Chemical and spectroscopic studies on organogermanes

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CHEMICAL AND SPECTROSCOPIC STUDIES ON ORGANOGERMANES

by

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A Thesis submitted for the Degree of Doctor
of Philosophy in the University of Durham

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I am indebted to the Science Research Council for a maintenance grant, and to all those members of the Chemistry Department, University of Durham, who so readily gave advice and assistance.

NOTE

The work described in this thesis was carried out in the University of Durham between September 1965 and June 1968. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

PUBLICATIONS

The work described in this Thesis has been the subject of the following publications:

"Mass Spectra of Organo-germanes and -stannanes" Chem. Comm., 282, (1966). (With D.B. Chambers, F. Glockling and M. Weston).

"Alkylation of Germanium Halides by Aluminium Alkyls" J. Chem. Soc. (A), 623, (1967). (With F. Glockling).

"Electron Impact Behaviour and Bond Energies of Beryllium and Group IVb Organometallic Compounds". 3rd Internat. Symp. on Organometallic Chem., Munich, (1967). (With D.B. Chambers, F. Glockling and M. Weston).

"Mass Spectra of Organogermanes" J. Chem. Soc.(A), 717, (1968). (With F. Glockling).

A review "Mass Spectra of Organometallic Compounds" (with D.B. Chambers and F. Glockling) has been accepted for publication in Quarterly Reviews.

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Part II. Spectroscopic Studies

Summary

The first part of this thesis describes the alkylation of germanium halides by organoaluminium compounds, and comparison is made with other alkylating reagents. The second part presents the first detailed analysis of the mass spectra of a wide range of organogermanes, and shows how this technique can be used in characterising new compounds. Some aspects of infrared and proton magnetic resonance spectroscopy of organogermanium compounds are included.

Part I.Chemical Studies.

Besides giving good yields of the tetraorganogermanes, the reaction between alkylaluminium compounds and germanium tetrachloride gives by-products containing up to seven germanium atoms. With germanium di-iodide a complex mixture of compounds containing up to ten germanium atoms is obtained. These compounds are fully alkylated, having Me_3Ge end groups and the germanium skeleton is usually highly branched. In addition to these compounds, both reactions gave products resulting from growth of the alkyl group e.g. Me_3Al gave compounds such as Me_5EtGe_2 and Me_5PrGe_2. The Wurtz reaction on Me_3GeBr also gives organopolygermanes containing up to five germanium atoms and compounds with $GeCH_2Ge$ linkages.

Part II. Spectroscopic Studies

The problem of characterising low-yield products like those described above, is acute. Infrared spectroscopy is too insensitive, and chemical methods are uncertain and destructive. A complete analysis is possible using a combination of mass spectrometry and proton magnetic resonance spectroscopy.

Before using mass spectrometry for characterising new compounds, it was necessary to establish the modes of fragmentation of typical known organogermanes. Examination of a wide range of compounds showed that almost all gave low abundance (odd-electron) molecular ions, which lost an odd-electron (radical) fragment giving abundant even-electron ions with three co-ordinate germanium. Subsequent fragmentation by elimination of stable molecules preserved the even-electron character of the ions. Hydrocarbon ions and ions resulting from C-C bond rupture were of low abundance. Alkyl compounds (except methyl) favour alkene elimination reactions, and aryl compounds, elimination of aromatic hydrocarbons or acetylene. Methylpolygermanes lose a methyl radical from the molecular ion, and then eliminate Me_2Ge fragments until Me_3Ge^+ is reached. Other alkylpolygermanes eliminate alkenes without rupture of the Ge-Ge bonds. Aryldigermanes break the Ge-Ge bond in the molecular ion itself. Having established the basic fragmentation modes it has proved possible to distinguish between such isomers as

Me_7EtGe_3 and $Me_5Ge_2CH_2GeMe_3$ or $Me_8Et_2Ge_4$ and Me_9PrGe_4.

At 220 Mc., the p.m.r. spectra of methylpolygermanes show considerable differences in chemical shift between Me_3Ge, Me_2Ge and MeGe units, and this distinguishes isomers such as $(Me_3Ge)_4Ge$ and $(Me_3Ge)_2Ge(Me)Ge_2Me_5$. The spectra of e.g. $EtMe_7Ge_3$ and $Me_5Ge_2CH_2GeMe_3$ are also distinctly different.

PART I. CHEMICAL STUDIES

Part I. Chemical Studies

1. Introduction: Formation and Properties of Germanium-Germanium Bonds.

Catenation is the basis of life, so it is natural that chemists should find it a peculiarly fascinating aspect of their subject. Interest has hitherto been concentrated on carbon, the basic element of life, but the question of why carbon should be unique is intriguing, and an obvious attack on the problem is to consider catenation in related elements. Preliminary enquiries have shown that true catenation, the formation of bonds between atoms of the same element, is a limited phenomenon and perhaps the most promising elements are the remaining main Group IV elements, silicon, germanium, tin and lead. Recent research has shown that lead is unlikely to form long chains of lead atoms, and so attention is more narrowly focused on the three remaining elements.

In the early part of this century, Stock turned his attention to the preparation of the silicon analogues of the alkanes, the silanes.[1] Unlike alkanes, silanes are very reactive. They inflame in air and are rapidly hydrolysed by aqueous base. They are strong reducing agents and are not very stable thermally, the ease of thermal decomposition increasing with the number of Si-Si bonds. Replacement of the hydrogen atoms by organic groups considerably reduces the reactivity, and enhances the thermal stability. The germanes are less readily attacked by air than the silanes, and are much more stable to hydrolysis. Once again, the organic derivatives show increased stability, and decreased reactivity. No catenated stannanes except Sn_2H_6[2] have been prepared, but the organic derivatives have been extensively studied. Because of the commercial applications of organo-silicon and tin compounds, they have been more widely studied than their germanium analogues which to date have found no wide-spread application. The theoretical importance of germanium has, however, been sufficient to compensate for this disadvantage and research in the field is expanding apace. If it should prove, as what evidence there is suggests, that germanium surpasses silicon and tin as a catenating element, then its theoretical interest will be increased considerably.

Historically, information on catenated compounds of germanium, has been obtained either as a result of studying by-products from the preparation of mono-germanes or from attempts to prepare organic derivatives of divalent germanium. In considering the methods of formation of Ge-Ge bonds therefore, their genesis as by-products will first be examined, and then the more recent methods which have been devised specifically for the preparation of di- and poly-germanium compounds. Preparations of the germanes themselves are discussed only briefly since these are not in general relevant to the experimental investigations described in this thesis.

1:1 Side-reactions in the Preparation of Tetraorganogermanes.

1:1:1 Grignard Reactions

Most of the reagents used in the preparation of alkyl- and aryl-germanes are organometallic reagents, and of these the Grignard reagents are the most widely used. Quantitative yields of the tetraorganogermanes are never obtained, and one of the major side-reactions is that leading to di- and poly-germanes. Even in the simplest possible systems, as exemplified by the reaction between $GeBr_4$ (or $GeCl_4$) and EtMgX, it is possible to isolate some digermane, Et_6Ge_2.[3] In some cases the yield of digermane approaches that of the monogermane. Vinylmagnesium bromide and germanium tetrachloride give 25% of hexavinyldigermane, compared with 35% of tetravinylgermane.[4] The explanation given for this coupling process has since been extended to account for the formation of digermanes in many Grignard syntheses. The final step, involving the reaction of a partially substituted germane with a germyl-Grignard reagent, seems eminently reasonable:

$$R_3GeX + R_3GeMgX \longrightarrow R_3GeGeR_3 + MgX_2$$

but there are two difficulties. First of all, the intermediate germyl-Grignard reagent has eluded isolation. Since isolation of Grignard reagents is notoriously difficult, this would not be a serious objection to the theory if a convincing route to the species could be devised. The path suggested goes by a Ge^{II} intermediate:

$$GeCl_4 + CH_2{=}CHMgBr \longrightarrow GeCl_2 + (CH_2{=}CH\cdot)_2 + 2MgClBr$$

$$GeCl_2 + 2CH_2{=}CHMgBr \longrightarrow Ge(CH{=}CH_2)_2 + 2MgClBr$$

$$Ge(CH{=}CH_2)_2 + CH_2{=}CHMgBr \longrightarrow (CH_2{=}CH)_3GeMgBr$$

This type of explanation has become very popular, not only in accounting for the complexities of the Grignard reaction, but also for those of organo-lithium and other reagents. If the evolution of $(CH_2{=}CH)_2$ were demonstrated, this would significantly strengthen the argument. Otherwise, the simpler:

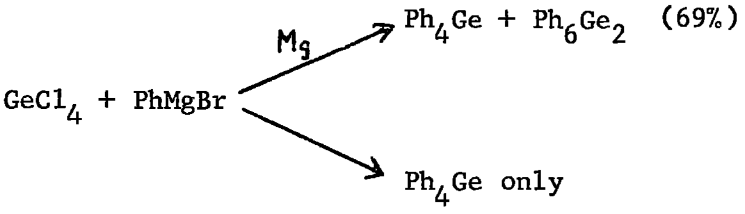
$$R_3GeX + RMgX \longrightarrow R_3GeMgX + RX$$

cannot be discounted. Again, a simple test of the proposition would be detection of the eliminant, in this case alkyl halide. Demonstration of its absence would not, however, be proof of the contrary, since the alkyl halide might be reconverted to the Grignard reagent by reaction with the free magnesium which is almost always present in these reactions.

Reductive coupling appears to be less common with silicon and tin[4] and this has been ascribed to the higher electronegativity of germanium. Thus if germanium is more like carbon than are either silicon or tin, then germyl-Grignard reagents should be more likely than silyl- and particularly stannyl-Grignard reagents.

Hexaphenyl- and hexa-p-tolyl-digermanes were also obtained as by-products from Grignard reactions.[5]

Observation of the high yield of catenated by-product from some of these preparations suggests that, by suitably adjusting conditions, they can be made to serve as a preparative method for the digermane, instead of the monogermane. This technique was recommended[6,7] for the preparation of hexaphenyldigermane. Removal of ether from the mixture immediately after addition of $GeCl_4$ dissolved in toluene produced Ph_4Ge; when the ether was left in the reaction mixture, Ph_6Ge_2 resulted. This supports the existence of an R_3GeMgX intermediate, since ether is well-known to be an essential part of Grignard reagents. A thorough study[8] of the reaction between germanium tetrachloride and phenylmagnesium bromide led to the formulation of optimum conditions for digermane formation. The apparent relationship between yield of digermane and lack of experimental care was pinned down to the presence or absence of free magnesium as the real determining factor.

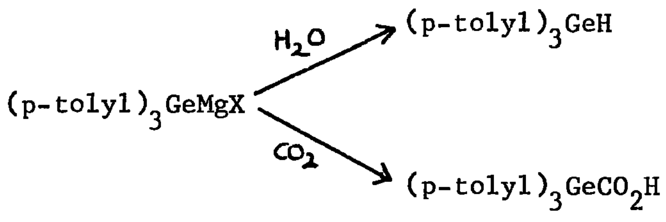


This provided yet another suggestion for the formation of the germyl-Grignard reagent:

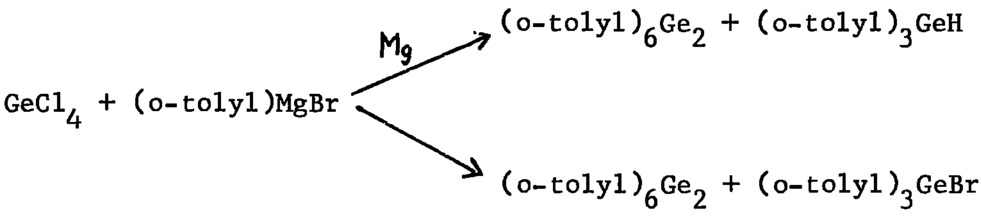
$$Ph_3GeBr + Mg \longrightarrow Ph_3GeMgBr$$

so that the Ph_3GeBr is to be regarded simply as a highly-branched alkyl halide. There was evidence that the finely divided magnesium not removed by filtration, rather than the bulk metal, was responsible for the formation of the germyl-Grignard reagent. In the total absence of magnesium, the yield of digermane was zero.

The existence of germyl-Grignard reagents has been well established in some cases. Germanium tetrachloride and tolylmagnesium halide react together in the presence of free magnesium giving germyl-Grignard reagents, as shown by hydrolysis or carbonation of the reaction mixture.



It was also shown that the o-tolyl-magnesium bromide (considered to be a sterically hindered reagent) reacted with $GeCl_4$ to form only the digermane both in the presence and the total absence of free magnesium. The reaction was, however, faster when free magnesium was present, and the hydride was formed on hydrolysis.



These observations were accounted for by assuming that two possible modes of formation of the germyl-Grignard are possible, one involving free magnesium:

$$(\text{o-tolyl})_3\text{GeBr} + \text{Mg} \xrightarrow{\text{fast}} (\text{o-tolyl})_3\text{GeMgBr}$$

and the other a halogen-Grignard exchange which is a slow, equilibrium process:

$$(\text{o-tolyl})_3\text{GeBr} + \text{o-tolylMgBr} \rightleftharpoons (\text{o-tolyl})_3\text{GeMgBr} + (\text{o-tolyl})\text{Br}$$

Some doubt has been cast[9] on this interpretation by the observation that colloidal magnesium is very difficult to remove by filtration, and it will also be apparent that the mechanism involving formation of an organic halide will account for all the reported facts, if its further reaction with free magnesium, when present, is assumed to drive the equilibrium to the right.

Cyclohexylmagnesium bromide and germanium tetrachloride can also be regarded as a sterically-hindered system and the yield of $(\text{cyclohexyl})_3\text{GeH}$ increases with the molar ratio of the Grignard reagent. The hydride is not present before hydrolysis.[10]

All the mechanisms proposed for digermane formation have the final stage in common:

$$R_3\text{GeX} + R_3\text{GeMgX} \longrightarrow R_6\text{Ge}_2 + \text{MgX}_2$$

The extent to which this reaction occurs must depend on, among other things, the rate of substitution of the final halogen atom in $R_3\text{GeX}$ i.e. the rate of the competing reaction:

$$R_3\text{GeX} + R\text{MgX} \longrightarrow R_4\text{Ge} + \text{MgX}_2$$

This reaction will be slow if either the R group is large, or X is large. Work already cited has shown that increase in the "bulk" of the R group increases the formation of digermane. The influence of the size of X is, perhaps, indicated by comparison of the reactions of benzylmagnesium chloride with germanium tetrachloride and tetraiodide respectively. With the chloride the yield of $(PhCH_2)_4Ge$ is almost quantitative, whereas with the iodide formation of hexabenzyldigermane decreases the yield of the monogermane.[11] With methyltri-iodogermane, benzylmagnesium bromide gives essentially equal amounts of $(PhCH_2)_3GeMe$ and $(PhCH_2)_4Ge_2Me_2$, and in the same quantities whether magnesium is present or not.[12]

The triorganogermylmagnesium halide is not the only intermediate of this type whose existence has been postulated. The reaction between isopropylmagnesium chloride and $GeCl_4$[9,13] gives a variety of products testifying to the presence of intermediates other than $Pr^i{}_3GeX$. In the context of this discussion the most relevant appears in the following sequence of reactions:

$$Pr^i{}_2GeCl_2 \xrightarrow[\text{or Mg}]{Pr^iMgCl} Pr^i{}_2Ge(Cl)MgCl$$

$$\xrightarrow{Pr^i{}_2GeCl_2} (Pr^i{}_2GeCl)_2$$

$$\xrightarrow{LiAlH_4} (Pr^i{}_2GeH)_2$$

Only about 1% of $Pr^i_6Ge_2$ was obtained from these $Pr^iMgX-GeX_4$ systems, but the system X=Cl also gave rise to $Pr^i_8Ge_4$. Some higher polymeric material was obtained, the proportion being higher for the iodide reaction, in accord with the benzylmagnesium bromide reactions already quoted. This polymeric material did, however, contain oxygen, and there was no evidence that Ge-Ge bonds were present. Earlier experiments[14] showed that the system $Pr^iMgBr-GeBr_4$ gave no $Pr^i_6Ge_2$, but some polymer was obtained which is probably analogous to that obtained in the other isopropyl systems, although it was assigned the composition $(Pr^iGe)_n$.

The formation of digermanes in reactions between $GeCl_4$ and mixed Grignard reagents has been studied[15] by adding a mixture of two alkyl halides and $GeCl_4$ to Mg in diethylether. It is interesting to note that reactions generally similar to those already discussed do take place, even though the Grignard reagent is not pre-formed. This means that if alkyl halides are eliminated in the formation of a germyl-Grignard reagent, as previously suggested, they may be removed by formation of further Grignard reagent. It is also worth noting that some trigermane was detected. Two possible routes to this are readily apparent:

$$R_2GeX_2 + R_3GeMgX \longrightarrow R_3GeGeR_2X + MgX_2$$

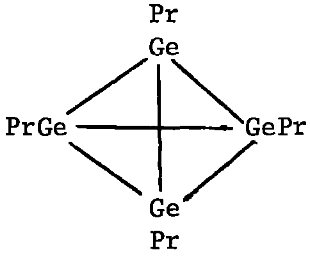
$$R_5Ge_2X + R_3GeMgX \longrightarrow R_8Ge_3 + MgX_2$$

or $$R_3GeMgX + R_2Ge(X)MgX \longrightarrow R_3GeGeR_2MgX + MgX_2$$

$$R_5Ge_2MgX + R_3GeX \longrightarrow R_8Ge_3 + MgX_2$$

1:1:2 Organolithium Syntheses

These give lower yields[16] of the symmetrical tetra-organogermanes than do the corresponding Grignard syntheses. From the $GeBr_4$/EtLi reaction, low yields of Et_4Ge (12%) and Et_6Ge_2 (9%) were obtained, together with much unidentified polymeric material, while n-propyllithium and germanium tetrachloride gave the three chloropropylgermanes, but at higher temperature only a propyl-germanium polymer, PrGe. This was distillable indicating a low molecular weight.[17] It is difficult to formulate a low molecular weight compound with this empirical formula, but a possibility is:



With some earlier work, however, characterisation was inadequate particularly before the spread of modern physical tools, such as infrared spectroscopy. Of course, with such reactive reagents as the organometallic compounds used in these syntheses generally are, the possibility of aerial oxidation and hydrolysis must always be recognised, and when ethereal solvents in particular are used, solvent-cleavage is also a danger. Putting these problems aside, there still remain a number of side-reactions which can occur. These in general can be classified as "halogen-metal exchange" (a term widely used, for a process whose mechanism is rarely explained in detail), and "reduction". Halogen-metal exchange could perhaps occur at any stage in the alkylation of the germanium halide, but the simple inductive effect suggests it to be most likely at the R_3GeCl stage:

$$GeCl_4 + 3RLi \longrightarrow R_3GeCl + 3LiCl$$

$$R_3GeCl + RLi \longrightarrow R_3GeLi + RX$$

The trialkylgermyl lithium reagent thus formed (c.f. the germyl-Grignard intermediate discussed in the preceding section) can then react with more R_3GeCl:

$$R_3GeLi + R_3GeCl \longrightarrow R_6Ge_2 + LiCl$$

or with less fully alkylated germanes:

$$R_3GeLi + R_2GeCl_2 \longrightarrow R_3GeGeR_2Cl + LiCl$$

with the possibility of forming long chains of germanium atoms.

Polymeric germanes might also result from preliminary reduction:

$$GeCl_4 \xrightarrow{RLi} GeCl_2 \xrightarrow{RLi} \text{polymer}$$

Unlike the alkyl-lithium reagents, phenyl-lithium and $GeCl_4$ can give as much as 90% Ph_4Ge,[18] but a similar system, sodium and p-BrC_6H_4Me with $GeCl_4$, produces a reasonable yield of hexa-p-tolyldigermane, along with some $(p\text{-tolyl})_4Ge$ and hexabenzyldigermane has also been prepared from tribenzylgermanium bromide in this way.[5] With β-bromostyrene however, only 0·5% of $(\beta\text{-styryl})_6Ge_2$ was obtained,[19]

$$GeCl_4 + PhCH{=}CHBr + Na \longrightarrow \underset{18\%}{(PhCH{=}CH)_4Ge} + \underset{0{\cdot}5\%}{(PhCH{=}CH)_6Ge_2}$$

whereas the reaction between Ph_3GeBr and $(NaC_5H_4)_2Fe$ gives 53-77% Ph_6Ge_2.[20] Hexabenzyldigermane has also been made from butyl-lithium[11] and tribenzylgermane. Two other interesting reactions are:

$$Me_3GeCl + Me_3GeCH{:}CHCl \xrightarrow{Na} (Me_3GeCH{:})_2 + Me_6Ge_2 \qquad 21$$

$$Me_3GeCl + Me_3GeC(Cl){:}CH_2 \xrightarrow{Na} \underset{68\%}{(Me_3Ge)_2C{=}CH_2} + Me_6Ge_2 \qquad 22$$

There do not seem to be any obvious trends here.

Instead of the germanium halides, germanium hydrides can be used with organolithium reagents for the preparation of tetra-organogermanes. Reactions of the type

$$Ph_3MH + RLi \longrightarrow Ph_3MR + LiH$$

where M = Si and R = Me, Bu^n, Ph give Ph_3SiR in high yield,[23] but when

M = Ge, complications occur due to competition between the two possible reactions:

$$\begin{tikzcd} & Ph_3GeR + LiH \\ Ph_3GeH + RLi \arrow[ur] \arrow[dr] & \\ & Ph_3GeLi + RH \end{tikzcd}$$

Which of these two competing processes is of most importance depends very much on the nature of R and the conditions of the reaction. When Ph_3GeH is added to an 8-fold excess of ethereal PhLi at reflux temperature, Ph_4Ge is obtained in 70% yield.[24] When the phenyl-lithium is added to Ph_3GeH instead, the main product is Ph_6Ge_2 (54-60%)[24,25]

$$Ph_3GeLi + Ph_3GeH \longrightarrow Ph_6Ge_2 + LiH$$

Reaction of MeLi with Ph_3GeH gives 10% Ph_6Ge_2.[25]

Tribenzylgermane undergoes both alkylation and metal-hydrogen exchange reactions with both n-butyl- and benzyl-lithium.[11] Conversion of the germyl-lithium reagent formed to digermane is not immediate, since methylation of the reaction mixture gives some $(PhCH_2)_3GeMe$:

$$\begin{tikzcd} (PhCH_2)_3GeH + Bu^nLi \arrow[d, "2\text{ hrs. at }-10^{o};\ MeI;\ H_2O"] \\ \underset{12{\cdot}5\%}{(PhCH_2)_6Ge_2} + \underset{16\%}{(PhCH_2)_4Ge} + \underset{26\%}{(PhCH_2)_3GeBu^n} + \underset{12\%}{(PhCH_2)_3GeMe} \end{tikzcd}$$

At room temperature, 50% $(PhCH_2)_3GeBu^n$ is obtained.

With diphenylgermane the picture is further complicated, since one or both of the hydrogen atoms can be replaced by lithium. In a reaction[11] with n-butyl-lithium, the reaction mixture was alkylated with ethylbromide.

$$\begin{array}{c} Ph_2GeH_2 + Bu^nLi \\ \Big\downarrow \text{ 4 hrs. at } -10^o\text{; EtBr; } H_2O \\ H_2 + \underset{2\%}{Ph_2GeEt_2} + \underset{20\%}{Ph_2GeEtBu^n} + \underset{12\%}{Ph_2GeBu^n{}_2} + \underset{28\%}{(Ph_2EtGe)_2} \end{array}$$

It is an interesting point that, although Ph_2GeBu^nLi must have been formed, since it gives rise to $Ph_2GeEtBu^n$, no $(Ph_2GeBu)_2$ or similar compound was reported. Thus the coupling reaction:

$$Ph_2GeBu^nLi + Ph_2GeX_2 \longrightarrow Ph_2GeBu^nGePh_2X + LiX$$

must be slow. The reaction

$$Ph_2GeLi_2 + Ph_2GeHLi \longrightarrow Ph_2GeLiGeLiPh_2 + PhLi$$

on the other hand must be fast, since $(Ph_2GeEt)_2$ is an abundant product, whereas Ph_2GeEt_2 is not, and Ph_2GeHEt is absent.

If the reaction mixture is hydrolysed instead, then hydrides are obtained:

$$Ph_2GeH_2 + Bu^nLi \xrightarrow[\text{Hydrolysis}]{\substack{\text{4 hr } -10^o \\ Et_2O}} \underset{22\%}{Ph_2GeH_2} + \underset{36\%}{Bu^nPh_2GeH} +$$

$$(Ph_2GeH)_2 + Ph_2Ge(H)GeBuPh_2{}^{26}$$

It has been shown[15] that the action of mixed alkyl-lithium reagents (MeLi and EtLi or Pr^nLi) on germanium tetrachloride gives rise to mixed di- and poly-germanes in greater proportions than in similar Grignard reactions. With a large excess of the lithium reagents (4 moles MeLi and 4 moles EtLi to 1 mole $GeCl_4$), 60% of the product was a mixture of Me_6Ge_2, Me_8Ge_3 and $Me_{10}Ge_4$ with a little Me_7Ge_3Et. When less of the lithium reagent was used, the incorporation of ethyl groups was greater. The isomer ratios for $Et_2Me_4Ge_2$ and $Pr^n{}_2Me_4Ge_2$ were found to be those expected for a random distribution of alkyl groups. This was not so for the analogous Grignard reactions.

Ph_6Ge_2 is produced as a by-product from the reaction:

$$Ph_3GeSnPh_3 \xrightarrow[CO_2]{Bu^nLi} Ph_6Ge_2 + Ph_3GeCO_2H \quad ^{27}$$

1:1:3 Organo-aluminium Syntheses

The alkylation of many metal and metalloid halides using aluminium alkyls has been studied.[28] Silicon and tin halides react in a series of equilibria which may be displaced by the addition of an alkali metal halide so that the stable complex salt $MAlCl_3X$ results. Ethers and amines also drive these reactions to completion. A patent report[29] describes the reaction between $GeCl_4$ and triethylaluminium in refluxing hexane, with added NaCl, as proceeding in about 90% yield according to the equation:

$$3GeCl_4 + 4Et_3Al + 4NaCl \longrightarrow 3GeEt_4 + 4NaAlCl_4$$

It was also claimed that Et_2GeCl_2 can be obtained in appreciable yield by suitably altering the stoichiometry.

Without added sodium chloride or a solvent[30], 73% yields of both Et_4Ge and $Bu^i{}_4Ge$ were obtained by reaction of the respective alkyls on $GeCl_4$ at 120-130° for 6 hours. Et_4Ge has also been prepared from $Et_3Al_2Br_3$ and sodium chloride, with $GeCl_4$.[31]

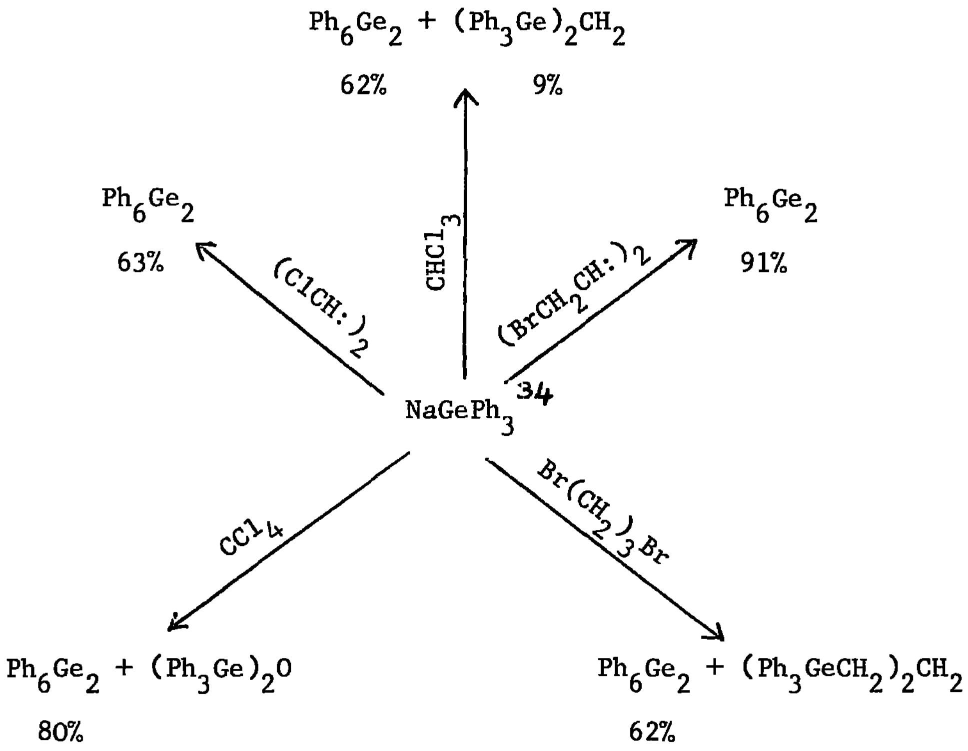
In none of these papers was there any suggestion that Ge-Ge bonded compounds were formed as by-products, but the original work to be discussed in this thesis does show that such compounds are formed.

1:1:4 Triorganogermylmetal Reagents

The formation of intermediate R_3GeLi compounds was postulated to account for some of the side reactions occurring with organolithium reagents. Although germyl-alkali metal compounds have never been isolated (with the possible exception of Ph_3GeNa prepared from Ph_6Ge_2 and sodium in liquid ammonia),[32] their existence is amply attested by the reactions they undergo.

