# DERIVATIVES OF MONOGERMANE

## PART II. PREPARATION AND PROPERTIES OF GERMYL PSEUDOHALIDES AND RELATED COMPOUNDS[1, 2]

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## ABSTRACT

Germyl isocyanate, isothiocyanate, and acetate have been prepared in almost quantitative yield by the interaction of germyl bromide with silver cyanate, thiocyanate, and acetate, respectively. Some of the physical properties of these new germyl derivatives are reported, and their thermal decompositions at moderate temperatures are described. The reaction of germyl bromide with silver oxide or carbonate produces germanium(II) hydride and water instead of digermoxane. Germyl bromide reacts with silver nitrite, forming germane, nitrous oxide, and nitric oxide as the only volatile products.

## INTRODUCTION

Only 24 volatile compounds containing the germyl group ($GeH_3$—) have been reported up to the present time. These are of three main types: (i) binary hydrides, $Ge_nH_{2n+2}$, with $n = 1$ up to 5 (1–5), (ii) monohalides $GeH_3X$, with X = F, Cl, Br, I (6–9), and (iii) monoalkylgermanes (10–12). Vinylgermane (13), germyl cyanide (14), and digermthian (8) have also been prepared. By contrast, about 50 silyl ($SiH_3$—) compounds were known up to 1956 when MacDiarmid (15) reviewed their chemistry. Several of these were first obtained by the action of silyl halides on silver salts. In this paper we describe the reactions of germyl chloride and bromide with some silver salts. Our object has been the preparation of new compounds containing the germyl group and to compare their properties with analogous silyl derivatives.

## RESULTS AND DISCUSSION

### *Preparation of Germyl Derivatives*

In our attempts to prepare new germyl compounds we followed the pattern suggested by the following silver salt conversion series for silyl compounds, as proposed by MacDiarmid (15):

$$(SiH_3)_2Te \rightarrow SiH_3I \rightarrow (SiH_3)_2Se \rightarrow (SiH_3)_2S \rightarrow SiH_3Br \rightarrow$$
$$SiH_3Cl \rightarrow SiH_3CN \rightarrow SiH_3NCS \rightarrow SiH_3NCO \rightarrow (SiH_3)_2O \rightarrow SiH_3F.$$

By reaction with the appropriate silver salt, any compound in this series can be converted into any other following it but not into one preceding it. This conversion series is similar to those described earlier for trialkylsilyl (16) and trialkylgermyl (17) compounds.

Contrary to the above series, we found that neither germyl chloride nor germyl bromide reacted with silver carbonate or oxide to yield digermoxane, $(GeH_3)_2O$. However, this

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compound might have been an unstable intermediate in the following observed reactions:

$$\begin{tikzcd}
2GeH_3Br + Ag_2CO_3 \arrow[r] & {[(GeH_3)_2O]} + 2AgBr + CO_2 \arrow[d] \\
& 2GeH_2 + H_2O \\
2GeH_3Br + Ag_2O \arrow[r] & {[(GeH_3)_2O]} + 2AgBr. \arrow[u]
\end{tikzcd}$$

Sujishi (8) reported that germyl iodide reacts with silver oxide or mercuric oxide to produce digermoxane, but it decomposes during purification into germane and water as the only volatile products. More recently, Sujishi and Goldfarb (18) claimed the detection of digermoxane by infrared spectral measurements on the hydrolysis products of germyl cyanide, but they could not isolate pure digermoxane. The apparent instability of germyl ethers containing Ge—H bonds is further evident from the recent observations that (i) hydrolysis of *n*-butylbromogermane does not yield the expected 1,1′-di-*n*-butyldigermoxane (19) and (ii) interaction of methylbromogermane with silver carbonate does not give 1,1′-dimethyldigermoxane (20). By contrast, stable silyl ethers with Si—H bonds are easily obtained by the reaction of silyl halides with either water or silver carbonate (15, 21, 22).

