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Chemistry of Germanium Atoms. IV. A New Method for Preparation of Organogermanium Halides by Co-condensation of Germanium Vapor with Tetrahydrofuran[1)]

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Synopsis. Germanium vapor (atom) when co-condensated with THF at 77 K was found to be reactive toward organic halides. Several organogermanium halides were prepared by the addition of organic halides to the resultant germanium atom-THF slurry at ambient temperatures.

The co-condensation of metal vapor (atom) with certain solvents has been reported to make very reactive metal surfaces (slurries in solution).[2)] With this method it is becaming feasible to synthesize organometallic compounds, which would be difficult to prepare by other methods, at ambient conditions. However, there have been few reports on the reactivities of group 4B metal vapor-solvent slurries.[3)] Particularly no reports on silicon and germanium atoms-solvent slurries have appeared. In studying the reaction of germanium atoms in the condensed phase,[4—6)] we have found that germanium vapor (atom)-THF co-condensate is reactive toward organic halides. Here, we report on a new method for the preparation of organogermanium halides using germanium atom-THF co-condensate (slurry) at ambient temperatures.

Results and Discussion

A reactive germanium metal surface was conveniently produced by the co-condensation of germanium vapor with THF and by the use of essentially the same apparatus and conditions described previously (ca. 1200—1300 °C, 5×10^{-3} Torr, 1 Torr=133.322 Pa).[4)] Germanium metal was evaporated at a rate of ca. 10 mg min^{-1}, while an excess of THF was co-condensed on the wall of a quartz reaction flask containing the crucible and a perforated inlet tube through which THF was introduced. The reaction flask was immersed in liquid nitrogen during the germanium evaporation. Germanium atoms that co-condensed with THF were warmed to room temperature. The ensuing germanium atom-THF slurry was found to react with organic halides under argon. The size of particles in the germanium atom-THF slurry ranged from 0.7 to 18 μm as shown in Fig. 1.[7)]

Reactions of germanium atom-THF slurry with organic halides were examined. Germanium-containing products are summarized in Table 1. Bromotrichloromethane ($BrCCl_3$) reacted with this germanium atom-THF slurry at 50 °C for 5 h to give germanium tetrachloride ($GeCl_4$) (ca. 1.0%) and (trichloromethyl)-tribromogermane (CCl_3GeBr_3) The yields of germanium-containing products increased slightly at 50 °C for 20 h, as shown in Table 1. On the other hand, no reaction of $BrCCl_3$ took place with commercially available germanium powder (200 mesh) under these reaction conditions.

Reactions of germanium atom-solvent slurries with $BrCCl_3$ were also examined using various solvents. The yields of germanium-containing products were extremely low when a germanium atom-hexane slurry was used. No reaction of $BrCCl_3$ with germanium-benzene slurry occurred. The yields of germanium-containing products decreased roughly in the order: THF $>$ DME $\simeq$ hexane $\gg$ benzene. The differences of reactivities of solvents employed in this study might be attributed to the size and shape of particles in the germanium atom-solvent slurries. Similar results have been reported for nickel[1e)] and calcium atoms.[8)] Carbon tetrachloride (CCl_4) reacted with germanium atom-THF slurry to give $GeCl_4$ (ca. 1.0%) and (trichloromethyl)trichlorogermane (CCl_3GeCl_3) (3.0%). When $GeCl_4$ was used as a substrate, germanium atom-THF slurry produced hexachlorodigermane (Ge_2Cl_6) (10.0%) and octachlorotrigermane (Ge_3Cl_8) (3.0%). The reactions of germanium atom-THF slurry with sulfur monochloride (S_2Cl_2) and trichlorophophine (PCl_3) gave only $GeCl_4$ in 6.0 and 2.0% yields, respectively. No reaction of germanium atom-THF slurry with chloroform occurred.