The most extensively used is Ph_3GeLi, prepared from Ph_4Ge and lithium shot in THF, but Ph_3GeNa is also known.[33] These reagents give quite good yields of tetraorganogermanes when reacted with alkyl halides, but reactions with di- or poly-halides must be carried out in liquid ammonia since in diethylether, digermanes are formed. Thus in the reaction[34] between Ph_3GeNa and trimethylenedibromide in ether, Ph_6Ge_2 is the main product, as it is in many other reactions of Ph_3GeNa

with organic halides.



With phenylbromide in ether, Ph_4Ge is the main product, but even so 10% Ph_6Ge_2 is obtained.[33]

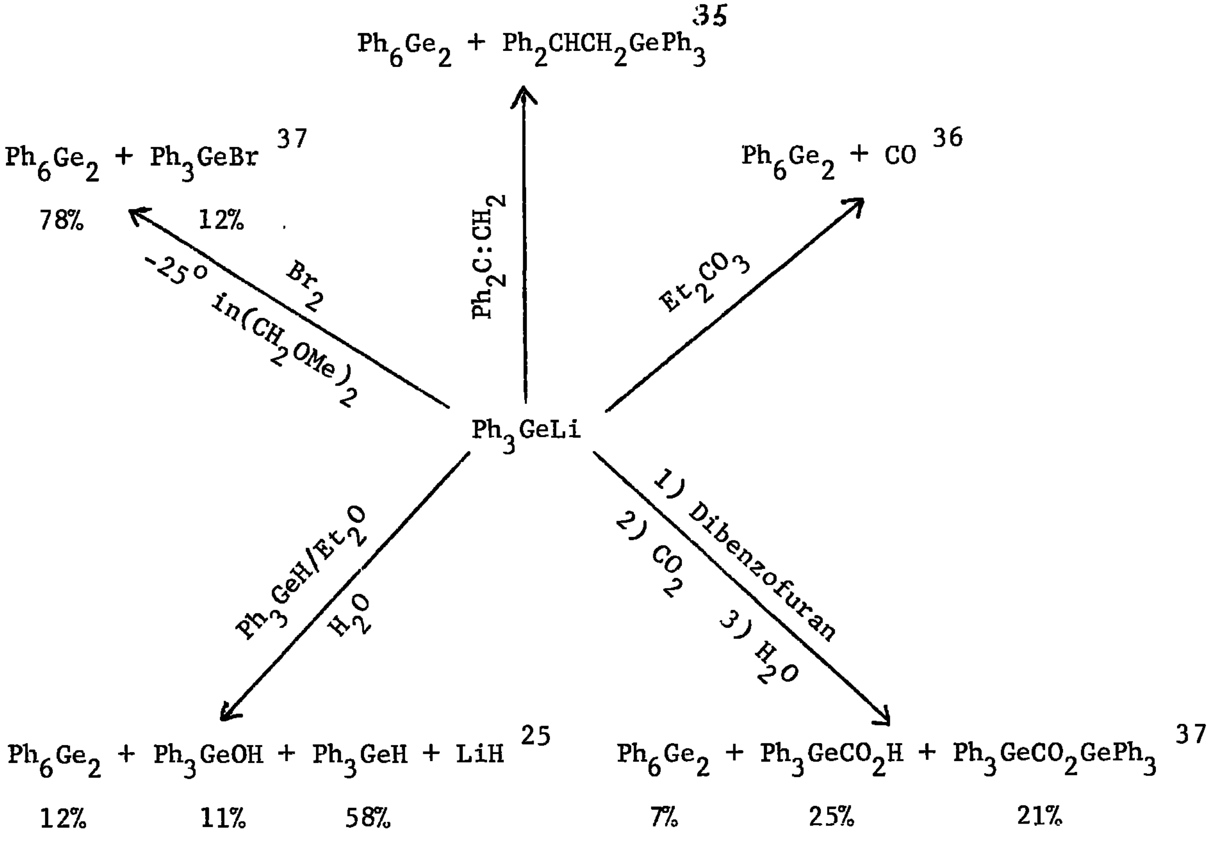
Once again the mechanism suggested for these reactions invokes "halogen-metal exchange".

$$\begin{tikzcd}
Ph_3GeNa + RX \arrow[r] & Ph_3GeX + RNa \arrow[d, "Ph_3GeNa"] \\
& Ph_6Ge_2 + NaX
\end{tikzcd}$$

and this idea derives some support from the reaction between triphenylgermylsodium and triphenylgermaniumfluoride.

$$Ph_3GeNa + Ph_3GeF \longrightarrow Ph_6Ge_2 + NaF$$ [33]

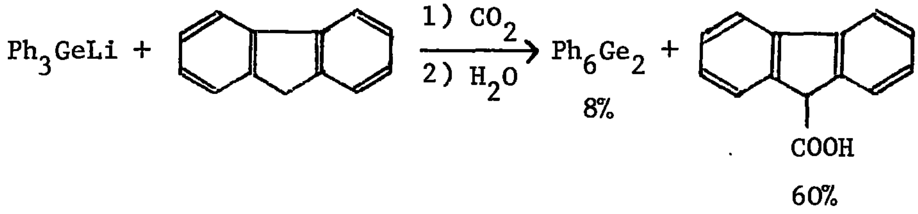
Some reactions of Ph_3GeLi which give Ph_6Ge_2 as a by-product are shown below.



For the reaction

$$Ph_3GeLi + Ph_3GeCO_2Me \longrightarrow Ph_6Ge_2 + CO + LiOMe$$ [36] (75%)

it was shown that with Ph_3SiLi, Ph_3GeCO_2Me gives $Ph_3SiGePh_3$ as the only product (84%). From this it was concluded that the digermane was formed in the Ph_3GeLi experiment from one molecule each of Ph_3GeLi and Ph_3GeCO_2Me. With fluorene only 8% Ph_6Ge_2 is formed:



The digermane is thought to be formed from Ph_3GeLi and Ph_3GeH, produced during the metallation.[37] An interesting reaction is:

$$Et_3GeBr + (CH_2CH_2Li)_2 \xrightarrow[Et_2O]{-5^{o}} \underset{56\%}{Et_6Ge_2} + \underset{12\%}{(Et_3GeCH_2CH_2)_2} \quad ^{38}$$

The attempted preparation of $(Ph_3Ge)_4M$ from MCl_4 (M = Ge, Sn) and Ph_3GeLi gave only Ph_6Ge_2. The preparation of $(Ph_3Ge)_4Pb$ was successful, although Ph_6Ge_2 was formed as a by-product.[39] A similar result was obtained with Ph_3GeNa and silicon tetrachloride.

$$Ph_3GeNa + SiCl_4 \longrightarrow \underset{46\%}{Ph_6Ge_2} + (Ph_3Ge)_4Si$$

From the product the tris(triphenylgermyl)silyl-lithium reagent can be prepared, and on reaction with ethylbromide some decomposition of this reagent occurs.

$$(Ph_3Ge)_3SiLi + EtBr \xrightarrow{NH_3} \underset{31\%}{Ph_6Ge_2} + \underset{63\%}{(Ph_3Ge)_3SiEt} + LiBr$$

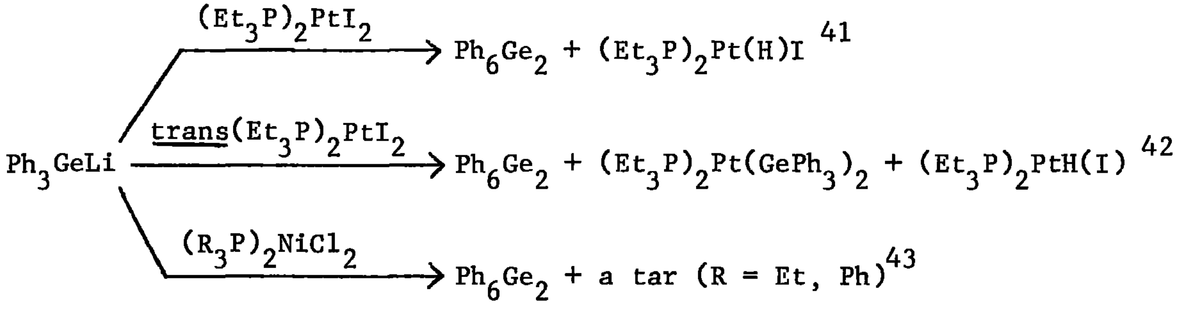
The preparation of other Ge-Si and Ge-Sn compounds from germyl-alkali metal reagents leads to the digermane as a by-product

$$Ph_3GeLi + Ph_3SnCl \longrightarrow Ph_6Ge_2 \quad (46\%)^{27}$$

$$Ph_3GeLi + R_3MX \longrightarrow Ph_3GeMR_3 + Ph_6Ge_2 + R_6M_2 + LiX \ ^{40}$$

$$Ph_3GeNa + Me_3SnBr \longrightarrow Ph_6Ge_2 + Me_6Sn_2 + Ph_3GeSnMe_3 \ ^{33}$$

Reactions of some transition metal complexes with triphenylgermyl-lithium give hexaphenyldigermane.



$$Ph_3GeLi \xrightarrow{(Et_3P)_2PtI_2} Ph_6Ge_2 + (Et_3P)_2Pt(H)I \ ^{41}$$

$$Ph_3GeLi \xrightarrow{\underline{trans}(Et_3P)_2PtI_2} Ph_6Ge_2 + (Et_3P)_2Pt(GePh_3)_2 + (Et_3P)_2PtH(I) \ ^{42}$$

$$Ph_3GeLi \xrightarrow{(R_3P)_2NiCl_2} Ph_6Ge_2 + \text{a tar } (R = Et, Ph)^{43}$$

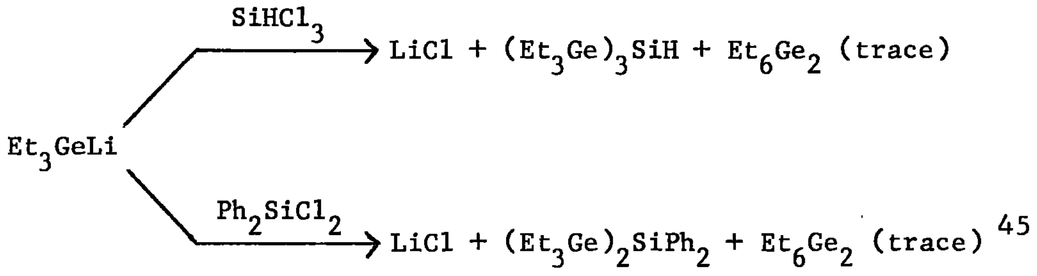
Because this method of preparing bonds from germanium to main group or transition metals, although often successful, does give digermanes as by-products it should provide an ideal route to symmetrical organodigermanes. One would expect that unsymmetrical digermanes could also be prepared in this way, but that the symmetrical digermanes would be formed as by-products. These expectations have been confirmed; the actual products depend to some extent on the conditions of the reaction

$$Ph_3GeNa + Et_3GeBr \xrightarrow{benzene} Ph_3GeGeEt_3$$ [32]

When $(PhCH_2)_3GeLi$ is added to Et_3GeH, extensive halogen-metal exchange occurs and only the symmetrical digermanes $(PhCH_2)_6Ge_2$ and Et_6Ge_2 were isolated. Reversing the order of addition gave the unsymmetrical digermane, $(PhCH_2)_3GeGeEt_3$.[11] Trigermanes can also be made

$$Ph_2GeCl_2 + Ph_3GeNa \longrightarrow Ph_8Ge_3 + 2NaCl$$ [44]

Trialkylgermyl-alkali metal reagents have until recently, been unknown, but several methods have now been developed for their preparation and they are full of promise for the preparation of polygermanes. Replacement of the silanes in these reactions should give the



$$Et_3GeLi \xrightarrow{SiHCl_3} LiCl + (Et_3Ge)_3SiH + Et_6Ge_2 \text{ (trace)}$$

$$Et_3GeLi \xrightarrow{Ph_2SiCl_2} LiCl + (Et_3Ge)_2SiPh_2 + Et_6Ge_2 \text{ (trace)}$$ [45]

corresponding Ge-Ge bonded compounds. Reagents such as R_3GeK have been prepared from the digermanes, R_6Ge_2, themselves and will be considered in Section 1:3:2:1.

It is likely that the celebrated Wurtz-Fittig reaction involves triorganogermyl-alkali metal intermediates. This reaction was used in 1925 to prepare the first organo-substituted digermane.[46]

$$2Ph_3GeBr + 2Na \longrightarrow Ph_6Ge_2 + 2NaBr$$ [33,46]

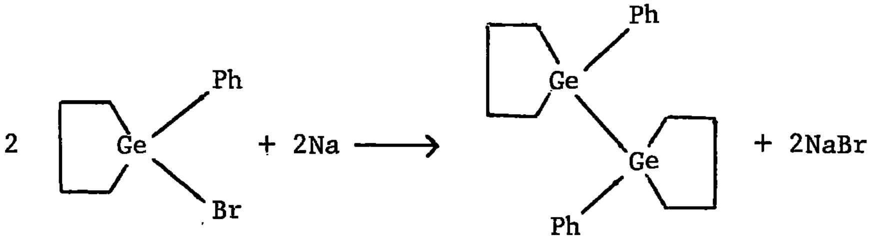
This reaction can give as much as 86% Ph_6Ge_2.[47] Alkyldigermanes can be made in like manner. Thus hexaethyldigermane is formed by refluxing Et_3GeBr with sodium in the absence of solvent, although it does not react in boiling xylene.

$$2Et_3GeBr + 2Na \longrightarrow Et_6Ge_2 + 2NaBr$$ [48,49,50]

Hexamethyldigermane can be prepared in a similar way.

$$2Me_3GeBr + 2K \longrightarrow Me_6Ge_2 + 2KBr$$ [51]

Other digermanes prepared in this way include $(PhCH_2)_6Ge_2$, $(p\text{-tolyl})_6Ge_2$ [5] and hexacyclohexyldigermane.[52] An interesting example of the reaction is the preparation of bis(phenylgermanocyclopentane) in 80% yield.[53]



It is possible that the greater success with the alkyl compounds in the absence of solvent is due to higher reaction temperatures. If lithium is used instead of sodium or potassium the reactions can be carried out with Et_3GeX in diethylether[54,55] or THF[49,54], or even ethylamine.

$$2Et_3GeBr + 2Li \longrightarrow Et_6Ge_2 + 2LiBr \quad (63\%)^{49}$$

$$2Et_3GeF + 2Li \xrightarrow{EtNH_2} 2LiF + Et_6Ge_2 \; ^{48}$$

More recently hexamethylphosphonictriamide has been introduced as a solvent, and gives good yields of hexa-alkyldigermanes with both lithium and sodium.[56]

The possible intermediacy of R_3GeM compounds is indicated by the reaction of Ph_3GeX with lithium in THF, where the reaction actually leads to the formation of triphenylgermyl-lithium.

$$Ph_3GeX + 2Li \longrightarrow Ph_3GeLi + LiX \quad (X = Cl^{57}, Br^{58})$$

A careful study of the reaction between $Pr^{i}_{3}GeCl$ and Na/K alloy[13] confirms this possibility since on hydrolysis of the reaction mixture both $Pr^{i}_{3}GeH$ and $(HPr^{i}_{2}Ge)_2$ are formed as well as $Pr^{i}_{6}Ge_2$.

$$\begin{tikzcd}
Pr^{i}_{3}GeCl + Na/K \arrow[r] & Pr^{i}_{6}Ge_2 + & Pr^{i}_{3}GeK \arrow[d, "H_2O"'] & + & (KPr^{i}_{2}Ge)_2 \arrow[d, "H_2O"'] \\
& & Pr^{i}_{3}GeH & & (HPr^{i}_{2}Ge)_2
\end{tikzcd}$$

The formation of the di-potassio intermediate requires the breaking of a Ge-C bond.

In some cases, the Wurtz reaction can be applied to the preparation of halogenated digermanes from polyhalogermanes

$$Ph_2GeBr_2 + Li/Hg \xrightarrow{Et_2O} (Ph_2GeBr)_2 \quad (60\%)$$

$$PhGeBr_3 + Li/Hg \xrightarrow{Et_2O} (PhGeBr_2)_2 \quad (20\%)$$ [59]

Attempts to produce Ge-Si and Ge-Sn bonds lead also to the digermane as the main product.

$$Et_3GeBr + Et_3SiBr + Na \xrightarrow{THF} \underset{27\%}{Et_3GeSiEt_3} + \underset{28\%}{Et_6Si_2} + \underset{42\%}{Et_6Ge_2}$$ [49]

$$Me_3GeBr + Me_3SiBr + K \longrightarrow \underset{20\%}{Me_3GeSiMe_3} + \underset{8\%}{Me_6Si_2} + \underset{70\%}{Me_6Ge_2}$$ [60]

Organo-germyl compounds of main group elements other than Group I are beginning to appear, and these decompose to digermanes.

$$\begin{tikzcd} Et_3GeH + Et_3Tl \arrow[r, "100^\circ"] & C_2H_6 + Tl + (Et_3Ge)_3Tl \quad (91\%) \arrow[d, "3\ hr./170^\circ"] \\ & Et_6Ge_2 + Tl \end{tikzcd}$$ [61]

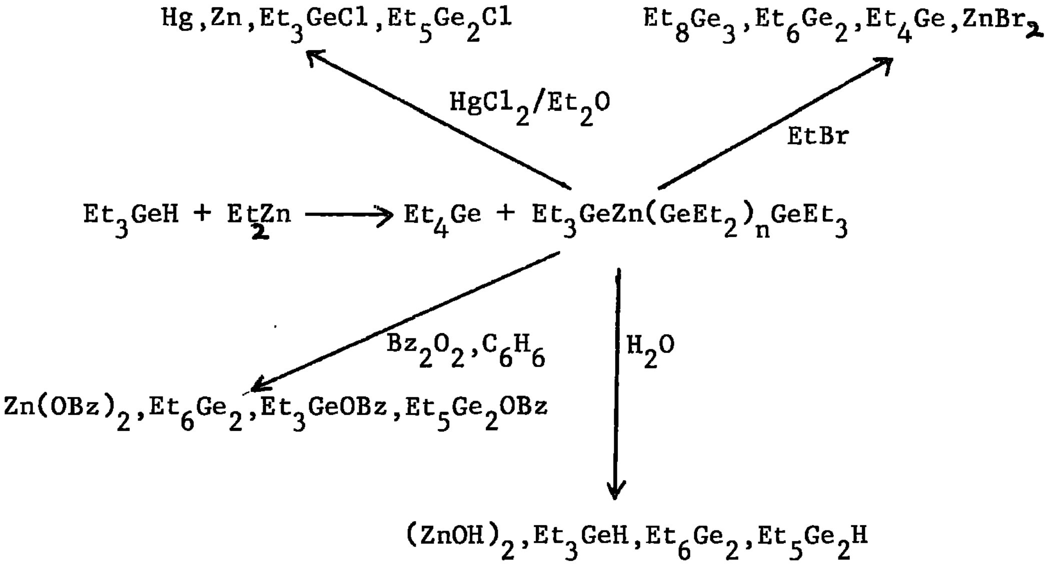
$$(Me_3Ge)_2Hg \xrightarrow{u.v.} Me_6Ge_2$$ [62]

$$(Et_3Ge)_2Hg \xrightarrow{u.v.} Et_6Ge_2 \quad (93\%) + Hg$$ [63,64]

The latter reaction occurs in Et_4Sn, cumene, Bu^tperoxide[63] neat or in benzene[64], but in brominated solvents (EtBr, α-bromonaphthalene, $PhCH_2Br$) it gives Et_3GeBr[63]. Bistriethylgermylmercury reacts with cyclohexyloxytriethylgermane and lithium to give hexaethyldigermane:

$$Et_3GeOC_6H_{11} + (Et_3Ge)_2Hg + Li \xrightarrow{C_6H_6} C_6H_5OH + Et_6Ge_2 \quad (64\%)$$

The reaction of triethylgermane with diethylzinc gives a compound or mixture of compounds of uncertain constitution:[65]



The cadmium analogue is more straightforward.

$$(Et_3Ge)_2Cd \xrightarrow[7\ hr.]{heat} Et_6Ge_2 + Cd$$

in 74% yield,[66] and 77% after 40 hr. at 80°C.[67] Tris(trimethylgermyl)-bismuthine has also been prepared,[68] and tristriethylgermylbismuthine gives hexaethyldigermane on heating:

$$(Et_3Ge)_3Bi \xrightarrow[4\text{-}5hr.]{270^{\circ}} Et_6Ge_2 + Bi \ (100\%)^{69}$$

Triorganogermyl transition metal complexes give rise to digermanes in some of their reactions e.g.[41,42]

$$\begin{tikzcd}[column sep=small]
(Et_3P)_2Pt(GePh_3)_2 + H_2 \arrow[r] & {[(Et_3P)_2Pt(H)_2(GePh_3)_2]} \arrow[dl, "5\%"'] \arrow[dr, "90\%"] & \\
Ph_6Ge_2 + (Et_3P)_2Pt(H)_2 & & (Et_3P)_2Pt(H)GePh_3 + Ph_3GeH
\end{tikzcd}$$

$$\begin{tikzcd}
(Pr^n{}_3P)_2Pt(GePh_3)_2 + MgI_2 \arrow[dr] & \\
& Ph_6Ge_2 + (Pr^n{}_3P)_2PtHGePh_3 \\
(Pr^n{}_3P)_2PtIGePh_3 + Ph_3GeMgI \arrow[ur] &
\end{tikzcd}$$

$$(R_3P)_2Pt(GePh_3)_2 \xrightarrow{220^o} Ph_6Ge_2 + Ph_4Ge + Et_3P + C_6H_6 \text{ etc.}^{42}$$

$$(R = Et,\ Pr^n)$$

Palladium complexes decompose at a lower temperature:[43]

$$(Et_3P)_2Pd(GePh_3)_2 \xrightarrow{100^o} Pd + Ph_6Ge_2 + Ph_4Ge + Et_3P + C_6H_6 \text{ etc.}$$

Hexamethyldigermane is a by-product in the preparation of trans-bistriethylphosphinepalladiumhydridochloride.

$$\underline{trans}(Et_3P)_2PdCl_2 + Me_3GeH \longrightarrow H_2 + Me_3GeCl + Pd + Me_6Ge_2$$
$$+ \underline{trans}(Et_3P)_2PdHCl$$

It is thought that this is a free-radical reaction, and this view is supported by the fact that Me_6Ge_2 is formed together with hydrogen by decomposition of Me_3GeH at room temperature in the presence of palladium black.[70]

1:1:5 Summary of Alkylation Reactions which do not give Ge-Ge By-products

The so-called direct synthesis of methylchlorogermanes[18] does not produce digermanes, so far as is known. Since it is a gas/solid reaction, and not a liquid/liquid or liquid/solid reaction like those previously discussed, it would not be surprising if it differed from them. The gas phase production of higher germanes (discussed in section 1:2:6) by the passage of an electric discharge through GeH_4 is not really analogous because of the known low thermal stability of germane.

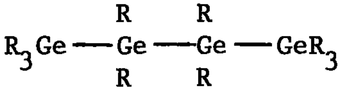
Redistribution reactions[71] using organogermanes, -stannanes and -plumbanes are not known to give Ge-Ge bonded compounds as by-products although it has been reported that the redistribution of Ph_3GeBr with $GeBr_4$ gives $(Ph_2GeBr)_2$ as a by-product.[72] A closer examination of such reactions might well reveal di- or poly-germanes in small amounts. This is particularly likely in those systems which use $AlCl_3$ as a catalyst, since here the conditions approximate to those occurring in the alkylation of $GeCl_4$ with aluminium alkyls.

Organo-zinc, -cadmium, and -mercury reagents (R_2M) seem to be free of the complications observed with the Grignard and organolithium compounds.[18] Since, however, these elements are able to form germyl compounds, which will decompose to give digermanes, it may be that here too a closer examination of the reactions would reveal catenated by-products.

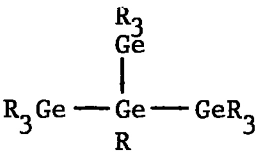
1:2 Deliberate Syntheses

Once interest in compounds containing germanium-germanium bonds had been aroused, more direct ways of preparing them were sought. As has already been described the Grignard and organolithium reactions on germanium-(IV) halides can in certain cases be made to give high yields of organo-digermanes, and triorganogermyl metallic reagents have been used to prepare both symmetrical and unsymmetrical organo-digermanes.

A number of attempts were made, quite early in the history of organogermanium chemistry, to prepare divalent organogermanium compounds, R_2Ge, analogous to the halides, GeX_2, all of which are known. These attempts were unsuccessful, giving amorphous, intractable, air-sensitive or otherwise unattractive materials. Where claims for R_2Ge compounds were made, further investigation showed that such compounds were in almost all cases polymeric, due either to the formation of germoxanes by contact with the air or hydrolysis, or to the production of poly-germanes, containing germanium to germanium bonds. In compounds where there are chains or networks of germanium atoms



$R_3Ge-\underset{R}{\overset{R}{Ge}}-\underset{R}{\overset{R}{Ge}}-GeR_3$



$R_3Ge-\underset{R}{\overset{\overset{R_3}{\overset{Ge}{|}}}{Ge}}-GeR_3$

the germanium is 4-co-ordinate and 4-covalent. Thus these compounds are not the sought-after $R_2Ge(II)$ species but are substituted germanes analogous to branched hydrocarbons. It is thus apparent that polygermanes must be sought among the products from reactions which might otherwise have been expected to give divalent germanium compounds. It is the nature of the germanium compound used which is all important, not the particular alkylating reagent, and so in this section the reactions will be classified according to the germanium compound.

1:2:1 Reactions of Germanium Dihalides

All of the halides, GeX_2, are known but alkylation and arylation of GeI_2 only has been attempted. Phenylation of GeI_2 by PhLi[73,74], PhMgBr[73] and Ph_3Al produces essentially similar results with all three reagents. With two or more equivalents of PhLi in ether, GeI_2 gives Ph_4Ge, a red-brown polymer of approximate composition $(PhGe)_{10}$ and a yellow polymer with an empirical formula midway between GeC_6H_5 and $GeC_{12}H_{10}$. Both of these polymers were free from oxygen and halogen, and therefore almost certainly contain Ge-Ge bonds. With a large excess of PhLi, GeI_2 gives a deep blood-red ether solution from which Ph_4Ge, Ph_3GeH and a yellow polymeric material were isolated after hydrolysis. The yellow polymer was oxidised by air, and was shown by controlled brominative degredation to contain Ph_3Ge, Ph_2Ge, PhGe and Ge groups. The formation of this polymer was attributed to halogen-metal exchange reactions during the phenylation, giving rise to intermediates such as PhGeLi, Ph_3GeLi and LiGeI. The following reactions account for all the products isolated.

$$\begin{tikzcd}
\mathrm{GeI_2 + 2PhLi} \arrow[r] & \mathrm{Ph_2Ge + 2LiI} \arrow[d, "\mathrm{PhLi}"] & \\
\mathrm{Ph_4Ge + LiI} & \mathrm{Ph_3GeLi} \arrow[l, "\mathrm{PhI}"'] \arrow[r, "\mathrm{H_2O}"] & \mathrm{Ph_3GeH}
\end{tikzcd}$$

$$\begin{tikzcd}
 & \mathrm{PhGeI + LiI} \arrow[r, "\mathrm{PhLi}"] & \mathrm{PhGeLi + PhI} \\
\mathrm{GeI_2 + PhLi} \arrow[ur] \arrow[dr] & & \\
 & \mathrm{LiGeI + PhI} &
\end{tikzcd}$$

With PhMgBr in THF, an exothermic reaction occurs and $\mathrm{Ph_4Ge}$ and the yellow polymer are formed. With excess mesitylmagnesium bromide, the result is essentially the same, $(\mathrm{mesityl})_3\mathrm{GeH}$ and a yellow amorphous mesityl-germanium polymer being formed, the polymer having a composition between $\mathrm{GeC_9H_{11}}$ and $\mathrm{GeC_{18}H_{22}}$. The reaction with $\mathrm{Ph_3Al}$ was incomplete, the polymers obtained containing oxygen and iodine.

Triphenylgermyl-lithium reacts with $\mathrm{GeI_2}$ to give, after hydrolysis, tristriphenylgermylgermane.

$$\begin{tikzcd}
\mathrm{Ph_3GeLi + GeI_2} \arrow[r] & \mathrm{(Ph_3Ge)_3GeLi + Ph_6Ge_2} \arrow[d, "\mathrm{H_2O}"] \\
 & \mathrm{(Ph_3Ge)_3GeH} \quad (36\%)\ [73]
\end{tikzcd}$$

With di-n-butylmercury[75] $\mathrm{GeI_2}$ gives 1,2-di-iodotetrabutyldigermane.

$$GeI_2 + Bu^n{}_2Hg \xrightarrow{acetone} Bu^nHgI + (Bu^n{}_2GeI)_2$$

No germanium compound was isolated from the reaction of Et_2Hg and GeI_2. Ethyl- and butyl-lithium probably gives complexes with GeI_2, and $Bu^n{}_2Zn$ and $Bu^i{}_2Zn$ give colourless solutions in benzene, containing a polymer of unknown structure, molecular weight $2 \times 10^4 - 10^5$.

