

# THE GERMANES AND THEIR ORGANO DERIVATIVES

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## I. INTRODUCTION

The position of germanium with reference to the other elements in the periodic table is unique in that it represents the midpoint in the transition from metallic to nonmetallic properties both vertically and horizontally. It is in truth the crossroads element, and its chemical behavior when compared with its nearest relatives, silicon and tin, indicates quite strongly the duality of its nature.

It has become common in the case of silicon to restrict the word "organosilicon" to those compounds having at least one carbon atom linked directly to silicon (15, 68). However, the present review will include in the discussion the germanes, and to a limited extent the tetrahalides, since the majority of the known organo-germanium compounds are viewed as derivatives of the germanes and the tetrahalides form the starting material for most of the present methods of organo-germanium syntheses.

The methods of preparation and the properties of all known organo-germanium compounds, and also many germanium compounds that are not strictly organic compounds but are prepared by organic procedures, will be summarized. Many of the physical constants of these compounds are given in tables in Section VI.

Since the number of organo-germanium compounds known at the present time is only about 230, all are included in the tables, making the survey complete to January, 1950.

## II. NOMENCLATURE

Present usage in the naming of organo-germanium compounds does not adhere rigidly to any discernible pattern. With the expectation that a considerable number of hitherto unknown germanium compounds will be isolated and identified within the next few years, it seems preferable to outline a general systematic procedure for naming these compounds as simply and effectively as possible. With this objective in view the following tentative recommendations are suggested.

1. The names "germane," "digermane," and "trigermane" are now accepted generally for the first three alkane-type compounds of germanium. Derivatives of these three compounds are structurally analogous to the derivatives of the first three members of the alkane series and the accepted rules for the nomenclature of such organic compounds (82) should be followed as closely as possible in the naming of analogous germanium compounds.

2. Where organic nomenclature is ambiguous or inapplicable, the recommendations of the Committee on Nomenclature, Spelling and Pronunciation of the American Chemical Society for the naming of silicon compounds (17) should be followed for the naming of analogous germanium compounds.

3. Inorganic nomenclature is recommended in accordance with present organic usage if such naming is simpler and more specific. Thus  $H_3GeBr$  becomes germyl bromide, analogous to methyl bromide.

Adherence to the above broad general rules would bring about some changes in present nomenclature. The compound  $HGeOOH$  is currently called "germanonic acid" in *Chemical Abstracts*. Volume II of *Inorganic Syntheses* however,

prefers conformity with organic usage and recommends "germanoic acid" for this compound (28, 81). This system of naming could well be extended to the analogous silicon, tin, and lead acids, which would then become silanoic acid, stannanoic acid, and plumbanoic acid. The compounds  $C_2H_5SiOOH$  and  $n-C_3H_7SiOOH$  (3) would then become ethylsilanoic acid and propylsilanoic acid. The name "germanic acid" is commonly used for inorganic compounds of the type  $H_4GeO_4$ .

The combining form "sil-" rather than "silic-" is recommended for silicon (17). The author believes that the shorter combining form "germ-" will cause less confusion than the longer "german-" for germanium. The radical  $H_3Ge-$  is then the "germyl" radical and  $H_3GeO-$  becomes "germoxy," corresponding to the silyl and siloxy radicals.

Using this shorter combining form the radical  $H_2Ge<$  is named "germylene," similar to the silylene radical,  $H_2Si<$ . The longer combining form is then available for the naming of radicals such as  $H_3GeGeH_2-$ , which becomes the digermanyl radical, corresponding to the disilanyl,  $H_3SiSiH_2-$ , radical. Likewise, the compound  $H_3GeOGeH_3$  becomes "digermoxane," in conformity with accepted usage for silicon.

The use of the shorter combining form "germ-" as advocated is not breaking with precedent, since its use is firmly established in the universal acceptance of the names "germane," "digermane," etc.

### III. THE SIMPLE GERMANES

#### A. GENERAL

The first hydride of germanium was made by Voegelen (96) in 1902. Voegelen worked with small quantities and did not obtain the hydride in pure state but confined himself to a determination of the composition of the hydride existing in dilute mixture with hydrogen from which he was unable to separate the hydride. The germanium hydride was caused to react with a silver salt, thus precipitating a silver germanide, and the mixture was also passed over finely divided sulfur, thus converting the hydride to the sulfide. The analysis of these two products suggested the formula  $GeH_4$ .

The next mention of germanium hydrides in the literature comes from Müller and Smith (64). These investigators reported on the use of the Marsh test for detecting germanium; in the course of their study they also investigated methods of preparing the hydride. They did not isolate the pure hydride but worked with mixtures of the hydride in hydrogen. Paneth (67) and Schenk (76) prepared small quantities by treating an alloy of germanium and zinc or of germanium and magnesium with an acid. Both of these investigators experimentally ascertained that the composition of the gas was  $GeH_4$  and Schenk also reported values of  $-165^\circ C.$  for the freezing point and  $-126^\circ C.$  for the boiling point.

For a period of several years the study of germanium compounds, including the hydrides, was greatly advanced through grants made to Cornell University by the Heckscher Foundation for the Advancement of Research. At Cornell

University Dennis, Corey, and Moore (19) studied methods of preparing germanium hydrides and finally adopted a method similar to the one used by Stock (88) for the preparation of the hydrides of silicon. This procedure consisted in the treatment of magnesium germanide with an acid. Application of this technique resulted not only in the formation of monogermane,  $\text{GeH}_4$ , but also produced the higher hydrides, digermane,  $\text{Ge}_2\text{H}_6$ , and trigermane,  $\text{Ge}_3\text{H}_8$ , which were isolated and identified for the first time. From 67.5 g. of magnesium germanide Dennis, Corey, and Moore (19) obtained 7.15 g. of monogermane, 2.12 g. of digermane, and 0.43 g. of trigermane. These products account for only 22.7 per cent of the germanium. This per cent conversion is closely similar to the yield of silicon hydrides obtained by Stock (88) from magnesium silicide. No attempt was made by Dennis to ascertain what became of the remaining 77.3 per cent of germanium. Later, Kraus and Carney (46) obtained yields of over 70 per cent by treating magnesium germanide with ammonium bromide in liquid ammonia instead of with hydrochloric acid in aqueous solution. Using this modification they obtained yields of mixed germanes ordinarily averaging between 60 and 70 per cent of the total germanium.

The gases obtained contained 30–40 per cent hydrogen, the remainder being the germanes, of which monogermane predominated. The gases may be purified by means of liquid air as described by Dennis, Corey, and Moore (19), but Kraus and Carney (46) found that monogermane of high purity could be obtained by passing the mixture of gases through a solution of sodium in liquid ammonia. In this process the monogermane reacts with sodium to form germylsodium (called sodium trihydrogermanide by Kraus and Carney) with the evolution of hydrogen. Digermane is apparently directly reduced to germylsodium, while trigermane forms a mixture of germylsodium and the disodium-substituted germane. These compounds are all soluble in liquid ammonia and are converted to monogermane on the addition of ammonium bromide. Monogermane of 99.7 per cent purity is obtained by this method and may be further purified by means of liquid air.

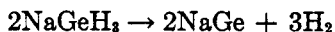
#### B. MONOGERMANE

The monogermane obtained by Dennis, Corey, and Moore (19) was further examined by Corey, Laubengayer, and Dennis (18). Because the boiling point for monogermane was much lower than that expected by comparison with the analogous hydrides ( $\text{CH}_4$ ,  $-160^\circ\text{C}$ .;  $\text{SiH}_4$ ,  $-112^\circ\text{C}$ .;  $\text{GeH}_4$ ,  $-126^\circ\text{C}$ .), they rechecked the values for the freezing point and the boiling point, obtaining  $-165^\circ\text{C}$ . and  $-90^\circ\text{C}$ ., respectively, as compared with the values  $-165^\circ\text{C}$ . and  $-126^\circ\text{C}$ . reported by Schenk (76). The vapor pressure curve for monogermane from  $-165^\circ\text{C}$ . to  $-90^\circ\text{C}$ . is given in reference 18.

The germylsodium formed by monogermane when it is added to an ammonia solution of sodium (46) is a white solid very soluble in liquid ammonia but insoluble in ethylamine. It reacts readily with oxygen, being oxidized to sodium orthogermanate. It decomposes slowly at liquid ammonia temperatures, be-

coming slightly yellow within 24 hr. At room temperatures the decomposition is more rapid, the product turning brown in several hours.

With rising temperatures germylsodium decomposes rapidly according to the equation:



The rate of evolution of hydrogen is greatest in the neighborhood of 125°C., although hydrogen is slowly evolved at 360°C. The residue is evidently the alloy NaGe and is apparently identical with the alloy prepared by Dennis and Skow (25) by the direct interaction of the two elements at elevated temperatures. Germylsodium crystallizes from liquid ammonia (46) with six molecules of ammonia of crystallization. At 315 mm. pressure  $\text{NaGeH}_3 \cdot 6\text{NH}_3$  is converted to  $\text{NaGeH}_3 \cdot 4.5\text{NH}_3$ , which in turn changes to  $\text{NaGeH}_3 \cdot 2\text{NH}_3$  at 23 mm. and finally to  $\text{NaGeH}_3$  at 3 mm.

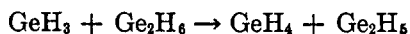
### C. DIGERMANE AND TRIGERMANE

Among the products obtained by Dennis, Corey, and Moore (19) were two substances that satisfied the analytical requirements for the formulas  $\text{Ge}_2\text{H}_6$  and  $\text{Ge}_3\text{H}_8$ , or digermane and trigermane, respectively. Digermane is a clear liquid which has a vapor pressure of about 560 mm. at room temperature and has a density as a liquid of about 1.98 at  $-109^\circ\text{C}$ .

Heating digermane under a pressure of 200 mm. brought about thermal decomposition starting at  $214^\circ\text{C}$ . Trigermane is somewhat less stable thermally, the dissociation beginning at  $194^\circ\text{C}$ . under similar conditions.

Addition of carbon tetrachloride to either digermane or trigermane brought about solution with evolution of heat, and when the liquid was exposed to air a white fog appeared in the liquid. The fog turned yellow almost immediately and finally disappeared.

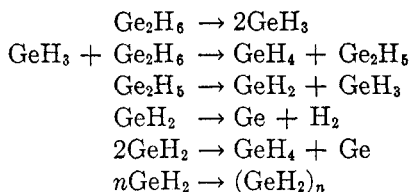
Emeléus and Jellinek (27) studied the pyrolysis of digermane and concluded that the decomposition of digermane within the temperature range  $195\text{--}222^\circ\text{C}$ . is kinetically similar to the decomposition of ethane and disilane. The reaction is apparently homogeneous and of the first order. Emeléus and Jellinek assume the initial reaction to be the rupture of the Ge—Ge bond, with which they associate the observed activation energy of 33.7 kcal. The mechanism of the subsequent reaction is largely speculative. Following a mechanism suggested by Rice and Herzfeld (69) for ethane, the assumption is made that the  $\text{GeH}_3$  radical produced initially reacts with  $\text{Ge}_2\text{H}_6$ :



The  $\text{Ge}_2\text{H}_5$  radical may decompose into  $\text{Ge}_2\text{H}_4$  and H or more probably into  $\text{GeH}_2$  and  $\text{GeH}_3$ , the latter acting as chain propagator. A solid germanium hydride is produced, which they compare to the polymerized hydride  $(\text{GeH}_2)_n$  described by Royen and Schwarz (75).

Emeléus and Jellinek (27) also observed that the decomposition of digermane induced polymerization in propene. This induced polymerization could be ex-

plained by the formation of the  $\text{GeH}_3$  radical, but they advanced an alternative explanation by assuming that atomic hydrogen is produced in the reaction. Such hydrogen-producing reactions are known to induce polymerization in alkenes. The addition of molecular hydrogen during the decomposition does not increase the relative amount of monogermene in the product, although such an effect is well marked in the decomposition of disilane. This implies that the reaction  $\text{GeH}_3 + \text{H}_2 \rightarrow \text{GeH}_4 + \text{H}$  is more endothermic than  $\text{SiH}_3 + \text{H}_2 \rightarrow \text{SiH}_4 + \text{H}$ , which is a direct consequence of the relative strengths of the Ge—H and Si—H bonds. The marked induction period experimentally observed is assumed to be associated with some reaction in which hydrogen participates. Normally this hydrogen is produced in the initial stages of the reaction and when hydrogen is added at the beginning, the induction period is considerably shortened. The following series of reactions are therefore suggested as representing the main course of the pyrolysis of digermene:



Hogness and Johnson (37) have shown that the decomposition of monogermene is heterogeneous, the rate of decomposition being proportional to the one-third power of the pressure of the undecomposed monogermene. No explanation is offered as to why this is different from the decomposition of monosilane, which Hogness, Wilson, and Johnson (38) have shown to be homogeneous and of the first order.

Emel us and Jellinek (27) found the latent heat of vaporization of digermene to be 6400 cal./mole.