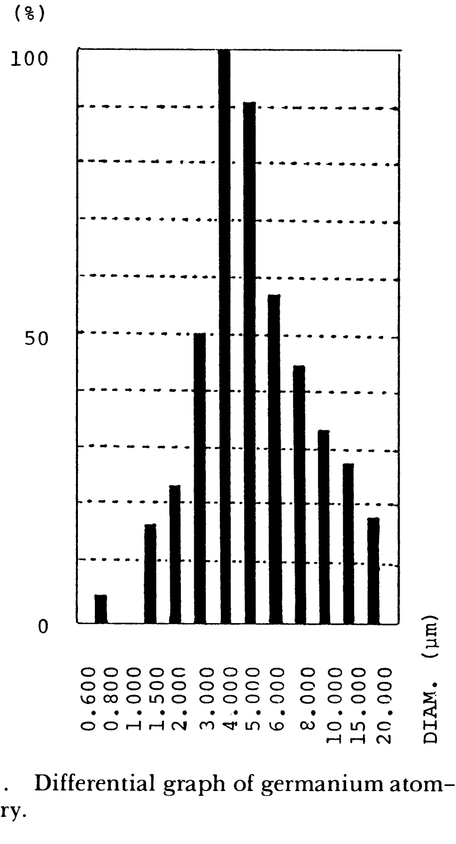

Fig. 1. Differential graph of germanium atom-THF slurry.

Table 1. Reactions of Germanium Atom-Solvent Slurries with Organic Halides

Halide (RX)	Solvent	Condition	Product (Yield/%)[a]
$BrCCl_3$	THF	50 °C, 5 h	$GeCl_4$ (ca. 1.0),[b] CCl_3GeBr_3 (2.5)
$BrCCl_3$	THF	50 °C, 20 h	$GeCl_4$ (ca. 1.0),[b] CCl_3GeBr_3 (3.5)
$BrCCl_3$	DME	50 °C, 5 h	$GeCl_4$ (trace), CCl_3GeBr_3 (1.5)
$BrCCl_3$	Hexane	50 °C, 5 h	$GeCl_4$ (trace), CCl_3GeBr_3 (1.0)
$BrCCl_3$	Hexane	50 °C, 20 h	$GeCl_4$ (trace), CCl_3GeBr_3 (1.5)
$BrCCl_3$	Benzene	50 °C, 20 h	No reaction
CCl_4	THF	50 °C, 5 h	$GeCl_4$ (ca. 1.0),[b] CCl_3GeCl_3 (3.0)
$GeCl_4$	THF	50 °C, 5 h	Ge_2Cl_6 (10.0), Ge_3Cl_8 (3.0)
S_2Cl_2	THF	50 °C, 5 h	$GeCl_4$ (6.0)
PCl_3	THF	50 °C, 5 h	$GeCl_4$ (2.0)
$CHCl_3$	THF	50 °C, 5 h	No reaction
MeI	THF	50 °C, 5 h	$MeGeI_3$ (1.0), Me_2GeI_2 (1.0)
EtI	THF	50 °C, 5 h	$EtGeI_3$ (1.0), Et_2GeI_2 (1.0)

a) Yields of products are based on the amount of germanium metal used. b) The retention time of $GeCl_4$ on GLC was partially overlapped with that of solvents.

Methyl iodide reacted with germanium atom-THF slurry to produce methyltriiodogermane ($MeGeI_3$) (1.0%) and dimethyldiiodogermane (Me_2GeI_2) (1.0%). With ethyl iodide, germanium atom-THF slurry produced ethyltriiodogermane ($EtGeI_3$) (0.5%) and diethyldiiodogermane (Et_2GeI_2) (0.5%).

The reactions of this germanium atom-THF slurry with organic halides proceed under milder conditions than a general direct synthesis of organogermanium halides,[9,10] although the yields of products are very low.

Experimental

GLC analyses were performed on a Shimazu GC-6A and 8A gas chromatograph equipped with a 2m×column packed with 20% SE-30 on celite 545. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. GC-MASS spectra were obtained with a JEOL JMS-DX 303 mass spectrometer and data analyses were performed on a JMN-DA 5000 mass data system. ^1H NMR spectra were recorded on a Varian FT 80A, using tetramethylsilane as an internal standard.

Materials. The organic halides were commercially available products. THF and other solvents were dried over benzophenone ketyl and distilled before use. $MeGeI_3$,[11] Me_2GeI_2,[9] $EtGeI_3$,[11] and Et_2GeI_2[12] were prepared according to the cited literature.