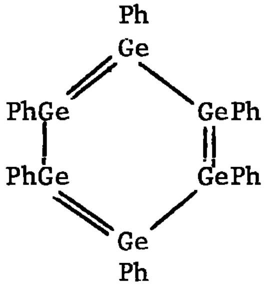
Phenylation[76] of the triphenylphosphine adduct of GeI_2 also gives rise to a phenylpolygermane, possibly $(Ph_2Ge)_4$.

$$Ph_3PGeI_2 \xrightarrow{PhMgBr} (Ph_2Ge)_x$$

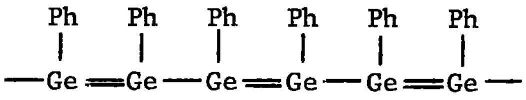
Methylation (reagent unspecified) of GeI_2 in pyridine/ether solution gives $Me(GeMe_2)_nMe$, $(n \geq 2)$, and small amounts of cyclopolymers, $(Me_2Ge)_n$, (n = 6 and probably 4).[77] Experiments described later in this thesis show that trimethyl-, triethyl- and tri-isobutyl-aluminium compounds react with GeI_2 to produce alkylpolygermanes.

1:2:2 Reactions of Trihalogermanes

The reduction of $PhGeCl_3$ with sodium[72] or potassium[78] in xylene under a CO_2 atmosphere gives an amorphous polymeric solid originally thought, from analysis and molecular weight determinations to be $(PhGe)_6$. Two structures were proposed.



or



Present knowledge indicates that delocalised pπ-pπ bonding (as implied in the benzene-like structure) does not occur in the elements of Group IV heavier than carbon. The other structure is unacceptable for the same reason, and also because it would be a di-radical.

The reaction has been re-investigated[59] and better yields of polymer were obtained by slightly altering the conditions. A yellow solid was formed which had a Ph:Ge ratio of 1:1, but analysis and infrared spectra indicated a 5-10% oxygen and 1-5% chlorine content. Molecular weight measurements gave values corresponding to 5 to 8 PhGe units. Reaction with bromine consumed the same quantity per PhGe unit as previously reported, and gave $Ph_2Ge_2Br_4$, Ph_2GeBr_2 and $PhGeBr_3$. The polymer is also obtained by the lithium amalgam reduction of $PhGeCl_3$, but with $PhGeBr_3$ it gives 20% $(PhGeBr_2)_2$.

A large number of the reactions of trichlorogermane, $HGeCl_3$[79,80,81] or its etherate[82] have been explained in terms of the following initial steps.

$$HGeCl_3 \longrightarrow GeCl_3^- \longrightarrow GeCl_2$$

If this interpretation is correct, it might be expected that $HGeCl_3$ would react with methyl compounds of metals to give methylpolygermanes, and indeed it does.[83,84]

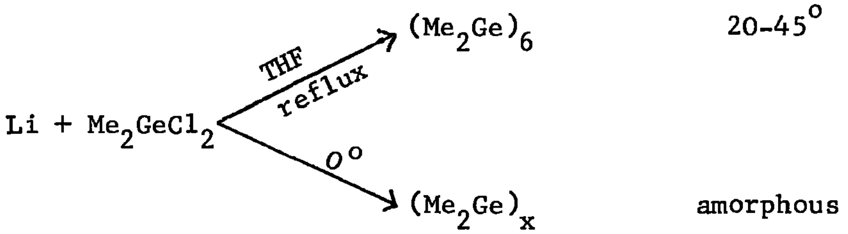
$$HGeCl_3 \xrightarrow{MCH_3} GeR_2 \xrightarrow{MCH_3} CH_3(GeR_2)_nCH_3 \xrightarrow{MCH_3} CH_3[Ge(CH_3)_2]_nCH_3$$

where M is Li or MgX; R is Cl or CH_3; and X is halogen; $n \geq 1$. No trimethyl- or tetramethyl-germane were obtained. Fractional distillation gave individual telomer homologues with n = 2 to 5 in 90-99% purity. Cyclic polymers $(Me_2Ge)_4$ and $(Me_2Ge)_6$ were also reported. Similar experiments gave ethyl and phenyl compounds. $HGeBr_3$ seems likely to behave in a similar way.[85] Reactions of etherates of $HGeCl_3$ have been described in more detail. Thus $HGeCl_3.R_2O$ or $HGeCl_3.2R_2O$ with MeMgBr or MeLi give $Me(GeMe_2)_nMe$, $n \geq 2$; (n = 2, 3-6%; n = 3, 5%; n = 4, 5%; n = 7, 5%; $n > 7$, a mixture of liquid and solid telomers, 70%). Reaction of $HGeCl_3.R_2O$ with magnesium followed by methylation gives the same products[83,86] and the methylation of GeI_2 has already been mentioned. Methylation of an $HGeCl_3$-pyridine complex in ether proceeds in the same way. In all cases small amounts of cyclopolymers were obtained.[86,87,88] $HGeCl_3.Et_2O$ reacts similarly with phenyl-lithium,[86] giving Ph_4Ge, Ph_6Ge_2 and linear telomer homologues[83] and with EtMgBr trichlorogermane and its etherates give $Et(GeEt_2)_nEt$.

The products from these reactions were identified by the nmr and infrared spectra, and by the linear dependence of the log of their retention times on n. No data were reported so it is diffuclt to make a critical appraisal of this work. As will be shown, methylation of GeI_2 with trimethylaluminium does not in general give linear telomers. The one concrete piece of evidence presented for the linear structures assigned is the formation of Me_2GeHCl and Me_2GeCl_2 on treatment of the telomers with dry HCl at 200-300°. There was, however, no mention of the formation of Me_3GeCl in these degradations. This fact takes some of the force out of the evidence.

1:2:3 Reactions of Dihalogermanes

Another possible route to R_2Ge compounds is the dehalogenation of dialkylgermaniumdichlorides. Using lithium, the end product is a mixture of cyclic oligomers and high polymers, in which the nature of the end groups has not yet been investigated.[88]



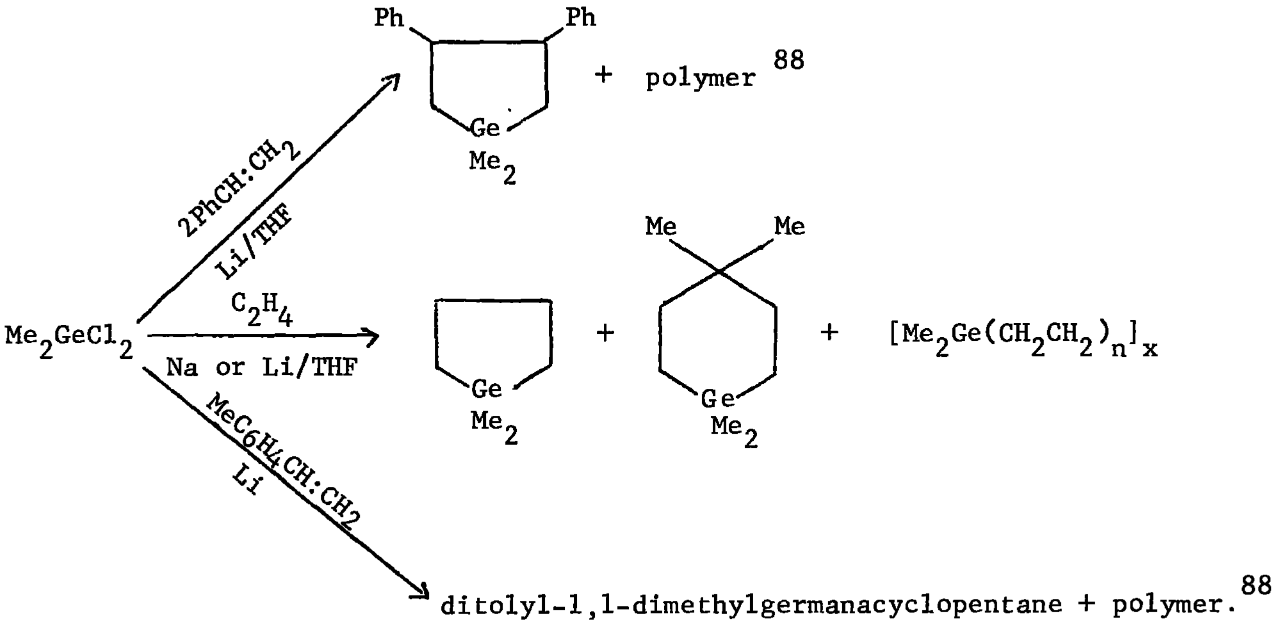
The reaction has been extended.

$$R_2MCl_2 \xrightarrow[THF]{Li\ or\ Na} (R_2M)_6 \qquad R = Me, Et. \quad M = Si, Ge.$$

High molecular weight polymers, presumed linear, were also formed, $(R_2M)_n$, with $n \geq 55$.[84] The mechanism proposed for these reactions is:

$$Me_2GeCl_2 \xrightarrow{Li} Me_2Ge(Li)Cl \longrightarrow Me_2Ge: + LiCl$$

followed by polymerisation.[88] Support for this theory has been obtained by carrying out the reactions in the presence of an olefin[89,90] when low yields of cyclic germanes were obtained.



Similar reactions occur with diphenyl-dihalogermanes, but the extent of polymerisation would appear to be less. With lithium amalgam, Ph_2GeBr_2 leads to 1,2-dibromotetraphenyldigermane[59]. The reaction of Ph_2GeCl_2 with sodium in xylene gave a product thought to be $(Ph_2Ge)_4$[44] which was later characterised as octaphenylcyclotetragermane.[91] Much yellow resinous material of approximate composition Ph_2Ge and a molecular weight of about 900 was also obtained.[44] Variation of the alkali metal and solvent leads to other cyclogermanes.

$$4Ph_2GeCl_2 + 8Na \longrightarrow \underset{35\%}{Ph_8Ge_4} + \underset{65\%}{(Ph_2Ge)_n} + 8NaCl \quad {}^{92}$$

$$Ph_2GeCl_2 + Li \xrightarrow{THF} \underset{33\%}{(Ph_2Ge)_5} + \underset{2\%}{(Ph_2Ge)_6} + \text{polymer} \quad {}^{92,93}$$

$$Ph_2GeCl_2 + C_{10}H_8Na \xrightarrow{(CH_3O)_2C_2H_4} \underset{37\%}{(Ph_2Ge)_5} + \underset{7\%}{(Ph_2Ge)_6} + (Ph_2Ge)_n \quad ^{91,92}$$

$$Ph_2GeCl_2 + Li \xrightarrow{EtNH_2} (Ph_2Ge)_n \quad ^{44}$$

Using the solvent hexamethylphosphoramide, dimetal derivatives of dialkyldichlorogermanes are obtained, instead of polymeric products.

$$Bu_2GeCl_2 + 4K \longrightarrow Bu_2GeK_2 \xrightarrow{H_2O} Bu_2GeH_2 \quad ^{94}$$

This could be utilized as a route to $(R_3Ge)_2GeR'_2$ compounds.

1:2:4 Reactions of Diorganogermanes

The alkylation of Ph_2GeH_2 by alkyl-lithium compounds has already been discussed, and it was found that the products were explicable on the basis of both hydrogen atoms being replaceable by lithium. With diethylmercury, diphenylgermane forms a germyl-mercury polymer, $(Ph_2GeHg)_n$ which decomposes under the influence of heat or u.v. light:

$$(Ph_2GeHg)_n \xrightarrow[u.v.]{heat} \underset{34\%}{(Ph_2Ge)_4}^{92,93} + \underset{66\%}{(Ph_2Ge)_n}^{92}$$

1:2:5 From other Organopolygermanes

Such preparations, which involve cleavage of Ge-Ge or Ge-C bonds and formation of new bonds in their place, will obviously be dependent on the properties of the organopolygermanes used as starting materials.

For this reason, they will be discussed with other properties of organopolygermanes.

1:2:6 Preparation of Polygermanes

The methods used for preparing germane itself, and higher homologues, are quite different from those used for the preparation of organo-substituted derivatives. They will be briefly summarised here.

Hydrolysis of magnesium germanide with dilute hydrochloric acid gives a 27% yield of a mixture of GeH_4, Ge_2H_6 and Ge_3H_8.[95,96] The reaction of magnesium germanide and ammonium bromide in liquid ammonia give 70% of the germanes with monogermane predominating.[97] Chromatography of the product gases from acid hydrolysis of magnesium germanide showed seven peaks, the first five of which were assigned to GeH_4, Ge_2H_6, Ge_3H_8, <u>iso</u>Ge_4H_{10} and n-Ge_4H_{10}.[98] In another study, Ge_4H_{10} and Ge_5H_{12} were isolated, but their structures were not determined, and they may have been mixtures of isomers.[99] The deuterides Ge_2D_6 and Ge_3D_8 have been prepared using DCl to hydrolyse magnesium germanide.[100] Smaller quantities of the higher germanes are obtained by reduction of germanium dioxide with KBH_4, (GeH_4, Ge_2H_6, Ge_3H_8)[101] or $NaBH_4$ (73% GeH_4 and a trace of Ge_2H_6).[102,103]

An alternative method for the higher germanes is the action of a silent electric discharge on GeH_4. In one experiment a mixture of Ge_2H_6 (20%), Ge_3H_8 (30%) and higher germanes up to Ge_8H_{18} was obtained. The hydrides were identified by their retention times on a gas-liquid chromatograph and some of them were separated by this means and characterised by their p.m.r. and mass spectra.[104] In another experiment, germanes up to nonagermane were obtained. All possible isomers up to Ge_5H_{12} were identified by vapour phase chromatography and tentative assignments of four hexagermanes, seven heptagermanes, three octagermanes and a nonagermane were made. The tetragermanes were separated and characterised fully.[101] The technique has been extended to the separation and complete characterisation of the three pentagermanes.[105] No cyclic germanes have been reported yet.

Persistant reports of polymeric lower hydrides $(GeH_2)_x$ and $(GeH)_x$ occur in the literature.

$$CaGe + 2HCl\ aq \longrightarrow CaCl_2 + (GeH_2)_x \quad ^{106}$$

$$GeO_2 + KBH_4 \longrightarrow GeH_4 + Ge_2H_6 + Ge_3H_8 + (GeH)_x \quad ^{101}$$

$$GeCl_4 + LiAlH_4 \xrightarrow{THF} GeH_4 + (GeH_2)_x \quad ^{107}$$

$$\begin{tikzcd} NaGeH_3 + PhBr \arrow[r, "NH_3"] & (GeH_2)_x + C_6H_6 + NaBr \arrow[d, "-NH_3"] \\ & GeH_4 + (GeH)_x \quad ^{108} \end{tikzcd}$$

$$NaGeH_3 + NH_4Br \longrightarrow (GeH)_x \quad ^{97}$$

$$Ge_2H_6 \xrightarrow{heat} GeH_4 + H_2 + Ge + (GeH_2)_x \quad ^{96}$$

$$NaGe \xrightarrow{acid} (GeH)_x \quad ^{109}$$

Some substance of the type Ge_xH_y must occur to give rise to so many reports, but recent work on the solvolysis of CaGe and $CaGe_2$[110] suggests a non-stoichiometric phase $GeH_{0\cdot9-1\cdot2}$ rather than a discrete compound.

1:3 Properties

Although a multitude of polygermanes have now been prepared, they have not been thoroughly studied. In particular there is a dearth of quantitative data concerning heats of formation and strengths of Ge-Ge bonds. This is equally true for silicon, tin and lead.

1:3:1 Thermal Stability

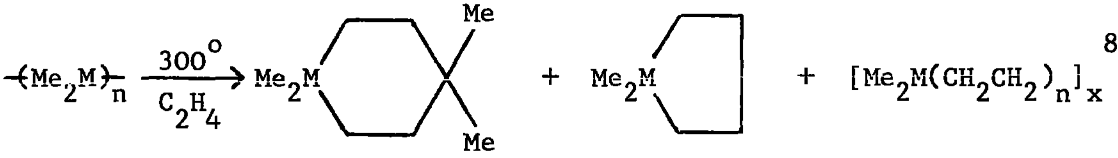
It has been said that the thermal stabilities of analogous catenated compounds of the Group IVB elements decrease from silicon to lead[55], but this is an instinctive expectation rather than an observational conclusion.

Three methods have been used to obtain the energy of the Ge-Ge bond. The heat of combustion of Et_6Ge_2 gave a value of 62 kcal. per mole.[50] Measurement of the heat of explosive decomposition of digermane in the presence of stibine gave a Ge-Ge bond energy of 38 kcal. per mole,[111] and the same method gave the Ge-Ge bond energy in trigermane as 39 kcal. per mole.[112] Measurement of the appearance potentials of the Ge^+ ion in Ge_2H_6 and Ge_3H_8 gave E(M-M) of 33 and 28 kcal. per mole respectively.[113] There is no positive evidence for the homolytic dissociation of the Ge-Ge bond.[46] The magnetic susceptibility of Ph_6Ge_2 in powder form and in benzene has been measured and a small upper limit of dissociation calculated, but the opinion was expressed that no dissociation in fact took place.[114] Hexaphenylethane, of course, readily dissociates but the mixed compound Ph_3GeCPh_3 does not.

Since there is little quantitative data, and what there is lacks consistency, a consideration of more qualitative observations may be instructive. The stability of inorganic polysilanes decreases with increasing chain length[115] and Ge_3H_8 begins to decompose to metallic germanium at 194°, whereas decomposition of Ge_2H_6 commences at 218°.[95] The hydride, or mixed isomers, Ge_4H_{10} decomposes slowly above 50° and rapidly above 100° to give GeH_4 and a higher liquid germane. The liquid germane or mixture Ge_5H_{12}, decomposes at 100° to give GeH_4 and a solid. Above 350° both these compounds decompose to germanium and hydrogen.[99] On the whole the germanes are less stable than the silanes. There is, however, no evidence that this is so for the organic derivatives of germanium. It seems that most organopolygermanes are quite stable to heat. Ph_6Ge_2 melts at 352-4° without decomposition[8], though at 450° some discolouration occurs.[116] Dodecamethylcyclohexagermane melts at 211-3°C also without decomposition.[84,88] Linear methylpolygermanes are pyrolysed at 300°, however

$$-\!\!(Me_2M)\!\!-_n \xrightarrow{350\text{-}400^o} (Me_2M)_x \qquad x = 4\text{-}6,\ M = Si,Ge$$

In the presence of C_2H_4, pyrolysis results in addition products.



[84]

There are isolated instances of decomposition at lower temperatures. Ph_8Ge_4 decomposes on melting at 238°C [93] whilst the analogous five- and six-membered rings do not melt or decompose below 360°C [91], and phenyl-germanium polymers are apparently stable until they decompose to germanium metal between 400 and 450°.[73] Hexacyclohexyldigermane decomposes on melting at 316°C.[52] Hexaethyldigermane may be distilled in air at 265°C.[48]

$Et_3GeGeEt_2Cl$ was recovered unchanged after heating for 6 hr. at 200° in N_2, but under the same conditions $(Et_2GeCl)_2$ underwent decomposition, although only to the extent of 8%.[117]

$$(Et_2GeCl)_2 \xrightarrow{heat} Et_2GeCl_2 + (Et_2Ge)_n$$

$(PhGeBr_2)_2$ is much less stable. It slowly decomposes in hexane solution, and on attempted sublimation (105°/0·1 mm Hg). It has a wide melting range (4°) another indication of thermal instability.[59] Iodogermane, Ge_2H_5I is unstable at room temperature,[118] more so than Ge_2H_5Br and Ge_2H_5Cl.[119]

It is convenient to note here that some ill-defined polymers presumably containing Ge-Ge bonds, have been obtained by pyrolysis of monogermanes. e.g.

$$(PhCH_2)_3GeH \xrightarrow{400^{\circ}} PhMe + (PhCH_2)_2 + (PhCH:)_2 + H_2 + \text{polymer}$$

The polymer had the approximate composition $Ge_3(CH_2Ph)_2$.[11]

1:3:2 Cleavage of Ge-Ge Bonds

1:3:2:1 Electropositive Metals

The Ge-Ge bond is susceptible to cleavage by alkali metals, forming germyl-metallic species. These compounds have never been isolated, but their existence is attested by their solution reactions described in section 1:1:4.

The first reaction of this type to be investigated was:

$$Ph_6Ge_2 + Na \xrightarrow{NH_3} 2Ph_3GeNa \qquad {}^{32,33,44,47}$$

and this became a standard method for the preparation of Ph_3GeNa. Sodium-potassium alloy gives the germyl-metallic reagent in mixtures of ether with THF, PhBr or Ph_4Ge [116,120] but in diethylether alone there are conflicting reports.[35,114] Other reagents which cleave Ph_6Ge_2 to give Ph_3GeM include lithium in 1,2-dimethoxyethane[35,37,116,121,122] or THF[57,123,124] but with Na/K alloy in 1,2-dimethoxyethane, di-n-butyl ether, THF, benzene/THF or xylene and cesium in ether the cleavage products are not Ph_3GeM.[116] With lithium in THF the reaction is swift, and prolongation decreases the yield of Ph_3GeLi. Thus immediate treatment of the reaction mixture with n-octadecyl bromide gives 79% n-octadecyltriphenylgermane. After 24 hrs. the yield is reduced to 68% and after 116 hr. to 48%. In addition a higher melting unidentified material is obtained, and after 8 days at 20° this was the only product.[18] A similar experiment showed that after 5 days 12% unreacted Ph_6Ge_2 was present, and solvent cleavage had occurred.[125] Hexaphenyldigermane is also cleaved by alkaline earth metals.

$$Ph_6Ge_2 \xrightarrow{M/NH_3} (Ph_3Ge)_2M \qquad (M = Sr,Ba)^{126}$$

Octaphenylcyclotetragermane is cleaved by lithium

$$(Ph_2Ge)_4 \xrightarrow{Li} Li(Ph_2Ge)_4Li \xrightarrow{PhBr} Ph(Ph_2Ge)_4Ph$$

Some $Ph_{10}Ge_5$ was also formed in this reaction[91,92,93]. With sodium in liquid ammonia, Ph_8Ge_4 is completely degraded to Ph_2GeNa_2, and with sodium-naphthalene in 1,2-dimethoxyethane all the Ge-Ge bonds in Ph_8Ge_4, $Ph_{10}Ge_5$, $Ph_{12}Ge_6$ and Ph_6Ge_2 were cleaved without cleavage of Ge-C bonds.[92,127]

$$Ph_8Ge_4 \xrightarrow[(MeO)_2SO_2]{Na/naphthalene} Ph_2GeMe_2 + MePh_2GeGePh_2Me$$

Cleavage of the Ge-Ge bond in $(PhCH_2)_6Ge_2$ by lithium in 1,2-dimethoxyethane was slow and incomplete (50% after 20 hr. at 0^o). The main product was $(PhCH_2)_3GeLi$, but some cleavage of Ge-benzyl bonds occurred giving toluene.[11]

The germanium-germanium bonds in alkylpolygermanes are less readily cleaved by metals than their aryl analogues. Thus although hexaethyldigermane is cleaved slowly by sodium in liquid ammonia/ether mixture or lithium or potassium in ethylamine[48], attempts to cleave hexa-alkyldigermanes in ethereal solvents[51,54] were unsuccessful.

Me_6Ge_2 was refluxed with Na/K alloy in 1,2-dimethoxyethane for 3 days, and recovered unchanged.[51] Refluxing Et_6Ge_2 with sodium in the presence of Et_3SiBr[49] or with sodium-naphthalene[127] gave only unreacted digermane. Me_6Ge_2 is unaffected by refluxing over potassium. Similarly, $Pr^i{}_6Ge_2$ is resistant to cleavage by lithium metal in refluxing 1,2-dimethoxyethane[13] and with Na/K alloy although Ge-C bonds were broken, the Ge-Ge bond remained intact.[9]

The solvent hexamethylphosphotriamide, $(Me_2N)_3PO$, has recently come into wide use as a solvent for cleavage reactions, and the use of potassium or lithium in this solvent gives high yields of R_3GeM from hexa-alkyldigermanes.[56] Other advantages of this solvent are the absence of ammonolysis reactions (which occur when liquid ammonia is used) and the greater reaction rate obtained compared with both ammonia and ethers, presumably due to the high solubility both of the metal and the digermane in $(Me_2N)_3PO$. Sodium reacts more slowly, being less soluble. A large number of ethylpolygermanes have been prepared starting from hexaethyldigermane in $(Me_2N)_3PO$.

$$Et_6Ge_2 + 2K \longrightarrow 2Et_3GeK$$

$$Et_3GeK + Et_5Ge_2Cl \longrightarrow Et_8Ge_3 + KCl$$

$$2Et_3GeK + Me_2GeCl_2 \longrightarrow (Et_3Ge)_2GeMe_2 + 2KCl$$

$$2Et_3GeK + (Et_2GeCl)_2 \longrightarrow Et_3Ge(GeEt_2)_2GeEt_3$$ [94]

$$Et_3GeM + Me_3GeX \longrightarrow Et_3GeGeMe_3 + Et_6Ge_2 + Me_6Ge_2$$

$$(M = Li,Na,K;\ X = F,Cl)^{56,94}$$

$$Bu^n{}_3GeK + Me_3GeCl \longrightarrow Bu_3GeGeMe_3 + KCl \quad ^{56}$$

For the reaction:

$$Et_3GeLi + Me_3GeX \xrightarrow{(Me_2N)_3PO} Et_3GeGeMe_3 + Me_6Ge_2 + Et_6Ge_2$$

it has been shown that the formation of the symmetrical by-products is not due to halogen-metal exchange (i.e. nucleophilic attack on halogen) but to nucleophilic attack of the germyl-alkali metal compound on the metal-metal bond of the mixed coupling product:[94]

$$Et_3Ge^-Li^+ + Me_3GeX \longrightarrow Et_3GeGeMe_3$$

$$Et_3Ge^-Li^+ + Et_3GeGeMe_3 \rightleftharpoons Et_6Ge_2 + Me_3Ge^-Li^+$$

$$Me_3Ge^-Li^+ + Et_3GeGeMe_3 \rightleftharpoons Me_6Ge_2 + Et_3Ge^-Li^+$$

$$Me_3Ge^-Li^+ + Me_3GeX \longrightarrow Me_6Ge_2$$

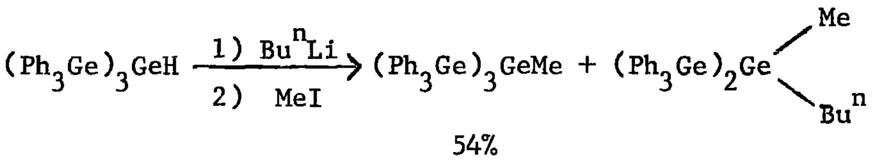
the two equilibria being established immediately on mixing the reagents, and for the overall reaction:

$$Me_3Ge_2Et_3 \overset{K}{\rightleftharpoons} Me_6Ge_2 + Et_6Ge_2$$

$K = 0{\cdot}1$. However, pure $Me_3Ge_2Et_3$ is apparently stable under these conditions towards disproportionation. The authors explain this as a kinetic effect, the disproportionation being catalysed by R_3GeM reagents and nucleophilic species in general (EtOK, PhLi etc.) which produce immediate equilibration.[128]

1:3:2:2 Organometallic Reagents

Some Ge-Ge bond cleavage occurs in the reaction between $(Ph_3Ge)_3GeH$ and Bu^nLi.[73]



Hexabenzyldigermane is, however, inert to butyl-lithium.[11] Hexaphenyldigermane is cleaved by PhLi in ether but the products were not identified.[116]

1:3:2:3 Halogens

Bromine readily cleaves both alkyl- and aryl-polygermanes giving bromogermanes. Reaction of Br_2 in refluxing CCl_4 with Ph_6Ge_2 gives only Ph_3GeBr[7,33], while in 1,2-dibromoethane some Ph_2GeBr_2 is also formed.

$$\mathrm{Ph_6Ge_2} \xrightarrow[\text{2) EtMgBr}]{\text{1) } \mathrm{Br_2/BrC_2H_4Br}} \underset{2\cdot7\%}{\mathrm{Et_2GePh_2}} + \underset{68\%}{\mathrm{Ph_3GeEt}} \quad {}^{73}$$

$$\mathrm{Ph_6Ge_2} \xrightarrow[\text{2) } \mathrm{LiAlH_4}]{\text{1) } \mathrm{Br_2/BrC_2H_4Br}} \underset{67\%}{\mathrm{Ph_2GeH_2}} + \underset{10\%}{\mathrm{Ph_3GeH}} \quad {}^{6}$$

Bromine cleaves octaphenyltrigermane at room temperature:

$$Ph_8Ge_3 \xrightarrow{Br_2/CCl_4} Ph_3GeBr + Ph_2GeBr_2 \quad ^{44}$$

Ph_6Ge_2 is not affected by iodine in refluxing chloroform and even from refluxing xylene 60% Ph_6Ge_2 was recovered, the only other product identified being 10% Ph_6Ge_2O.[116] The two cyclogermanes, $Ph_{10}Ge_5$ and $Ph_{12}Ge_6$ are also inert towards iodine in benzene, but the more reactive Ph_8Ge_4 is cleaved giving 1,4-di-iodo-octaphenyltetragermane.[91,92]

$$(GePh_2)_4 \xrightarrow[20^o]{I_2} I(GePh_2)_4I$$

The bromination (Br_2 in EtBr) of Et_6Ge_2 gives exclusively Et_3GeBr.[48] The cleavage of some alkylpolygermane Ge-Ge bonds with bromine is said to be explosive.[15] Hexavinyldigermane is cleaved by bromine or iodine to give the trivinylgermanium halide, without effecting the C=C double bond.

$$(CH_2{=}CH)_6Ge_2 \xrightarrow{Br_2} 2(CH_2{=}CH)_3GeBr \quad ^{4}$$

Brominative degradation has been much used as a method of investigating the structure of intractable organopolygermanes.[15,59,73] The results of such investigations must be treated with caution, because of the possibility of Ge-C bond cleavage also occurring. Meaningful results are often obtained with the lower polygermanes however:

$$R_2ClGe_2ClR_2 \xrightarrow{X_2} 2R_2GeClX \quad 117$$

distinguishing this compound from $R_3GeGeRCl_2$.