Emel us and Gardner (26) studied the oxidation of monogermene and digermene. Monogermene is sufficiently stable thermally so that they were able to study the oxidation at a temperature at which it did not undergo thermal decomposition. Monogermene was found to be less inflammable than monosilane, but much more so than methane. Evidence was obtained that the oxidation took place by a chain mechanism, but it was shown to differ from that of other hydrides in that the solid product formed in the oxidation, which is either germanium dioxide or a hydroxylated derivative of it, had a remarkable catalytic effect upon the reaction. They also studied the slow oxidation of monogermene and found that oxidation in a clean glass vessel required a considerable induction period at higher temperatures. The suggestion was made that this might represent a homogeneous reaction producing active centers in the oxide surface first formed and that a heterogeneous reaction then takes place on the oxide surface with a chain reaction in the gas phase taking place around the active centers.

Emel us and Gardner also studied the effect of pressure on the ignition of

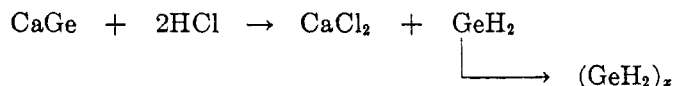
monogermane-oxygen mixtures and found that increasing the pressure lowered the ignition temperature. Typical results for a 20 per cent monogermane-oxygen mixture showed that no explosion resulted at a pressure of 29.8 mm. at 346°C. but increasing the pressure to 31 mm. caused ignition of the mixture. At 237°C. a pressure of 70.7 mm. did not produce an explosion, while a pressure of 73.5 mm. did.

Irradiation of a monogermane-oxygen mixture reduced the induction time considerably. At 230°C., for example, the induction period is of the order of 100 min. and this was reduced to 12 sec. by irradiation with a quartz mercury arc. Mahneke and Noyes (60) found that monogermane exhibits no banded absorption at wave lengths greater than 1550 Å. and continuous absorption extends from about 1700 Å. to shorter wave lengths. Emel us and Gardner concluded therefore that the effect was due to the absorption of energy by the oxygen.

#### D. OTHER GERMANIUM-HYDROGEN COMPOUNDS

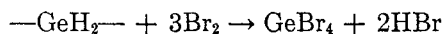
Dennis and Skow (25) treated sodium germanide with cold water and obtained a brown solid which instantaneously dissociated with an explosive puff when the dry, or nearly dry, substance was brought in contact with air. The formula  $(\text{GeH})_x$  was proposed for the compound. It is a strong reducing agent and unites with free halogens to form compounds of the type  $\text{GeX}_4$ . This same brown solid was obtained by Kraus and Carney (46) on treating sodium germanide alloy with ammonium bromide in liquid ammonia.

Another solid hydride, which has been assigned the formula  $(\text{GeH}_2)_x$ , was prepared by Royen and Schwarz (73, 74, 75). Treatment of calcium germanide with hydrochloric acid yielded a yellowish, apparently unsaturated, polymeric hydride.

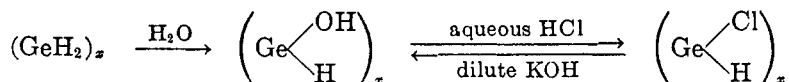


The low volatility of the substance, its insolubility in organic solvents, and its failure to react with hydroxyl ions or elementary halogens in stoichiometric ratios suggest that the hydride is a long chain-like polymer terminated by  $\text{H}_2\text{O}$  or  $\text{HCl}$ , as indicated by the formula:  $\text{H}-\text{GeH}_2-\text{GeH}_2 \cdots \text{GeH}_2-\text{Cl}$ .

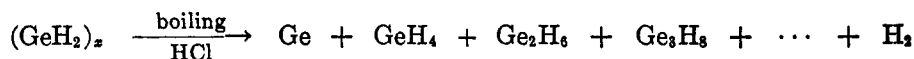
The unsaturated nature of the compound is shown by its behavior towards bromine in hydrochloric acid solution, in which the following reaction presumably occurs:



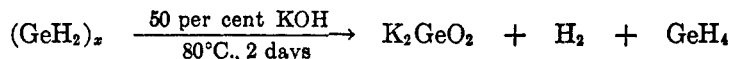
The polymer also reacts with water to form dark red polyhydroxy compounds which are labile to hydrochloric acid.



Heating the substance with hydrochloric acid converts it into a mixture of saturated germanes, together with some elementary germanium and hydrogen.



Hot alkalis ultimately convert some of the germanium to the germanite.



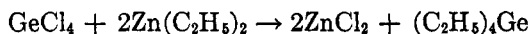
Glarum (34) found that germylsodium and phenyl bromide reacted, with the quantitative production of sodium bromide, benzene, and so-called germanoethylene,  $\text{GeH}_2$ . Germanoethylene appears to be stable in liquid ammonia. Upon warming or removing the ammonia at  $-33^\circ\text{C}$ . it decomposes with the evolution of monogermene and the formation of germanoacetylene,  $\text{GeH}$ . This latter compound decomposes into its elements upon heating to  $180^\circ\text{C}$ .

The properties of the six known simple germanes are summarized in table 1 of Section VI.

#### IV. GENERAL METHODS FOR THE SYNTHESIS OF ORGANOGERMANIUM COMPOUNDS

##### A. SUBSTITUTION BY ZINC DIALKYLs

It is of historical interest that the organogermanium compound first reported was prepared by Clemens Winkler (99). Winkler prepared tetraethylgermane by treating germanium tetrachloride with diethylzinc:



This one paper by Winkler is the sole reference to appear on the organic compounds of germanium until 1925, thirty-eight years later, when Dennis and Hance (20) investigated further the preparation of tetraethylgermane by means of diethylzinc and described the properties of tetraethylgermane more fully.

##### B. SUBSTITUTION BY MERCURY DIARYLS

Aryl compounds of mercury have been used (66) in the synthesis of aryltrichlorogermanes. Diphenylmercury with germanium tetrachloride in a sealed tube reacts, at  $140^\circ\text{C}$ ., to form phenyltrichlorogermane.



Benzyltrichlorogermane, *p*-tolyltrichlorogermane, and *p*-dimethylaminophenyltrichlorogermane were prepared in the same manner. No modifications of this method have come into common use.

##### C. SUBSTITUTION BY GRIGNARD REAGENTS

With the renewal of interest in germanium in 1925 the Grignard technique was immediately applied (49, 63, 90). As ordinarily carried out, the Grignard reagent is prepared in the usual manner and then added to a stirred solution



of germanium tetrachloride in ether. Magnesium halide precipitates and the substituted germanium compounds remaining in solution are then separated by distillation.

For sluggish reactions involving the higher arylmagnesium halides, the ether may be replaced by a higher boiling solvent such as toluene, and the reaction mixture heated for a period of time. The organogermanium compounds may then be separated by destroying any excess Grignard reagent and recrystallizing the product from a suitable solvent.

All variations of the Grignard reaction, or similar substitutions involving alkyls of different metals, result in a mixture of products. With germanium tetrachloride the substitution products  $RGeCl_3$ ,  $R_2GeCl_2$ ,  $R_3GeCl$ , and  $R_4Ge$  are possible and form in varying percentages, so that if a specific intermediate is desired the conditions yielding the highest percentage of that particular compound must first be investigated if an efficient reaction is desired.

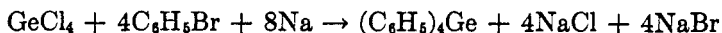
Mixed alkyl- or aryl-germanes are obtained by the stepwise alkylation or arylation of intermediates.

#### D. PREPARATION BY ALKYL- OR ARYL-LITHIUM COMPOUNDS

In some instances the use of the now common alkyl- or aryl-lithium techniques is advantageous. Johnson and Nebergall (43) observed that the use of organolithium compounds in the preparation of tetrasubstituted germanes often gave better yields than the standard Grignard or Fittig procedures. Johnson and Harris (41) studied the reaction between triphenylgermane and phenyllithium and found that the principal product could be either tetraphenylgermane or hexaphenyldigermane, depending upon the sequence of mixing the reactants.

#### E. COUPLING REACTIONS WITH SODIUM

Wurtz or Fittig type reactions were first used with germanium compounds by Tabern, Orndorff, and Dennis (90). Germanium tetrachloride and phenyl bromide were found to react vigorously with sodium in ether:



Using this procedure these workers prepared tetra-*p*-tolylgermane, tetrapropylgermane, tetraisoamylgermane, and tetraethylgermane.

The Wurtz reaction as a method for alkylating germanium tetrachloride has never achieved the popularity of the Grignard reaction, chiefly because the difficulty of control made it reasonably successful only as a means of preparing the fully substituted tetraalkyls or tetraaryls. The partially substituted germanium halides appear only in low yields, because the reaction as usually conducted goes to complete substitution. One explanation is based upon the heterogeneity of the system. The sodium is unavoidably present in relatively large masses, and a molecule of germanium tetrachloride which comes in contact with the surface of a lump of sodium has an excess of sodium atoms immediately available and derives enough energy from the first substitution to continue right on with the substitution of the remaining three germanium-chlorine bonds.

A two-stage synthesis (77), which has been successfully used with silicon and which should be applicable to germanium, allows better control. The sodium is first allowed to react with a halide such as chlorobenzene in a solvent to yield phenylsodium. After the heat of the reaction is dissipated, the phenylsodium is mixed with the silicon halide in solution and a milder reaction ensues. Phenyltrichlorosilane was made by the action of less than one equivalent of phenylsodium on silicon tetrachloride. The use of a separately prepared sodium alkyl or aryl in this way provides about the same degree of control as in a Grignard synthesis.

#### F. DIRECT SYNTHESIS

A general reaction of alkyl halides with elementary germanium to produce the corresponding organogermanium halides has been developed (70, 71). By the action of methyl chloride upon elementary germanium in the presence of a copper catalyst, a mixture of related organogermanium chlorides is obtained from which the individual substances may be separated by distillation. The composition of the mixture is influenced by the temperature of the reacting mass, the type of catalyst used, the manner in which the catalyst is associated with the germanium, and possibly the time of contact.

The direct synthesis is best suited to the preparation of dialkyl- or diaryl-dihalogermanes. Compounds of the type  $R_3GeCl$  and  $R_4Ge$  represent only a small fraction of the total yield.

### V. THE CHEMISTRY OF ORGANOGERMANIUM COMPOUNDS

#### A. PARTIALLY SUBSTITUTED ALKYL- AND ARYL-GERMANES

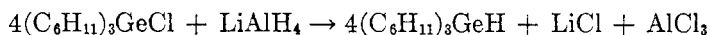
Only three partially substituted germanes—triethylgermane, tricyclohexylgermane, and triphenylgermane—have been described in the literature. All three are trisubstituted compounds of the type  $R_3GeH$ , and rather oddly comprise one example each of the aliphatic, the alicyclic, and the aromatic series. The constants of the alkyl- and aryl-substituted germanes are given in table 1 of Section VI.

The first one to be prepared was triphenylgermane,  $(C_6H_5)_3GeH$ , which forms quantitatively when triphenylgermysodium reacts with ammonium bromide or with water (49). This compound exists in two monotropic forms. The more stable  $\alpha$ -form melts at  $47^\circ C$ . and the less stable  $\beta$ -form melts at  $27^\circ C$ . Under ordinary conditions, triphenylgermane is stable in air but on very long standing there are indications of oxidation. It reacts immediately with the halogens to form triphenylgermyl halides, and the same compounds are formed on treatment with strong halogen acids.

Triethylgermane,  $(C_2H_5)_3GeH$  (48), was prepared in the same manner as the triphenylgermane by the ammonolysis of triethylgermyllithium. This compound is a liquid boiling at  $124.4^\circ C$ . (751 mm.) and has a camphor-like odor.

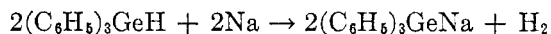
The newly developed reduction technique, using lithium aluminum hydride as a reducing agent in organic solvents, lends itself admirably to the preparation

of partially substituted germanes. Applying this procedure to the reduction of chlorotricyclohexylgermane, Johnson and Nebergall (43) obtained a yield of 87 per cent of tricyclohexylgermane. The reduction may be represented by the equation:



This technique has been used by Johnson and Harris (40) for the preparation of the first diaryl-substituted germane,  $(\text{C}_6\text{H}_5)_2\text{GeH}_2$ , to be isolated. Since the hydrides react immediately with halogens to form the corresponding halides, this method is valuable for the laboratory preparation of dialkyldihalogermanes.

The trisubstituted germanes are readily reduced by sodium in liquid ammonia, compounds of the type  $\text{R}_3\text{GeNa}$  being formed and hydrogen being evolved. The reaction is not quantitative, however, the amount of hydrogen obtained always being less than that required by the following equation:



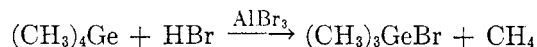
The solution, on the completion of the reaction, is always tinged with red, a fact which has been accepted (49) as evidence for the presence of  $(\text{C}_6\text{H}_5)_2\text{GeNa}_2$ . On treatment of the liquid ammonia solution with ammonium bromide, a mushy precipitate was formed which was thought to be  $(\text{C}_6\text{H}_5)_2\text{GeH}_2$ . The latter compound was not isolated or identified.