In agreement with the silyl conversion series, we found that germyl bromide reacted with silver cyanide to produce germyl cyanide, $GeH_3CN$. However, we could not isolate a pure sample due to its decomposition at 25° in the presence of an unidentified impurity. Sujishi and Keith (14) obtained pure germyl cyanide from the reaction of germyl bromide with silver cyanide. The infrared spectrum of pure germyl cyanide reveals that, like silyl cyanide (23), it exists mainly in the normal form at room temperature (24, 25).

The fact that germyl bromide is more reactive than the chloride toward silver salts is evident from our observation that germyl bromide but not germyl chloride reacted with silver cyanate to produce germyl isocyanate, $GeH_3NCO$. The iso structure, confirmed by its infrared spectrum (24), is not surprising because cyanic acid and its esters have the iso structure. Covalent normal cyanates have not yet been detected, presumably because they are thermodynamically unstable with respect to their iso forms. Interestingly, silyl isocyanate, $SiH_3NCO$, has not yet been isolated, though MacDiarmid tried to prepare it by the reaction of silyl iodide with silver cyanate; he obtained silicon tetraisocyanate instead (26).

As expected, germyl bromide reacted with silver thiocyanate to form germyl isothiocyanate, $GeH_3NCS$, in high yield. This is similar to the preparation of silyl isothiocyanate from silyl iodide and silver thiocyanate. Infrared spectra of germyl and silyl isothiocyanates confirm their iso structures (24, 27).

We found that other silver salts, such as silver acetate and nitrite, reacted with germyl bromide. Thus, germyl acetate was obtained conveniently by the reaction of germyl bromide with silver acetate. Germyl nitrite was probably an unstable intermediate in the reaction between germyl bromide and silver nitrite which produced germane, nitrous oxide, and nitric oxide as the only volatile products.

### *Thermal Decomposition of Germyl Derivatives*

Germyl isocyanate, isothiocyanate, and acetate were stable at ambient temperatures, but they decomposed at higher temperatures (50–200°) into polymeric germanium(II) hydride and the corresponding hydroacid, as represented by the equation

$$xGeH_3X \rightarrow (GeH_2)_x + xHX,$$

where X = NCO, NCS, or $OCOCH_3$. Germanium(II) hydride decomposes in a complex manner, yielding hydrogen, germane, germanium, and $(GeH)_x$, in amounts which depend on the temperature and duration of heating (28, 29). Germyl fluoride, like silyl halides (15), disproportionates at 25°, yielding germane and difluorogermane in equimolar quantities (6):

$$2GeH_3F = GeH_4 + GeH_2F_2.$$

Germyl chloride, however, decomposes at room temperature as follows (7):

$$2GeH_3Cl = GeH_4 + 2HCl + Ge.$$

As yet there is no quantitative data for the thermal decomposition of germyl bromide and iodide.

The fact that germyl halides and pseudohalides are less stable than the corresponding silyl compounds might be attributed to a difference in the polarities of the Ge—H and Si—H bonds in these compounds. Germanium and silicon have almost identical electronegativities, 1.90 and 2.00 respectively (30, 31), and their tetracovalent radii are not appreciably different, 1.17 and 1.22 Å, respectively (32). In spite of these similarities, the dipole moments of germyl chloride (2.12 D) and silyl chloride (1.30 D) differ significantly (33). These values suggest that the Ge—Cl bond is more polar than the Si—Cl bond. This might be due, in part, to the lesser tendency of germanium to use its vacant 4*d*-orbitals in $d_\pi$–$p_\pi$ partial double bonding with the chlorine atom. If this is true, the electron-withdrawing effect of the chlorine atom might make the hydrogen atoms, also bonded to germanium, electropositive with respect to germanium and hence more susceptible to nucleophilic attack than the hydrogen atoms bonded to silicon, which are electronegative with respect to silicon. We believe that this protonic (or acidic) nature of the hydrogen atoms in germyl halides and pseudohalides accounts for their lesser thermal stability compared with their silicon analogues. Replacement of all hydrogen atoms in germyl halides and pseudohalides with electron-releasing methyl groups gives trimethylgermyl halides and pseudohalides which are known to be more stable thermally than the corresponding germyl derivatives (34, 24).