Cleavage by bromine has been used in the analysis of mixed hexaalkyldigermanes.

$$Me_3GeGeMe_2Et \xrightarrow{Br_2} Me_3GeBr + Me_2EtGeBr$$

In this reaction, and that with $Me_7Ge_2Pr^n$, the bromogermanes were formed in the 1:1 ratio expected. Octamethyltrigermane gives a 2:1 ratio of bromide and dibromide.

$$Me_8Ge_3 \longrightarrow 2Me_3GeBr + Me_2GeBr_2$$

A reaction between $GeCl_4$ and a MeLi/EtLi mixture gave $EtMe_7Ge_3$ as one fraction. There are two possible isomers with this formula, and bromination showed that a mixture of the two was present in a 3:1 ratio, as expected for a random distribution between $EtMe_2GeGe_2Me_5$ and $EtMeGe(GeMe_3)_2$.

$$EtMe_7Ge_3 \xrightarrow[2)\ Bu^nMgCl]{1)\ Br_2} Me_3GeBu^n + Me_2GeEtBu^n + Me_2GeBu^n{}_2 + GeMeEtBu^n{}_2$$

The agreement between duplicate determinations was about 10%. The same technique was used to analyse the isomer ratios for $Et_2Me_4Ge_2$, $Et_3Ge_2Me_3$, $Me_4Ge_2Pr^n{}_2$ and $Pr^i{}_2Ge_2Me_4$ from mixed Grignard reagents. The results showed that for the Grignard reaction, the isomer ratios were not as expected for a completely random distribution.[15]

The two phases formulated as $(GeH_2)_x$ and $(GeH)_x$ react with halogens to give GeX_4.[106,109]

1:3:2:4 Oxygen

As far is known, all fully organo-substituted polygermanes are stable in air. Ph_6Ge_2 does not react with oxygen in refluxing benzene[116] and Ph_8Ge_3 is stable towards moist air.[44] Hexavinyldigermane is said to be "moderately" stable in air.[4] It is to be expected that functionally substituted polygermanes will be stable in air only if the corresponding substituted monogermanes are. Thus $Bu_3Ge_2Bu_2H$ is air-sensitive,[117] and Ge_2H_6 and Ge_3H_8 react slowly with oxygen and water[95], digermane rapidly at 100°.

$$2Ge_2H_6 + 7O_2 \longrightarrow 4GeO_2 + 6H_2O$$

Monogermane reacts only slowly with oxygen at 160-183°. The lower hydride phases, formulated as $(GeH_2)_x$ and $(GeH)_x$ were said to react explosively with air.[106,109] The combustion of Me_6Ge_2 has been studied.[129]

1:3:2:5 Acids

Phenylgermanium polymers, in which there is probably extensive metal-metal bonding, takes fire in concentrated nitric acid.[73] Me_6Ge_2 is not attacked appreciably by concentrated H_2SO_4.[51] The telomers $Me(Me_2Ge)_nMe$ are degraded by dry HCl at 200-250° giving Me_2GeCl_2 and Me_2GeHCl.[86] With boiling aqueous HCl, $(GeH_2)_x$ yields H_2, Ge, GeH_4,

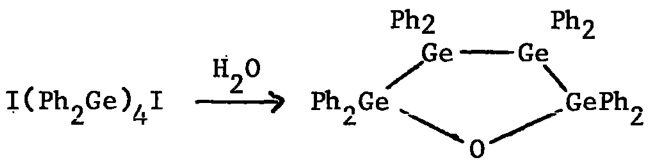
Ge_2H_6 and Ge_3H_8.[106] HCl slowly cleaves the Ge-Ge bond in Ge_2H_6, only in the presence of $AlCl_3$, not alone. Ge_2H_6 also reacts with BCl_3.[119]

1:3:2:6 Alcoholic Silver Nitrate

Hexaphenyldigermane reacts slowly with boiling alcoholic silver nitrate.[46] Alkylpolygermanes might well be more reactive, but there is no experimental evidence.

1:3:2:7 Aqueous Alkali

It has been shown that the by-products Et_6Ge_2 and Me_6Ge_2 which occur in the preparation of $Me_3GeGeEt_3$, arise from nucleophilic attack on the Ge-Ge bond, and that the disproportionation is catalysed by nucleophiles. From this it might be expected that Ge-Ge bonds would be susceptible to attack by aqueous alkali. Ph_6Ge_2 is not affected by boiling aqueous alkali, however, but this may be due to the insolubility of the digermane in the reagent.[46] Hexa-β-styryl-digermane reacts slowly with aqueous NaOH.[19] The Ge-I bonds in 1,4-di-iodo-octaphenyl-tetragermane are hydrolysed without appreciable cleavage of the Ge-Ge bonds.[91,92]



1:3:3 Substitution Reactions

Reactions which lead to the replacement of groups attached to germanium by new groups, without cleavage of Ge-Ge bonds, are discussed in this section.

1:3:3:1 Redistribution Reactions

Redistribution reactions of substituted monogermanes have been widely investigated. Less work has been done with polygermanes, but there are indications that this could be a most important method for preparing functionally substituted polygermanes, and so of increasing chain length in a more predictable fashion than has been possible hitherto.

Redistributions of general type:

$$R_4Ge + GeCl_4 \longrightarrow R_3GeCl + RGeCl_3$$

have been studied extensively[71], and GeI_2 is one of many catalysts for these systems. Similar reactions have been carried out with digermanes:

$$Et_6Ge_2 + GeCl_4 \longrightarrow Et_5Ge_2Cl$$

$$Bu^n{}_6Ge_2 + GeCl_4 \xrightarrow{200^o} \underset{60\%}{Bu^n{}_3GeGeBu^n{}_2Cl} + Bu^nGeCl_3 \qquad 117$$

$Bu^n{}_4Ge$ does not react under these conditions so that the Ge-C bond in the digermane is more reactive than in the monogermane. Furthermore, Bu_6Ge_2 catalyses the redistribution of $Bu^n{}_4Ge$ and $GeCl_4$. At 250° some Ge-Ge bond cleavage occurs. From the study of monogermanes[71] it was concluded that substitution of Cl for C took place more quickly on the species with most R groups. It is not surprising, therefore, that further substitution in R_3GeGeR_2Cl should give the symmetrical compound.[117] As well as using 2 moles

$$R_6Ge_2 \xrightarrow{GeCl_4} R_3GeGeR_2Cl \xrightarrow{GeCl_4} ClR_2GeGeR_2Cl$$

of $GeCl_4$ per mole of digermane, it is necessary to prolong the reaction or use GeI_2 as a catalyst to effect this further substitution. CCl_4, $SiCl_4$ and $SnCl_4$ were also tried as halogenating reagents, and $SnCl_4$ was the most successful for the preparation of $R_4Ge_2Cl_2$.

Possible mechanisms for these redistribitions have been discussed at length, but there is really insufficient data for firm conclusions.

A similar sort of reaction is that between digermanes and alkyl-halides, but here a catalyst (AlX_3) is required.

$$Et_6Ge_2 + Pr^iBr \xrightarrow{AlCl_3} Et_5Ge_2Br + Et_4Ge + Et_3GeBr + tar$$

Disproportionation of Et_6Ge_2 occurs on heating with aluminium bromide alone.

$$Et_6Ge_2 \xrightarrow{AlBr_3} Et_4Ge\ (45\%) + tar$$

32·6% Et_6Ge_2 remained unchanged after 15 hr. The tar contained 1·04 ethyl groups per germanium, was stable to atmospheric oxygen (which suggests it does not contain Ge^{II}) and had no unpaired electrons (ESR). It was thought to contain many multi-germanium-germanium bonds. Similar results were obtained with $AlCl_3$.[130]

Unlike Et_6Ge_2, hexamethyldigermane does not react with Pr^iBr in the presence of $AlBr_3$,[60] although Me_4Ge does. With a halopolygermane it is the alkyl group of the alkyl halide which is transferred to germanium.

$$I(GePh_2)_4I + 2MeI \longrightarrow Me(Ph_2Ge)_4Me$$ [92]

Digermane reacts with iodine without apparent cleavage of the Ge-Ge bond,

$$Ge_2H_6 + I_2 \xrightarrow{-63^{\circ}} Ge_2H_5I + HI$$ [118]

but with bromine there is extensive cleavage to give GeH_2Br_2.[119] Iododigermane exchanges halogen with silver chloride[116], or bromide.[119]

$$Ge_2H_5I + AgX \xrightarrow{0^{\circ}} Ge_2H_5X + AgI$$

Digermane itself will react with AgCl or AgBr

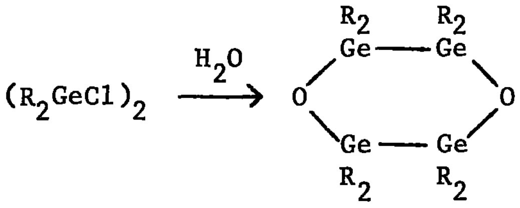
$$Ge_2H_6 + AgX \longrightarrow Ge_2H_5X + Ag + \tfrac{1}{2}H_2$$

but some cleavage of the Ge-Ge bond occurs with AgBr.[119]

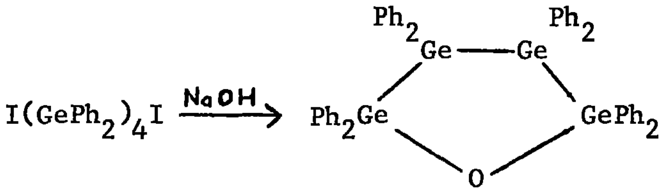
1:3:3:2 Hydrolysis

As with monogermanes, the Ge-C bond is not susceptible to hydrolysis. Germanium-halogen bonds can be hydrolysed.

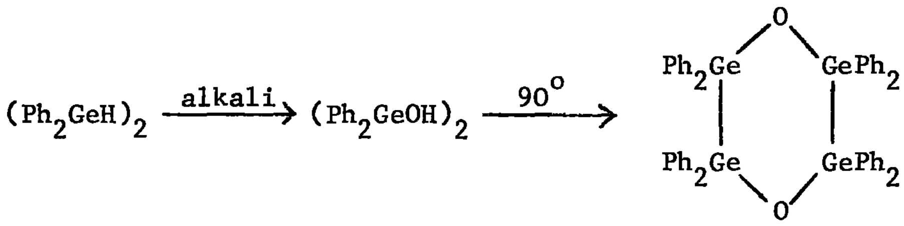
$$R_3GeGeR_2Cl \xrightarrow{H_2O} (R_3GeGeR_2)_2O$$



The nature of R and the conditions were not specified.[117] With longer germanium chains, cyclisation can take place on hydrolysis with incorporation of only one oxygen atom.[91,92]



The Ge-H bond is also hydrolysable.



1:3:3:3 Reduction

Halopolygermanes behave in a similar fashion to the monogermanes.

$$(Ph_2GeBr)_2 \xrightarrow{LiAlH_4} (Ph_2GeH)_2$$

$$I(Ph_2Ge)_4I \xrightarrow{LiAlH_4} H(Ph_2Ge)_4H \quad {}^{131}$$

$$Bu_3Ge_2(Cl)Bu_2 \xrightarrow{LiAlH_4} Bu_3Ge_2Bu_2H$$ [117]

1:3:3:4 Organometallic Compounds

Organolithium compounds alkylate halopolygermanes satisfactorily,

$$(Ph_2GeBr)_2 \xrightarrow{MeLi} (Ph_2GeMe)_2$$ [127]

$$I(Ph_2Ge)_4I \xrightarrow{PhLi} Ph(GePh_2)_4Ph$$ [91,92]

and so do Grignard reagents.

$$Bu_5Ge_2Cl \xrightarrow{MeMgBr} Bu_5Ge_2Me$$ [117]

Wurtz coupling can be effected.

$$2Et_3GeGeEt_2Cl + 2M \longrightarrow Et(GeEt_2)_4Et + 2MCl$$ [94]

Even iododigermane can be alkylated by means of a Grignard reagent.

$$Ge_2H_6 \xrightarrow{I_2} Ge_2H_5I \xrightarrow{EtMgBr} EtGe_2H_5$$

The product was also synthesized by hydrogermylation of ethylene, but the reaction was quite complicated, giving among other compounds Ge_3H_8;

$$Ge_2H_6 + C_2H_4 \longrightarrow EtGe_2H_5$$

1,1-$Et_2Ge_2H_4$; 1,2-$Et_2Ge_2H_4$; 2-$EtGe_3H_7$; 1-$EtGe_3H_7$; n-Ge_4H_{10} and 1,1,2-$Et_3Ge_2H_3$.[132]

1:3:4 Spectroscopic Properties

These are discussed in Part II of this Thesis.

1:3:5 Uses

Up to now, germanium-germanium bonded compounds have found very little use outside the laboratory. Hexacyclohexyldigermane is said to reduce static charge in synthetic polymer filaments when small amounts are added during polymerisation.[133]

2. Experimental Investigations: Alkylation of Germanium Halides by Alkylaluminium Compounds

2:1 Discussion

The alkylation of germanium tetrachloride and of germanium di-iodide will be described separately. Certain problems common to both reactions will be discussed under the alkylation of germanium di-iodide.

2:1:1 Germanium Tetrachloride

Prior to this investigation, work on the alkylation of germanium tetrachloride by alkylaluminium compounds was confined to triethyl- and tri-isobutyl-aluminium and ethylaluminium sesquibromide. Furthermore this work showed only that the main product of the reaction was the tetra-alkylgermane, except in one case in which it was claimed that diethyldichlorogermane could be prepared (Section 1:1:3). The absence of information on side-reactions meant that no meaningful comparison could be made with Grignard and organolithium reactions.

The results described here indicate that, as in the Grignard and organolithium syntheses, the use of organoaluminium reagents leads to the formation of di- and poly-germanes as by-products. Complications due to partial alkylation of the germanium tetrachloride seem, however, to be absent, as no alkylchlorogermanes were isolated. In all cases however unreacted germanium tetrachloride was recovered. These observations are consistent with the rate of monoalkylation being slower than subsequent stages, in contrast with the Grignard reaction, where substitution of the fourth halogen atom is usually the slowest step,[18] but in keeping with redistribution studies on alkylgermanium compounds (Section 1:3:3:1)

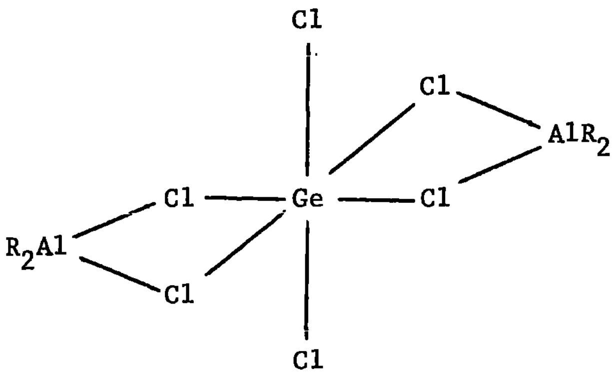
$$(R_3Al)_2 + GeCl_4 \xrightarrow{\text{slow}} RGeCl_3 + R_5Al_2Cl$$

$$RGeCl_3 + (R_3Al)_2 \xrightarrow{\text{fast}} R_2GeCl_2 + R_5Al_2Cl$$

$$2R_2GeCl_2 \rightleftharpoons R_3GeCl + RGeCl_3$$

$$R_3GeCl + (R_3Al)_2 \longrightarrow R_4Ge + R_5Al_2Cl$$

This will lead to an accumulation of partially chlorinated aluminium compounds in the reaction mixture, which still contains appreciable $GeCl_4$. It is quite possible that, at this stage, formation of 6-coordinate halogen-bridged complexes between $(R_2AlCl)_2$ and $GeCl_4$ would occur. Germanium tetrachloride is known to form octahedral complexes (such as $GeCl_6^{2-}$), but substitution of Cl by R greatly reduces the acceptor power of the germanium.[134] Because of this last fact, any

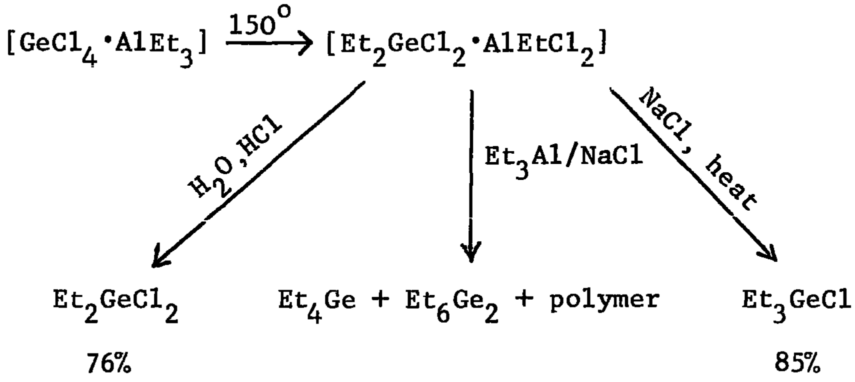


transfer of R to the germanium would cause immediate disruption of the complex,and the $RGeCl_3$ liberated would be rapidly alkylated. In the final distillation, the complex is destroyed and the $GeCl_4$ driven off.

Evidence for the formation of similar complexes has been published since this work was completed. It was found that on mixing triethylaluminium and germanium tetrachloride in the absence of sodium chloride, heat was evolved. After 3-5 hrs. at 130°, a sudden evolution of heat and a deepening in colour occurred. Distillation at this point removed the surplus $GeCl_4$, leaving the reagents in a 1:1 mixture. Diethylgermanium dichloride could then be distilled from the mixture with some Et_3GeCl. Further distillation gave another substance which on hydrolysis yielded Et_2GeCl_2, and from which $AlCl_3$ could be obtained by vacuum distillation. The authors suggested the formation of a complex (of unspecified structure).

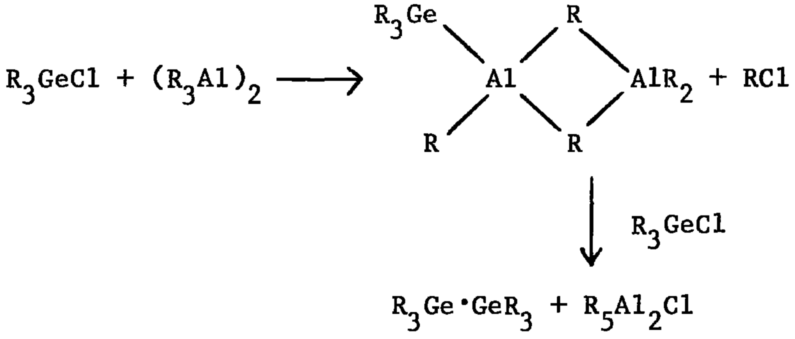
$$GeCl_4 + Et_3Al \longrightarrow [GeCl_4{\cdot}AlEt_3]$$

This rearranges.



It was claimed that analogous results were obtained with $Et_3Al_2Cl_3$, Pr^n_3Al, Bu^i_3Al and Bu^i_2AlCl. The authors further stated that using the conditions obtaining in the present work, these phenomena did not occur i.e. at lower temperatures and in the presence of sodium chloride, the only product isolated was Et_4Ge.[135]

In all of the systems studied, di- and poly-germanes were evident, and the proportion formed increased in the order Me $<$ Et $<$ Bu^i. There are several possible routes to their formation. The most obvious is by way of reactive intermediates containing a Ge-Al bond, analogous to germyl-Grignard and germyl-metal compounds.



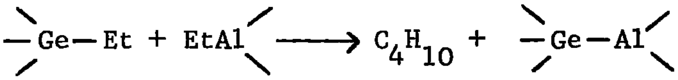
Such complexes would have to be highly reactive; they are not present immediately prior to hydrolysis, since no R_3GeH is formed. In the methyl and ethyl reactions, traces of methyl and ethyl chloride respectively, were in fact detected. No isobutyl chloride was obtained from the isobutyl reactions, despite the fact that more coupling was apparent in these than in the other reactions. Isobutane was a product, and it is possible that in this case any isobutyl chloride formed is reduced to the alkane, either by $(Bu^i{}_2AlH)_2$ or an isobutylgermanium hydride.[136] Such reducing agents were certainly formed in the reactions of tri-isobutylaluminium at elevated temperatures. At room temperature, no reduction products were isolated, but the proportion of digermane in this reaction was increased. Thus the explanation is not entirely satisfactory. A clue to the resolution of this difficulty may be in the observation that isobutyl chloride in the presence of aluminium chloride will dephenylate trimethylphenylgermane.[60] So the following reaction is a possibility

$$Bu^i{}_4Ge + Bu^iCl \longrightarrow Bu^i{}_3GeCl + C_8H_{18}$$

It is interesting to note the differences in behaviour of tetramethyl- and tetraethyl-germane on the one hand and tetraisobutylgermane on the other, towards dealkylation by iodine in the presence of aluminium iodide.[137]

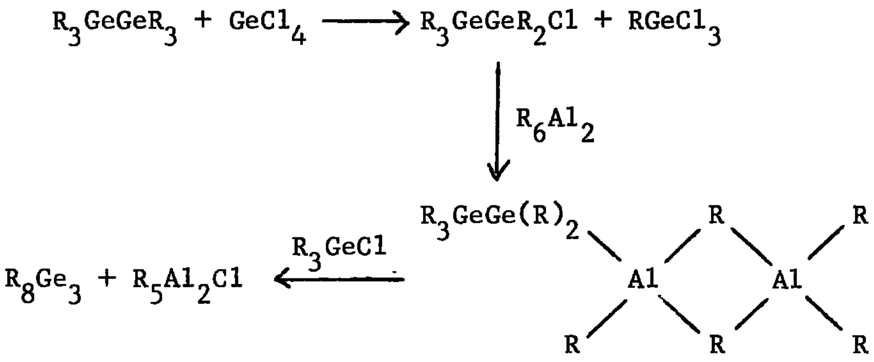
$$\begin{tikzcd}[row sep=small] & R_3GeI + RI \qquad (R = Me,Et) \\ R_4Ge + I_2 + AlI_3 \arrow[ur] \arrow[dr] & \\ & R_3GeI + R_2 \qquad (R = Bu^i) \end{tikzcd}$$

In the recent paper described above, di- and poly-germanes were isolated from a triethylaluminium preparation of tetraethylgermane, and the route suggested to the germyl-aluminium intermediate was:[135]



n-butane having been observed as a by-product of the reaction.

The formation of organopolygermanes would require some sort of redistribution, (Section 1:3:3:1), followed

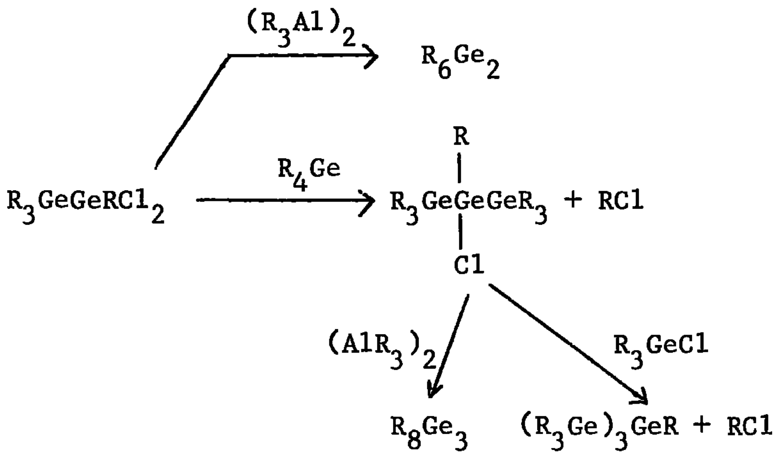


by a second coupling reaction, and so on. The actual structures of the tetra- and higher-germanes were not determined, but products from the GeI_2 reactions were highly branched. Recent work[135] suggests that $Et_{10}Ge_4$ formed as a by-product in triethylaluminium reactions with $GeCl_4$ is the branched isomer, but the structure determination (by brominative degradation) is suspect since besides Et_3GeBr, Et_2GeBr_2 and $EtGeBr_3$, some ethylbromide was obtained.

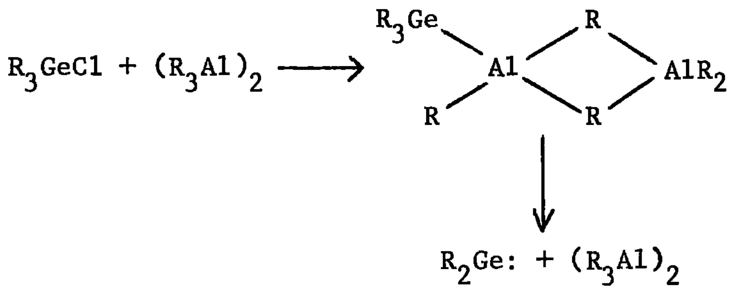
A second route to polygermanes involves a $Ge^{IV} \rightarrow Ge^{II}$ reduction.

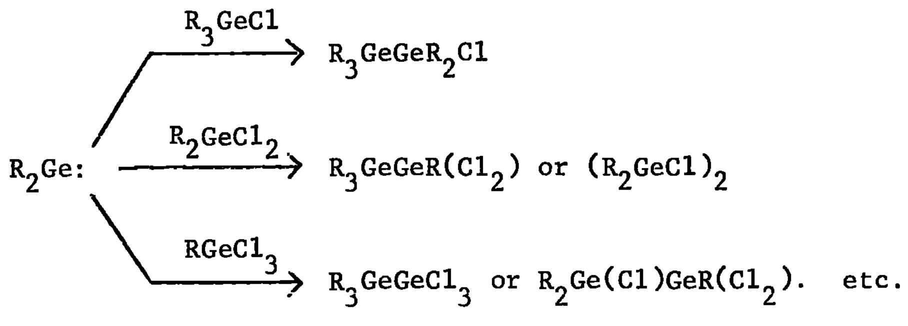
$$RGeCl_3 \longrightarrow GeCl_2 + RCl \xrightarrow{R_4Ge} R_3GeGeRCl_2$$

In this case, the aluminium compounds present would play no part at all, except as alkylating reagents. The formation of organopolygermanes from this intermediate follows easily.



A third possible route has features of both the other two.





In this connection, the following observations[138] are pertinent.

$$\begin{tikzcd}
3(Me_3Si)_2Hg + 2Al \arrow[r] & 2(Me_3Si)_3Al + 3Hg \arrow[d] \\
Me_2AlSiMe_3 \arrow[r] & AlMe_3 + :SiMe_2 \arrow[d, "(Me_3Si)_2Hg"] \\
 & Me_8Si_3 + Me(SiMe_2)_4Me
\end{tikzcd}$$

It will be appreciated that the differences arising from these processes are marginal, and no decision among them is possible on the evidence available. All of the schemes involve elimination of alkylchloride, and participation of alkylchlorogermanes, which must be present as transitory intermediates in the main alkylation process, and which in any case are available by redistribution between R_4Ge and $GeCl_4$. The increase in proportion of di- and poly-germanes formed in the series Me < Et < Bu^i may be a result of the decreased reactivity of the alkylaluminium compound, and therefore of a slower rate for the main reaction.

2:1:1:1 Methylaluminium Compounds and Germanium Tetrachloride

For the methylaluminium reagents, some conclusions additional to the general ones already discussed, were reached. In the Me_3Al-$GeCl_4$ system, addition of sodium chloride increased the reaction rate, but not the yield of tetramethylgermane. The use of ethereal solvents leads to undesirable complications.

Reaction of germanium tetrachloride with a 1•5-fold excess of trimethylaluminium (based on $4Me_3Al + 3GeCl_4 \longrightarrow 3Me_4Ge + 4AlCl_3$) gave, after 4hr. reflux, a 46% yield of tetramethylgermane. Continued reflux gave more Me_4Ge (21% after 3 hr. and 14% after a further 4 hr.). Even after this period, 5% of unreacted $GeCl_4$ was isolated, together with methyl chloride but there was no evidence for methylchlorogermanes. Increasing the initial reflux period (6 hr. at 120^o) with a 2·3-fold excess of Me_3Al gave Me_4Ge in 70% yield. Again a further period of reflux gave Me_4Ge (8%) together with 13% unreacted $GeCl_4$. Hydrolysis of residues gave hexamethyldigermane in low yield, and a trace of ethylpentamethyldigermane, and probably propylpentamethyldigermane. The formation of these last two compounds will be discussed later together with that of all such compounds. A 1·1-fold excess of trimethylaluminium and germanium tetrachloride, at a slightly lower temperature (100^o)gave, after 2 hr., 33% Me_4Ge. A further 7 hr. reflux gave 2% Me_4Ge and 9% $GeCl_4$. Addition of more Me_3Al gave finally a total yield of 52% Me_4Ge and 20% recovered $GeCl_4$. Refluxing a 1·1-fold excess of Me_3Al with $GeCl_4$ for 38 days gave 57% Me_4Ge and 8% $GeCl_4$.