## B. NORMAL ALKYL OF THE TYPE $\text{R}_4\text{Ge}$ , $\text{R}_3\text{GeGeR}_3$ , ETC.

### 1. *Substituted monogermanes*

Compounds of the type  $\text{R}_4\text{Ge}$ , in which all of the organic radicals are alkyl or aryl hydrocarbon groups, are the most stable substances known to organogermanium chemistry. They are readily prepared by the usual Grignard and organolithium techniques, Kraus and Flood (48) reporting practically quantitative yields of tetraethylgermane from the action of ethylmagnesium bromide on germanium tetrabromide. Tetraethylgermane (20), as a typical simple alkyl derivative of monogermane, is a colorless oily liquid having a pleasant odor somewhat reminiscent of the lighter alkanes. It burns in air, giving a flame with a dark yellow outer portion and a red inner portion, shading off to blue at the surface of the burning liquid. Tetraethylgermane is insoluble in water but is known to be soluble in some eighteen organic solvents.

Tetraethylgermane reacts slowly with bromine in ethyl bromide solution to yield bromotriethylgermane and ethyl bromide (48). Tetramethylgermane (24) may be brominated by treatment with hydrogen bromide in the presence of aluminum bromide according to the equation:



The following normal tetraalkylgermanes have been prepared and described in the literature: methyl, ethyl, *n*-propyl, *n*-butyl, isoamyl, and benzyl. They are listed in table 1 together with their known physical constants.

Tetraphenylgermane is a typical example of the tetraarylgermanes. Kraus and Foster (49) obtained a 95 per cent yield of this compound by the Grignard reaction, using germanium tetrabromide as starting material.

Tetraphenylgermane (49) is a white crystalline substance melting at 235.7°C. and is readily soluble in hot benzene and toluene, the solubility decreasing greatly with a decrease in temperature. It is soluble in chloroform, moderately soluble in carbon tetrachloride, carbon disulfide, and acetone, and slightly soluble in alcohol, ether, and petroleum ether.

Tetraphenylgermane likewise is brominated very readily but substitution beyond one phenyl group is difficult. A quantitative yield of bromotriphenylgermane was obtained (49) by direct bromination in boiling carbon tetrachloride for a period of 7 hr. The use of ethylene bromide as a solvent (66) was found to be greatly superior to carbon tetrachloride and gave substitution of one phenyl group by bromine on warming for a few minutes. Replacement of two phenyl groups by bromine was accomplished (44) by prolonged boiling of tetraphenylgermane with two moles of bromine in carbon tetrachloride.

Tetraphenylgermane reacts slowly with metallic sodium dissolved in liquid ammonia to form triphenylgermylsodium,  $(C_6H_5)_3GeNa$ , sodium amide, and benzene (49). The slowness of the reaction may be due to the low solubility of the tetraphenylgermane in liquid ammonia. When concentrated solutions are used a second phenyl group is replaced, giving  $(C_6H_5)_2GeNa_2$ , which may be recognized by the characteristic red color which it imparts to the solution.

Tetraphenylgermane is stable even at higher temperatures and may be volatilized without decomposition. It is insoluble in cold concentrated sulfuric acid but is sulfonated (63) upon warming.

In addition to tetraphenylgermane, the tetrasubstituted *o*-, *m*-, and *p*-tolyl-, *p*-biphenyl-, and benzyl-germanes have been described and are listed in table 1.

The phenomenon of steric hindrance apparently prohibits the formation of some tetrasubstituted germanes. Nebergall (65) observed that while germanium tetrachloride and phenylmagnesium bromide reacted to form the tetraphenyl derivative, the corresponding reaction with cyclohexylmagnesium bromide produced only the trisubstituted bromotricyclohexylgermane. Attempts to force the reaction over to tetracyclohexylgermane by the use of higher boiling solvents and by the use of the more reactive cyclohexyllithium resulted only in the formation of the trisubstituted cyclohexyl compound.

Simons (85) carried out an interesting study to test the stability of various substituted germanes. He found that tetrabenzylgermane was much more resistant towards cleavage by hydrogen bromide and bromine than the tetraarylgermanes. The following groups are arranged in order of decreasing reactivity: *p*-tolyl, *m*-tolyl, phenyl, benzyl.

Besides the normal alkyl and aryl derivatives in which all four groups are identical, there is a long series of related compounds containing two, three, or four different radicals. These compounds were almost always prepared by successive reactions of different Grignard reagents upon germanium tetrachloride.

Because of the analogy of the tetrahedral carbon atom to the tetravalent germanium atom it was to be expected that compounds containing an asymmetric

germanium atom would exhibit the property of optical activity. Schwarz and Lewinsohn (78) demonstrated optical activity in germanium compounds by preparing bromoethylisopropylphenylgermane and resolving the mixture through the use of *d*-bromocamphorsulfonate.

### 2. *Substituted digermanes and trigermanes*

Completely substituted derivatives of the higher germanes of the type  $R_3\text{Ge-Ge}R_3$  and  $R_3\text{GeGe}R_2\text{Ge}R_3$  are generally more difficult to prepare and are much more reactive than the tetrasubstituted monogermanes.

Hexaphenyldigermane,  $(\text{C}_6\text{H}_5)_3\text{GeGe}(\text{C}_6\text{H}_5)_3$ , may be prepared by a Wurtz reaction by treating bromotriphenylgermane with sodium in boiling xylene (63), by the reaction of phenyllithium with triphenylgermane (41), or by the use of a large excess of Grignard reagent with germanium tetrachloride (40). Hexaphenyldigermane is a white crystalline substance that melts at  $340^\circ\text{C}$ . and is only slightly soluble in ordinary organic solvents. The bond between the germanium atoms is apparently quite stable. The compound is almost insoluble in liquid ammonia, and when a suspension of this material in liquid ammonia is treated with sodium, reaction takes place quite slowly with the formation of triphenylgermysodium (49). Hexaphenyldigermane is converted to bromotriphenylgermane by treatment with bromine in boiling carbon tetrachloride.

The sequence of the addition of the reactants in the organolithium reaction, that is, the relative concentrations of the two major reactants, is important. Johnson and Harris (41) observed that if phenyllithium is present in large excess, as is the case in the addition of a dilute solution of triphenylgermane to a refluxing concentrated solution of phenyllithium, the resulting product contained as much as 60 per cent of the germanium in the form of hexaphenyldigermane, the remainder being principally tetraphenylgermane.

Contrary to the conclusions of Morgan and Drew (63) it has been found (41) that about 50 per cent of the germanium could be transformed to hexaphenyldigermane with the Grignard reaction by using a ratio of ten moles of phenylmagnesium bromide to one mole of germanium tetrachloride and refluxing in a mixture of five volumes of ether and two volumes of toluene.

In contrast to the corresponding triphenyl compound, bromotriethylgermane does not react with sodium in boiling xylene but may be reduced by the direct action of sodium at elevated temperatures (48). The resulting hexaethyldigermane is a colorless mobile liquid of rather pleasant odor. It is soluble in ordinary organic solvents but is insoluble in water and in liquid ammonia. It is relatively stable towards oxygen and may be distilled in air without noticeable change. The germanium-germanium bond is readily broken by bromine, and hexaethyldigermane reacts quantitatively with this element to form bromotriethylgermane.

Owing to the low solubility of hexaethyldigermane in liquid ammonia, there is little reaction with sodium in that solvent. Addition of ether increases the reaction slightly. Lithium and hexaethyldigermane are both soluble in ethylamine, and the reaction was found to proceed readily in this solvent without the evolution of gas which indicates the formation of a lithium salt.



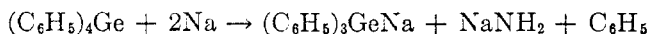
Kraus and Brown (44, 45) prepared octaphenyltrigermane,  $(C_6H_5)_3GeGe(C_6H_5)_2Ge(C_6H_5)_3$ , by the reaction of triphenylgermysodium on dichlorodiphenylgermane in benzene solution:



Octaphenyltrigermane is readily soluble in warm benzene and in chloroform. On rapid crystallization a fine white crystalline powder is obtained, while slow crystallization gives plate-like crystals. It is stable towards air and moisture. Treatment with bromine in carbon tetrachloride at room temperature resulted in some bromotriphenylgermane, some dibromodiphenylgermane, and unchanged octaphenyltrigermane, indicating further that the bond between neighboring germanium atoms is weaker than the carbon-germanium bond.

#### C. ALKALI METAL SALTS OF THE TYPE $R_3GeM$

Triphenylgermysodium,  $(C_6H_5)_3GeNa$ , is obtained when tetraphenylgermane is treated with metallic sodium dissolved in liquid ammonia (49):



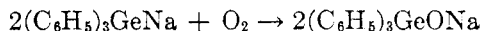
The reaction is slow, probably because of the low solubility of the tetraphenylgermane in liquid ammonia, and a better yield is obtained by treating hexaphenyldigermane with an equivalent amount of sodium in liquid ammonia. Here also the reaction is slow, again presumably owing to the low solubility of the hexaphenyldigermane. If the concentration of sodium is high, additional phenyl groups are substituted by the sodium.

Triphenylgermysodium is very soluble in liquid ammonia. Dilute solutions are faintly yellow, while more concentrated solutions are orange. The concentrated solutions are extremely viscous. Triphenylgermysodium crystallizes from ammonia with three molecules of ammonia of crystallization. It is fairly soluble in ether and in pure benzene and very soluble in benzene saturated with ammonia. Solutions of triphenylgermysodium in liquid ammonia are as highly ionized as ordinary salts, and its solutions in benzene saturated with ammonia conduct electricity with considerable facility.

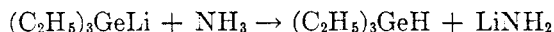
Triphenylgermysodium is extremely reactive towards electronegative elements or towards compounds containing such elements (49). This is to be expected, since the triphenylgermyl anion is only weakly electronegative. In the presence of electronegative elements, or nonionic compounds of such elements, the germyl ion loses its electron to the negative element. The sodium, or other strongly positive element, plays no part in the reaction, merely supplying the balancing electrical charge.

With ammonium bromide or with water, triphenylgermysodium yields triphenylgermane quantitatively. With fluorotriphenylgermane in liquid ammonia a small quantity of hexaphenyldigermane is obtained. Treatment of an ether solution with bromobenzene gave principally tetraphenylgermane with about 10 per cent hexaphenyldigermane. With bromotrimethylstannane the principal product was trimethylstannyltriphenylgermane,  $(CH_3)_3SnGe(C_6H_5)_3$ , together with small amounts of hexaphenyldigermane and hexamethyldistannane.

Triphenylgermysodium is oxidized in liquid ammonia, in benzene, or in the dry state (49) to the germanolate, a compound analogous to the alkoxides of carbon chemistry:



The triethylgermyllithium resulting from the action of metallic lithium on hexaethyldigermene is ammonolyzed completely in liquid ammonia and, to a considerable extent, in ethylamine. This reaction has been used for the preparation of triethylgermane (48):



Since potassium amide is a much stronger base than lithium amide, hexaethyldigermene was treated with metallic potassium to see if the triethylgermyl-potassium formed would be stable in liquid ammonia. The triethylgermyl-potassium was found to be fairly stable and may be prepared in practically quantitative yield in ethylamine (48):

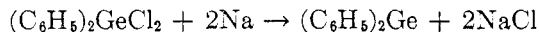


Triethylgermylpotassium in ammonia solution reacts with ethyl bromide with the formation of tetraethylgermane.

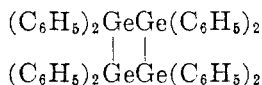
Kraus and Nelson (51) treated triethylsilyl bromide with triphenylgermysodium and obtained triethylsilyltriphenylgermane. This compound crystallizes readily from ethanol. It is soluble in benzene and petroleum ether, moderately soluble in hot methanol and ethanol, but only slightly soluble in cold ethanol. It is practically insoluble in liquid ammonia but is readily soluble in ethylamine. Bromine converts triethylsilyltriphenylgermane into triphenylgermyl bromide and triethylsilyl bromide. Lithium in ethylamine gives an equimolecular mixture of triethylsilyllithium and triphenylgermyllithium. These latter two compounds react with ammonium bromide to give triethylsilane and triphenylgermane, respectively.

#### D. ALKYL-SUBSTITUTED RING COMPOUNDS OF GERMANIUM

Inorganic compounds of divalent germanium are common. Kraus and Brown (45) attempted to synthesize the divalent organic compound, diphenylgermanium, by the reduction of dichlorodiphenylgermane by sodium in boiling xylene.



Molecular weight determinations of the crystalline product, however, gave results approximately four times as large as the simple empirical formula required, and so it is quite possible that the compound is a derivative of cyclotetragermene:



When treated with metallic sodium in liquid ammonia the compound added two sodium atoms for each germanium atom and gave a red solution previously reported as characteristic of the compound  $(\text{C}_6\text{H}_5)_2\text{GeNa}_2$ .

A compound containing germanium in a ring with five carbon atoms was obtained by Schwarz and Reinhardt (79) by making a Grignard reagent with 1,5-dibromopentane and treating with germanium tetrachloride. The resulting pentamethylenegermanium dichloride,  $\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{GeCl}_2}$ , was then treated with ethylmagnesium bromide, thus replacing the two chlorine atoms by ethyl groups.