## EXPERIMENTAL

### *Apparatus and Methods*

The apparatus, techniques, and measurements of vapor pressure, molecular weight (M), and melting point have been described in a previous paper (20). In each reaction of germyl chloride or bromide with a silver salt, the vapor of the halide was passed slowly through a column loosely packed with a mixture of the dry salt and powdered glass wool.

### *Materials*

Germane was prepared by the reduction of an aqueous acidic solution of germanium dioxide with sodium borohydride. Piper and Wilson (35), who first described this method, reported yields of germane in the range 60–75%. We obtained yields of 90–95% by allowing the reduction to occur at 35° instead of at 0°.

Germyl chloride was obtained by the reaction of germane with hydrogen chloride in the presence of aluminum(III) chloride as catalyst (7). It was separated from the mixture of products by several distillations at −96° (20% yield). (Found: M, 110.5; v.p. 69.7 mm at −23.6°; lit. (7) v.p. 70.2 mm at −23.6°. Calc. for $GeH_3Cl$: M, 111.1.)

Germyl bromide can be prepared by the reaction of germane with hydrogen bromide using aluminum(III) bromide as catalyst (7), but the yield is usually less than 10%. Yields of 60–90% were obtained by the reaction of germane with bromine, using a method similar to that described by Sujishi and Witz (36) for the preparation of silyl bromide. In one of our typical preparations bromine (7.9 mmole) was condensed in successive small portions onto germane (8.1 mmole) cooled to −196°. After each addition of bromine the mixture was warmed slowly until the color of bromine just disappeared, then the mixture was frozen again before the next addition of bromine. Germyl bromide was recovered from the product mixture by several distillations at −78° (91% yield). (Found: M, 156.0; v.p. 25.7 mm at −23°; lit. (7) v.p. 25.0 mm at −23°. Calc. for $GeH_3Br$: M, 155.5.)

The silver salts $Ag_2O$, $Ag_2CO_3$, AgOCN, and AgSCN were prepared by treating aqueous solutions of silver nitrate with equivalent amounts of aqueous NaOH, $Na_2CO_3$, KOCN, and $NH_4SCN$, respectively. Commercial samples of AgCN, $AgC_2H_3O_2$, and $AgNO_2$ were used. All silver salts were dried in a high vacuum for several days before they were used.

### *Reactions of Germyl Chloride*

*(a) With Silver Cyanide*

Upon reaction with germyl chloride (1.50 mmole) at 25°, silver cyanide changed from white to brown, and a volatile material, which sublimed without melting, resulted. This volatile product was separated by distillation at −80° into: (i) a distillate (0.78 mmole) (found: M, 49.2) which was mainly hydrogen cyanide (calc. M, 27.0), as evident from its infrared spectrum and (ii) a residue which was crude germyl cyanide (0.62 mmole) (found: M, 100.1; calc. for $GeH_3CN$: M, 101.6). The molecular weight of the crude germyl cyanide decreased from 100.1 to 48.4 after it had been kept at 25° for 16 hours, and its vapor pressure became 89.1 mm at −22.9°, slightly higher than that of pure hydrogen cyanide (lit. (37) v.p. 85.2 mm at −22.9°). A non-volatile, yellow amorphous powder, undoubtedly germanium(II) hydride, remained on the walls of the storage bulb after the hydrogen cyanide had been removed. Evidently the crude germyl cyanide contained impurities, probably germyl chloride and hydrogen cyanide, which catalyzed its decomposition at 25° into hydrogen cyanide and germanium(II) hydride, as represented by

$$x\mathrm{GeH_3CN} \rightarrow (\mathrm{GeH_2})_x + x\mathrm{HCN}.$$

*(b) With Silver Carbonate*

Silver carbonate changed gradually from greenish-yellow to black when it reacted with germyl chloride (1.91 mmole). The condensable products consisted of carbon dioxide (0.28 mmole) (found: M, 44.3; calc. for $CO_2$: M, 44.0) and unchanged germyl chloride (1.43 mmole) (found: M, 106.9; calc. for $GeH_3Cl$: M, 111.1). Digermoxane $(GeH_3)_2O$, the expected product, was not obtained. The ratio of consumed germyl chloride to carbon dioxide produced was 1.72:1, rather than 2:1, as would be expected if the reaction