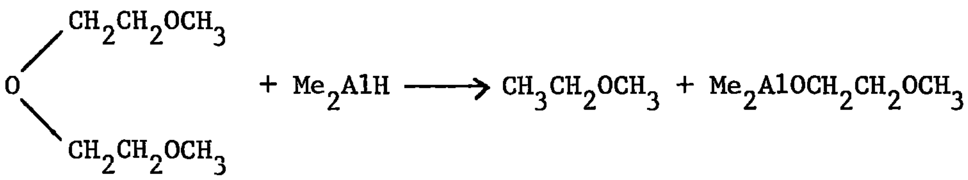
When sodium chloride was added to mixtures of $GeCl_4$ and excess of Me_3Al, tetramethylgermane could be isolated in 73% yield after only 30 min. reflux, but again there was unreacted germanium tetrachloride present and further reflux did not produce Me_4Ge. Again Me_6Ge_2 was isolated. The accelerating effect of sodium chloride probably relates to the displacement of equilibria by the formation of sodium tetrachloraluminate,[139] and this effect was most apparent with methylaluminium sesquichloride. In the absence of NaCl 22% of Me_4Ge was formed after 5 hr. reflux, but after adding the theoretical quantity of NaCl, the total conversion to Me_4Ge was 75%. Even with added sodium chloride, a mixture of trimethylaluminium and germanium tetrachloride heated for 30 min. at only 70° gave a much reduced yield (17%) of tetramethylgermane. However, yields of tetramethylgermane seemed to be very dependent on work up procedures. Thus distillation through a packed column gave good fractionation, but a Vigreau column was insufficient. Reaction in a sealed tube at 80° for one month gave 76% Me_4Ge, a little $GeCl_4$, and some hydrogen, methane, and carbon.

Excess germanium tetrachloride reacted with a mixture of trimethylaluminium and sodium chloride gave 25% Me_4Ge after 30 min. at 100°, and 61% $GeCl_4$ was recovered. A little propane was detected, together with methyl chloride. Hydrolysis of the residue gave a mixture of Me_8Ge_3, Me_7Ge_3Et, $Me_6Ge_3Et_2$ or Me_7Ge_3Pr, $Me_{10}Ge_4$, Me_9Ge_4Et and $Me_{12}Ge_5$.

A 2·2-fold excess of trimethylaluminium with $GeCl_4$ and NaCl gave, after 30 min. at 110°, 43% Me_4Ge with a trace of Me_3GeH. Continued reflux at 140° for a futher hour gave another 18% Me_4Ge, but no more trimethylgermane. With a 13·1-fold excess of Me_3Al, 72% Me_4Ge containing some trimethylgermane was obtained. With a 9·4-fold excess, 78% Me_4Ge containing less than 10% Me_3GeH was formed. Hydrolysis of the residue gave a mixture of Me_8Ge_3, $Me_{10}Ge_4$, $Me_{12}Ge_5$ and $Me_{14}Ge_6$

together with some compounds which might be ethyl-containing. The formation of trimethylgermane in these reactions will be discussed later, when the formation of ethyl groups is considered.

Addition of ethers in the reaction of tin tetrachloride with aluminium alkyls enhances the yield of the tetra-alkyl, due to the preferential formation of stable complexes of the type $AlCl_3 \cdot OEt_2$.[139] As the addition of sodium chloride to the $GeCl_4$ reactions was most effective with methylaluminium sesquichloride, the reaction of this with germanium tetrachloride in diethylether and diglyme was tried. Only 10% of mixed methylgermanium chlorides was obtained. With added sodium chloride in diglyme, a 65% yield of tetramethylgermane was obtained, together with solvent cleavage products, including β-chloroethylmethylether. Ether cleavage of this type has been noted in similar systems. Thus ethylmethylether was isolated from the reaction between dimethylaluminium hydride and diglyme.[140]



$$O(CH_2CH_2OCH_3)_2 + Me_2AlH \longrightarrow CH_3CH_2OCH_3 + Me_2AlOCH_2CH_2OCH_3$$

It has been established that ethers form adducts with alkylaluminium compounds, as well as with aluminium chloride (e.g. Me_3Al, Me_2AlCl, and $MeAlCl_2$ all form several complexes with diglyme[140]), and it may well be that for the two ethers studied here, the difference in stability between the $AlCl_3$-ether complex and the other complexes possible, is insufficient to drive the reaction towards completion.

The reaction between trimethylaluminium and germanium tetraiodide in methylcyclohexane at 100^o gave, after 5 hr. reflux, 21% tetramethylgermane. No other organogermanes were isolated.

To sum up, it may be said that for the preparation of tetramethylgermane, the use of trimethylaluminium has three advantages over the Grignard reaction. Firstly, the aluminium compound may be bought, whereas the Grignard reagent must be prepared; secondly with sodium chloride added the reaction is rapid and the by-products are minor and easily left behind by a simple fractionation, and thirdly no solvent need be used.

2:1:1:2 Triethylaluminium and Germanium Tetrachloride

The system triethylaluminium-germanium tetrachloride-sodium chloride in the absence of solvent gave tetraethylgermane in 77% yield after 30 min. reflux. There were indications that prolonged periods of reflux reduced the yield, giving more di- and poly-germanes. Unreacted $GeCl_4$ was always recovered. Even when a 2-fold excess of $GeCl_4$ was used, the products were tetraethylgermane and unreacted $GeCl_4$, and not the ethylchlorogermanes. (This conclusion has since been confirmed by other workers[135]). Similarly, rapid addition of germanium tetrachloride to cold triethylaluminium did not lead to ethylchlorogermanes. This again indicates that monoalkylation of $GeCl_4$ is the slow stage. These reactions gave ethyl chloride as a by-product, as well as Et_6Ge_2, Et_8Ge_3 and $Et_{10}Ge_4$, and compounds of the type Et_3GeBu^n, $Et_3Ge(C_6H_{13})$, $Et_3Ge_2Et_2Bu$, $Et_3Ge_2Et_2(C_6H_{13})$, $Et_7(Bu)Ge_3$ and $Et_7(C_6H_{13})Ge_3$.

2:1:1:3 Tri-isobutylaluminium and Germanium Tetrachloride

The system tri-isobutylaluminium-germanium tetrachloride-sodium chloride shows some extra features. At 60-80° over 3 days the reaction paralleled those of the methyl and ethyl reagents; tetraisobutylgermane (44%) and unreacted $GeCl_4$ (26%) were isolated together with a much higher proportion of isobutylpolygermanes, mainly $Bu^i_6Ge_2$ (21%) and some butane. At a higher temperature (140-150°) additional reactions occur due to thermal decomposition of the aluminium alkyl.

$$2Bu^i_3Al \longrightarrow (Bu^i_2AlH)_2 + 2C_4H_8$$

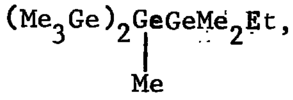
The rate of reduction of Ge-Cl bonds by di-isobutylaluminium hydride is competitive with the rate of alkylation, and germane and isobutylgermane were among the reaction products. Analogous compounds were obtained from the tri-isobutylaluminium-silicon tetrachloride system.[139] The reactions appeared to be much slower than those with the methyl and ethyl compounds, and greater proportions of $GeCl_4$ were recovered unreacted. The amount of isobutylpolygermane formed was always considerable and included $Bu^i_6Ge_2$, $Bu^i_8Ge_3$ and $Bu^i_{10}Ge_4$ in decreasing quantities.

2:1:2 Germanium Di-iodide

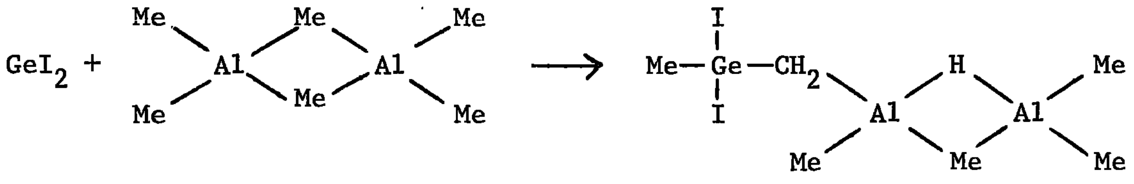
The reaction between germanium-(II) iodide and triphenylaluminium etherate has been described as giving phenylgermanium polymers containing residual iodine (Section 1:2:1). With the more reactive trimethyl- and triethyl-aluminium complete displacement of the iodine occurs giving fully alkylated oligomers. Polymeric oxides were obtained on hydrolysis, presumably from any remaining Ge-I bonds. Tri-isobutylaluminium is less reactive, iodine-containing oligomers being formed, and these survive hydrolysis.

Unlike the germanium-(IV) halides, germanium di-iodide would be expected to give di-alkylgermanium polymers, and the real problem here is to discover how the end groups arise, since no cyclic compounds were isolated. As with the germanium tetrachloride reactions, ethyl-containing compounds were obtained from the methyl reactions.

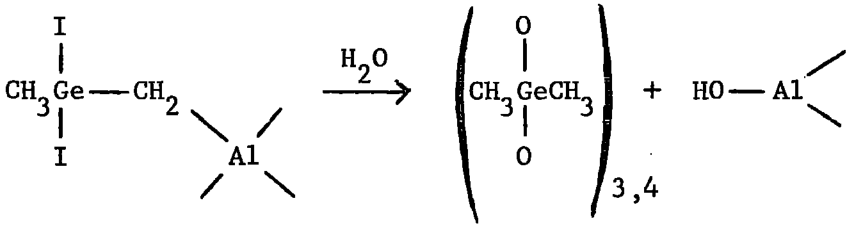
2:1:2:1 Trimethylaluminium and Germanium Di-iodide

The reaction of trimethylaluminium with germanium di-iodide is essentially the same whether carried out at room temperature or 120°. No tri- or tetra-methylgermane is formed, but a colourless viscous liquid is recovered on hydrolysis of the reaction mixture. This is separated by alumina chromatography into two main fractions, the first being a mixture of methylgermanium oligomers, and the second a mixture of dimethylgermanium oligomeric oxides including $(Me_2GeO)_n$, where n is 4 and probably 3 also. A small amount of material was obtained, which appeared to be unsaturated, since on exposure to air it became opalescent and viscous. Mass spectrometric examination of this showed it to contain a greater proportion of oxygen than the $(Me_2GeO)_n$ oligomers. Vacuum distillation of the polygermane further separated this, and preparative gas-liquid chromatography on the more volatile fraction gave a variety of compounds. These were shown, by mass spectrometry, to be $Me_{10}Ge_4$, Me_9Ge_4Et, Me_9Ge_4Pr, $Me_8Ge_4Et_2$, $Me_{12}Ge_5$, $Me_{11}Ge_5Et$ and $Me_{14}Ge_6$. The exact structure of some of these was elucidated by proton magnetic resonance spectroscopy, showing them to be $(Me_3Ge)_3GeMe$,  $(Me_3Ge)_2Ge(Me)GeMe_2Et$, $Me(GeMe_2)_5Me$, $(Me_3Ge)_2Ge(Me)Ge(Me)_2GeMe_3$, $(Me_3Ge)_2Ge(Et)Ge(Me)_2GeMe_3$, $Me(GeMe_2)_3Ge(Me)(GeMe_3)_2$, $(Me_3GeGeMe_2)_2Ge(Me)GeMe_3$, $((Me_3Ge)_2GeMe)_2$ and $Me(GeMe_2)_6Me$. The less volatile fraction was shown by mass spectrometry to contain $Me_{14}Ge_6$, $Me_{16}Ge_7$, $Me_{18}Ge_8$, $Me_{20}Ge_9$ and $Me_{22}Ge_{10}$.

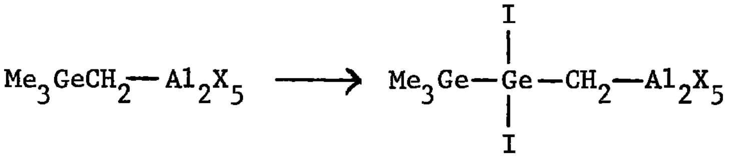
A mechanism can be written to explain these facts but it is essentially speculative. The initiating step is the formation of a methylene-bridged aluminium-germanium complex.



For aluminium compounds containing one or fewer Al-H bonds for each aluminium, the Al-H bond is much less reactive than the Al-R bond, because the hydrogen forms a stronger bridging group than does an alkyl group.[141] Since a large excess of trimethylaluminium was present in these reactions, no transfer of H from Al to Ge would be expected. Any of this complex remaining at the hydrolysis stage would be converted to the oligomeric dimethylgermanium oxide, and aluminium hydroxide.



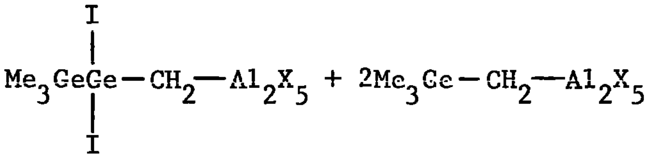
Exchange of the iodine atoms for methyl groups leads to Me_3Ge CH_2 Al , and this is followed by insertion



$$Me_3GeCH_2—Al_2X_5 \longrightarrow Me_3Ge—GeI_2—CH_2—Al_2X_5$$

where X is Me and/or I and not more than 2H.

The two iodine atoms are then exchanged for methyl or trimethylgermyl groups. In the latter case:



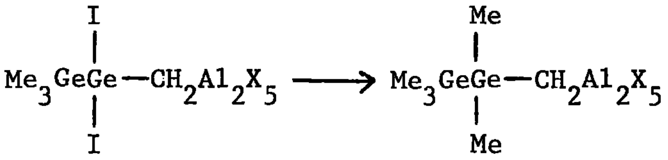
$$Me_3GeGeI_2—CH_2—Al_2X_5 + 2Me_3Ge—CH_2—Al_2X_5$$

$$\longrightarrow (Me_3Ge)_3GeCH_2Al_2X_5 + 2ICH_2Al_2X_5$$

On hydrolysis the main product of the reaction is obtained.

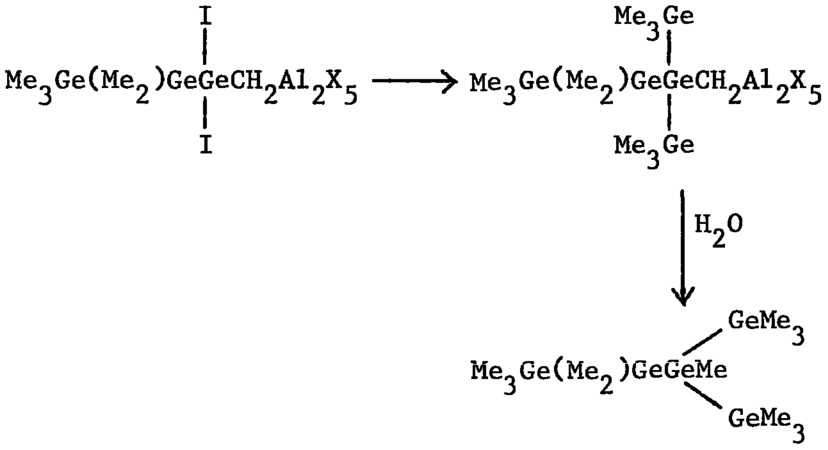
$$\mathrm{(Me_3Ge)_3GeCH_2Al_2X_5} \xrightarrow{\mathrm{H_2O}} \mathrm{(Me_3Ge)_3GeMe} + \mathrm{HOAl}<$$

The other products containing only methyl groups are formed in similar ways,

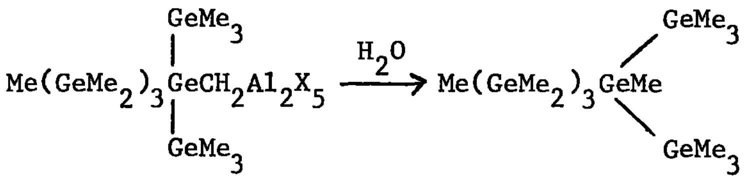


$$\mathrm{Me_3Ge}\overset{\mathrm{I}}{\underset{\mathrm{I}}{\mathrm{Ge}}}\mathrm{{-}CH_2Al_2X_5} \longrightarrow \mathrm{Me_3Ge}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Ge}}}\mathrm{{-}CH_2Al_2X_5}$$

and this is repeated a number of times to give $\mathrm{Me(GeMe_2)_n{-}CH_2{-}Al_2X_5}$ which on hydrolysis forms $\mathrm{Me(GeMe_2)_nMe}$. Routes to branched compounds are readily envisaged.

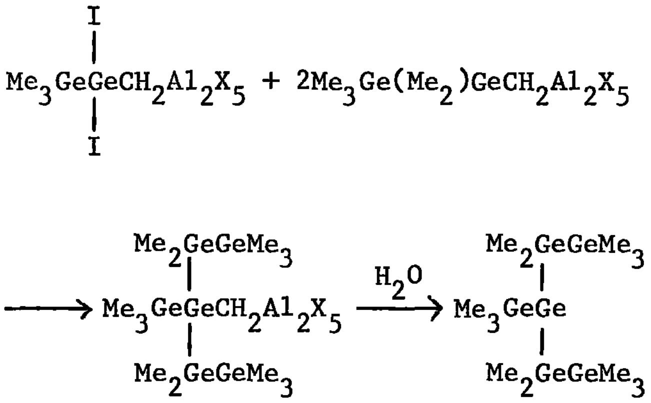


A longer chain compound of this type would be formed similarly.



$$\mathrm{Me(GeMe_2)_3\overset{\displaystyle GeMe_3\atop|}{\underset{\displaystyle |\atop GeMe_3}{Ge}}CH_2Al_2X_5 \xrightarrow{H_2O} Me(GeMe_2)_3\overset{\displaystyle GeMe_3\atop /}{\underset{\displaystyle \backslash\atop GeMe_3}{GeMe}}}$$

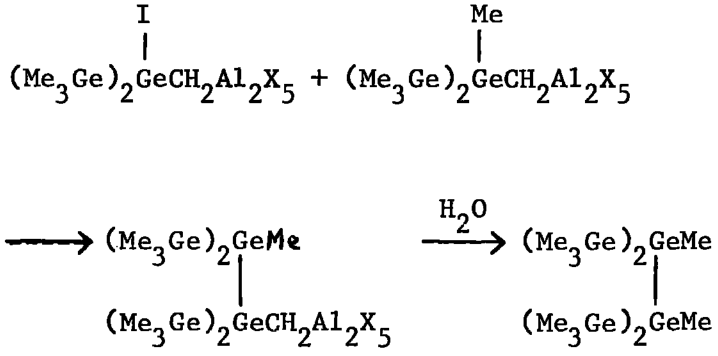
Combination of intermediates at various stages of development leads to more highly branched products.



$$\mathrm{Me_3Ge\overset{\displaystyle I\atop|}{\underset{\displaystyle |\atop I}{Ge}}CH_2Al_2X_5 + 2Me_3Ge(Me_2)GeCH_2Al_2X_5}$$

$$\longrightarrow \mathrm{Me_3Ge\overset{\displaystyle Me_2GeGeMe_3\atop|}{\underset{\displaystyle |\atop Me_2GeGeMe_3}{Ge}}CH_2Al_2X_5 \xrightarrow{H_2O} Me_3Ge\overset{\displaystyle Me_2GeGeMe_3\atop|}{\underset{\displaystyle |\atop Me_2GeGeMe_3}{Ge}}}$$

Likewise:

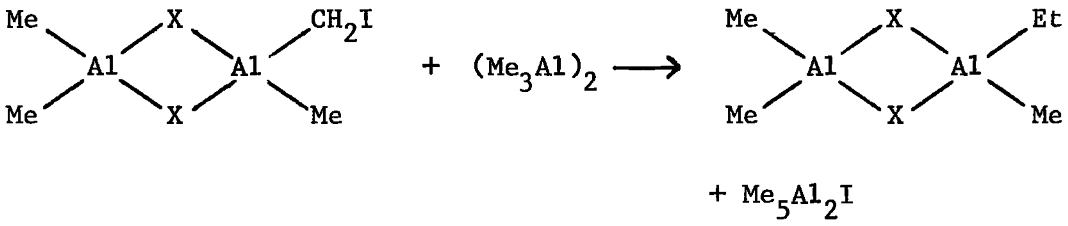


$$\mathrm{(Me_3Ge)_2\overset{\displaystyle I\atop|}{Ge}CH_2Al_2X_5 + (Me_3Ge)_2\overset{\displaystyle Me\atop|}{Ge}CH_2Al_2X_5}$$

$$\longrightarrow \begin{array}{l}\mathrm{(Me_3Ge)_2GeMe}\\ \qquad\quad|\\ \mathrm{(Me_3Ge)_2GeCH_2Al_2X_5}\end{array} \xrightarrow{H_2O} \begin{array}{l}\mathrm{(Me_3Ge)_2GeMe}\\ \qquad\quad|\\ \mathrm{(Me_3Ge)_2GeMe}\end{array}$$

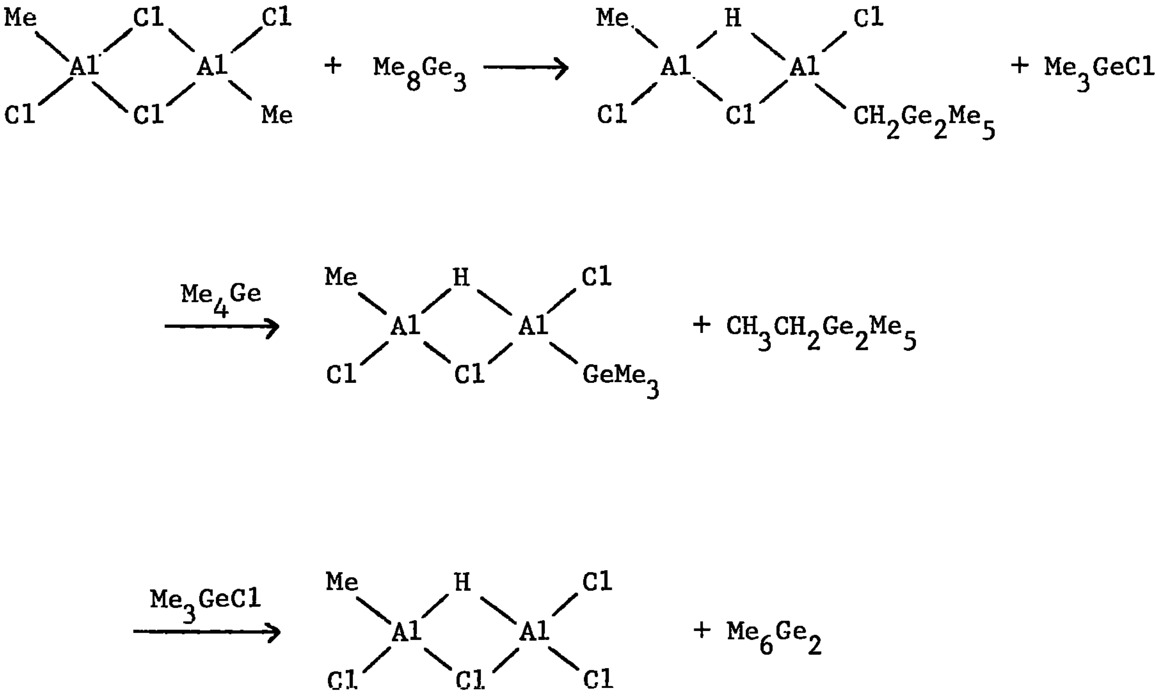
The formation of compounds containing ethyl groups from a reaction of trimethylaluminium is not easy to explain. Splitting out and insertion of ethylene is known to occur in triethylaluminium to give butyl and hexyl groups,[139] but this is not really expected under the mild conditions used in all these reactions. However, no reaction analogous to this can occur for trimethylaluminium. It is thermally very stable, pyrolysing only at high temperature to give methane and aluminium carbide, although in the course of the pyrolysis compounds such as $Me_2AlCH_2AlMe_2$ are thought to occur.[142] Because of this the obvious explanation that the trimethylaluminium is impure requires careful examination. Hydrolysis of a sample of the trimethylaluminium used gave no ethane and established an upper limit for C_2H_5 content of one mole per 5800 moles of Me_3Al. The mass spectrum also showed complete absence of ethyl groups. The mass spectrum of the triethylaluminium used showed no higher alkyl groups.

The presence in the reaction mixture of compounds of the general form $ICH_2Al_2X_5$ is a possible source of ethyl groups.

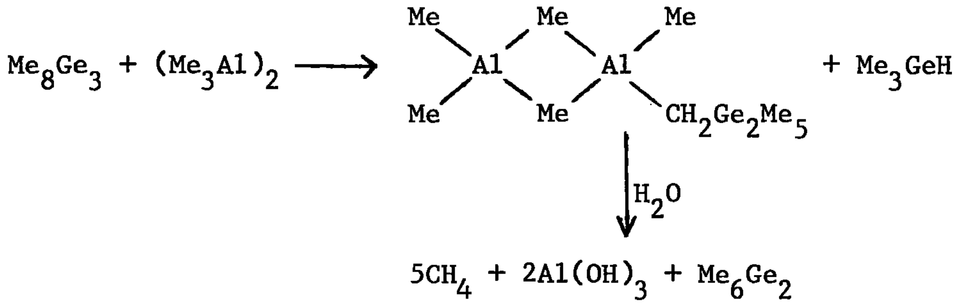


These ethyl groups can then be transferred to germanium in the same ways that the methyl groups are. In the unlikely event of an ethyl group undergoing further chain lengthening, a propyl group would be formed, but only one such compound was isolated. Its structure was not determined, but it might be expected to be an isopropyl group.

It is convenient at this point to consider the formation of ethyl groups in the germanium tetrachloride reactions. Towards the end of the reaction when some methylpolygermane has been formed, one of the more abundant aluminium species will be $(MeAlCl_2)_2$. The following reaction sequence can be envisaged.



In reactions with a large excess of trimethylaluminium species such as $(MeAlCl_2)_2$ will be almost entirely absent, and a cleavage reaction on a polygermane could conceivably take a different path.



Another possible route to ethyl compounds depends on the observation that compounds like Me_3GeCH_2Cl when heated in the presence of aluminium chloride rearrange.[143]

$$Me_3GeCH_2Cl \xrightarrow[4hr./110^{o}]{AlCl_3} Me_2GeEtCl$$

Thus if a reaction of the type

$$Me_4Ge + AlCl_3 \longrightarrow Me_3GeCH_2Cl + HAlCl_2$$

could occur an ethyl group attached to germanium would result.

Approximately equimolar proportions of Me_4Ge and $AlCl_3$ were mixed, and sufficient Me_3Al added to give the sesquichloride. After heating NaCl was added to remove the aluminium chloride so that any $Me_3GeEtCl$ formed would be alkylated. Work up of the reaction gave only tetramethylgermane. This does not, of course, exclude the possibility that Me_6Ge_2 or some higher homologue would react in the required way.

2:1:2:2 Triethylaluminium and Germanium Di-iodide

A 12-fold excess of Et_3Al stirred with GeI_2 at 20° for 22 hr. gave, after hydrolysis, a mixture of Et_6Ge_2, Et_8Ge_3 and $Et_{10}Ge_4$ with diethylgermanium oxides, probably including $Et_8Ge_4O_4$ and $Et_6Ge_3O_3$. No Et_4Ge was found. The mechanism postulated for the trimethylaluminium reaction is easily adapted to explain this reaction.

2:1:2:3 Tri-isobutylaluminium and Germanium Di-iodide

The reaction between a 9-fold excess of tri-isobutylaluminium and germanium di-iodide proceeded much more slowly than with the other reagents. After 38 hr. the remaining solid was filtered off and found to be a mixture of GeI_4 with Bu^iGeI_3. On hydrolysis the filtrate gave a viscous yellow liquid which was a mixture of $Bu^i{}_5Ge_2I$ and $Bu^i{}_7Ge_3I$, with other, probably oxygen-containing materials.

The formation of the iodo-di- and -tri-germanes shows that the isobutyl group is bulky enough to reduce the sensitivity of the Ge-I bond to SN2 hydrolysis. The mechanism of this reaction is probably slightly different from the others, since tri-isobutylaluminium is monomeric, although the hydride is associated.[139]

2:1:3 Selective Synthesis of Some Methylpolygermanes

To assist in the structural analysis of compounds formed in the Me_3Al-GeI_2 reactions, attempts were made to prepare similar compounds by less random methods.

2:1:3:1 Reaction of Germanium Tetrachloride with Trimethylgermyl-lithium

It was hoped that the main product of this reaction would be tetrakistrimethylgermylgermane.

$$4Me_3GeLi + GeCl_4 \longrightarrow (Me_3Ge)_4Ge + 4LiCl$$

In fact a solid mixture of two compounds, probably $(Me_3Ge)_4Ge$ and probably $(Me_3Ge)_3GeGe(GeMe_3)_3$, was obtained.

$$GeCl_4 + 3Me_3GeLi \longrightarrow (Me_3Ge)_3GeCl + 3LiCl$$

$$\begin{tikzcd}
 & (Me_3Ge)_4Ge + LiCl \\
(Me_3Ge)_3GeCl + Me_3GeLi \arrow[ur] \arrow[dr] & \\
 & (Me_3Ge)_3GeLi + Me_3GeCl
\end{tikzcd}$$

$$(Me_3Ge)_3GeLi + (Me_3Ge)_3GeCl \longrightarrow (Me_3Ge)_3GeGe(GeMe_3)_3 + LiCl$$

2:1:3:2 Wurtz Reaction on Trimethylbromgermane

Refluxing trimethylbromogermane with potassium for 12 hr. at 140° gave 58% of hexamethyldigermane

$$2Me_3GeBr \xrightarrow{K} Me_6Ge_2$$

Examination of the residue after removal of the digermane showed the presence of a number of higher germanes. These were separated by preparative v.p.c. and their structures determined by mass and p.m.r. spectroscopy.