#### E. THE ORGANOHALOGERMANES

The first halogen-substituted derivatives of the germanes to be prepared were the mono and dichloro derivatives of monogermane and the analogous bromo and iodo compounds. Dennis and Judy (22) prepared monochloro- and dichloro-germanes and monobromo- and dibromo-germanes by the action of hydrogen halides upon monogermane. The corresponding iodo compounds were also prepared but were not isolated because of their instability.

Both chlorogermane and dichlorogermane are colorless mobile liquids with peculiarly nauseating odors. They fume when exposed to moist air, the walls of the container becoming coated with a film which is white at first and then becomes yellow, finally deepening to an orange tint. The reaction is accompanied by the evolution of considerable heat.

Water hydrolyzes both monochlorogermane and dichlorogermane with the evolution of hydrogen. Absolute ethanol precipitates a white substance which dissolves to a yellow solution when an equal volume of water is added. Solutions of alkali hydroxides precipitate an orange compound, liberating considerable hydrogen. Alcoholic potassium hydroxide solution yields a pale yellow precipitate, no hydrogen being evolved until water is added to the mixture. Hydrogen chloride, in the presence of aluminum chloride, converts chlorogermane to dichlorogermane with the liberation of hydrogen. The dichlorogermane does not react further with hydrogen chloride.

Ammonia acts instantly on both chlorogermane and dichlorogermane, forming nonvolatile colored substances which decompose with explosive violence when heated in air.

Chlorogermane decomposes slowly at room temperature in accordance with the equation:



Dichlorogermane decomposes more rapidly, yielding a variety of products among which germanium, germanium dichloride, germane, hydrogen chloride, chlorogermane, tetrachlorogermane, and hydrogen have been identified.

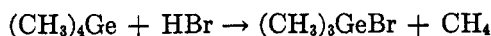
The chemical properties of the bromo compounds are similar to those of their chlorine analogs.

##### 1. Alkyl-substituted halogermanes

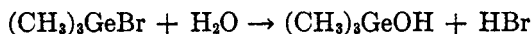
Although the first aryl-substituted halogermane, bromotriphenylgermane, had been prepared in 1925, it was not until 1930 that the first alkyl-substituted halogermane was isolated.



Dennis and Patnode (24) selected bromotrimethylgermane for investigation. By a series of reactions they converted germanium tetrachloride into tetramethylgermane by the method of Dennis and Hance (21), and then converted the tetramethylgermane into bromotrimethylgermane by treatment with hydrogen bromide, using the method devised by Dennis and Judy (22) for making halogen derivatives of monogermane.



Bromotrimethylgermane is a colorless oily liquid with a characteristic odor resembling turpentine and onions. It is soluble in the usual organic solvents. The compound is hydrolyzed by water, and silver nitrate precipitates silver bromide from the water solution. The hydrolysis product is a volatile liquid. Germanium disulfide is not precipitated when an aqueous solution of bromotrimethylgermane is acidified and treated with hydrogen sulfide. The reason for the nonprecipitation of the sulfide is believed to be the formation of the non-polar germanol:



The trimethylgermanol may or may not condense with itself with the elimination of a molecule of water. This is in contrast to the phenyl analog, which condenses readily (63). Bromotrimethylgermane is readily oxidized by sodium peroxide and by hot chromic acid but only slowly by ammoniacal hydrogen peroxide. Hot concentrated sulfuric acid liberates bromine. When bromotrimethylgermane was dissolved in benzene and dry ammonia bubbled through the solution, a white crystalline precipitate of ammonium bromide appeared. Evaporation of the filtrate yielded a compound believed to be an amine.

Kraus and Flood (48) prepared all four of the monohalotriethylgermanes. They observed that fluorotriethylgermane was generally more stable towards hydrolysis than the other analogous halogen compounds. Comparison of the bromo compound with the silicon and tin analogs reveals the expected intermediate properties. Bromotriethylsilane is immediately and completely ammonolyzed in the presence of ammonia, either vapor or liquid. Bromotriethylstannane (50) combines with one molecule of ammonia to form a stable solid that is not ammonolyzed in liquid ammonia.

On condensing ammonia on bromotriethylgermane, which is a solid at liquid ammonia temperatures, two liquid layers are formed, the upper layer occupying the greater volume. As the ammonia evaporates, both layers gradually disappear, leaving a white solid. The formation of the two layers was accepted as an indication of ammonolysis, the heavier layer comprised of di(triethylgermyl)-amine and the upper layer containing ammonium bromide. As the ammonia evaporates interaction takes place between the two layers, forming again the bromotriethylgermane with one molecule of ammonia.

Di(triethylgermyl)amine,  $[(\text{C}_2\text{H}_5)_3\text{Ge}]_2\text{NH}$ , is a colorless mobile liquid insoluble in liquid ammonia. It reacts vigorously with water to form bis (triethylgermanium oxide,  $[(\text{C}_2\text{H}_5)_3\text{Ge}]_2\text{O}$ .

Compounds of the type  $R_3AX$ , if they do not ammonolyze, may be reduced by means of alkali metals in liquid ammonia with the formation of the free group, which is usually obtained as the dimer. Since the halotriethylgermanes are readily ammonolyzed in liquid ammonia, their reduction cannot be carried out in this solvent. The weaker ammonolyzing agent ethylamine may be used as a solvent and the reaction may be carried out in this solvent with the evolution of more or less hydrogen. Since the fluoride has less tendency to hydrolyze than the other halides, Kraus and Flood (48) carried out the reaction with fluorotriethylgermane, using lithium in ethylamine. Very little hydrogen was liberated and hexaethyldigermene was formed:



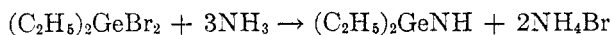
The formation of triethylgermyllithium,  $(C_2H_5)_3GeLi$ , was postulated as part of the mechanism.

Hydrolysis of bromotriethylgermane by potassium hydroxide yielded 97 per cent of bis(triethylgermanium) oxide,  $[(C_2H_5)_3Ge]_2O$  (48).

Flood (30) observed that the relative rate of reaction of bromine with fluorotriethylgermane was about six times more rapid than with the corresponding chloride and that the reaction with the chloro compound, in turn, was about six times more rapid than with the bromo compound. Furthermore, it was observed that while the reaction of bromine with bromotriethylgermane liberated considerable quantities of hydrogen bromide, no detectable hydrogen bromide was evolved when fluorotriethylgermane was brominated under similar conditions. These observations led to a satisfactory method of preparing dihalo derivatives wherein the fluorotriethylgermane was brominated and the crude dihalodiethylgermanes converted into diethylgermyl oxide by hydrolysis. When treated with concentrated halogen acids the oxide is converted to the corresponding dihalodiethylgermane.

Horvitz and Flood (39) have devised a method of preparing dihalodiethylgermanes by an obscure reaction involving the heating of triiodoethylgermane with an excess of 40–60 lead–bismuth alloy and extracting with ethyl iodide. Hydrolyzing the impure diiodo mixture with boiling aqueous sodium hydroxide converts the dihalo compound to diethylgermyl oxide, which may be filtered off upon cooling the solution.

Dibromodiethylgermane is a colorless liquid with a sharp odor suggestive of hydrogen chloride. When treated with water or with aqueous alkaline solutions the compound is hydrolyzed, forming diethylgermanium oxide. With liquid ammonia ammonolysis takes place, yielding diethylgermanium imine.



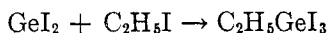
A molecular weight determination indicates polymerization of the imine to the tetramer.

Information concerning the relative reactivity of alkyl and aryl groups is given by an indirect method of obtaining dibromodiethylgermane developed by Flood (30). Dibromodiphenylgermane can be prepared by the action of bromine

on tetraphenylgermane (44), but the preparation of dibromodiethylgermane by reaction of bromine with tetraethylgermane is not practical. All attempts to substitute a second bromine atom for an ethyl group in bromotriethylgermane by the direct action of bromine gave complex mixtures from which only low yields of dibromodiethylgermane could be obtained. Flood accordingly prepared diethyldiphenylgermane by the action of ethylmagnesium bromide on dibromodiphenylgermane, which was brominated with the preferential replacement of the phenyl groups, yielding dibromodiethylgermane.

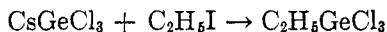
Treatment of diethylgermanium oxide with hydrobromic acid also yields dibromodiethylgermane (30).

The first trihaloalkylgermane was prepared by Flood (31), who made triiodoethylgermane by heating germanium(II) iodide and ethyl iodide in an air-free sealed tube at 110°C. for several days.



At 140°C. a mixture of products is obtained, the principal constituents being germanium tetraiodide, unidentified gases, and only a very little triiodoethylgermane.

Tchakirian (92) devised a method whereby  $\text{CsGeCl}_3$ , formed by the addition of germanium(II) chloride to cesium(I) chloride, is treated with alkyl or aryl iodide. A yield of 60 per cent was obtained for the ethyl compound.



Triiodoethylgermane is a mobile lemon-yellow liquid, the color becoming deep red above 250°C. It is soluble in ordinary organic solvents and is relatively stable towards thermal decomposition, withstanding heating to 300°C. without appreciable change. This stability is in marked contrast to the behavior of triiodogermane, which is reported (22) to decompose at room temperature to give germanium(II) iodide and hydrogen iodide. When heated above 350°C. triiodoethylgermane decomposes, with the formation of gas and germanium tetraiodide. Triiodoethylgermane is quite stable towards oxidation and may be distilled in dry air without change (31). Exposure to moist air causes marked decomposition.

The application of Rochow's direct synthesis method (70) yields dichlorodimethylgermane and trichloromethylgermane by the action of methyl chloride on elementary germanium at temperatures over 320°C. with an equal weight of copper used as a catalyst. The method yields principally the dichloro derivative with both ethyl chloride and phenyl chloride. With methyl bromide the products, while not definitely examined, appeared to be principally dibromodimethylgermane and tribromomethylgermane, together with some monobromo compound.

## 2. Aryl-substituted halogermanes

Bromotriphenylgermane was first isolated by Morgan and Drew (63) as one of the partial substitution products of the reaction between germanium tetra-

bromide and a large excess of phenylmagnesium bromide. It is prepared in greater yield by simple bromination of tetraphenylgermane (44, 49, 66). Earlier workers used carbon tetrachloride as a solvent during the bromination, heating the mixture for several hours. Ethylene dibromide as a solvent greatly facilitates the bromination, replacing the first phenyl group by bromine within a few minutes and giving a much greater proportion of the dibromo compound.

Bromotriphenylgermane is very soluble in ordinary organic solvents such as chloroform, carbon tetrachloride, benzene, and toluene. It hydrolyzes slowly in water and more readily in aqueous solutions of alkalis. The product of hydrolysis is not the hydroxide but the oxide,  $(C_6H_5)_3GeOGe(C_6H_5)_3$ . The bromide is readily soluble in liquid ammonia and on evaporation of the solvent, tri(triphenylgermyl)amine,  $[(C_6H_5)_3Ge]_3N$ , is obtained (49).

The fluoro, chloro, and iodo derivatives have been prepared by the action of the corresponding halogen acid upon bis(triphenylgermanium) oxide. The fluoride is the most stable of the halotriphenylgermanes in that it hydrolyzes very slowly, even when boiled with alcoholic potassium hydroxide. Iodotriphenylgermane is very unstable. It hydrolyzes readily and its solutions in petroleum ether acquire a pink color, due to free iodine, after exposure to the atmosphere for a short time.

Dihalogermanes of the type  $R_2GeX_2$  are also synthesized by the Grignard reaction, by direct bromination of tetraarylgermanes, using ethylene dibromide as the solvent, or by direct synthesis from the metal and aryl halide.

Bromotriarylgermane may be separated fairly easily by fractionation of the mixture but it is difficult to separate the dibromo and tribromo compounds. To overcome this difficulty Kraus and Brown (44) converted them to the chlorides with concentrated hydrogen chloride. Dichlorodiphenylgermane is a colorless liquid distilling readily at  $100^\circ C$ . under a pressure of 0.005 mm. It is readily soluble in ordinary organic solvents. It is slightly hydrolyzed in moist air, more rapidly in water and alcohol, and still more rapidly in aqueous alkaline solutions. Dibromodiphenylgermane is obtained by treating the dichloro compound with strong hydrobromic acid. The difluoro compound was obtained by hydrolyzing dichlorodiphenylgermane and treating the resulting diphenylgermanium oxide with concentrated hydrofluoric acid.

Separation of the dihalo compound from the trihalo can also be accomplished by converting them into the corresponding arylgermanes by reduction with lithium aluminum hydride (40). The diphenylgermane made in this way is very easily separated by fractionation and is readily converted to the dibromide by simple bromination.

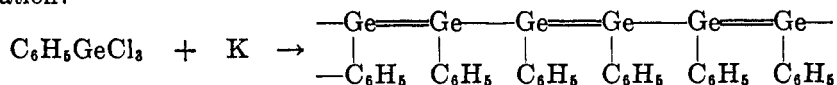
The first trihalogermane to be isolated was trichlorophenylgermane. This compound was prepared (80) by heating tetraphenylgermane with germanium tetrachloride in a sealed tube at  $210-290^\circ C$ .



