chem.* **1986**, *315*, 157.

(12) Synthesis of $Cl_3GeCH_2CH_2OCH_3$ from $Cl_3Ge^-Et_3NH^+$: To a benzene solution (5 mL) of $GeCl_4$ (3.71 g, 17 mmol), Cl_3SiH (2.31 g, 17 mmol), and Et_3N (1.73 g, 17 mmol)[6] was added $ClCH_2CH_2OCH_3$ (1.6 mL, excess), and the mixture was heated in a Carius tube at 120 °C for 48 h. Addition of C_6H_6 (5 mL) caused precipitation of $[Et_3NH]^+Cl^-$, which was filtered out. Distillation of the filtrate gave $Cl_3GeCH_2CH_2OCH_3$ (0.65 g, 16%): bp 98 °C (35 mmHg); ^1H NMR (C_6D_6) δ 1.73 (t, 2 H, CH_2), 3.13 (t, 2 H, CH_2O), 2.93 (s, 3 H, OCH_3) ppm. Anal. Calcd for $C_3H_7GeCl_3$: C, 15.14; H, 2.90; Cl, 44.67. Found: C, 14.81; H, 2.47; Cl, 44.73.

(13) Manuel, G. Thesis, Toulouse, France, 1970.

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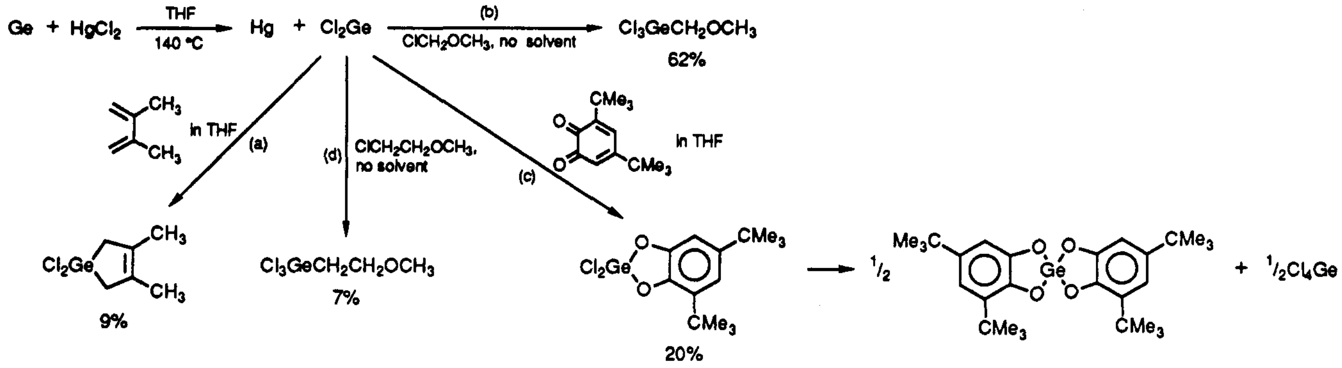
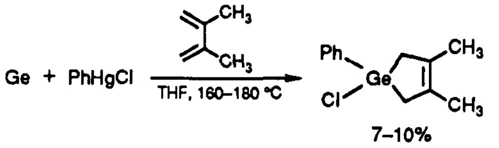
Scheme I



erate GeF_4·THF (^{19}F NMR: δ(F) = −51 ppm).[15]

All mercury(II) halides did not show the same reactivity. Thus, the reaction of HgI_2 with germanium powder (THF, 140 °C) in the presence of 1,3-dimethylbutadiene did not generate the expected diiodogermacyclobutene. The formation of elemental mercury is only partially observed in this last reaction at 140 °C, which is the upper limit for the stability of 1,1-diiodo-3,4-dimethyl-1-germa-3-cyclopentene.[13] The formation of free iodine suggests some decomposition process.

Reaction between Germanium Powder and Phenylmercury(II) Chloride. Phenylmercury(II) chloride was less reactive than $HgCl_2$. The reaction, carried out in THF in a Carius tube, started only at 160 °C. The high temperature led to partial decomposition of the generated organochlorogermylene, which could be trapped in only low yield:



(7)

The generated phenylchlorogermacyclopentene[5] was fully characterized with use of GC and ^1H NMR and mass spectroscopy.

Although these results show that direct synthesis of divalent and tetravalent germanium compounds is possible, we believe that a substantial increse in the yields of the reactions could be obtained by using ultrasound, Ge/Na and Ge/Hg amalgams,[16] copper catalysis,[17] or more reactive germanium obtained by evaporation from a tungsten filament (ca. 1200–1300 °C and 5 × 10^{-3} Torr)[18,19] or by an electron-beam evaporation source.[20] The results of such studies will be reported at a later date.

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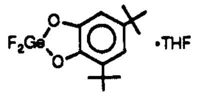
(14) A mixture of Ge powder (0.107 g, 1.47 mmol) and HgF_2 (0.30 g, 1.47 mmol) was slowly heated (oil bath) in a curved Carius tube sealed under vacuum (0.08 mmHg). At 160–165 °C a violent reaction was observed with distillation of Hg and sublimation of crystalline GeF_2 on the cold upper walls of the tube. The Carius tube was cooled in dry ice and opened under argon. GeF_2 was extracted with 4 mL of THF. The GeF_2·THF so obtained was treated with a solution of 3,5-di-*tert*-butyl-*o*-quinone (0.32 g, 1.47 mmol) in THF (2 mL) according to ref 11 until persistent red coloration. Only 20% of the quinone solution was necessary for the GeF_2·THF trapping, which gives after solvent evaporation the product in 19% yield:



^1H NMR (C_6D_6) δ 1.37 (s, 9 H, tBu), 1.70 (s, 9 H, tBu), 1.10 (m, 4 H, CH_2), 3.80 (m, 4 H, OCH_2), 7.10 and 7.30 (m, 2 H, C_6H_2).

(15) Identification of GeF_4 was effected by carrying the GeF_4 formed in an argon flow into THF (2 mL) and comparing the ^{19}F NMR spectrum of this solution with that of an authentic sample of GeF_4·THF obtained by treatment of a solution of $Ge(OMe)_4$ in THF with 40% aqueous HF (δ(^{19}F) = −51 ppm, CF_3COOH).

(16) Tchakirian, A.; Bévillard, P.; Godfrin, A. In *Nouveau traité de Chimie minérale*; Pascal, P., Ed.; Masson: Paris, 1963, Vol. 8.

(17) Lee, M. E.; Bobbitt, K. L.; Lei, D.; Gaspar, P. P. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 77.

(18) Mochida, K.; Yoshida, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1789.

(19) Mochida, K.; Tashiro, K.; Yoshida, Y.; Mizumo, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1247.

(20) Ozin, G. A.; Andrews, M. P.; Francis, C. G.; Hüber, H. X.; Molnar, K. *Inorg. Chem.* **1990**, *29*, 1068.