Octamethyltrigermane must be formed by germanium-carbon bond cleavage, either by potassium or by trimethylgermylpotassium.

$$\begin{tikzcd}
 & Me_5Ge_2K + MeK \\
Me_6Ge_2 \arrow[ur, "2K"] \arrow[dr, "Me_3GeK"'] & \\
 & Me_5Ge_2K + Me_4Ge
\end{tikzcd}$$

$$Me_5Ge_2K + Me_3GeBr \longrightarrow Me_8Ge_3$$

The isolation of trimethylgermylpentamethyldigermanylmethane indicates that some C-H bond cleavage occurs.

$$Me_6Ge_2 + 2K \longrightarrow Me_3GeGeMe_2CH_2K + KH$$

This reaction resembles those postulated in the aluminium reactions, but in this case the result is a methylene bridged trigermane.

$$Me_3GeGeMe_2CH_2K + Me_3GeBr \longrightarrow Me_3GeGe(Me_2)CH_2GeMe_3 + KBr$$

The formation of tetrakistrimethylgermylgermane in this reaction is interesting. Like Me_8Ge_3 it must be a result of Ge-C bond cleavage. The obvious starting point is octamethyltrigermane, in which the most nucleophilic germanium is the central one.

$$(Me_3Ge)_2GeMe_2 \xrightarrow{K} (Me_3Ge)_2GeMeK \xrightarrow{Me_3GeBr}$$

$$(Me_3Ge)_3GeMe \xrightarrow{K} (Me_3Ge)_3GeK \xrightarrow{Me_3GeBr} (Me_3Ge)_4Ge$$

The substitution of a methyl on the central germanium atom of Me_8Ge_3 by a trimethylgermyl group makes it more nucleophilic still, and so the end product is the symmetrical pentagermane.

A methylene bridged tetragermane was also formed, but its exact structure was not determined. In addition, some attack on benzene (with which the potassium was washed) occurred giving Me_3GePh and $(Me_3Ge)_3C_6H_3$.

2:1:3:3 Redistribution of Germanium Tetrachloride and Hexamethyldigermane

Refluxing equimolar proportions of germanium tetrachloride and hexamethyldigermane appeared to give pentamethylchlorodigermane in a very smooth reaction. A Wurtz reaction on the product gave, very largely, $Me_{10}Ge_4$ (presumably the linear isomer) with a trace of $Me_{12}Ge_5$ and cyclic germanium oxides.

2:2 Experimental

2:2:1 General

All reactions and operations involving air sensitive compounds or intermediates were carried out in an atmosphere of pure, dry nitrogen. Further purification of commercial "white spot" nitrogen was achieved by passing the gas through a tower containing heated copper (to remove traces of oxygen) and a column of molecular sieve and a long spiral trap cooled to -196° to remove traces of moisture. Where convenient, volatile products were isolated by fractionation on a mercury float-valve vacuum system. Most of the preparative work was carried out in ordinary "Quick-fit" apparatus.

Germanium di-iodide was prepared from freshly sublimed GeI_4,[144] and excess GeI_4 was removed by sublimation at 130° under high vacuum. An X-ray powder photograph showed the GeI_2 to be free of GeO_2. Other reagents were commercially available ($GeCl_4$ from Johnson, Matthey and Co. Ltd., and alkylaluminium compounds from the Ethyl Corporation and Borax Consolidated Ltd.). The trimethylaluminium was purified by fractional recrystallisation and distillation, and the ethyl and tri-isobutyl compounds by distillation. Their purity was confirmed by mass spectroscopy, and an infrared spectrum showed no Al-H in the tri-isobutylaluminium. Solvents were purified by distillation and dried by standing over sodium, or refluxing with lithiumaluminium hydride.

Infrared spectra were recorded in the region 2•5-25μ on either a Grubb-Parsons G.S.2A or "Spectromaster" spectrophotometer. Solids were examined as pressed discs in KBr, or as mulls in Nujol or perfluorokerosene. Semi-solids and liquids were examined as thin films between KBr, NaCl or AgCl plates. Gas and vapour spectra were recorded in gas cells with KBr or NaCl windows. The region 20-50μ was recorded on a Grubb-Parsons D.M. 2/D.B.3 instrument, and Raman spectra on a Cary-81.

P.m.r. spectra were recorded on a Perkin-Elmer R.10 instrument using a 60 Mc./s. R.F. field at 33°C, with benzene as solvent and internal standard (τ = 2•73), and on an A.E.I.-R.S.2 instrument. The spectrum of Bu^i_4Ge was recorded at 100 Mc/s. by Dr. J. Feeney of Varian Associates Ltd. The 220 Mc/s. spectra of methylpolygermanes were recorded by Dr. J. Walker of Imperial Chemical Industries Ltd.

Details of infrared, p.m.r. and mass spectra relevant to the identification of compounds described in the preparative work, will be noted in the spectroscopic studies.

A variety of gas-liquid chromatographs were employed, all manufactured by W.G. Pye and Co. Ltd. Most of the analytical work was carried out on Pye 104 single or dual column machines equipped with flame ionisation detectors, using 0•01-1 μl injections. A variety of stationary phases was employed. The most generally useful was a 10% Apiezon-L on 100-120 mesh "Celite" packing in 4 mm. diamter, 5 ft. and

10 ft. long columns, (approx. 400 plates per ft.), but the use of a 5% neopentyl glycol adipate phase was helpful for high molecular weight material, which was less strongly retained by this substance than by Apiezon-L. The carrier gas employed was nitrogen, flow rate 50 ml./min. A Kent "Chromalog" integrator was connected in parallel with the (Honeywell-Brown) recorder. Germanium tetrachloride does not trigger a flame-detector, so analysis of mixtures containing this compound was effected using a gas density balance detector fitted in a Pye "Panchromatograph". The peak area to weight per cent conversion factor was calculated as described in the literature.[145] This machine, with a flame-ionisation detector, was also used for small-scale preparative separations using a 9 ft., 1 cm. diamter, 10% Apiezon-L column and a Hamilton fraction collector. Volatile compounds were collected on quartz sand in U-tubes sealed with serum caps and cooled to -196°, -78° or 0° as appropriate. The compounds were removed from the sand by washing with ether. Larger amounts of material were less tediously separated on a Pye 105 automatic chromatograph, with a 30 ft. long column. High efficiency spiral traps were used in place of the packed U-tubes.

Mass spectra were recorded by Mr. P. Nutter on an A.E.I. M.S.9 double-focusing mass spectrometer, using a 70 eV, 100μA ionising beam and 8 kV accelerating potential, with the ionisation chamber at 200°. Volatile liquids were introduced through a cold inlet, gallium cell or hot box, and solids by direct insertion probe. The precise masses of species as measured at high resolution (1:10,000) by comparison with perfluoro-tri-n-butylamine peaks of known mass, by the peak switching method, were compared with a table of calculated masses for all chemically possible combinations of Ge, C, H or Ge_2, C, H as appropriate. This table was compiled using a simple computer program, which selects the possible species, calculates their precise masses, sorts these into ascending order of mass and prints them out in blocks according to their nominal mass, as in the examples.

The program was written initially for an Elliott 803 computer, using the eight channel telecode. As given here, the program contains extensive comment to explain the processes involved. It was later translated into KDF9 code (also given, but without commentary).

The input of data requires:

1) The lowest nominal mass to be considered,

2) The maximum nominal mass to be considered <u>plus</u> <u>one</u>,

3) The number of metal isotopes or isotope combinations,

4) The effective valence of the central atom or group of atoms (for Ge this is 4; for Ge_2 it is 6),

5) The parameter "size" which fixes the boundary of the array used in the sorting procedure, and which must have a value large enough to include the maximum numbers of species expected for any nominal mass under consideration. It can of course be larger than is necessary, so that the maximum number need not be known exactly,

6) The accurate masses of the metal isotopes or metal isotope combinations. Besides Ge, Ge_2......Ge_n, the central "element" could be Sn, Sn_2, Ge-O, Ge-Cl, Pb-N etc.

The values for the accurate masses of ^{12}C (=12) and ^{1}H (= 1·00782522) are written into the program, and all masses used were on the ^{12}C atomic mass scale.[146] The examples of output given are for Ge (nominal masses 90 to 98) and Ge_2 (nominal masses 267 and 268).

Program for Elliott 803 Computer (with commentary):

```
ACCURATE MASS TABLE;
begin  integer nominal,residue,combination,Catoms,number,Hatoms,isotope,
               total,maximum,limit,line,valence,column,size;
       real Hmass,Cmass,hold;
       comment nominal = nominal  mass  of species  and  maximum = upper
               limit of this. residue = nominal  mass of organic  part.
               Catoms = no. of carbon atoms in the species, and Hatoms =
               no. of hydrogen  atoms. number = no. of metal  isotope
               combinations, combination = no. assigned to each of these
               in turn, and valence = their maximum  effective  valency.
               isotope = nominal  mass of metal isotope  combination in
               species. total = no. of species for  each nominal  mass.
               limit = point after which no more comparisons  are  made.
               line = vertical position  of  array  element and column =
               horizontal  position.  size =  maximum  number of species
               expected for any one mass number.  Hmass = accurate  mass
               of hydrogen  atom  and  Cmass that of carbon atom. hold =
               storage  location  during  sorting;
       read nominal;
       comment This reads in lowest nominal mass;
       read maximum,number,valence,size;
       Cmass:=12;
       Hmass:=1·00782522;
       begin real array METAL[1:number],SPECIES[1:4,1:size];
             for combination:=1 step 1 until number do
             read METAL[combination];
             comment This reads in metal isotope combinations;
             for nominal:=nominal,nominal+1 while maximum>nominal do
```

```
begin switch s:=again;
      line:=1;
      for combination:= 1 step 1 until number do
      begin residue:=nominal-METAL[combination];
            if residue≥0 then
            begin Catoms:=residue div 12;
                  for Catoms:=Catoms,Catoms-1 while Catoms≥0
                      do
                  begin Hatoms:= residue - Catoms*12;
                        comment The  chemically  possible
                                species  are  now  selected;
                        if Hatoms ≤ 2*Catoms + valence  then
                        begin SPECIES[1,line]:=
                              METAL[combination] + Catoms*
                              Cmass + Hatoms*Hmass;
                              SPECIES[2,line]:=
                              METAL[combination];
                              SPECIES[3,line]:=Catoms;
                              SPECIES[4,line]:=Hatoms;
                              line:=line + 1
                        end
                  end
            end
      end of selection and calculation routine. Species  are
          next sorted into ascending order of mass;
      total:=line-1;
      limit:=total-1;
      for line:= 1 step 1 until limit do
      again: begin if SPECIES[1,line]>SPECIES[1,line+1] then
             begin for column:=1,2,3,4 do
```

```
                                      begin hold:=SPECIES[column,line];
                                            SPECIES[column,line]:=
                                            SPECIES[column,line+1];
                                            SPECIES[column,line+1]:=hold
                                      end;
                                      if line>1 then
                                      begin line:=line-1;
                                            goto again
                                      end
                               end
                         end of sorting routine;
                  print ££s10??,sameline,digits(3),nominal,
                        ££s11?Ge£s5?C£s5?H£1??;
                  for line:=1 step 1 until total do
                  begin isotope:=SPECIES[2,line];
                        Catoms:=SPECIES[3,line];
                        Hatoms:=SPECIES[4,line];
                        print ££s10??,sameline,aligned(3,6),
                              SPECIES[1,line],digits(5),isotope,Catoms,
                              Hatoms,££1??
                  end;
                  print ££12??
           end Next nominal mass is now considered
     end Having reached maximum
end;
```

Output, first example

```
90              Ge      C       H
89.937010       76      1       2
89.952451       74      1       4
89.962486       73      1       5
89.968691       72      1       6

91              Ge      C       H
90.944835       76      1       3
90.960276       74      1       5
90.970311       73      1       6

92              Ge      C       H
91.952660       76      1       4
91.968101       74      1       6

93              Ge      C       H
92.960486       76      1       5

94              Ge      C       H
93.924277       70      2       0
93.968311       76      1       6

95              Ge      C       H
94.932102       70      2       1

96              Ge      C       H
95.921740       72      2       0
95.939927       70      2       2

97              Ge      C       H
96.923360       73      2       0
96.929565       72      2       1
96.947752       70      2       3

98              Ge      C       H
97.921150       74      2       0
97.931185       73      2       1
97.937390       72      2       2
97.955578       70      2       4
```

Output, 2nd example

```
267            Ge     C     H
266.844510     147    10    0
266.851180     146    10    1
266.860747     145    10    2
266.868249     144    10    3
266.878937     143    10    4
266.885140     142    10    5
266.897495     152     9    7
266.903329     140    10    7
266.912936     150     9    9
266.922972     149     9   10
266.928569     148     9   11
266.938412     147     9   12
266.945082     146     9   13
266.954650     145     9   14
266.962153     144     9   15
266.972839     143     9   16
266.979047     142     9   17
266.991396     152     8   19
266.997232     140     9   19
267.006838     150     8   21
267.016874     149     8   22

268            Ge     C     H
267.842493     148    10    0
267.852335     147    10    1
267.859005     146    10    2
267.868574     145    10    3
267.876075     144    10    4
267.886761     143    10    5
267.892967     142    10    6
267.905318     152     9    8
267.911154     140    10    8
267.920761     150     9   10
267.930795     149     9   11
267.936395     148     9   12
267.946237     147     9   13
267.952907     146     9   14
267.962477     145     9   15
267.969978     144     9   16
267.980666     143     9   17
267.986870     142     9   18
267.999222     152     8   20
268.005059     140     9   20
268.014663     150     8   22
```

Program for KDF9.

```
ACCURATE MASS TABLE →
begin library A0 ,A1,A4,A5,A15;
      integer nominal,residue,combination,Catoms,number,Hatoms,isotope,
              total,maximum,limit,line,valence,column,size;
      real Hmass,Cmass,hold;
      open (20);
      nominal:=read (20);
      maximum:=read (20);
      number:=read (20);
      valence:=read (20);
      size:=read(20);
      Cmass:=12;
      Hmass:=1.00782522;
      begin real array METAL[1:number],SPECIES[1:4,1:size];
            for combination:=1 step 1 until number do
            METAL[combination]:=read (20);
            for nominal:=nominal,nominal+1 while maximum>nominal do
            begin line:=1;
                  for combination:= 1 step 1 until number do
                  begin residue:=nominal-METAL[combination];
                        if residue≥0 then
                        begin Catoms:=residue÷12;
                              for Catoms:=Catoms,Catoms-1 while
                                  Catoms≥0 do
                              begin Hatoms:=residue-Catomsx12;
                                    if Hatoms≤2xCatoms+valence then
                              begin SPECIES[1,line]:=METAL[combination]
                                    +CatomsxCmass+HatomsxHmass;
                                    SPECIES[2,line]:=METAL[combination];
```

```
                        SPECIES[3,line]:=Catoms;
                        SPECIES[4,line]:=Hatoms;
                        line:=line+1
                  end
             end
      end
end;
total:=line-1;
limit:=total-1;
for line:=1 step 1 until limit do
again: begin if SPECIES[1,line]>SPECIES[1,line+1] then
             begin for column:=1,2,3,4 do
                   begin hold:=SPECIES[column,line];
                         SPECIES[column,line]:=
                         SPECIES[column,line+1];
                         SPECIES[column,line+1]:=hold
                   end;
                   if line>1 then
                   begin line:=line-1;
                         goto again
                   end
             end
       end;
       open (30);
       write (30,format ([10sndd]),nominal);
       write text (30,[[11s]Ge[5s]C[5s]H[c]]);
       for line:= 1 step 1 until total do
       begin isotope:=SPECIES[2,line];
             Catoms:=SPECIES[3,line];
             Hatoms:=SPECIES[4,line];
             write (30,format ([10sndd.dddddd]),SPECIES[1,line]);
```

```
                   write (30,format ([nddddd]),isotope);
                   write (30,format ([nddddd]),Catoms);
                   write (30,format ([nddddddc]),Hatoms)
              end;
              write text (30,[[cc]]);
              close (30)
         end
    end;
    close (20)
end→
```

2:2:2 Reactions of Germanium Tetrachloride with Methylaluminium Compounds

2:2:2:1 Trimethylaluminium and Germanium Tetrachloride

29•9 g. (0•415 mole) of Me_3Al were reacted with 46•1 g. (0•215 mole) of $GeCl_4$, by slow addition of the latter, a 1•45-fold excess of the aluminium alkyl. Heat was evolved. The mixture was refluxed for 4 hr., and then fractionated through a 9" column packed with glass helices, giving 13•2 g. (46•2% on the basis of $GeCl_4$) of Me_4Ge (b.pt. = 43•5°C, confirmed by i.r. spectrum and v.p.c. comparison). The mixture was refluxed for another 3 hr., and fractionation gave an additional 6•0 g. (21•0%) of Me_4Ge (b.pt., i.r., v.p.c.). A further 4 hr. reflux gave 6•6 g. distillate, boiling range 36-43°, shown by v.p.c. analysis to contain 4•1 g. (14•4%) of Me_4Ge and 2•5 g. (5•4%) of $GeCl_4$, with a little methyl chloride (i.r., v.p.c.). Material recovered from a -196° trap attached to the top of the reflux system (water condenser, topped by CO_2 pistol) contained traces of Me_4Ge and CH_3Cl (i.r., v.p.c.) and $GeCl_4$ (i.r.). Total yield of Me_4Ge was 81•6%.

In another experiment, 23•1 g. (0•320 mole) of Me_3Al were heated to 100°C and 22•4 g. (0•104 mole) of $GeCl_4$ were added slowly over 30 min., giving a 2•30-fold excess of Me_3Al. The mixture was refluxed for 6 hr. at 120°, and fractionation gave 9•7 g. (69•9%) of Me_4Ge (b.pt., i.r., v.p.c.). A further 5 hr. reflux at 130° gave 4•2 g. of liquid (b.range 43-110°) shown by v.p.c. to contain Me_4Ge (1•2 g., 8•3%) and $GeCl_4$

(2·8 g., 12·5%). The residue was hydrolysed with water, extracted with diethylether, dried over $MgSO_4$ and the ether removed leaving 0·8 g. of liquid. This was distilled at $20^{o}/2 \times 10^{-2}$mm.Hg, giving a few drops of Me_6Ge_2 (i.r., m.s., found M = 235·9848, deviation 2 p.p.m. for ${}^{146}Ge_2C_6H_{18}{}^{+}$). The undistilled residue contained Me_6Ge_2, $Me_3GeGeMe_2Et$ (m.s., found M = 250·0001, deviation 1 p.p.m. for ${}^{146}Ge_2C_7H_{20}{}^{+}$) and $Ge_2C_8H_{22}$ (m.s., found, M = 264·0155, deviation 1 p.p.m.). This last compound is either $Me_4Et_2Ge_2$ or Me_5PrGe_2, but the mass spectrum was too weak for the metastables necessary for distinction to be descried. There was also a trace of a compound $Ge_2C_{10}H_{24}$, for which several isomers are possible (m.s.).

In a third experiment, 22·1 g. (0·103 mole) of $GeCl_4$ were added to 11·3 g. (0·157 mole, 1·14-fold excess) of Me_3Al at 100°. The mixture was refluxed for 2 hr. and fractionation then gave 4·5 g. (32·9%) of Me_4Ge (b.pt., i.r., v.p.c.). Further reflux at 110° for 7 hr. produced 2·3 g. of liquid, a mixture of 0·3 g. of Me_4Ge and 2·0 g. of $GeCl_4$ (v.p.c., i.r.). 1·5 g. of Me_3Al were added to the reaction mixture, and after 2 hr. reflux at 130-140°, 0·2 g. of Me_4Ge and 0·8 g. of $GeCl_4$ were distilled off. Another 1·9 g. of Me_3Al were added and after 7 hr. reflux, 0·8 g. of distillate were obtained; 0·5 g. Me_4Ge and 0·3 g. $GeCl_4$. 1·6 g. of liquid were recovered from the -196° trap, and this was 0·9 g. of Me_4Ge and 0·7 g. of $GeCl_4$. The residue was hydrolysed, and during hydrolysis 1·4 g. of liquid collected in the trap, 0·7 g. Me_4Ge and 0·7 g.

$GeCl_4$. The total yield of Me_4Ge was 7•1 g. (51•9%) and 4•5 g. (20•4%) of the $GeCl_4$ was recovered.

19•7 g. (0•0920 mole) of $GeCl_4$ were added to 9•8 g. (0•136 mole, a 1•09-fold excess) of Me_3Al at -196°. The mixture was sealed in an all-glass apparatus with a double-surface water condenser leading to a 10 cm. mercury blow-off. The mixture was refluxed at 110° for 38 days. Work-up gave 6•9 g. (56•5%) of Me_4Ge (b.pt., i.r.) and 1•6 g. of $GeCl_4$ (8•1%). The residue was largely aluminium chloride. It was extracted with pentane, and the extract hydrolysed and normal work up gave a trace of $Me_{10}Ge_4$ (m.s.). There was a suggestion of an ethyl compound (Me_2GeEt^+ appeared in a mass spectrum) but none could be identified.

2:2:2:2 Trimethylaluminium, Germanium Tetrachloride and Sodium Chloride

22•5 g. (0•105 mole) of $GeCl_4$ was added to a mixture of 23•3 g. (0•323 mole, a 2•31-fold excess) of Me_3Al and 18•3 g. (0•313 mole) of NaCl at 100° over 45 min. The mixture was refluxed at 130-140° for 30 min., after which fractionation gave 10•2 g. (73•2%) of Me_4Ge (b.pt., i.r., v.p.c.). Continued reflux for another 30 min. gave no more Me_4Ge. The residue contained some Me_4Ge and $GeCl_4$ (v.p.c.), and part of it was hydrolysed and worked up in the usual way to give a little Me_6Ge_2 (m.s.).

In a second experiment 33•2 g. (0•155 mole) of $GeCl_4$ were added to a mixture of 16•7 g. (0•232 mole, a 1•12-fold excess) of Me_3Al and 12•2 g. (0•209 mole) of NaCl. The mixture was refluxed at 70° for 30 min., when distillation through a Vigreau column gave 9•7 g. distillate (40-52°).

This was hydrolysed with water, extracted with ether, dried over $MgSO_4$ and filtered. The filtrate was cooled to -30°C, and concentrated H_2SO_4 added. The upper layer was separated and distilled giving 3•5 g. (17•0%) of Me_4Ge (b.pt., i.r., v.p.c.). A further 4 hr. reflux at 130° gave 2 g. distillate (43°) and this was combined with 0•8 g. material recovered from the -196° trap, hydrolysed and extracted with toluene, from which the tetramethylgermane could not be recovered by distillation.

In a third reaction 22•1 g. (0•103 mole) of $GeCl_4$ were added to 11•1 g. (0•154 mole, a 1•12-fold excess) of Me_3Al and 13 g. (0•222 mole) of NaCl. After 30 min. at 140° distillation through a Vigreau column gave 4•6 g. of distillate (boiling range 44-48°, 33•6% Me_4Ge). Further reflux at 140° for 7½hr. gave 2•7 g. distillate (45-80°), a mixture of Me_4Ge and $GeCl_4$.

In a fourth experiment, 19•4 g. (0•0903 mole) of $GeCl_4$ were added dropwise to 9•8 g. (0•136 mole, a 1•13-fold excess) of Me_3Al and 7•9 g. (0•135 mole) of NaCl at 100°. The mixture was refluxed at 120° for 30 min., after which fractionation gave 5•4 g. (45%) of Me_4Ge (b.pt., i.r.). Some Me_4Ge (i.r.) had collected in the -78° trap. A second fraction distilled at 90° (5•2 g.) and was a mixture of Me_4Ge and $GeCl_4$ with a little Me_3Al (i.r.). Work up of the residue gave a mixture of cyclic germoxane (possibly the trimer $Me_6Ge_3O_3$) and methylpolygermanes, probably including some with ethyl groups (m.s. showed ions $Me_5Ge_2^+$, $Me_4EtGe_2^+$ and $Me_5Ge_3O_3^+$, together with others unidentified).

2·5 g. (0·0346 mole, a 1·18-fold excess) of Me_3Al and 4·7 g. (0·0219 mole) of $GeCl_4$ were condensed from a vacuum line into a break-seal tube containing 2·0 g. (0·0342 mole) of NaCl, and the tube was sealed. It was kept at 80° for 1 month, cooled, sealed to a vacuum line, frozen at -196°, and the seal broken. 7·7 Nccs. of non-condensable gas were obtained. This gas contained methane (i.r.). It was sparked with 49·7 Nccs of oxygen, and the CO_2 frozen out at -196°. The remaining gas contained no CH_4 or CO_2. Water was removed from the CO_2 by allowing this to evaporate at -78°, and 5·9 Nccs of CO_2 were obtained. Calculation of the % H_2 in the gas from the oxygen consumed and from the CO_2 produced (from the methane) gave a mean value of 0·0325 mmoles H_2 produced in the reaction (the two values agreed to within 5%). Some of the methane was produced by reaction of Me_3Al with H_2O adsorbed on the glass of the vacuum system. The H_2 may have been produced in a similar way from Al-H bonds. The remaining volatile components were $GeCl_4$ and Me_4Ge (i.r.). These were separated by repeated vacuum evaporation at -96° giving small samples of pure $GeCl_4$ (i.r.) and Me_4Ge (i.r.). The bulk of this mixture was removed from the line, cooled and hydrolysed with conc. H_2SO_4. The organic layer was pipetted off giving 2·2 g. (75·7%) of Me_4Ge (i.r.). The H_2SO_4 was diluted and a precipitate of GeO_2 (i.r.) formed. The involatiles were worked up in the usual way but no germanium compounds were obtained. The black insoluble solid was presumably carbon.

In an experiment using excess $GeCl_4$ (156•8 g., 0•731 mole, a 1•24-fold excess) added slowly to a mixture of 56•8 g. (0•788 mole) of Me_3Al and 63•5 g. (0•805 mole) of NaCl, the mixture was refluxed for 30 min. at 100° when fractionation gave 24•7 g. (25•4%) of Me_4Ge (b.pt., i.r.). Another 2 hr. reflux at 110-120° gave 4•5 g. of distillate on fractionation (boiling range 43-60°). The rest of the liquid was removed under vacuum, leaving a solid residue, and fractionated at atmospheric pressure. This gave 55•3 g. (35•3%) of $GeCl_4$ (b.pt.84°, i.r., v.p.c.) with a trace of Me_4Ge (i.r.); 46•5 g. of a fraction (84-90°); and 54•0 g. of a final pyrophoric fraction (112-126°), leaving a dark brown residue. The second fraction was redistilled giving 40•4 g. (25•8%) of $GeCl_4$ (b.pt., i.r.) with traces of Me_4Ge and MeCl (gas i.r.). The residue was worked up in the usual way and gave probably Me_5Ge_2Et and possibly a little $Me_4Ge_2Et_2$ (or Me_5Ge_2Pr), (m.s.). The solid residue remaining from the initial vacuum distillation was hydrolysed, and normal work up gave a mixture of Me_8Ge_3, Me_7Ge_3Et, $Ge_3C_{10}H_{28}$ ($Me_6Ge_3Et_2$ or Me_7Ge_3Pr), $Me_{10}Ge_4$, $Me_{12}Ge_5$ and Me_9Ge_4Et (m.s., i.r.). Volatile material which collected in a -196° trap during this hydrolysis was fractionated by repeated evaporation on the vacuum line, and found to contain Me_4Ge, $GeCl_4$ (i.r.), propane (10^{-3} mole, i.r, m.s.) and methanol (i.r.), and possibly Me_2GeCl_2, $MeGeCl_3$, Me_3GeEt, and other unidentified compounds (m.s.). Some material had also collected during the two reflux periods, and similar treatment showed Me_4Ge, $GeCl_4$, MeOH, and MeCl (i.r.).

Trimethylgermane was detected in some experiments. 18·4 g. (0·0860 mole) of $GeCl_4$ were added dropwise to a mixture of 18·0 g. (0·250 mole, a 2·18-fold excess) of Me_3Al and 14·4 g. (0·246 mole) of NaCl at 100°, and heated for 30 min. at 110°. A little Me_3GeH (i.r.) collected in a -78° trap during reflux. 4·9 g. (42·9%) of Me_4Ge with a trace of Me_3GeH (i.r.) were distilled from the mixture. Reflux at 140° for a further hr. gave no more Me_3GeH, but 2·0 g. (17·5%) of Me_4Ge with a trace of $GeCl_4$ were distilled from the reaction. Hydrolysis of the residue gave no germanium compounds.

8·3 g. (0·0387 mole) of $GeCl_4$, 48·9 g. (0·678 mole, a 13·1-fold excess) of Me_3Al and 4 g. (0·0684 mole) of NaCl were refluxed at 100° for 30 min. Me_3GeH (i.r.) collected in a -78° trap. Fractionation of the reaction mixture gave 3·7 g. (72·0%) Me_4Ge, with a trace of Me_3GeH (i.r.). Distillation continued at 126-128° (Me_3Al, b.pt.). The residue exploded on attempted hydrolysis, but $(Me_2GeO)_4$ was detected (m.s.).