The treatment of cesium germanium trichloride with aryl halide (92) has been discussed under the trihaloalkylgermanes.

The dihalo and trihalo compounds hydrolyze and ammonolyze readily. These

reactions will be discussed in detail under oxides and germanoic acids. Schwarz and Schmeisser (80) synthesized an interesting compound by reduction of trichlorophenylgermane with metallic potassium. They wrote the following equation:



The terminal valences are not united to give the cyclo compound.

The fact that inorganic compounds of divalent germanium are common prompted Kraus and Brown (45) to attempt to prepare diphenylgermanium. The reduction of dihalodiphenylstannane is readily effected by means of the alkali metals in liquid ammonia and it was expected that a similar reaction might hold for germanium. The dihalodiphenylgermanes ammonolyze readily, however; accordingly ethylamine was used as a solvent with lithium metal as a reducing agent, since the dihalogermanes are not ammonolyzed to any great extent in this solvent and lithium is soluble in it. The reduction product was a resinous material whose composition approximated that of diphenylgermanium but which could not be purified. The diphenyl compound was obtained in crystal form, however, by the reduction of dichlorodiphenylgermane by sodium in xylene. The yields were small, the greater proportion of the product again appearing as a resinous material resembling that obtained with lithium in ethylamine. The product was considered a tetramer,  $[(\text{C}_6\text{H}_5)_2\text{Ge}]_4$ , and was very likely octaphenylcyclotetragermane.

#### F. THE SUBSTITUTED GERMANIUM OXIDES

Dennis and Patnode (24) indicated the existence of bis(trimethylgermanium) oxide as resulting from the loss of water from the germanol but no constants were given and the compound has not been investigated.

Kraus and Flood (48) obtained bis(triethylgermanium) oxide in 97 per cent yield by the hydrolysis of an impure sample of triethylgermyl bromide by aqueous potassium hydroxide. The principal impurity was diethylgermanium oxide, formed by the dibromodiethylgermane present in the starting material.

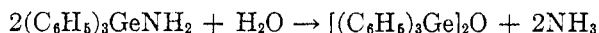
Bis(triethylgermanium) oxide is a colorless liquid with a camphor-like odor. It boils at 253.9°C. (760 mm.) and does not solidify at  $-50^\circ\text{C}$ . It is soluble in common organic liquids and in ethylamine but is insoluble in water and in liquid ammonia. It is quite stable towards oxidation and may be heated to 250°C. in air without appreciable decomposition. It burns readily with a smoky flame. When treated with concentrated aqueous halogen acids the oxide is converted into the corresponding halide. The oxide reacts readily with lithium in ethylamine with the formation of a reddish solution and without evolution of gas, probably according to the equation:



On evaporation of the ethylamine, the triethylgermyllithium ammonolyzes to triethylgermane.

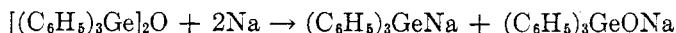
Bis(tribenzylgermanium) oxide has been prepared (12) by treating tribenzylgermanium bromide with silver nitrate and also by boiling the bromide with alcoholic potassium hydroxide. Treatment with concentrated halogen acids yields the corresponding monohalide.

Bis(triphenylgermanium) oxide was first prepared by Morgan and Drew (63). They obtained the compound in quantitative yield by boiling an alcoholic solution of triphenylgermanium bromide with silver nitrate. It is quantitatively reconverted by concentrated hydrobromic acid. Kraus and Wooster (54) obtained the oxide by the hydrolysis of triphenylgermylamine.



They observed that triphenylgermylamine was extremely sensitive towards hydrolysis, differing markedly in this respect from its carbon analog, which is comparatively stable.

Bis(triphenylgermanium) oxide reacts with sodium in liquid ammonia:



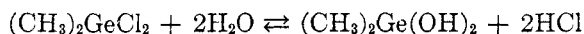
The sodium readily breaks down the first of the germanium-oxygen bonds but attacks the second only with difficulty, if at all.

Refluxing tri-*p*-tolylgermyl bromide for 10 hr. with 0.5 *N* sodium hydroxide gave bis(tri-*p*-tolylgermanium) oxide (86). The same compound is obtained by the action of alcoholic silver nitrate on the bromide. Bis(tri-*p*-tolylgermanium) oxide is a white, densely crystalline solid, crystallizing in small well-developed anisotropic prisms. It is insoluble in water, very slightly soluble in methanol and ethanol, and soluble in hot ligroin and cold benzene.

Bis(tri-*m*-tolylgermanium) oxide was prepared in quantitative yield (86) by reaction of the bromide with alcoholic silver nitrate solution. It crystallizes in thick ill-formed crystals. It reacts with concentrated hydrochloric acid in alcoholic solution to form tri-*m*-tolylgermanium chloride. It is insoluble in water, soluble in ethanol, and soluble in benzene.

Crude tri-*o*-tolylgermanium chloride gave the germanol when treated with alcoholic silver nitrate.

Rochow (71) investigated dimethylgermanium oxide and compared it with the silicon analogs. Methyl silicones may be prepared by hydrolyzing the corresponding chlorosilanes, separating the water-insoluble methyl siloxane, and processing it to produce the desired polymer. The behavior of germanium analogs is entirely different. Dimethylgermanium dichloride did not produce a water-repellent film on solids as does dimethyldichlorosilane; instead it dissolved completely in water. When the water solution was evaporated to dryness, no residue was left. When dimethylgermanium dichloride was hydrolyzed in dilute ammonium hydroxide and the resulting clear solution was evaporated, only ammonium chloride remained. It was found that the hydrolysis was reversible to an extent which makes impractical the preparation of dimethylgermanium oxide by the techniques used for preparing the analogous silicones



Hydrolysis of the dichloride was accordingly abandoned in favor of the hydrolysis of the sulfide.

Hydrolysis of  $[(\text{CH}_3)_2\text{GeS}]_x$  in 10 per cent aqueous hydrogen peroxide yields a water-clear solution of methylgermanium oxides or hydroxides, from which resinous and crystalline substances are obtained on evaporation. If the treatment with hydrogen peroxide is sufficiently vigorous to oxidize a minor fraction of the methyl groups, there is obtained a sirupy mass which becomes resinous when chilled. The resins are soluble in hot water, benzene, and ethanol. On long standing white crystals, presumably the hydroxide, grow slowly in the mass but disappear on heating. A resinous sample with a  $\text{CH}_3:\text{Ge}$  ratio of 1.2:1 did not crystallize on standing and was found to be infusible although slightly soluble in water.

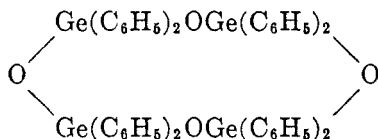
The following is proposed as a possible mechanism: The sulfide ion is oxidized to the sulfate, which is followed by acid hydrolysis of the rest of the dimethylgermanium sulfide. The addition of dilute sulfuric acid as such yielded a mixture of polymeric oxides, one of which was identified as the tetramer,  $[(\text{C}_2\text{H}_5)_2\text{GeO}]_4$ .

Flood (30) prepared diethylgermanium oxide by the hydrolysis of triethylgermanium bromide by aqueous sodium hydroxide. He found that the compound existed in two polymeric forms. At room temperature the stable form is a white amorphous solid melting at about  $175^\circ\text{C}$ . when heated rapidly. It is insoluble in organic solvents, water, and liquid ammonia. The oxide also exists in an unstable liquid form which crystallizes at about  $18^\circ\text{C}$ . In this form the oxide is soluble in organic solvents, but insoluble in water and in liquid ammonia. Cryoscopic measurements indicate that the unstable form is trimeric while the high-melting stable form is assumed to be dimeric. Transition between the two forms occurs in the vicinity of  $110^\circ\text{C}$ . and is accelerated by a trace of water.

When treated with concentrated halogen acid diethylgermanium oxide is converted into the dihalide. It reacts readily with lithium in ethylamine solution and is fairly stable towards oxidation, no decomposition occurring when it is heated to  $290^\circ\text{C}$ . in air.

Anderson (2) repeated Flood's work on diethylgermanium oxide and concluded that the polymer was tetrameric.

Morgan and Drew (63) obtained two well-characterized compounds from the hydrolysis of diphenylgermanium dibromide. One of these was assigned the formula,  $\text{HOGe}(\text{C}_6\text{H}_5)_2\text{OGe}(\text{C}_6\text{H}_5)_2\text{OGe}(\text{C}_6\text{H}_5)_2\text{OGe}(\text{C}_6\text{H}_5)_2\text{OH}$ , and called trianhydrotetrakis(diphenyl)germanediol. The other was given a cyclic formula



and called tetraanhydrotetrakis(diphenyl)germanediol.

Kraus and Brown (44) hydrolyzed pure diphenylgermanium dibromide by boiling with strong aqueous ammonium hydroxide and obtained a white powder practically insoluble in organic solvents. They were unable to obtain compounds

with definite boiling points and concluded that a mixture of complex oxides was produced. A similar mixture of oxides was obtained by the hydrolysis of diphenylgermanium imine.

In general, it appears that the oxides obtained from the dihalogermanes are structurally similar to the siloxanes. While the structures have not been determined by the usual methods for structural analysis, it seems highly probable that lack of agreement between the small amount of data available on these compounds is entirely due to the large variations in structure that may occur with rather minor differences in the conditions under which the oxides were synthesized.

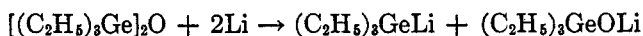
#### G. THE SUBSTITUTED GERMANOLS

The first alcohol-type germanium compound to be prepared was triphenylgermanol. Contrary to expectations, monohalotriphenylgermanes are not hydrolyzed by water or alkaline solutions, and attempts by Morgan and Drew (63) and Kraus and Foster (49) to obtain triphenylgermanol in this manner ended in failure. The product of hydrolysis of bromotriphenylgermane (49, 63) is not triphenylgermanol but bis(triphenylgermanium) oxide,  $[(C_6H_5)_3Ge]_2O$ . Triphenylgermanol is best obtained by treating a benzene solution of sodium triphenylgermanolate (49) with water and recrystallizing the product from petroleum ether.

Triphenylgermanol is soluble in organic solvents to about the same extent as bromotriphenylgermane (49). It crystallizes from petroleum ether in the pure state but crystallizes from benzene with solvent of crystallization. It melts at  $134.2^\circ C$ . (corr.) without appreciable loss of water, but above this temperature water is lost with the formation of the oxide.

Sodium triphenylgermanolate is practically insoluble in liquid ammonia, extremely soluble in benzene, and readily soluble in petroleum ether (49). The product crystallized from petroleum ether melts at about  $100^\circ C$ . but the dry product obtained on crystallization from liquid ammonia failed to melt at temperatures up to  $250^\circ C$ . The crystals obtained from liquid ammonia contain one molecule of ammonia of crystallization and it is thought that the crystals obtained from petroleum ether also contain solvent of crystallization. Sodium triphenylgermanolate in liquid ammonia reacts readily with water to form the germanol.

Among the alkyl-substituted germanols the existence of trimethylgermanol was postulated by Dennis and Patnode (24) but the compound was not isolated. The next higher analog, triethylgermanol, behaves very much like the phenyl compound in that it is not formed by the hydrolysis of triethylgermanium bromide (48), the oxide being formed instead. Bis(triethylgermanium) oxide is a colorless liquid with a camphor-like odor. Treating the oxide with lithium in ethylamine as a solvent gives a reddish solution, presumably according to the equation:

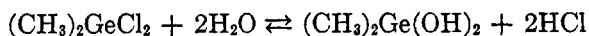


Among other monogermanol compounds reported is tricyclohexylgermanol (9, 43), prepared by the reaction of tricyclohexylgermanium bromide with



alcoholic silver nitrate solution. Tri-*o*-tolylgermanol (86) has been prepared from the corresponding chloride by a similar reaction. The latter compound was obtained as an oily residue distilling at 212–214°C./1 mm.

In the attempted hydrolysis of dichlorodimethylgermane to dimethylgermanium oxide, Rochow (71) suggests either the formation of volatile hydrolysis products or the existence of a readily reversible reaction:



This reaction is reversible to an extent which makes it impractical for the preparation of the oxide.

Laubengayer and Allen (56) studied the hydrolysis of methyltrichlorogermane and found the hydrolysis and subsequent condensation to the highly polymeric methylgermanium oxide to be reversible. Although methylgermanetriol was not isolated, there is strong evidence for its existence in solution.

#### H. GERMANOIC ACIDS, ANHYDRIDES, AND THIO ACIDS

One of the earliest references to germanoic acids is that of Morgan and Drew (63). They hydrolyzed tribromophenylgermane and obtained a colorless amorphous product that was soluble in caustic alkalies. The properties of the product in regards to the degree of hydration were found to vary with the experimental conditions of its preparation and isolation. Their results indicate the presence of hydroxyl groups, and they believed the product to be intermediate in composition between the limits represented by the acid,  $\text{C}_6\text{H}_5\text{GeOOH}$ , and the anhydride,  $(\text{C}_6\text{H}_5\text{GeO})_2\text{O}$ .