Preparation of Gremanium Atom-Solvent Slurries. Germanium atom-solvent slurries were produced using essentially the same apparatus and conditions described previously.[4] A typical procedure is described below. Germanium metal (0.5 g, 6.9 mmol) was vaporized at a rate of ca. 10 mg min^{-1}, at a temperature of 1200—1300 °C using a resistence-heated, alumina-coated tungsten spiral crucible (5.0—6.0 V, 15 A) connected to copper electrodes, in vacuo (ca. 5×10^{-3} Torr). During the vaporization of germanium metal, a large excess of THF (20 cm^3) was introduced as a vapor through a perforated inlet tube. The THF was cocondensed onto the wall of a quartz reaction flask was immersed in liquid nitrogen during the entire operation. Then, the reaction flask was allowed to warm to room temperature and was left to stand for 1 h. The reaction flask was evacuated and then filled with argon.

Reactions of Germanium Atom-THF Slurry with Organic Halides. The reaction with $BrCCl_3$ is described as a typical example. The germanium atom-THF slurry was shaken vigorously and a given volume of the germanium atom-THF slurry was quickly placed in a two-necked 50-cm^3 flask equipped with a serum cap and a reflux condenser in an argon-filled glove box. Ten times molar amounts of $BrCCl_3$ were then syringed in. The reaction mixture was stirred at 50 °C for 5 h under argon. The products were identified by comparing their GC-MASS[4,5] and their retention times on GLC with those of authentic samples.

Identification of Products. The known compounds were identified by comparing their GC-MS and retention times on GLC with those of authentic samples. The unkown compounds were carefully identified by comparing their GC-MS with those of similar samples and by parent peaks and cleavage patterns considering natural abundance of germanium (ratio, $^{70}Ge/^{72}Ge/^{73}Ge/^{74}Ge/^{76}Ge=56/75/21/100/21$) and chlorine (ratio, $^{35}Cl/^{37}Cl=75.4/24.6$). $^{74}Ge_2{}^{35}Cl_6$[13] (parent ion peak at m/z=358), m/z=323 (6), 253 (12). $^{74}Ge_3{}^{35}Cl_8$ (parent ion peak at m/z=502), m/z=327 (21), 288 (7), and 253 (7).

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References

1) Chemsitry of germanium atoms. III. See; Ref. 6.

2) For examples; a) R. D. Rieke and P. M. Hundnall, *J. Am. Chem. Soc.*, **94**, 7178 (1972); b) R. D. Rieke, S. J. Uhm, and P. M. Hundnall, *J. Chem. Soc., Chem. Commun.*, **1973**, 269; c) D. F. Stark and A. Streitwieser, *J. Am. Chem. Soc.*, **95**, 3423 (1973); d) K. J. Klabunde, H. F. Efner, T. O. Murdock, and W. Donley, *J. Organomet. Chem.*, **71**, 309 (1974); e) K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. Ropple, *J. Am. Chem. Soc.*, **98**, 1021 (1976); f) K. J. Klabunde, "Chemistry of Free Atoms and Particles," Academic Press, New York (1980); g) Y. Imizu, *Shokubai*, **27**, 480 (1985).

3) K. J. Klabunde, "Reactive Intermediates," ed by R. A. Abramovitch, Plenum Press (1980), Vol. 1, Chap. 2, p. 140.

4) K. Mochida and K. Tashiro, *Nippon Kagaku Kaishi*, **1987**, 1168.

5) K. Mochida and K. Tashiro, *Chem. Lett.*, **1987**, 1105; K. Mochida, K. Tashiro, Y. Yoshida, and Y. Mizuno, *Bull. Chem. Soc. Jpn.*, **61**, 1247 (1988).

6) K. Mochida and Y. Yoshida, *Bull. Chem. Soc. Jpn.*, **61**, 1785 (1988).

7) The size of particles in the germanium atom–THF slurry was measured by a coulter method (Coulter Counter Model TA-II, Coulter Electronics Co., Ltd.,) and a centrifugal sedimentation method.

8) K. Mochida and T. Yamanishi, *J. Organomet. Chem.*, **332**, 247 (1987).

9) K. Moedritzer, *J. Organomet. Chem.*, **6**, 282 (1966).

10) K. Moedritzer and J. R. V. Wazer, *Inorg. Chem.*, **5**, 547 (1966).

11) E. A. Flood, *J. Am. Chem. Soc.*, **55**, 4935 (1933).

12) L. Horvitz znd F. A. Flood, *J. Am. Chem. Soc.*, **55**, 5055 (1933).

13) N. N. Kochanova and I. I. Lapidas, *Zh. Fiz. Khim.*, **47**, 2937 (1973); *Chem. Abstr.*, **80**, 41634e (1974).