Addition of 10·6 g. (0·0494 mole) of $GeCl_4$ over 90 mins. to a mixture of 35·7 g. (0·611 mole) of NaCl and 44·8 g. (0·621 mole, a 9·43-fold excess) of Me_3Al at 100° gave, after 30 mins. reflux at 110-120° 5·1 g. (77·7%) Me_4Ge (v.p.c., i.r., m.s.), containing $<10\%$ (v.p.c.) of Me_3GeH (νGe-H = 2039; literature value 2041 cm^{-1}).[147] Distillation continued at 120-128° to give Me_3Al, with traces of Me_4Ge and $GeCl_4$ (v.p.c.). Hydrolysis of this gave no germanium compounds, but a little ethylene collected in a -196° trap (i.r., m.s.). Hydrolysis of the residue gave 0·3 g. of a mixture (i.r., m.s.) of Me_8Ge_3 (Found, M =

337·9525, deviation 4 p.p.m. for $^{218}Ge_3C_8H_{24}$), $Me_{10}Ge_4$ (Found, M = 439·9223, deviation 2 p.p.m. for $^{290}Ge_4C_{10}H_{30}$), $Me_{12}Ge_5$ (Found, M = 543·8907, deviation 1 p.p.m. for $^{364}Ge_5C_{12}H_{36}$) and $Me_{14}Ge_6$ (Found, M = 645·8614, deviation 1 p.p.m. for $^{436}Ge_6C_{14}H_{42}$). Traces of $Ge_4C_{11}H_{32}$, $Ge_5C_{13}H_{38}$ and $Ge_5C_{14}H_{40}$ were also found (m.s.).

2:2:2:3 Methylaluminium Sesquichloride and Germanium Tetrachloride

46·1 g. (0·215 mole) of $GeCl_4$ were added to 108·7 g. (0·529 mole, a 1·85-fold excess) of $Me_3Al_2Cl_3$. After 5 hr. reflux, fractionation gave 6·3 g. (22·1%) of Me_4Ge (b.pt., i.r., v.p.c.). 56 g. (0·958 mole) of NaCl were added and the mixture refluxed for 2 hr., after which distillation gave 13·1g of crude distillate. A further 2 hr. reflux yielded another 5·6 g. of crude distillate. Refractionation of the combined crude distillate gave 14·4 g. (50·5%) of Me_4Ge (b.pt., i.r., v.p.c.). Me_4Ge (0·8 g.) was recovered from the -196° trap attached to the reflux system (i.r.). Total yield of Me_4Ge was 75·3%.

2:2:2:4 Methylaluminium Sesquichloride and Germanium Tetrachloride in Ethereal Solution

8·3 g. (0·0387 mole) of $GeCl_4$ and 10·9 g. (0·0531 mole, a 1·03-fold excess) of $Me_3Al_2Cl_3$ were refluxed in 50 ml. of Et_2O for $5\frac{1}{2}$ hr. The mixture was hydrolysed with conc. HCl, and the ethereal layer separated and dried over $MgSO_4$. It contained Me_3GeCl and $MeGeCl_3$ (combined yield $<$0·5%) and 8 other components (v.p.c.).

In a similar experiment 4•6 g. (0•0215 mole) of $GeCl_4$ and 15•8 g. (0•0769 mole, a 2•68-fold excess) of $Me_3Al_2Cl_3$ were refluxed in 50 ml. of Et_2O for 2 hr., and hydrolysed with conc. HCl. Work up gave a liquid which was separated by preparative v.p.c. and shown to contain $MeGeCl_3$ (m.s.) and Me_2GeCl_2 (m.s.), combined yield 6•0% (v.p.c.) and Me_3GeCl (4•6%, v.p.c.).

4•6 g. (0•0215 mole) of $GeCl_4$ and 16•3 g. (0•0794 mole, 2•77-fold excess) of $Me_3Al_2Cl_3$ were refluxed for 6½ hr. at 150° in 50 ml. of diglyme. Work up as before showed a trace of $MeGeCl_3$ (v.p.c.).

In an identical experiment, but with 22 g. (0•376 mole) of NaCl present, the mixture was refluxed for 11 hr. at 150°, after which v.p.c. analysis showed the presence of a little Me_4Ge with unreacted $GeCl_4$.

36•9 g. (0•172 mole) of $GeCl_4$, 76•1 g. (0•370 mole, a 1•61-fold excess) of $Me_3Al_2Cl_3$ and 103•2 g. NaCl (1•77 mole) were refluxed for 4 hr. in 80 ml. of diglyme, and then distilled up to 90°. The crude distillate was fractionated giving Me_4Ge (14•9 g., 65•3%; b.pt., i.r., m.s., v.p.c.). A second fraction was collected (44-90°) and separated by preparative v.p.c., when Me_4Ge, $MeGeCl_3$ and Me_2GeCl_2 were identified (m.s.), together with C_3H_7ClO, whose fragmentation pattern fitted $MeOCH_2CH_2Cl$, which must result from solvent cleavage. A third fraction (92°) contained a little Me_4Ge but was mainly $GeCl_4$ (v.p.c.). Some MeCl had collected at -196° during reflux (v.p.c., i.r.).

2:2:2:5 Trimethylaluminium and Germanium Tetra-iodide

7·52 g. (0·1042 mole, a 1·16-fold excess) of Me_3Al were added dropwise to 39·2 g. (67·5 mole) of GeI_4 and 30 ml. of methylcyclohexane at 100°. The reaction was vigorous and all the GeI_4 went into solution. After 5 hr. reflux (100°) the liquid had changed from orange to pale yellow. On cooling, white NaCl-like crystals separated. Distillation gave 1·9 g. (21·2%) of Me_4Ge (i.r.). No material had collected in the -78° trap during reflux. Normal work up of the residue gave no organogermanium compounds.

2:2:3 Reaction of Germanium Tetrachloride with Triethylaluminium

20·3 g. (0·0946 mole) of $GeCl_4$ were added to a mixture of 16·1 g. (0·141 mole, a 1·11-fold excess) of Et_3Al and 9·8 g. (0·168 mole) of NaCl at 20°C. A vigorous exothermic reaction ensued, and the mixture was refluxed for 30 min., and then distilled through a Vigreau column giving 1·5 g. (7·4%) of $GeCl_4$ (b.pt.) and 13·7 g. (76·7%) of Et_4Ge (v.p.c.) containing small amounts of EtCl and Et_6Ge_2 (v.p.c.). The minor components were separated by preparative v.p.c., giving 0·2 g. (1·0%) of Et_3GeBu^n (m.s., i.r., v.p.c., Found, C = 55·3, H = 11·1, $GeC_{10}H_{24}$ requires C = 55·4, H = 11·2%) and Et_3Ge (C_6H_{13}) or Et_2GeBu_2 (m.s.). (log t_R secs on 10% Apiezon-L at 150°: Et_4Ge = 3·189, Et_3GeBu^n = 3·537, suspected $Et_3Ge(C_6H_{13})$ = 3·938).

A mixture of $GeCl_4$ (20·3 g., 0·0946 mole), Et_3Al (16·7 g., 0·147 mole, a 1·16-fold excess) and NaCl (9·8 g., 0·168 mole) was refluxed for 2 hr. at 130° and fractionation gave 11·8 g. (66·0%) of Et_4Ge (v.p.c., i.r.) with traces of EtCl and Et_6Ge_2 (v.p.c.).

An identical mixture was heated for 4hr. at 130°, after which fractionation gave 2·7 g. (13·3%) of $GeCl_4$ (b.pt., v.p.c., m.s.). The remaining volatiles were removed by vacuum distillation and hydrolysed. Normal work up gave a mixture of Et_4Ge (10·2 g., 57·1%), Et_6Ge_2 (2·3 g., 15·0%), and Et_8Ge_3 (0·1 g., 0·8%), (v.p.c., m.s.). The residue from the distillation was also hydrolysed with water, dried, filtered and the ether removed by evaporation, leaving 0·5 g. of ethylpolygermanes (i.r.) including Et_6Ge_2 (m.s., Found, M = 320·0786, deviation 2 p.p.m. for $^{146}Ge_2C_{12}H_{30}$) and Et_8Ge_3 (m.s., Found, M = 450·0795, deviation 1 p.p.m. for $^{218}Ge_3C_{16}H_{40}$). Separation by preparative v.p.c., followed by mass spectral identification showed the presence of Et_6Ge_2, Et_5Ge_2Bu, $Et_5Ge_2(C_6H_{13})$, $Ge_2C_{18}H_{42}(Et_3Bu_3Ge_2?)$, Et_8Ge_3, Et_7Ge_3Bu (Found, M = 478·1102, deviation 0 p.p.m. for $^{218}Ge_3C_{18}H_{44}$), $Et_7Ge_3(C_6H_{13})$ and $Et_{10}Ge_4$.

Addition of 30·7 g. (0·269 mole) of Et_3Al to 92·2 g. (0·430 mole, a 2·13-fold excess) of $GeCl_4$ produced a vigorous reaction. The mixture was refluxed for 7½ hr., and fractionation gave 67·5 g. (73·2%) of $GeCl_4$ (b.pt.) and 19·2 g. of crude Et_4Ge. The latter was hydrolysed, extracted with ether and distilled at 160-162·5° giving 12·8 g. (15·8%) of Et_4Ge (b.pt., i.r., v.p.c.).

2:2:4 Reactions of Germanium Tetrachloride with Tri-isobutylaluminium

21·2 g. (0·0989 mole) of $GeCl_4$ were added over 3 hr. to a mixture of 29·5 g. (0·149 mole, a 1·13-fold excess) of Bu^i_3Al and 10·5 g. (0·180 mole) of NaCl at 60°, and the mixture stirred at 60-80° for 68 hr. It was then distilled at $20^o/2 \times 10^{-3}$ mm. Hg, giving 6·7 g. (25·9%) of $GeCl_4$ (v.p.c.), containing some isobutane (i.r., v.p.c.). Continuation of the distillation up to $100^o/1{\cdot}5 \times 10^{-4}$ mm.Hg gave 22·2 g. of distillate, which was hydrolysed and extracted in the usual way giving 13·1 g. (44·0%) of Bu^i_4Ge (v.p.c., i.r.). Hydrolysis and extraction of the residue from the distillation gave 5·0 g. (20·7%) of <u>hexaisobutyldigermane</u> (v.p.c., i.r., m.s.) containing small amounts of higher isobutylpolygermanes.

At a higher temperature, a more complicated reaction occurred. 25·9 g. (0·110 mole) of $GeCl_4$ were added over 30 min. to 10·1 g. (0·173 mole) of NaCl and 37·3 g. (0·183 mole, a 1·13-fold excess) of Bu^i_3Al at 100-120°C, and the mixture was refluxed at 140-150° for 4 hr. 9·2 g. of volatile material collected in a trap at -196°, and repeated fractionation of this on a vacuum line gave isobutene (m.s., i.r.), GeH_4 (i.r., m.s.), isobutane (i.r., m.s.) and a clear colourless liquid, <u>isobutylgermane</u>, Bu^iGeH_3 (m.s., i.r.). Distillation of the reaction mixture gave 3·3 g. (13·0%) of $GeCl_4$ (v.p.c.,m.s.). A second fraction (15·4 g.) collected at $50\text{-}64^o/5 \times 10^{-4}$ mm.Hg, contained 14·6 g. (39·2%) of Bu^i_4Ge (i.r., m.s.) and a third fraction (7·3 g.) collected at $98\text{-}114^o/5 \times 10^{-4}$ mm. Hg. This viscous liquid consisted of Bu^i_4Ge (1·6 g., 4·2%)

and $Bu^i_6Ge_2$ (5·7 g., 19·6%). Redistillation gave $Bu^i_6Ge_2$, recrystallised from methanol as white needles (m.p., 48-9°), (Found, C = 60·1, H = 11·4, M = 488·2636; $Ge_2C_{24}H_{54}$ requires C = 59·1, H = 11·2%, deviation ($^{146}Ge_2$) 5 p.p.m.). Hydrolysis of the residue gave a little H_2 (m.s.) and some butane (i.r., m.s.). Normal work up of the hydrolysate gave 4·2 g. of a clear, viscous liquid, containing isobutylpolygermanes (i.r.), including $Bu^i_6Ge_2$ (m.s.; Found, M = 488·2648, deviation 2 p.p.m.) and octaisobutyltrigermane (m.s.; Found, M = 674·3273, deviation 3 p.p.m. for $^{218}Ge_3C_{32}H_{72}$) and $Bu^i_{10}Ge_4$, together with higher polygermanes. The presence of $Bu_3Ge(C_8H_{17})$ was a distinct possibility (m.s.).

24·5 g. (0·124 mole, a 1·08-fold excess) of Bu^i_3Al, 10 g. (0·171 mole) of NaCl and 18·4 g. (0·0860 mole) of $GeCl_4$ produced a vigorous, exothermic reaction. After being refluxed for 7 hr. at 106°, it was fractionated giving 0·6 g. of impure $GeCl_4$ containing Bu^i_3GeCl (?) and Bu^i_4Ge (m.s.) followed by 15·5 g. of crude Bu^i_4Ge which, after hydrolysis, yielded 13 g. (50·2%) of Bu^i_4Ge (b.pt. 78·3°/10^{-2} mm.Hg. Found C = 63·4, H = 11·8, M = 302·2034. Calculated for $GeC_{16}H_{36}$, C = 63·8, H = 12·1%, deviation 2 p.p.m. for ^{74}Ge). No detectable isomerisation had occurred (i.r., p.m.r., v.p.c.). Hydrolysis of the residue gave 5·4 g. of viscous liquid. Vacuum distillation separated this into liquid and semi-solid fractions. Preparative v.p.c. separation of the liquid gave $Bu^i_6Ge_2$ (m.s., Found, M = 488·2671, deviation 2 p.p.m.) and $Bu^i_8Ge_3$ (m.s.). The semi-solid contained $Bu^i_{10}Ge_4$ and higher organopolygermanes (m.s.). The highest species positively identified in the mass spectrum was $Bu^{i}{}_{11}Ge_5{}^{+}$ (Found, M = 989·3826, deviation 3 p.p.m. for $^{362}Ge_5$).

2:2:5 Reactions of Germanium Di-iodide with Trimethylaluminium

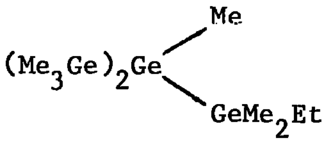
In a preliminary experiment, 3·4 g. (52·1 mmole, a 13·4-fold excess according to the equation $3GeI_2 + 2Me_3Al \longrightarrow 3Me_2Ge + 2AlI_3$) of Me_3Al were added to 1·9 g. (5·82 mmole) of GeI_2 and 15 ml. of decane, in a flask fitted with a water condenser leading to a -78° trap. There was no visible sign of reaction, or evolution of heat. After 2 hr. at 80°, when the yellow GeI_2 had given way to a buff solid, the temperature was raised to 100° for 24 hr. The mixture was distilled up to 200°, and the residue hydrolysed with water and extracted with ether. This gave 0·3 g. of semi-solid whose infrared spectrum resembled that of $(Me_2Ge)_n$.[88] The mass spectrum suggested a high molecular weight (>1400) methylpolygermane, with considerable chain branching (large Me_3Ge^+ ion). The buff solid remained in the aqueous layer. It was filtered off and found to be GeO_2 (i.r.).

In a larger scale experiment 15·4 g. (0·214 mole, a 10·7-fold excess) of Me_3Al were added to 9·8 g. (30 mmole) of GeI_2 and 100 ml. of decane. After 2 hr. at 80° the yellow crystals of GeI_2 had again given way to a buff solid, and the mixture was heated for a further 19 hr. at 120°. No Me_4Ge was produced. Decane and excess trimethylaluminium were distilled off (151-160°) and the residue filtered. The solid was GeO_2 (i.r., X-ray powder photograph), 3·0 g. The filtrate was hydrolysed and extracted with benzene giving, after removal of solvent, 2·0 g. of an opalescent, very viscous liquid. 1·8 g. of this was dissolved in heptane and chromatographed on alumina (Brockman Activity 1). Elution with heptane gave a main fraction (0·9 g), a clear colourless liquid of lower viscosity, $(Me_2Ge)_n$ (i.r., Found, C = 24·0, H = 5·4, GeC_2H_6 requires C = 24·3, H = 6·1%). The mass spectrum showed a mixture of $Me_{10}Ge_4$ (M = 441·9210, deviation 2 p.p.m. for $^{292}Ge_4$), $Me_{12}Ge_5$ (M = 543·8932, deviation 3 p.p.m. for $^{364}Ge_5$), $Me_{14}Ge_6$ (M = 645·8608, deviation 0 p.p.m. for $^{436}Ge_6$) and $Me_{16}Ge_7$ (M = 747·8207, deviation 13 p.p.m. for $^{507}Ge_7$). Again the presence of a large Me_3Ge^+ ion indicated branching, and the p.m.r. spectrum was very complicated. Elution with a 1:1 benzene-heptane mixture, then benzene and finally ethanol gave minor fractions, some of these being $(Me_2Ge)_n$ and some oxygen-containing (i.r.). The mass spectra were confusing, but the assignment of some peaks, such as $Me_5{}^{218}Ge_3O_3{}^+$ (Found, M = 340·8669, deviation 3 p.p.m.), $Me_7{}^{290}Ge_4O_4{}^+$ (Found, M = 458·8345, deviation 5 p.p.m.), $Me_7{}^{364}Ge_5O_6{}^+$ (Found, M = 564·7451, deviation 3 p.p.m.) and $Me_7{}^{436}Ge_6O_8{}^+$ (Found, M = 668·6586, deviation 5 p.p.m.) suggested the presence of the cyclic tetrameric oxide $(Me_8Ge_4O_4)$ and perhaps the trimer $(Me_6Ge_3O_3)$ together with material containing a higher proportion of oxygen.

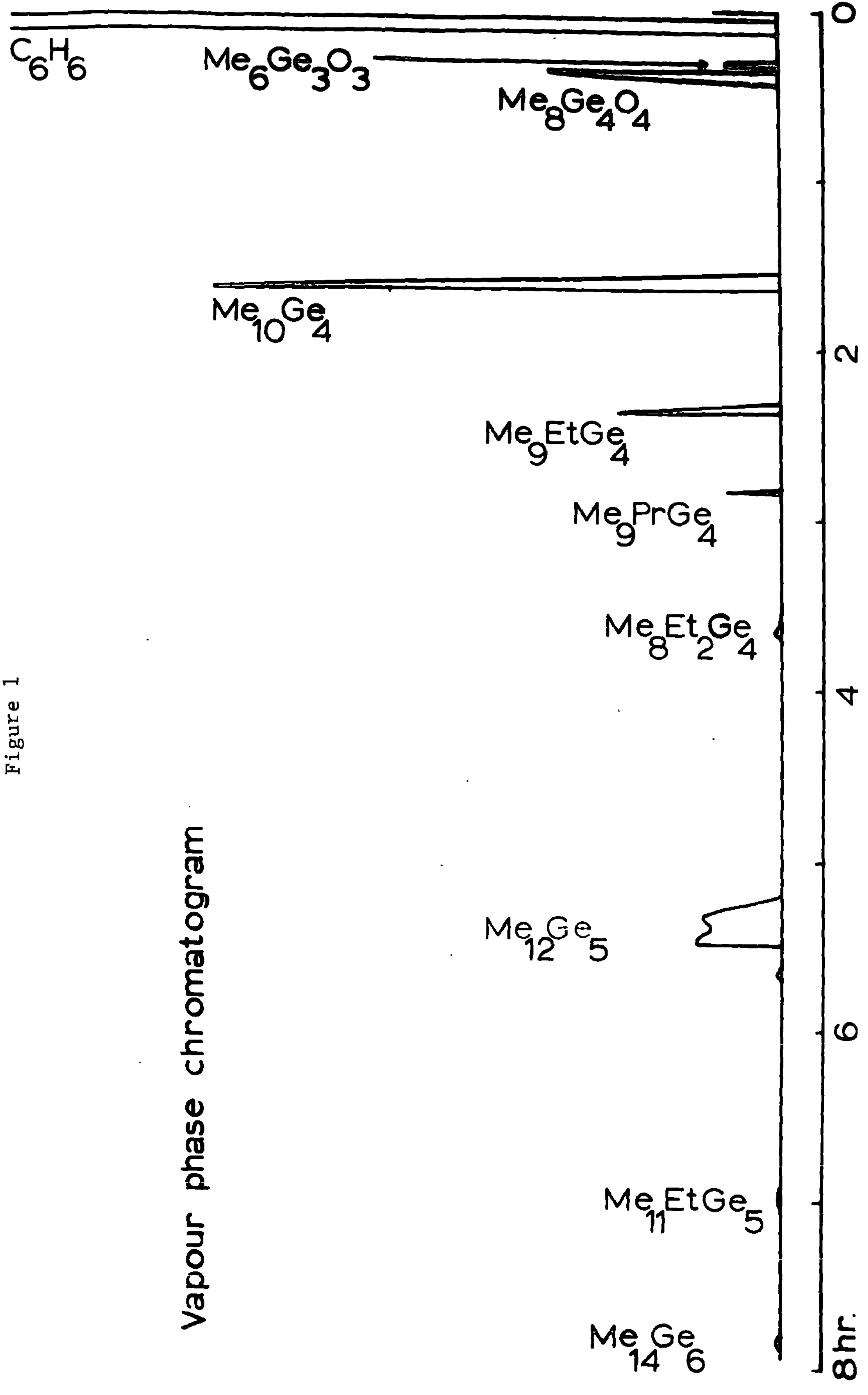
In a third experiment, 37·6 g. (0·5214 mole, a 9·56-fold excess) of Me_3Al were added to 26·7 g. (81·8 mmole) of GeI_2 and 160 ml. of cyclohexane and the mixture was stirred for 18 hr. at 20°, after which time most of the solid had gone into solution, leaving a buff residue.

Nothing collected in the -78^{o} trap. The cyclohexane and unreacted Me_3Al were distilled off. More cyclohexane was added to the residue, and the mixture filtered. The solid was returned to the flask and the cyclohexane/Me_3Al distillate added. Reflux at 100^{o} for 210 hrs. followed by hydrolysis and normal work up gave no organogermanium compounds. The filtrate from the initial reaction was hydrolysed with H_2O and dilute HCl, filtered and the organic layer separated and dried over $MgSO_4$. It was filtered and evaporated at $20^{o}C$ to 5×10^{-2} mm.Hg, leaving 7·3 g. of a viscous liquid, a mixture of $Me_{2n+2}Ge_n$ and $Me_xGe_yO_z$ (i.r.). 7·1 g. of this were dissolved in 10 ml. cyclohexane and chromatographed on an alumina column (67 cm x 2 cm.) by elution with cyclohexane; 50/50 cyclohexane/benzene mixture; benzene; and ethanol. The main fraction (2·7 g.) was a viscous, clear, colourless liquid with a pleasant smell, Ge_nMe_{2n+2} (i.r.). The low resolution mass spectrum showed a mixture of Ge_7Me_{16}, Ge_6Me_{14}, Ge_5Me_{12}, Ge_4Me_{10} and possibly Ge_3Me_8, with a very strong Me_3Ge^+ ion. V.p.c. on 5% NGA at 150^{o} showed many peaks, but separation of these was better at 200^{o} on 10% APL. 150μ l were separated (Pye Panchromatograph) and some of the components partially characterised by mass spectrometry as (in order of elution) $Me_6Ge_3O_3$, $Me_8Ge_4O_4$, $Me_{10}Ge_4$, $Me_{12}Ge_5$, $Me_{11}Ge_5Et$, $Me_{14}Ge_6$, $Me_{16}Ge_7$ and finally methylpolygermoxane of high molecular weight. The rest of the material was vacuum distilled in a microcup apparatus to concentrate the more volatile components. On distillation up to 110^{o}

at 2 x 10^{-4} mm. Hg a colourless liquid collected in the cup (0·9 g.), and this was separated by preparative v.p.c. (Pye 105). The chromatograph recording is shown in Figure 1. The compounds were partially characterised by mass spectrometry as $Me_8Ge_4O_4$ (378·7 mg.), $Me_{10}Ge_4$, Me_9Ge_4Et, Me_9Ge_4Pr, $Me_8Ge_4Et_2$, $Me_{12}Ge_5$ (two), $Me_{11}Ge_5Et$ and $Me_{14}Ge_6$. A solution of $Me_{10}Ge_4$ in benzene showed a single symmetrical peak when v.p.c.'d on 5% NGA, 5% SE30 and 10% APL stationary phases. This strongly suggested a single compound, not a mixture of the two possible isomers. The Raman spectrum showed no bands in the region expected for ν(Ge-Ge), (about 270 cm^{-1}) probably due to insufficiency of material. There were two bands at c.150 and 170 cm^{-1} which were attributed to Ge-Me deformation, by comparison with the spectrum of Me_6Ge_2.[148] The 60 Mc/s. p.m.r. spectrum showed a resonance at $9{\cdot}43\tau$ (as expected for a germanium methyl proton), and the 220 Mc/s spectrum showed unequivocably that the compound was methyltristrimethylgermylgermane, $(Me_3Ge)_3GeMe$. It was a colourless liquid (180·2 mg.) readily soluble in organic solvents. The compound, Me_9Ge_4Et (42·9 mg.) was a single isomer (v.p.c.), a colourless liquid readily soluble in organic solvents. The 220 Mc/s p.m.r. spectrum showed it to be methyl(bistrimethylgermyl)ethyldimethylgermylgermane.



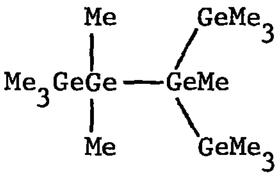
The next two compounds obtained were isomeric, but clearly distinguished



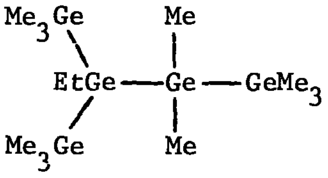
Vapour phase chromatogram

Figure 1

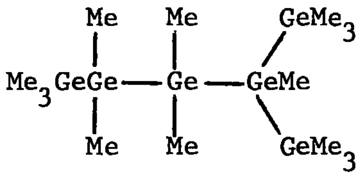
by their mass spectra as Me_9Ge_4Pr (18•6 mg.) and $Me_8Ge_4Et_2$ (9 mg.). A plot of log (retention time) against molecular weight for the three compounds $(Me_3Ge)_3GeMe$, $(Me_3Ge)_2Ge(Me)GeMe_2Et$ and $Me_8Ge_4Et_2$ gave a straight line, but Me_9Ge_4Pr did not lie on this line. This suggests that $Me_8Ge_4Et_2$ has the same germanium skeleton as the other two compounds. Since it is unlikely that the propyl compound is the only one with a straight chain of germanium atoms, the difference here probably arises from the propyl group itself and suggests it may be an isopropyl group. The first of the two $Me_{12}Ge_5$ fractions (94 mg. of colourless liquid) seemed, from its 60 Mc/s p.m.r. spectrum to be <u>methylbistrimethylgermyl(pentamethyldigermanyl)germane</u>



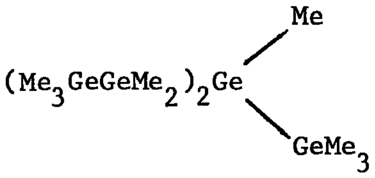
and the 220 Mc/s spectrum confirmed this assignment. The second half of the $Me_{12}Ge_5$ peak (24•4 mg.) also contained this compound, with some of the linear isomer $Me(Me_2Ge)_5Me$ also. The next fraction ($Me_{11}Ge_5Et$, 27•3 mg.) seemed, from its 220 Mc/s spectrum to be <u>ethylbistrimethylgermyl-(pentamethyldigermanyl)germane</u>

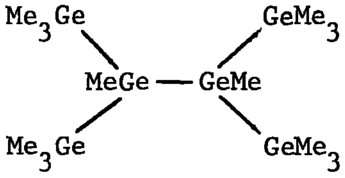


The final peak collected, $Me_{14}Ge_6$ (89•9 mg.) seemed from its 60 Mc/s spectrum to be methylbistrimethylgermyl(heptamethyltrigermanyl)germane



and the 220 Mc/s spectrum confirmed this and indicated that in addition the following compounds were present





$Me(GeMe_2)_6Me$

Thus out of 900 mg. injected, 865 mg. were accounted for. Continued microcup distillation up to 180° gave 0•36 g. of colourless liquid in the cup, which on cooling formed an opalescent, fluid gell. It was a mixture of $(Me_2Ge)_n$ and $Me_xGe_yO_x$ (i.r.), and contained $Me_8Ge_4O_4$, $Me_{14}Ge_6$, $Me_{16}Ge_7$, $Me_{18}Ge_8$, $Me_{20}Ge_9$ and $Me_{22}Ge_{10}$ (m.s.). The residue (0•6 g.) was a high molecular weight methylgermanium oxide (m.s., i.r.). During the distillation, 0•4 g. of $Me_6Ge_3O_3$ (v.p.c., i.r., m.s.) collected in a -196° trap, but appeared to isomerise to the tetramer on standing (m.s.). The presence of so much oxide in apparently oxide-free material suggests that the mixture as obtained after alumina chromatography contains unsaturated Ge^{II} which gradually oxidises. Two other major fractions (of 0•9 g. and 0•8 g.) were obtained from the alumina chromatography, and these like numerous minor fractions, were oxygen-containing. It was noted that some of the fractions immediately succeeding the main fraction, although clear at first, rapidly became opaque (in about 15 min.) and increased in viscosity. This again suggests aerial oxidation of Ge^{II} species, and the final product contained $Me_8Ge_4O_4$ and higher oxides (m.s., i.r.). As in the preceding experiment, some of the oxide material showed evidence for germanium bonded to more than two oxygen atoms (m.s.).