$$2\mathrm{GeH_3Cl} + \mathrm{Ag_2CO_3} \rightarrow \mathrm{GeH_2} + \mathrm{H_2O} + \mathrm{Ag_2O} + \mathrm{CO_2}$$

had occurred exclusively. Additional carbon dioxide probably resulted from thermal decomposition of some silver carbonate.

*(c) With Silver Oxide*

There was no noticeable change when germyl chloride (2.18 mmole) was passed 12 times through a column of dry silver oxide. Hydrogen was not produced and the recovery of germyl chloride (2.07 mmole) was almost quantitative. Therefore, no reaction occurred between germyl chloride and silver oxide.

### *Reactions of Germyl Bromide*

*(a) With Silver Cyanate*

An exothermic reaction between germyl bromide (2.63 mmole) and dry silver cyanate produced germyl isocyanate in almost quantitative yield (2.43 mmole, 93% yield). (Found: M, 116.7; v.p. 27.7 mm at 0°. Calc. for $GeH_3NCO$: M, 117.6.) This new compound melts at −44.0±0.5° and its vapor pressures in the range −23° to 23° are given by $\log_{10} p_{\mathrm{mm}} = 8.369 - (1891/T)$, which gives an extrapolated boiling point of 71.5°, a latent heat of vaporization of 8651 cal $mole^{-1}$, and a Trouton constant of 25.1.

Germyl isocyanate (2.24 mmole) did not decompose when heated for 40 hours at 110°, but after 12 hours at 200–220°, a lustrous silvery mirror of metallic germanium appeared uniformly on the walls of the flask. The volatile products were: (i) hydrogen (0.20 mmole), (ii) cyanic acid (0.21 mmole) (found: M, 44.1; v.p. 18.7 mm at −45°; lit. (38) v.p. 18.4 mm at −45°; calc. for HNCO: M, 43.0), and (iii) unchanged germyl isocyanate (1.99 mmole). Only 10% of the original germyl isocyanate decomposed and the ratio of hydrogen to cyanic acid was approximately 1:1; the ratio of decomposed germyl isocyanate to either hydrogen or cyanic acid was also about 1:1. These facts indicate that decomposition of germyl isocyanate occurred according to the equation

$$\mathrm{GeH_3NCO} \rightarrow \mathrm{Ge} + \mathrm{H_2} + \mathrm{HNCO}.$$

*(b) With Silver Thiocyanate*

Germyl bromide (2.08 mmole) and dry silver thiocyanate gave an exothermic reaction which yielded germyl isothiocyanate almost quantitatively (2.01 mmole, 97% yield). (Found: NCS, 43.6%. Calc. for $GeH_3NCS$: NCS, 43.33%.) This new germyl derivative has a melting point of 18.6±0.3° and its vapor pressures in the range 19 to 50° are given by $\log_{10} p_{\mathrm{mm}} = 8.268 - (2280/T)$, which indicates a latent heat of vaporization of 10.4 kcal $mole^{-1}$, an extrapolated boiling point of 150°, and a Trouton constant of 24.6. After germyl isothiocyanate (3.13 mmole) was heated for 20 hours at 55°, it decomposed completely into germane (1.07 mmole) (found: M, 77.2; calc. for $GeH_4$: M, 76.6) and a yellow, non-volatile residue. This residue did not dissolve in carbon disulphide, indicating that it did not contain free sulphur. The residue was non-homogeneous and could not be analyzed. It probably consisted of polymeric thiocyanic acid and solid germanium hydrides.