Orndorff, Tabern, and Dennis (66) prepared phenylgermanoic anhydride by heating an equimolecular mixture of diphenylmercury and germanium tetrachloride in dry xylene in a sealed tube at 140°C. for 2 days. The resulting mixture of trichlorophenylgermane and phenylmercuric chloride was treated with very dilute ammonium hydroxide and the phenylgermanoic anhydride,  $(\text{C}_6\text{H}_5\text{GeO})_2\text{O}$ , formed by the hydrolysis gathered at the liquid interface as a granular precipitate.

The anhydride of phenylgermanoic acid is described as a white, fluffy, amorphous solid, insoluble in water and organic solvents but soluble in an excess of alkali. It is precipitated in lustrous flakes from alkaline solution by carbon dioxide. A definite melting point could not be found.

Benzylgermanoic anhydride, *p*-tolylgermanoic anhydride, and dimethylamino-phenylgermanoic anhydride were prepared (66) in somewhat similar fashion.

Bauer and Burschkies (9) prepared a number of substituted germanoic anhydrides, together with their thio analogs. Phenyl- and naphthyl-germanoic anhydrides were prepared by the mercury diaryl method just described (66). Various substituted anilino-germanoic anhydrides were made by heating the substituted aniline with germanium tetrachloride in an autoclave. The latter reaction is contrary to earlier reports (94) that germanium tetrachloride would not react under such conditions.

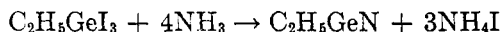
The thio analogs were obtained by the simple procedure of heating an acetic acid solution of germanoic anhydride with hydrogen sulfide.

The first reference to an alkylgermanic acid is a report by Flood (30) of the formation of a small quantity of white solid in the residue from the bromination of fluorotriethylgermane. He believed this to be impure ethylgermanic acid. Later Flood (31) boiled an aqueous solution of triiodoethylgermane with freshly prepared silver oxide, filtered the hot solution, concentrated the filtrate by evaporation, and obtained a transparent "cellophane-like" film on the surface of the hot solution. Removal of the material from the surface caused the formation of another solid film. Analysis indicated that the substance was ethylgermanic anhydride,  $(C_2H_5GeO)_2O$ . Evaporation of the filtrate yielded a residue which was also found to be the anhydride.

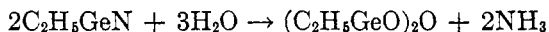
Almost quantitative yields are obtained by another method in which triiodoethylgermane is ammonolyzed in liquid ammonia. The insoluble white ammonolytic product is washed first with liquid ammonia and then with cold water until free from iodine. The residual solid is dissolved in boiling water, and the solution filtered. The ethylgermanic anhydride is obtained upon evaporation of the filtrate.

Ethylgermanic anhydride is a white solid which does not melt when heated to  $300^\circ C$ . At higher temperatures and reduced pressures sublimation and decomposition occur. The anhydride is soluble in water and alcohol and insoluble in petroleum ether. When treated with concentrated halogen acids, the corresponding trihalide is formed in solution and in the case of the trichloride may be extracted with ether. Attempts to find a hydrated form of ethylgermanic anhydride through vapor pressure measurements were not successful.

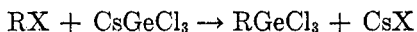
When liquid ammonia is condensed into trichloroethylgermane, a reaction occurs immediately, yielding a white solid insoluble in liquid ammonia. The reaction apparently proceeds with the formation of complex intermediate compounds but the overall reaction is given by the equation:



Hydrolysis of the ethylgermanium nitride then gives the anhydride:



Tchakirian (92) describes a method of obtaining germanic acids by heating an alkyl or aryl halide with cesium germanium chloride in a sealed tube:



Hydrolysis of the trichloride then gives the acid. Heating the cesium compound with methylene iodide gave  $CH_2(GeCl_3)_2$ , which on hydrolysis yielded the acid,  $CH_2(GeOOH)_2$ . Treatment of germanium dioxide with oxalic acid (92) is reputed to give the compound  $H_2[Ge(C_2O_4)_3]$ .

## I. MISCELLANEOUS GERMANIUM COMPOUNDS

### 1. Sulfides and thio compounds

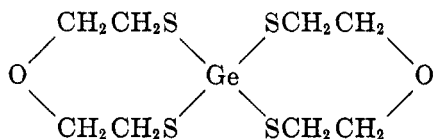
Omitting from present consideration the thio acids and anhydrides mentioned in the preceding section, there are only two types of sulfur compounds that have

been investigated to any extent. These are given in table 3, where the normal sulfides are listed first, followed by the sulfur analogs of the ortho esters. Only seven normal sulfides have been described in the literature. Burschkies (16) prepared most of them by interaction of the substituted monobromogermane with sodium sulfide under varying conditions. Of the six compounds prepared and described by Burschkies, five were the normal sulfides, that is, with one sulfur atom, but the tricyclohexylgermanium bromide reacted differently, giving the persulfide,  $(C_6H_{11})_3GeSSGe(C_6H_{11})_3$ .

When dimethylgermanium dichloride is dissolved in 6 *N* sulfuric acid and treated with hydrogen sulfide, a waxy white precipitate of dimethylgermanium sulfide is formed (71). This sulfide crystallizes in flat plates and has a peculiar pepper and onion odor. It hydrolyzes very slowly in moist air, liberating hydrogen sulfide. Hydrolysis is also slow in boiling water but more rapid in dilute acids or dilute solutions of hydrogen peroxide.

Schwarz and Reinhardt (79) prepared germanium tetrathiophenolate by the Grignard reaction between germanium tetrachloride and thiophenol and by the reaction of sodium with thiophenol and germanium tetrachloride. Backer and Stienstra (5, 7) prepared a whole series of analogous compounds by similar reactions.

Other sulfur compounds include a thiophene derivative,  $(C_4H_3S)_4Ge$  (55), and a compound with an ether linkage (5):



### 2. The germanium ortho esters

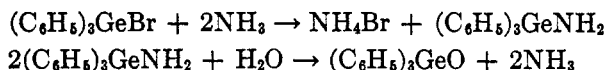
Germanium tetrachloride does not react with boiling ethanol. Addition of sodium (90) causes reaction, with formation of tetraethoxygermane. The only other analogous compound described in the literature is tetraphenoxygermane, prepared in similar fashion (79). Tetraethoxygermane is a colorless mobile liquid which is extremely hygroscopic and hydrolyzes readily in air with the separation of germanium dioxide. Laubengayer and Brandt (57) hydrolyzed tetraethoxygermane and obtained a germanium dioxide gel with properties somewhat similar to those of silica gel.

Sugden (89) predicted that the atomic parachor for germanium should be 36. Sidgwick and Laubengayer (84), using tetrahalo- and tetraethyl-germanes, obtained experimental values ranging from 36 to 39. With tetraethoxygermane a value of 30 was found. The low result is explained by a possible association due to the ethoxy groups.

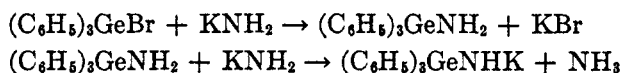
### 3. Amines and imines

A comparison of triphenylgermylamine with its carbon analog reveals several contrasting differences. The germylamine is extremely susceptible to hydrolysis, while the organic amine is comparatively stable. Triphenylgermylamine results

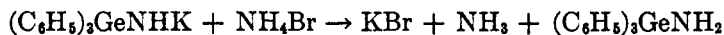
from the action of gaseous ammonia upon triphenylgermanium bromide, or other halides, in organic solvents (49, 54). The compound is so sensitive towards moisture that it is largely hydrolyzed in the operations incident to its separation unless extreme precautions are taken. Since the amine yields the oxide and ammonia on hydrolysis, the overall process is expressed by the equations:



Triphenylgermylamine may also be formed by the action of potassium amide upon the bromide in ammonia solution. An excess of the potassium amide facilitates the reaction, forming the monopotassium salt.



The amine is then liberated from its salt by ammonium bromide and appears as a fine white precipitate.



The germylamine also differs from its carbon analog by its marked tendency to lose ammonia with the formation of the secondary amine,  $[(\text{C}_6\text{H}_5)_3\text{Ge}]_2\text{NH}$ . This deamination sometimes occurs immediately upon precipitation. Attempts to recrystallize the amine invariably yield mixtures of the primary amine, the secondary amine, and even of the tertiary amine,  $[(\text{C}_6\text{H}_5)_3\text{Ge}]_3\text{N}$ .

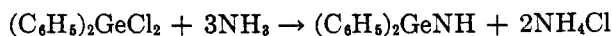
Complete conversion of the amine to the nitride is effected by heating the primary amine above 200°C. at atmospheric pressure and then evacuating. The tertiary amine may be purified by fractional sublimation under reduced pressure or by recrystallization from dry petroleum ether, which yields colorless crystals.

The amine decomposes when treated with hydrochloric acid and may be analyzed by separating the resulting ammonium chloride from the triphenylgermanium chloride. Treatment with nitric or sulfuric acid fails to give the corresponding nitrate or sulfate.

It was concluded that compounds of germanium with electronegative groups are more reactive than their carbon analogs.

Kraus and Nutting (52) pointed out the formation of the  $(\text{C}_6\text{H}_5)_3\text{Ge}^-$  ion resulting from the solution of triphenylgermysodium in liquid ammonia. The triphenylgermysodium reacts with methylene chloride in liquid ammonia to form a number of germanium compounds, one of which is triphenylgermylamine. The amine was not recovered, since it is hydrolyzed readily to the triphenylgermanium oxide.

Ammonolysis of a dihalodiphenylgermane with liquid ammonia gives the corresponding imine (44).



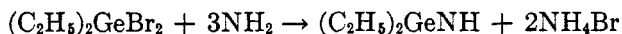
Diphenylgermanium imine is a colorless liquid which is extremely viscous at ordinary temperatures but becomes markedly more fluid at higher temperatures.

It is readily soluble in ordinary organic solvents and is hydrolyzed with extreme ease.

Only slight, if any, ammonolysis occurs when dichlorodiphenylgermane is dissolved in ethylamine (45).

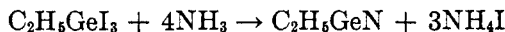
Treatment of bromotriethylgermane with sodium in liquid ammonia yielded bis(triethylgermyl)amine (48). This compound is a colorless mobile liquid, insoluble in liquid ammonia. It reacts vigorously with water to form bis(triethylgermanium) oxide.

Dibromodiethylgermane gave the diethylgermanium imine when treated with ammonia (30).

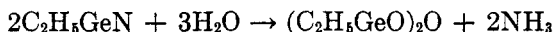


Diethylgermanium imine is a colorless liquid. It hydrolyzes very easily, being decomposed rapidly on exposure to air, liberating ammonia and forming diethylgermanium oxide. Molecular weight determinations indicate polymerization, possibly to the trimer or tetramer or a mixture of the latter two compounds.

Triiodoethylgermane reacts with liquid ammonia to give a white precipitate insoluble in liquid ammonia (31). The overall reaction is represented by the equation:



Hydrolysis of the nitride yields ethylgermanoic anhydride.



Tribromoethylgermane gives similar results.

#### 4. *The germanium isocyanates*

Germanium isocyanate,  $Ge(NCO)_4$ , was prepared (32, 58) by treating germanium tetrachloride in benzene with silver isocyanate. A small quantity of a solid residue also resulted which may have been germanium cyanate,  $Ge(OCN)_4$ .

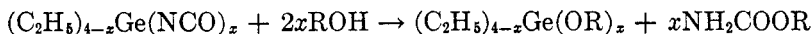
Anderson (1) has prepared a series of ethylgermanium isocyanates by the reaction of silver isocyanate with the appropriate ethylgermanium halide. A comparison of their properties showed that there is a regular decrease in the rate of hydrolysis from germanium tetrakisocyanate to the more inert tetraethylgermane. Germanium tetrakisocyanate is hydrolyzed rapidly with the evolution of considerable heat. Ethylgermanium triisocyanate is also hydrolyzed fairly rapidly and is characterized by the formation of a water-repellent solution. Diethylgermanium diisocyanate is hydrolyzed at a moderate-to-slow rate at 25°C., moderately rapidly at 55°C., and dangerously rapidly when shaken with water at 80°C. or above. Tetraethylgermane does not undergo hydrolysis at 25°C.

All four ethylgermanium isocyanates are colorless liquids. There is a gradual decrease in densities from germanium tetrakisocyanate to tetraethylgermane, a similar decrease in refractive indices, and good agreement with the calculated molar refractions.

On exposure to moist air germanium tetrakisocyanate becomes yellow and the

refractive index increases. The formulas  $[\text{GeO}(\text{CN})_2]_n$  or  $\text{Ge}_2\text{O}(\text{CN})_6$  have been suggested for the resulting compound.

The isocyanates react with alcohols yielding the alkoxy compounds:



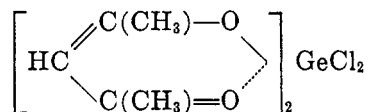
Forbes and Anderson (33) found that germanium halides and isocyanates undergo redistribution readily at elevated temperatures.

#### 5. Organic acid esters

Johnson and Nebergall (43) prepared acetoxytricyclohexylgermane (tricyclohexylgermanium acetate) by the reaction of tricyclohexylgermanol with acetic anhydride. Additional work by Anderson (4) on the reactions of ethyl-substituted germanium oxides with the appropriate aliphatic organic acid or anhydride has yielded a series of these ester-type compounds that includes triethylgermanium formate, diethylgermanium diformate, triethylgermanium acetate, diethylgermanium diacetate, and triethylgermanium *S*-triethylgermanium mercaptoacetate.

#### 6. Acetonate compounds of germanium

Germanium tetrachloride reacts energetically with acetylacetone in anhydrous solvents, evolving hydrogen chloride and forming germanium bisacetylacetone dichloride,



in quantitative yield (62, 83). The reaction with germanium tetrabromide is much slower and gives a small yield of germanium bisacetylacetone dibromide.

The bisacetylacetone compounds are sparingly soluble in organic solvents suitable for molecular weight determinations. Accordingly, the more soluble germanium bispropionylacetone dichloride was prepared and the molecular weight determined. Both boiling-point and melting-point determinations indicated the monomeric structure, and this structure was assumed for all three diketonic derivatives.

Germanium tetrachloride and copper acetylacetone interact in cold chloroform to form a greenish white intermediate additive product, while germanium tetrabromide yielded a purple-black product under the same conditions. These colored compounds are unstable in organic solvents and decompose, yielding colorless germanium trisacetylacetone cuprobromide and germanium trisacetylacetone dicuprobromide.

## VI. TABLES OF GERMANES AND THEIR ORGANO DERIVATIVES

TABLE I

*The germanes and the alkyl- and aryl-substituted germanes*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
GeH <sub>4</sub> .....	-165	-90	(18, 19, 26, 29, 37, 46, 60, 64, 67, 69, 76, 96)
Ge <sub>2</sub> H <sub>6</sub> <sup>(a)</sup> .....	-109	29/760 mm.	(19, 26, 27, 69)
Ge <sub>3</sub> H <sub>8</sub> <sup>(b)</sup> .....	-105.6	110.5/760 mm.	(19)
GeH.....			(25, 34, 46)
GeH <sub>2</sub> .....			(34, 93)
(GeH <sub>2</sub> ) <sub>2</sub> .....			(69, 73, 74, 75)
CH <sub>3</sub> GeH <sub>3</sub> .....			(34, 93)
(C <sub>2</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>11</sub> )GeH <sub>2</sub> .....		20/10 mm.	(34)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> GeH.....		124.4/751 mm.	(34, 48, 93)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>11</sub> )GeH.....		20/2 mm.	(34)
C <sub>6</sub> H <sub>7</sub> GeH <sub>3</sub> .....			(93)
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> GeH.....	24-25		(43)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeH(α).....	47		(41, 49, 51)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeH(β).....	27		(41, 49, 51)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeH <sub>2</sub> .....			(36, 40, 49)
RGeH <sub>3</sub> .....			(93)
(CH <sub>3</sub> ) <sub>4</sub> Ge <sup>(c)</sup> .....	-88	43.4/760 mm. 0/139.3 mm.	(21, 24, 71)
(CH <sub>3</sub> ) <sub>2</sub> GeC <sub>6</sub> H <sub>5</sub> .....		182-183	(11)
CH <sub>3</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	70.5-71.0		(52)
CH <sub>3</sub> Ge(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> .....			(42)
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Ge <sup>(d)(e)</sup> .....	-90	162.5/760 mm.	(20, 48, 90, 99)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>5</sub> .....		116-117/13 mm.	(11)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> .....		125-126/12 mm.	(11)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Ge[1,1-cyclo(CH <sub>2</sub> ) <sub>6</sub> ].....		52/13 mm.	(79)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> .....		316/760 mm.	(30)
C <sub>2</sub> H <sub>5</sub> Ge( <i>sec</i> -C <sub>3</sub> H <sub>7</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> .....		175-190 (?)	(78)
C <sub>2</sub> H <sub>5</sub> Ge( <i>sec</i> -C <sub>3</sub> H <sub>7</sub> )(C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>5</sub> - <i>p</i> ) <sub>2</sub> .....			(78)
C <sub>2</sub> H <sub>5</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	78-78.5 75-76		(20, 52, 66)
C <sub>2</sub> H <sub>5</sub> Ge(C <sub>6</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> ) <sub>2</sub> .....	55		(78)
C <sub>2</sub> H <sub>5</sub> Ge(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	56-57		(12)
C <sub>2</sub> H <sub>5</sub> Ge(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> .....			(42)
C <sub>2</sub> H <sub>5</sub> Ge(C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>5</sub> - <i>p</i> ) <sub>3</sub> .....	154-156		(78)
(C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>4</sub> ) <sub>4</sub> Ge.....	57		(16)
( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> Ge <sup>(f)(g)</sup> .....	-73	225/746 mm.	(90)
( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	86-86.5		(53)
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> Ge.....		178-180/733 mm.	(66)
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Ge(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> .....			(42)
( <i>i</i> -C <sub>6</sub> H <sub>11</sub> ) <sub>4</sub> Ge <sup>(h)(i)</sup> .....		163-164/10 mm.	(90)
( <i>n</i> -C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	42-43		(53)
( <i>n</i> -C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> Ge(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> .....			(42)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>4</sub> Ge.....	110		(66, 85)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	107-108		
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Ge(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> .....	82.5-83.5		(53)
			(42)

TABLE 1—Concluded

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Ge.....	230-231 235.7		(49, 63, 78, 90, 95)
C <sub>6</sub> H <sub>5</sub> Ge(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> .....			(43)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>m</i> .....	136.5-138.5		(85, 86)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> .....	123-124		(66, 85)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> .....	140-141		(66)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> .....	158-159		(66)
C <sub>6</sub> H <sub>5</sub> Ge(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> ) <sub>3</sub> .....	191		(78)
( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>4</sub> Ge.....	175-176		(85, 86)
( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>4</sub> Ge.....	146 150.1		(85, 86)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>4</sub> Ge.....	224, 227		(12, 78, 86, 90)
( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> .....	98.5-100.5		(85)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>o</i> .....	164-166		(85)
( <i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>4</sub> Ge.....	270-272		(78)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeGe(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> .....		265/758 mm.	(48)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeGe(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	89.5-90.5		(47, 53)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>3</sub> GeGe(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	183-184		(12)
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> GeGe(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> .....			(42)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeGe(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	336-337 340		(12, 40, 41, 49, 52, 63)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>2</sub> ·3C <sub>6</sub> H <sub>6</sub> .....	340		(49, 52, 63)
(HSO <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ) <sub>4</sub> Ge.....			(66)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeGe(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> ) <sub>3</sub> .....	345		(12)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeGe(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	247-248		(44, 45)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Ge] <sub>4</sub> .....	294-295		(35, 45)
(R <sub>2</sub> Ge) <sub>4</sub> .....			(34)
(C <sub>4</sub> H <sub>9</sub> N) <sub>4</sub> Ge.....	202		(79)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeCH <sub>2</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	132-133		(52, 87)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge(CH <sub>2</sub> ) <sub>3</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	133		(52)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge(CH <sub>2</sub> ) <sub>5</sub> Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> .....	133		(52)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Ge] <sub>6</sub> .....			(78, 80)
(C <sub>4</sub> H <sub>9</sub> O) <sub>4</sub> Ge.....	99-100	163/1 mm.	(59)

(a)  $d = 1.98$  ( $-109^{\circ}\text{C}.$ ).(b)  $d = 2.20$  ( $105.6^{\circ}\text{C}.$ ).(c)  $d = 1.006$  ( $0^{\circ}\text{C}.$ ).(d)  $d = 0.9911$  ( $24.5^{\circ}\text{C}.$ ).(e)  $n_D^{17.5^{\circ}} = 1.443$ .(f)  $d = 0.9539$  ( $20^{\circ}\text{C}.$ ).(g)  $n_D^{17.5^{\circ}} = 1.451$ .(h)  $d = 0.9147$  ( $20^{\circ}\text{C}.$ ).(i)  $n_D^{17.5^{\circ}} = 1.457$ .

TABLE 2

*The halogen-substituted germanes*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
H <sub>3</sub> GeCl <sup>(a)</sup> .....	-52	28	(22)
H <sub>3</sub> GeBr <sup>(b)</sup> .....	-32	52	(22)
H <sub>3</sub> GeI.....			(22)
H <sub>2</sub> GeCl <sub>2</sub> <sup>(c)</sup> .....	-68	69.5	(22)
H <sub>2</sub> GeBr <sub>2</sub> <sup>(d)</sup> .....	-15	89	(22)



TABLE 2—Continued

COMPOUND	MELTING POINT °C.	BOILING POINT °C.	REFERENCES
H <sub>2</sub> GeI <sub>2</sub> .....			(22)
HGeCl <sub>3</sub> .....		75.2/759 mm.	(13, 14, 23, 91, 97, 98, 99)
HGeBr <sub>3</sub> .....	-24	0/1.9 mm.	(14, 97)
(CH <sub>3</sub> ) <sub>3</sub> GeCl.....		115	(70)
(CH <sub>3</sub> ) <sub>3</sub> GeBr <sup>(a)</sup> ( <sup>b</sup> ).....	-25	113.7/760 mm.	(24, 70)
(CH <sub>3</sub> ) <sub>2</sub> GeCl <sub>2</sub> <sup>(a)</sup> ( <sup>b</sup> ).....	-22	124	(70, 71)
(CH <sub>3</sub> ) <sub>2</sub> GeBr <sub>2</sub> .....			(70)
CH <sub>3</sub> GeCl <sub>3</sub> <sup>(1)</sup> .....		111	(56, 70)
CH <sub>3</sub> GeBr <sub>3</sub> .....			(70)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeF.....		149.0/751 mm.	(48)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeCl.....		175.9/760 mm.	(48, 70)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeBr.....	-33	190.9/760 mm.	(48)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeI.....		212.3/760 mm.	(48)
(C <sub>2</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> GeBr.....			(78)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> GeCl <sub>2</sub> .....	37-39	175/758 mm.	(39, 70, 72)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> GeBr <sub>2</sub> .....		202/760 mm.	(30, 95)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> GeI <sub>2</sub> .....	-(1-2)	252/759 mm.	(39)
C <sub>2</sub> H <sub>5</sub> GeF <sub>3</sub> .....	-(15.5-16.5)	112/750 mm.	(31)
C <sub>2</sub> H <sub>5</sub> GeCl <sub>3</sub> .....		144/762 mm.	(31, 70, 72, 92)
		60/18 mm.	
C <sub>2</sub> H <sub>5</sub> GeBr <sub>3</sub> .....		200/763 mm.	(31)
C <sub>2</sub> H <sub>5</sub> GeI <sub>3</sub> .....	-(1.5-2.5)	281/755 mm.	(31)
(C <sub>2</sub> H <sub>5</sub> )( <i>sec</i> -C <sub>3</sub> H <sub>7</sub> )(C <sub>6</sub> H <sub>5</sub> )GeBr.....		130-135/13 mm.	(78)
(C <sub>2</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> )( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )GeBr.....			(78)
( <i>sec</i> -C <sub>3</sub> H <sub>7</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeBr.....		215-250/13 mm.	(78)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>3</sub> GeF.....	96		(12)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>3</sub> GeCl.....	154		(12)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>3</sub> GeBr.....	145, 146.5- 146.7		(12, 85)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>3</sub> GeI.....	141		(12)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> )GeCl <sub>3</sub> .....			(66)
(CH <sub>2</sub> ) <sub>3</sub> GeCl <sub>2</sub> .....		55-60/12 mm.	(79)
CH <sub>2</sub> (GeCl <sub>3</sub> ) <sub>2</sub> .....			(92)
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> GeF.....	92		(9)
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> GeCl.....	102		(9)
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> GeBr.....	110		(9, 42)
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> GeI.....	99-100		(9)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeF.....	76.6		(49)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeCl.....	116, 117-118		(54, 66)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeBr.....	138.5, 136.6-138.1		(49, 63, 66, 85, 86)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeI.....	157		(49, 78)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeF <sub>2</sub> .....		100/0.007 mm.	(44)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeCl <sub>2</sub> .....	9		(44, 45)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeBr <sub>2</sub> .....		120/0.007 mm.	(36, 40, 44, 45, 63, 78, 95)

TABLE 2—Concluded

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeI <sub>2</sub> .....	70-71		(36, 40)
C <sub>6</sub> H <sub>5</sub> GeCl <sub>3</sub> .....		105-106/12 mm. 115/19 mm.	(10, 66, 78, 80, 92)
C <sub>6</sub> H <sub>5</sub> GeBr <sub>3</sub> .....		120-122/13 mm.	(10, 44, 63, 78)
C <sub>6</sub> H <sub>5</sub> GeI <sub>3</sub> .....	55-56		(11)
C <sub>6</sub> H <sub>5</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> GeBr.....	119		(78)
( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeCl.....		216-222/1 mm.	(86)
( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeCl.....	79	221-224/2 mm.	(86)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeCl.....	121		(85)
( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> GeBr.....		205-210/1 mm.	(85, 86)
( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> GeBr.....	78-78.9	222-223/1 mm.	(85, 86)
( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> GeBr <sub>2</sub> .....		189-190/4 mm.	(85)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> GeBr.....	128	229-234/1 mm.	(78, 86)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> GeBr <sub>2</sub> .....		230-233/13 mm.	(78)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )GeCl <sub>3</sub> .....		115-116/12 mm.	(11)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )GeBr <sub>3</sub> .....		155-156/13 mm.	(11)
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )GeI <sub>3</sub> .....	72		(11)
( <i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> GeBr.....	242		(78)
C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub> GeCl <sub>3</sub> .....			(66)
[(CH <sub>3</sub> ) <sub>3</sub> CS] <sub>3</sub> GeCl.....			(6)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeBrGeBr(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> .....	165		(78)

(a) *d* (liquid) = 1.75 (−52°C.).<sup>(1)</sup> *n*<sub>D</sub><sup>18°</sup> = 1.4705.(b) *d* (liquid) = 2.34 (29.5°C.).<sup>(s)</sup> *d* = 1.492 (20°C.), 1.488 (26°C.).(c) *d* (liquid) = 1.90 (−68°C.).<sup>(b)</sup> *n*<sub>D</sub><sup>29°</sup> = 1.4552.(d) *d* (liquid) = 2.80 (0°C.).<sup>(1)</sup> *d* = 1.73 (24.5°C.).(e) *d*<sub>4</sub><sup>18°</sup> = 1.544.