The ratio of decomposed germyl isothiocyanate to germane was approximately 3:1, as one might expect if decomposition had occurred according to the following scheme:

$$\begin{aligned} GeH_3NCS &\rightarrow GeH_2 + HNCS, \\ 3GeH_2 &\rightarrow GeH_4 + 2GeH, \\ x\,HNCS &\rightarrow (HNCS)_x. \end{aligned}$$

*(c) With Silver Oxide*

Germyl bromide (4.20 mmole) reacted completely with silver oxide, producing carbon dioxide (0.27 mmole) (found: M, 44.7; calc. for $CO_2$: M, 42.0) and water (2.63 mmole) (found: M, 19.0; v.p. 12.6 mm at 15°; lit. (39) v.p. 12.8 mm at 15°; calc. for $H_2O$: M, 18.0), but no digermoxane. Evidently the main reaction was

$$2GeH_3Br + Ag_2O \rightarrow 2GeH_2 + 2AgBr + H_2O,$$

and the additional water (0.53 mmole) probably came from the silver oxide, which may not have been completely dry even though it had been evacuated for several days.

*(d) With Silver Carbonate*

Germyl bromide (2.31 mmole) was completely consumed in a highly exothermic reaction with silver carbonate. Digermoxane, the expected product, was not found among the products, which were carbon dioxide (7.46 mmole) and water (2.01 mmole). The reaction appeared to be

$$2GeH_3Br + Ag_2CO_3 \rightarrow 2GeH_2 + 2AgBr + CO_2 + H_2O.$$

The excess carbon dioxide undoubtedly resulted from the thermal decomposition of silver carbonate and the additional water probably came from the incompletely dry silver carbonate.

In another experiment the reaction between germyl bromide (1.84 mmole) and silver carbonate was allowed to occur at −28° for 5 hours. Again carbon dioxide (2.36 mmole) and water (0.90 mmole) were the only products. This time, the ratio of consumed germyl bromide to water was almost exactly 2:1, in accord with the above equation for the overall reaction.

*(e) With Silver Acetate*

Germyl bromide (3.20 mmole) reacted completely with dry silver acetate to form germyl acetate (3.07 mmole, 96% yield). (Found: M, 136.1; $C_2H_3O_2$, 43.6%; v.p. 9.7 mm at 0°. Calc. for $GeH_3C_2H_3O_2$: M, 134.7; $C_2H_3O_2$, 43.85%.) This new compound has a melting point of 12.8±0.1° and vapor pressures in the range −10 to 40° expressed by $\log_{10} p_{\mathrm{mm}} = 9.227-(2256/T)$, which gives a latent heat of vaporization of 10.3 kcal mole$^{-1}$, an extrapolated boiling point of 82.4°, and a Trouton constant of 30.0.

The yellow deposit which appeared after germyl acetate (1.80 mmole) was heated for only 10 minutes at 100–110° became orange-red after 16 hours of heating. The volatile products were: (i) hydrogen (1.09 mmole) and (ii) a mixture (1.38 mmole) (found: M, 95.6) of acetic acid (calc. M, 60.0) and germyl acetate (calc. M, 134.7) which could not be separated by fractional distillation. Assuming ideal gaseous behavior, we estimated that this mixture contained 0.72 mmole acetic acid and 0.66 mmole undecomposed germyl acetate. These results indicate that decomposition occurred to an extent of about 60%, probably according to the following scheme:

$$\begin{aligned} GeH_3C_2H_3O_2 &\rightarrow GeH_2 + HC_2H_3O_2, \\ 2GeH_2 &\rightarrow 2GeH + H_2. \end{aligned}$$

*(f) With Silver Nitrite*

The interaction of germyl bromide (1.87 mmole) with dry silver nitrite for 5 hours at −28° resulted in darkening of the silver nitrite and in complete consumption of germyl bromide. The volatile product mixture consisted of: (i) a fraction (0.69 mmole) (found: M, 65.4) which was shown by infrared measurements to be a mixture of germane (calc. M, 76.6) and nitrous oxide (calc. M, 44.0), (ii) nitric oxide (1.31 mmole) (found: M, 31.5; calc. for NO: M, 30.0), and (iii) water (0.88 mmole). There was no evidence of the expected germyl nitrite.

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