TABLE 3

## Thio germanium compounds and substituted germanium sulfides

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
(CH <sub>3</sub> ) <sub>2</sub> GeS.....	55.5	302	(72)
[(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>2</sub> S.....		148/12 mm.	(16)
[(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>3</sub> Ge] <sub>2</sub> S.....	124		(16)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>2</sub> S.....	138		(16)
[(CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> Ge] <sub>2</sub> S.....	156		(16)
[(C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> Ge] <sub>2</sub> S.....	238		(16)
[(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> Ge] <sub>2</sub> S <sub>2</sub> .....	87		(16)
Ge(SCH <sub>3</sub> ) <sub>4</sub> <sup>(a)</sup> .....	−3	139/4 mm.	(5, 7)
Ge(SC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> <sup>(b)</sup> .....		165/5 mm.	(5, 7)
Ge( <i>n</i> -SC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> <sup>(c)</sup> .....		191/4 mm.	(5)
Ge( <i>i</i> -SC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> <sup>(d)</sup> .....	15	163/4 mm.	(5, 7)
Ge( <i>n</i> -SC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> <sup>(e)</sup> .....		223/4 mm.	(5, 7, 93)
Ge( <i>i</i> -SC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> <sup>(f)</sup> .....		200/5 mm.	(5, 7)
Ge( <i>sec</i> -SC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> <sup>(g)</sup> .....		200/5 mm.	(5, 7)
Ge( <i>tert</i> -SC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> .....	172-173	Sublimes at 170/4 mm.	(5, 7)
Ge( <i>n</i> -SC <sub>5</sub> H <sub>11</sub> ) <sub>4</sub> <sup>(h)</sup> .....		240/3 mm.	(7)
Ge(SC <sub>6</sub> H <sub>11</sub> ) <sub>4</sub> .....	88		(7)

TABLE 3—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
Ge(SC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> .....	104		(5, 7, 79)
Ge(SC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> ) <sub>4</sub> .....	110-111		(5, 7)
Ge( <i>p</i> -SC <sub>6</sub> H <sub>4</sub> - <i>tert</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> .....	155		(7)
Ge(SC <sub>6</sub> H <sub>4</sub> Br- <i>p</i> ) <sub>4</sub> .....	196		(5)
Ge[S(CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub> ] <sub>4</sub> .....	50		(7)
(C <sub>4</sub> H <sub>9</sub> S) <sub>4</sub> Ge.....	149		(55)
[(SCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O] <sub>2</sub> Ge.....	159		(5)
(a) $d_4^{25^\circ} = 1.4364$ ; $n_D^{25^\circ} = 1.6379$ .		(e) $d_4^{25^\circ} = 1.1072$ ; $n_D^{25^\circ} = 1.5439$ .	
(b) $d_4^{25^\circ} = 1.2574$ ; $n_D^{25^\circ} = 1.5886$ .		(f) $d_4^{25^\circ} = 1.0984$ ; $n_D^{25^\circ} = 1.5381$ .	
(c) $d_4^{25^\circ} = 1.1662$ ; $n_D^{25^\circ} = 1.5612$ .		(g) $d_4^{25^\circ} = 1.1119$ ; $n_D^{25^\circ} = 1.5497$ .	
(d) $d_4^{25^\circ} = 1.1478$ ; $n_D^{25^\circ} = 1.5535$ .		(h) $n_D^{25^\circ} = 1.5336$ .	

TABLE 4  
*The germanols*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
(CH <sub>3</sub> ) <sub>2</sub> GeOH.....			(24)
(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> GeOH.....	176-177		(9, 43)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> OLi.....			(48)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeOH.....	132.2		(49, 63)
( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )GeOH.....		212-214/1 mm.	(86)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeONa.....			(49, 63)
(CH <sub>3</sub> ) <sub>2</sub> Ge(OH) <sub>2</sub> .....			(71)
[HOGe(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> OGe(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> O.....	149		(63)
CH <sub>3</sub> Ge(OH) <sub>3</sub> .....			(56)
C <sub>2</sub> H <sub>5</sub> Ge(OH) <sub>3</sub> .....			(31)

TABLE 5  
*The substituted germanium oxides*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
[(CH <sub>3</sub> ) <sub>2</sub> Ge] <sub>2</sub> O.....			(24)
[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ge] <sub>2</sub> O.....		253.9/760 mm.	(1, 2, 48)
[(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> Ge] <sub>2</sub> O.....	135		(12)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Ge] <sub>2</sub> O.....	184		(43, 49, 54, 63)
[( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Ge] <sub>2</sub> O.....	125		(86)
[( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Ge] <sub>2</sub> O.....	147-148		(86)
[(CH <sub>3</sub> ) <sub>2</sub> GeO] <sub>4</sub> .....	133.4	211	(71)
[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> GeO] <sub>2</sub> .....	175		(2, 30)
[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> GeO] <sub>3</sub> .....	18		(2, 30, 95)
[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> GeO] <sub>4</sub> .....	27.1	291/762 mm. 129/3 mm.	(2)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeO] <sub>4</sub> .....	218		(44, 63)

TABLE 6  
Germanoic acids, anhydrides, and thio acids

COMPOUNDS	REFERENCES	COMPOUNDS	REFERENCES
HGeOOH	(92)	[3-NO <sub>2</sub> -4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>3</sub> GeO] <sub>2</sub> O	(16)
CH <sub>3</sub> GeOOH	(92)	[p-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> GeO] <sub>2</sub> O	(9)
CH <sub>2</sub> (GeOOH) <sub>2</sub>	(92)	[p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> GeO] <sub>2</sub> O	(66)
C <sub>2</sub> H <sub>5</sub> GeOOH	(30, 92)	[p-HOOC <sub>2</sub> H <sub>4</sub> GeO] <sub>2</sub> O	(16)
(C <sub>2</sub> H <sub>5</sub> GeO) <sub>2</sub> O	(31)	H <sub>2</sub> [Ge(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]	(8, 92)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> GeO) <sub>2</sub> O	(66)	(C <sub>6</sub> H <sub>5</sub> GeS) <sub>2</sub> S	(9, 66)
C <sub>6</sub> H <sub>5</sub> GeOOH	(63, 66)	(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> GeS) <sub>2</sub> S	(9, 66)
(C <sub>6</sub> H <sub>5</sub> GeO) <sub>2</sub> O	(9, 63, 66)	(α-C <sub>10</sub> H <sub>7</sub> GeS) <sub>2</sub> S	(9)
(α-C <sub>10</sub> H <sub>7</sub> GeO) <sub>2</sub> O	(9)	[p-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> GeS] <sub>2</sub> S	(9)
[p-CH <sub>3</sub> NHC <sub>6</sub> H <sub>4</sub> GeO] <sub>2</sub> O	(9)	[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> GeS] <sub>2</sub> S	(66)
[p-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> GeO] <sub>2</sub> O	(9, 16, 66)		

TABLE 7  
Miscellaneous germanium compounds

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
Ge(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>		185-187/760 mm.	(57, 84, 90)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2-3</sub> Ge(OR) <sub>2</sub>			(1)
Ge(OC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>		210-220/0.1 mm.	(79)
H <sub>3</sub> GeNH <sub>2</sub>			(93)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeNH <sub>2</sub>			(45, 52, 54, 87)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeNK			(54)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> GeNH		ca. 100/0.01 mm.	(30)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeNH			(44)
[(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>2</sub> NH		ca. 100/0.1 mm.	(48)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>2</sub> NH			(54)
C <sub>2</sub> H <sub>5</sub> GeN	163-164		(31)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>2</sub> N			(49, 54)
Ge(NC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>			(94)
Ge[N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>			(94)
Ge(NC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>			(94)
Ge(NHC <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>			(94)
Ge(NC <sub>6</sub> H <sub>10</sub> ) <sub>4</sub>			(94)
H <sub>3</sub> GeNa			(34, 46, 93)
H <sub>3</sub> GeK			(93)
CH <sub>3</sub> GeH <sub>2</sub> Na			(34)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeLi			(48)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeK			(48)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeLi			(51)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeNa			(44, 45, 49)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeNa <sub>2</sub>			(45, 49)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> SiLi			(61)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeNa·3NH <sub>3</sub>			(49)
$\begin{array}{c} \text{O} \\    \\ (\text{C}_2\text{H}_5)_3\text{GeOCH} \end{array}$		186/760 mm.	(4)
$\begin{array}{c} \text{O} \\    \\ (\text{C}_2\text{H}_5)_2\text{Ge}(\text{OCH})_2 \end{array}$		210/760 mm.	(4)

TABLE 7—Concluded

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeOCOCH <sub>3</sub> .....		190/760 mm.	(4)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ge(OCOCH <sub>3</sub> ) <sub>2</sub> .....		217/760 mm.	(4)
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> GeOCOCH <sub>3</sub> .....	82		(43)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> GeOCOCH <sub>2</sub> Ge(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> .....		326/760 mm.	(4)
GeCl <sub>3</sub> OCN.....			(33)
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Ge(NCO) <sup>(a)</sup> .....	-26.4	200.4	(1)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ge(NCO) <sub>2</sub> <sup>(b)</sup> .....	-32	226.0	(1)
C <sub>2</sub> H <sub>5</sub> Ge(NCO) <sub>3</sub> <sup>(c)</sup> .....	-31	225.4	(1)
Ge(NCO) <sub>4</sub> <sup>(d)</sup> .....	-8	204.0	(32, 58)
[GeO(NCO <sub>2</sub> ) <sub>n</sub> .....			(1)
Ge <sub>2</sub> O(NCO) <sub>6</sub> .....			(1)
(SO <sub>3</sub> HC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ) <sub>4</sub> Ge.....			(66)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> B.....			(87)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeSi(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> .....			(51)
α-[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> SiH.....	188		(61)
β-[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> SiH.....	170		(61)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> SiC <sub>2</sub> H <sub>5</sub> .....	283 (decomposes)		(61)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> SiCl.....	230		(61)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> SiBr.....	241		(61)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>3</sub> SiOH.....	197		(61)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeSn(CH <sub>3</sub> ) <sub>3</sub> .....	88		(49)
[(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>2</sub> SO <sub>4</sub> .....	-4	165/3 mm.	(2)
[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Ge(SO <sub>4</sub> )] <sub>2</sub> .....	116		(2)
[CH(CCH <sub>3</sub> O) <sub>2</sub> ] <sub>2</sub> GeCl <sub>2</sub> .....	240		(62)
[CH(CCH <sub>3</sub> O) <sub>2</sub> ] <sub>2</sub> GeBr <sub>2</sub> .....	226		(62)
[CH(CC <sub>2</sub> H <sub>5</sub> O)(CCH <sub>3</sub> O)] <sub>2</sub> GeCl <sub>2</sub> .....	128		(62)
[CH(CCH <sub>3</sub> O) <sub>2</sub> ] <sub>3</sub> GeCuCl <sub>2</sub> .....	147		(62)
[CH(CCH <sub>3</sub> O) <sub>2</sub> ] <sub>3</sub> GeCuBr <sub>2</sub> .....	165		(62)
[CH(CCH <sub>3</sub> O) <sub>2</sub> ] <sub>3</sub> GeCuBr <sub>3</sub> .....	139		(62)
[CH(CCH <sub>3</sub> O) <sub>2</sub> ] <sub>3</sub> GeCu <sub>2</sub> Br <sub>3</sub> .....	195		(62)

(a)  $d_{4}^{20^{\circ}} = 1.1514$ ;  $n_{D}^{20^{\circ}} = 1.4519$ .(c)  $d_{4}^{20^{\circ}} = 1.5344$ ;  $n_{D}^{20^{\circ}} = 1.4739$ .(b)  $d_{4}^{20^{\circ}} = 1.330$ ;  $n_{D}^{20^{\circ}} = 1.4619$ .(d)  $d_{4}^{20^{\circ}} = 1.7714$ ;  $n_{D}^{20^{\circ}} = 1.4824$ .

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