2:2:6 Reaction of Germanium Di-iodide with Triethylaluminium

13•8 g. (0•121 mole, a 11•9-fold excess) of Et_3Al were added to 5 g. (15•3 mmole) of GeI_2 and 30 ml. of cyclohexane and the mixture stirred at 20° for 17 hr. after which time almost all the solid had gone into solution. After another 5 hr., the mixture was filtered giving 0•5 g. of unidentified solid, and a lime-green filtrate. The filtrate was distilled at 20°C and 10^{-3}mm.Hg and work up of the distillate showed no germanium compounds. The residue was hydrolysed, extracted with ether and removal of the solvent left 2•7 g. of mixed liquid and semi-solid, $(Et_2Ge)_n$ and $Ge_xEt_yO_z$ (i.r.). It was chromatographed on alumina using the same procedure as for the methyl compounds. In all, 2•5 g. of material was recovered. The first fraction (0•5 g.) was a colourless fairly mobile liquid, containing ethylpolygermanes (i.r.) with no oxide. Mass spectrum showed Et_6Ge_2, Et_8Ge_3 and higher ethylpolygermanes, but no

Et_4Ge. Separation by preparative v.p.c. (Pye 105) on 25% SE30 allowed identification of Et_6Ge_2, Et_8Ge_3 and $Et_{10}Ge_4$ (m.s.), and a high molecular weight ethylpolygermane was also obtained. A second fraction (0·2 g.) was very viscous ethylpolygermane (i.r.) which oxidised in air, the mass spectrum showing $Et_5Ge_3O_3^+$, $Et_7Ge_4O_4^+$ and higher oxygen-containing ions. Other fractions were similar, and the final one (1·5 g.) showed the ions $Et_5Ge_2O^+$, $Et_3Ge_3O_3^+$ and $Et_7Ge_4O_4^+$ ions, among many others, in its mass spectrum.

2:2:7 Reaction of Germanium Di-iodide with Tri-isobutylaluminium

17·4 g. (87·6 mmole, an 8·59-fold excess) of Bu_3^iAl were added to 5 g. (15·3 mmole) of GeI_2 in 30 ml. of cyclohexane. After 32 hr. at 20°, almost all the solid had gone into solution, and after a further 6 hr. the mixture was filtered. The solid residue was a mixture of GeI_4 and Bu^iGeI_3 (i.r., m.s.). The filtrate was worked up in the usual way, and gave, after hydrolysis, 4·2 g. of yellow liquid, a mixture of $Bu^i_7Ge_3I$ and $Bu^i_5Ge_2I$ (m.s.), with some material of higher molecular weight.

2:2:8 Experiments to Elucidate Formation of Ethyl Groups in the Methyl Reactions

2:2:8:1 Hydrolysis of Trimethylaluminium

The mass spectrum of the trimethylaluminium used showed the complete absence of ethyl-containing species, the only impurity being dimethylaluminium methoxide. Nevertheless, the purity was also checked by hydrolysis, when any ethyl groups present should give ethane. 11·3 g. (0·156 mole) of Me_3Al were hydrolysed with cyclohexanol in methylcyclohexane and the issuing gases collected at -196°. The methane was pumped away at -196°, and the remaining material fractionated on a vacuum line to remove $CH_3C_6H_{11}$ and $C_6H_{11}OH$ and a trace of methanol (i.r.). There remained 0·6N ccs of gas which appeared to be hydrocarbon, although not ethane. Even if it were ethane, this would give a maximum ethyl content of 1 mole per 5800 moles Me_3Al.

2:2:8:2 Attempted Ethylation of Tetramethylgermane

To test the possibility of the reactions:

$$Me_4Ge + AlCl_3 \longrightarrow Me_3GeCH_2Cl + HAlCl_2$$

$$Me_3GeCH_2Cl \longrightarrow Me_2GeEtCl$$

2·9 g. (21·8 mmole) of Me_4Ge were added to 3·4 g. (25·5 mmole) of pure $AlCl_3$, followed by 1·8 g. (25·0 mmole) of Me_3Al. The mixture was heated for 3½ hr. at 70°, and then 6 hr. at 100°. 1·6 g. (27·3 mmole) of NaCl were added, and the mixture heated for 1 hr. at 100°. Normal work up gave Me_4Ge as the only germanium-containing compound.

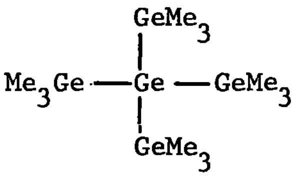
2:2:9 Selective Synthesis of Some Methylpolygermanes

2:2:9:1 Reaction of Germanium Tetrachloride and Trimethylgermyl-lithium

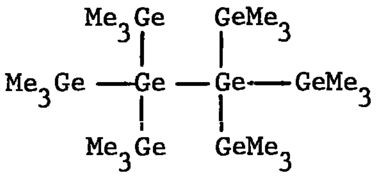
24 g. (0·181 mole) of Me_4Ge and 32 g. (0·200 mole) of Br_2 in 30 ml. of Pr^nBr were refluxed for 20 hr.[60] Distillation gave Pr^nBr (b.pt. 69°) and 33·8 g. (0·171 mole, 95%) of Me_3GeBr.

A 0•5% sodium amalgam was prepared (690 g. Hg and 3•5 g. Na) and poured into a flask fitted with a large paddle stirrer. 30 g. of redistilled Me_3GeBr were added, and the mixture stirred for 14 days in 60 ml. of cyclohexane. The product was extracted with benzene and the solvent removed and the residue sublimed in a Schlenck tube at 95°C/ $2{\cdot}5 \times 10^{-2}$ mm.Hg giving 6•4 g. (9•7%) of bistrimethylgermylmercury.[149] The unsublimable residue contained polymeric methylgermanium oxides.

2•9 g. (6•6 mmole) of $(Me_3Ge)_2Hg$ were dissolved in 15 ml. of tetrahydrofuran, and 1•2 g. (0•173 mole, a 13•1-fold excess) of lithium chips were added. The mixture was stirred for 4 hr. and then filtered through a sinter to remove excess Li and Hg, giving a port-coloured solution. 0•7 g. of $GeCl_4$ were added (giving a calculated excess of Me_3GeLi of 1•03-fold), the mixture immediately became hot and a brown precipitate was formed. The mixture was stirred for 15 hr. and refluxed for a further 2 hr. The THF was distilled off and the residue hydrolysed. Ether extraction gave 2•1 g. of a mixture of $Me_{12}Ge_5$ and $Me_{18}Ge_8$ (m.s.). Sublimation (200°/10^{-4} mm.Hg) gave a white solid, but achieved no separation of the two germanium compounds (p.m.r.). Both compounds appeared to be perfectly symmetrical, tetrakistrimethylgermylgermane and hexakis(trimethylgermyl)digermane



$$Ge(GeMe_3)_4$$



$$(Me_3Ge)_3Ge{-}Ge(GeMe_3)_3$$

2:2:9:2 Wurtz Reaction on Trimethylbromgermane

3•5 g. (89•5 mmole, a 1•13-fold excess) of potassium and 15•6 g. (78•9 mmole) of Me_3GeBr were refluxed for 12 hr. at 140°.[51] The potassium melted and gradually swelled into a puffy mass. The volatiles were removed by vacuum evaporation giving 5•4 g. (58•1%) of Me_6Ge_2 (i.r., m.s., v.p.c.) containing no Me_3GeBr, but with a little benzene (used to wash the potassium). Hydrolysis of the residue and extraction with ether gave a mixture of Me_6Ge_2, $Ge_3C_9H_{26}$, $Me_{12}Ge_5$ and other unidentified compounds (m.s.). Separation by v.p.c. (Pye 105) on 25% SE30 gave, besides Me_6Ge_2 (m.s.), trimethylgermylpentamethyldigermanylmethane, $Me_3Ge(Me_2)Ge\text{-}CH_2\text{-}GeMe_3$ (m.s., p.m.r.), Me_8Ge_3 (m.s.) and $Ge_4C_{11}H_{32}$ (m.s.). This last compound contained a $Ge\text{-}CH_2\text{-}Ge$ linkage, not an ethyl group, but there was insufficient for a p.m.r. spectrum. $(Me_3Ge)_4Ge$ was also obtained (m.s., p.m.r.). In addition a number of compounds which could only have come from attack on the benzene occurred, Me_3GePh (m.s.) and $(Me_3Ge)_3C_6H_3$ (m.s.).

2:2:9:3 Redistribution of Hexamethyldigermane and Germanium Tetrachloride

3•7 g. (15•7 mmole) of Me_6Ge_2 and 3•3 g. (15•4 mmole) of $GeCl_4$ were heated for 110 hr. at 130°. The resulting solution contained no Me_6Ge_2 (v.p.c.) but two new compounds were present, one of longer and one of shorter retention times. The volatiles were removed, and consisted of a mixture of benzene (from the preparation of Me_6Ge_2) and $MeGeCl_3$, with traces of $GeCl_4$, Me_3GeCl and Me_2GeCl_2 (m.s., i.r.) and the infrared spectrum of the involatile material was consistent with pentamethylchlorodigermane, Me_5Ge_2Cl.

2:2:9:4 Wurtz Reaction on Pentamethylchlorodigermane

4·5 g. (17·5 mmole) of Me_5Ge_2Cl and 0·8 g. (20·4 mmole, a 1·17-fold excess) of potassium were heated to 120° forming a solid mass. 4 ml. of benzene was added and the mixture refluxed at 100° for 21 hr. The volatiles were removed and the residue hydrolysed and extracted with ether giving 0·8 g. of a viscous liquid, mainly $Me_{10}Ge_4$ with some $Me_6Ge_3O_3$ and traces of $Me_8Ge_4O_4$ and $Me_{12}Ge_5$ (m.s.).

PART II. SPECTROSCOPIC STUDIES

Part II. Spectroscopic Studies

3. Introduction: Use of Spectroscopic Methods in Organogermanium Chemistry

In recent times the importance of spectroscopic methods in inorganic, organic and organometallic chemistry has been growing rapidly. Compared with them, traditional chemical methods of analysis and degradative determination of structure are lengthy and often imprecise. In organogermanium chemistry, infrared spectroscopy has long been of importance, but it is a relatively insensitive tool with which to deal with organopolygermanes. A combination of mass spectrometry and high frequency proton magnetic resonance spectroscopy can provide complete answers to analytical problems in this field.

An enormous quantity of data has been published concerning the spectra of organogermanes, and in the discussion which follows no attempt is made at completeness. Aspects which are most relevant to the original work presented later will be emphasised.

3:1 Infrared Spectroscopy

The great value of infrared spectroscopy as far as germanium compounds are concerned, is in the identification of groups bound to germanium. Many frequencies characteristic of particular X-Ge groupings have been identified, and these are often confined to a narrow band of the spectrum for a wide range of compounds. While this is invaluable for the detection of groups present, it means that differences between the spectra of similar compounds are minor. For example, the germanium-hydrogen stretch in the germanes occurs at 2030-2080 cm^{-1}. The presence of the Ge-H unit is almost always apparent from the infrared spectrum but it is much less obvious to which particular hydride or hydrides it belongs. It may be possible to decide this by careful comparison with the spectra of known compounds, but for the investigation of new compounds this is not a helpful approach.

Characteristic frequency ranges for groups bonded to germanium have been established by comparing large numbers of compounds.[18,26,40] In some cases the physical process producing the absorption of radiation has been identified, but there remain many characteristic frequencies whose origins are obscure. Some frequency ranges which have proved useful in the present work are tabulated below. (Key references only are given) These ranges cover poly- as well as mono-germanes. In some cases, the similarity between analogous mono- and poly-germanes is quite remarkable. For example, the methyl rock in Ph_3GeMe falls at 788 cm^{-1}. In $(Ph_3Ge)_3GeMe$ it is at 787 cm^{-1}. The frequencies of the

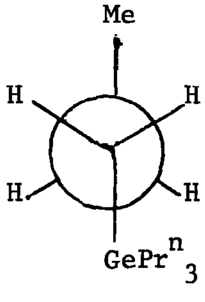
Table 1. Infrared Frequency Ranges for Groups Bonded to Germanium

Range (cm^{-1})	Assignment	References
3651	νGeO-H	40
2080-1953	νGe-H	40,150,151,152,153,154
1462-1449	$\delta_{asym}CH_3$(Et)	26
1428-1414	$\delta_{asym}CH_2$(Et)	26
1437-1405	$\delta_{asym}CH_3$(Me)	18,155
1379-1368	$\delta_{sym}CH_3$(Et)	26
1259-1227	$\delta_{sym}CH_3$(Me)	26,155
1234-1209	$\delta_{sym}CH_2$(Et)	26
926-820	νGe-O-Ge	26,156,157
850-787	ρCH_3(Me)	18,26,155
799-680	δ(Ge-H)	40,150,151,152,153
648-635	νGe-C(Bu^n, *trans*)	18,26
641-535	νGe-C(Me)	18,26,155
608-556	νGe-C(Et)	18,26
568-556	νGe-C(Bu^n, *gauche*)	26
425-362	νGe-Cl	40
283-263	νGe-I	26
228	νGe-Ge	73

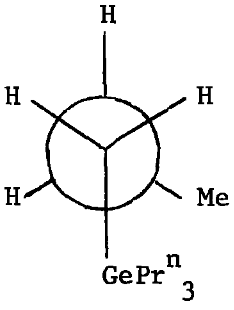
methyl rock in $(MeGe(CH_2Ph)_2)_2$ and $MeGe(CH_2Ph)_3$ are 801 and 800 cm^{-1} respectively.[26] Similar cases have been commented on in the literature.[15]

There are a number of bands characteristic of ethylgermanes which have not been assigned unequivocably. Those at 1030-1010 cm^{-1} and 970-950 cm^{-1} are thought to be ν(C-C) and δ(C-H) whilst those at 325 and 300-290 cm^{-1} are possibly δ(Ge-C-C). The band at 710-680 cm^{-1} is probably a methylene rock.[26]

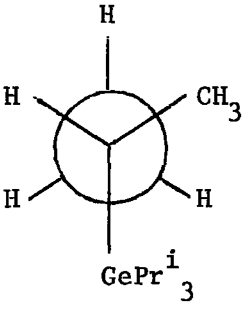
The n-propyl group can give rise to gauche and trans conformers, whereas the isopropyl group cannot, and two widely separated bands are seen in the spectrum of $Pr^n{}_4Ge$, one corresponding to the trans



trans



gauche



conformation and one to the gauche.[13] (These should not be confused with the symmetric and asymmetric Ge-C stretches, which occur much closer together, and are often not clearly separated). Two bands occur in tetra-n-butylgermane for the same reason.[26]

Characteristic frequency ranges have been ascribed to many organic groups, such as Ph-Ge, $PhCH_2$-Ge and (tolyl)-Ge,[26] besides those listed in the Table.

Germanium dioxide absorbs most strongly at 880 cm^{-1}, and many organogermanes such as $(R_3Ge)_2O$ and $(R_2GeO)_n$ absorb at about this frequency. These vibrations are always broad and in cyclic oxides such as $(Me_2GeO)_n$, the extent of polymerisation affects the frequency of absorption.[156,157]

3:2 The Raman Effect

In theory it should be possible to derive the structures of higher germanes from the Ge-Ge stretching modes in their far infrared spectra. In practice more success has attended consideration of their Raman spectra in this region. For the germanium hydrides, ν(Ge-Ge) produces strong bands in the region 200-300 cm^{-1}. All the predicted bands in the spectra of Ge_2H_6, Ge_3H_8, n-Ge_4H_{10} and i-Ge_4H_{10} have actually been observed, and the three pentagermanes have been characterised by this effect.[158]

The Raman spectrum of hexamethyldigermane has been analysed thoroughly, and ν(Ge-Ge) placed at 273 cm^{-1}.[148]

3:3 Ultraviolet Spectroscopy

In the ultraviolet spectrum of Ph_6Ge_2 there is a very intense band which masks the fine structure typical of a phenyl group. This band is not present in Ph_4Ge, and it was at first ascribed to interaction of phenyl groups via the Ge-Ge bond.[159] The observation that compounds of the type Ph_3MMR_3 also exhibit this band caused the explanation to be modified.[160] Furthermore, it was subsequently shown that even compounds of the type R_3GeGeR_3 (where R is alkyl, e.g. Pr^i)[13] have a band in this region of the ultraviolet. Thus the excitation is a characteristic of the M-M bond itself, and has been observed in silicon, tin and lead compounds as well as germanium ones.[161] In $Ph(Me_2Si)_nPh$, both λ max and ϵ increase as n increases.[162]

Table 2. Ultraviolet Absorption Maxima

	λ max (mμ)	ϵ	Reference
$Pr^i{}_6Ge_2$	210	$6{\cdot}46 \times 10^3$	13
Ph_6Ge_2	239	$30{\cdot}4 \times 10^3$	159

The cyclic compounds $(GePh_2)_n$, n = 4,5,6 also absorb in this region.[91]

3:4 Proton Magnetic Resonance Spectroscopy

The only naturally occurring isotope of germanium (^{73}Ge) with a nuclear spin ($^{9}/2$) is of such low abundance (7·6%) that side-bands due to coupling with it are not normally seen. Only in the p.m.r. spectrum of liquid Me_4Ge has J('H-C-^{73}Ge) been reported, as 2·94 cps. Only the six outside lines of the expected decaplet were observed, the other four falling under the main resonance.[163]

The resonance of hydrogen bonded directly to silicon, germanium and tin is to low-field of tetramethylsilane, showing that there is little diamagnetic shielding (Table 3). It is worth considering the use of p.m.r. spectra to identify some of these germanes, since a similar, though not identical, problem occurs in the characterisation of the methylpolygermanes. The spectrum of $(GeH_3)_3GeH$ is approximately first order, a doublet (GeH_3) and a decet (GeH).[158] The coupling constant $J_{GeH-GeH_3}$ is 4 cps, compared with J_{CH-CH_3} which is 5 cps.[152] The spectrum of $H(GeH_2)_4H$ is more complicated, being a second order spectrum, almost a mirror image of the spectrum of n-butane. $(GeH_3)_4Ge$ is again a first order spectrum, showing only a single peak. The other pentagermanes have second order spectra. In all these compounds, the GeH_2 and GeH signals occur up-field from GeH_3.[158] Successive replacement of hydrogen in germane by methyl groups, on the other hand, moves the Ge-H resonance to low-field. At the same time, the methyl C-H resonance moves progressively to high-field, until Me_4Ge is reached. Spin-spin coupling of the methyl protons with the germanium protons occurs in

Table 3. Some Ge-H and GeC-H Resonances (τ values)

	GeH_3	GeH_2	GeH	$GeCH_3$	$GeCH_2$	Ref.
GeH_4	6•73					164
Ge_2H_6	6•79					165
Ge_2H_5Cl	6•37	4•61				119
Ge_2H_5Br	6•21	5•31				119
Ge_2H_5I	5•96	6•57				119
Ge_3H_8	6•7	6•89				152
$(H_3Ge)_3GeH$	6•64		7•1			158
$(H_3Ge)_4Ge$	6•43					158
$MeGeH_3$	6•51			9•65		164
Me_2GeH_2		6•27		9•71		164
Me_3GeH			6•08	9•79		164
Me_4Ge				9•87		164,166
Me_6Ge_2				9•79		166
$(Me_2Ge)_6$				8•63		88
$(Me_3Ge)_2O$				9•69		167
Me_2GeEt_2				9•92	9•31	168
$(Me_3Ge)_2CH_2$				9•89	10•13	169
$(Me_3GeCH_2)_2$				9•94	9•28	169
$(Me_2GeO)_3$				9•51		170
$(Me_2GeO)_4$				9•53		170

these compounds, J_{CH-GeH} being approximately 4 cps.[164] The GeH_3-GeH_2 coupling constants for the digermanyl halides are also of this order.[119]

Some attempt has been made to resolve the Group IV electronegativity controversy from p.m.r. data. This is essentially a risky undertaking, since chemical shifts depend on many inter-related effects, and electronegativity itself cannot be defined rigorously. On the assumption that change in electronegativity of the central atom was the only factor affecting the chemical shift of the methyl protons in the tetramethyl compounds of carbon, silicon, germanium, tin and lead, electronegativity values were obtained which suggested that they decreased in the order $C > Pb > Ge > Sn > Si$.[171] This work has been subjected to detailed criticism. It was shown that the electronegativity of carbon in these compounds varies in a way not dependent on the electronegativity of the central atom, and this invalidates the use of chemical shift for determining the electronegativity sequence from these compounds.[172] Differences in chemical shift between MH_3 and MH_2 for germanium and silicon[152,165] and in the size of coupling constants in hexavinyldigermane and the vinylsilanes[173] have also been cited as evidence for equal or slightly larger electronegativity of germanium compared with silicon. In spite of this, and of some chemical evidence[171] in favour of the anomolous electronegativity order, the question is still quite open.

A p.m.r. study of polymeric dimethylgermanium oxides has shown that an equilibrium exists between the trimer and the tetramer.

$$4(Me_2GeO)_3 \rightleftharpoons 3(Me_2GeO)_4$$

Pure forms of either oligomer undergo equilibration on standing, and the position of equilibrium depends on conditions, particularly temperature. Thus the trimeric form is more stable at high temperature. Both forms age to give high molecular weight polymers. The processes involved can be followed by observing changes in the methyl proton resonance.[170]

Some chemical shift values relevant to the experiment work are included in Table 3.

3:5 Electron Impact Spectrometry

Most of the work on the mass spectra of organogermanes reported in the literature appeared concurrent with or subsequent to the experimental studies presented in this thesis. For this reason, such work will be discussed and acknowledged at appropriate points in the discussion of the experimental work itself. The principle exceptions are the studies of Me_4Ge[174] and of isopropylgermanes.[13] Since the results reported for these have been confirmed and extended during the present investigation, they too are best referred to later.

It is however, convenient, to mention the mass spectra of the germanes themselves at this juncture. GeH_4 has been the subject of several papers.[175,176] In the most careful and recent of these isotopically pure germanium, ^{74}Ge, was used.[175] The abundances obtained for the ions present were essentially those reported in the experimental section. Appearance potentials were measured for all of the ions, and for all possible processes leading to them. The values fall in the range 10-20 e.V. The energy of the Ge-H bond calculated from these measurements (68•4 kcals/mole) agreed well with the calorimetrically determined value (69•0 kcals/mole).[111]

In a similar study of Ge_2H_6,[113] for which isotopically pure germanium was again used, the most abundant ion was $Ge_2H_2^+$ (100%) followed by Ge_2^+ (66%). Appearance potentials were measured for all ions, and the energy of the Ge-Ge bond was calculated to be 33•2 kcals/mole, compared with a calorimetric value of 37•9 kcals/mole.[111] In the mass spectrum[113] of $^{74}Ge_3H_8$, Ge_3^+ was the base peak and all ions of greater abundance than 20% of it contained more than one metal atom. The Ge-Ge bond energy obtained from appearance potential measurements on this compound was 27·9 kcals/mole.

The mass spectrum of $H(GeH_2)_4H$ had a similar fragmentation pattern to n-butane, in that the relative abundance of fragments was in the order $M_3^+ > M_2^+ > M_4^+ > M_1^+$, (M = Ge or C). The other isomer, $(H_3Ge)_3GeH$ had a similar spectrum to isobutane, the order of ion types being $M_3^+ > M_2^+ > M_1^+ > M_4^+$.[152]

Mass spectrometry was used to confirm the identity of the digermanyl halides. The abundance of the Ge-halogen containing ions decreased in the order Cl > Br > I.[119]

A number of organogermanes have been partly characterised by their mass spectra.[132,149,177,178,179,180,181,182,183]

3:6 Electron Diffraction

Electron diffraction studies of Ge_2H_6 and Ge_3H_8 gave the Ge-Ge bond distance in both molecules as 2·41 ± 0·02 Å.[184]

4. Experimental Investigations: Spectra of Organogermanes.

Details of the type and operation of spectroscopic equipment have been given in Section 2:1:1 and will not be repeated here.

4:1 Infrared and Raman Spectra

In tetra-alkylgermanes ν(Ge-C) moves to lower frequency in the series[13,26] $Me_4Ge > Et_4Ge > Pr^i_4Ge$ but for Pr^n_4Ge, Bu^n_4Ge and Bu^i_4Ge a shift to higher frequency is observed. Both Pr^n_4Ge and Bu^n_4Ge show a band which has been assigned[26] to ν(Ge-C) _gauche_, but Pr^i_4Ge has no _gauche_ form (Section 3:1). Two conformations can be written for Bu^i_4Ge, but only one ν(Ge-C) band is visible in the neat liquid at 20-190°. This band is presumably due to (A), which may be compared with

(A) (B)

Projections along a Ge-C bond.

the _gauche_ form of Bu^n_4Ge, while (B) is more cluttered. From this it is concluded that Bu^i_4Ge exists entirely in the (A) form even at 190°.

In hexa-alkyldigeramnes, the germanium-carbon stretching frequency is lower than in the corresponding tetra-alkylgermanes and an additional

Table 4. ν(Ge-C) for Mono- and Di-germanes, (cm^{-1})

R	R_4Ge				R_6Ge_2		
Me	602 (gas)				592		552
Et	570				565		528
Pr^i [9]	559	549(s)			543	536(s)	505
Pr^n [9]	639(t)		567(g)	553(s)			
Bu^n [26]	641(t)		556(g)				
Bu^i	647	641(s)			639		610

(t = *trans*, g = *gauche*, s = symmetric)

weaker band occurs at even lower frequency. In monogermanes, the Ge-C stretch (either *trans* or *gauche*) sometimes has a shoulder due to separation of the symmetric stretch from the asymmetric stretch. In general, the symmetric stretch, when visible, is at lower frequency. In Et_6Ge_2O, there are two Ge-C stretches quite widely separated (Ge-Et$_{asym}$, 582 cm^{-1} and Ge-Et$_{sym}$, 536 cm^{-1})[185], and it is probable that the two bands due to ν(Ge-C) in alkyldigermanes are produced in the same way. (Table 4).

Infrared spectra (3000-400 cm^{-1}) of the higher organogermanes, Ge_nR_{2n+2}, were strikingly similar to those of the corresponding digermanes (as noted by previous workers[15]). The figures quoted in Table 5 must be treated with caution, since it was difficult to obtain sufficient material for infrared spectra in a high state of purity. The spectra of some

Table 5. Infrared Spectra of Methylpolygermanes

		ν(C-H)	$\delta_{sym}CH_3$	ρCH_3	νGe-C cm^{-1}
Me_4Ge	g	2967,2907	1248	828	602
Me_6Ge_2	1	2967,2899	1231	823	592,552
$(Me_3Ge)_4Ge$	1	2967,2899	1236	826	593,556
$(Me_3Ge)_4Ge$ $(Me_3Ge)_6Ge_2$	s	2941,2899	1229	811	584,553
$Me_{12}Ge_5$-$Me_{16}Ge_7$	1	2967,2907	1235	823,772	588,558
$Me_{14}Ge_6$-$Me_{22}Ge_{10}$	ss	2985,2898	1235	825,775	590,559

(g = gas, 1 = liquid, s = solid, ss = semi-solid)

mixtures have been included, and serve to illustrate the close similarity between the higher oligomers. The spectra appear quite clean, and could easily be mistaken for those of single compounds. The intensity of the second Ge-C stretch increases with the number of germanium atoms and when this is 5 or greater, the two Ge-C stretches are of equal intensity. For the ethyl- and isobutyl-polygermanes, the same general remarks could be made.

The methylpolygermoxanes resembled the polygermanes quite closely especially in the frequency of $\delta_{sym}CH_3$, but the methyl rock at about 805 was flanked by two bands of variable intensity at 855 and 763 cm^{-1}. These are due to ν(Ge-O-Ge), and their variation with degree of polymerisation has been noted. The germanium-carbon stretches varied very little in frequency, being at 588 and 556 cm^{-1}, the latter usually being the weaker. It will be noted that these are almost identical with ν(Ge-C) in the methylpolygermanes. A third band in this region at 625 cm^{-1} is more difficult to assign. It is probably associated with the Ge-O-Ge system rather than Ge-C. In some cases, broad bands were apparent below 500 cm^{-1}. The exact nature of the species present in the oxide mixtures obtained was rarely discovered, and it is unlikely that any of the spectra were of pure compounds especially since equilibration and ageing occurs on standing (Section 3:4). In addition, the phase of the mixture was dependent on its mode of preparation, and ranged from solid to mobile liquid. In some cases the phase itself appeared to be mixed. For these reasons a more detailed discussion of individual spectra is not appropriate. It is sufficient that the spectra were readily recognisable as oxides as distinct from methylgermanium polymers, and that they usually approximated to the spectra described for[156,157] trimer, tetramer and high polymer. Again, ethyl- and isobutyl- spectra had similar characteristics.

Isobutylgermane, Bu^iGeH_3, as gas, showed, in addition to isobutyl vibrations, ν(Ge-H) at 2089 and 2075 cm^{-1}, and two poorly resolved bands at 844 and 839 cm^{-1}. These are probably due to $\delta(GeH_3)$, (δGeH_3 bands of $MeGeH_3$[186] and $EtGeH_3$[187] occur in this region, 800-900 cm^{-1}), ν(Ge-C) was at 581 cm^{-1}.

A list of the main bands found in $Bu^i{}_4Ge$ is as follows:

2899s (complex), 2793sh, 1466s, 1410m, 1383s, 1368s, 1326m, 1211m, 1164s, 1092m, 1040m, 947w, 917w, 822w, 759s (some structure to low frequency, typically 4 step-like shoulders), 647m; and in $Bu^i{}_6Ge_2$: 2941s (complex), 2801sh, 1462s, 1408m, 1379s, 1364s, 1321m, 1211w, 1163s, 1089s, 1038s, 947m, 917w, 823m, 752s (structure more pronounced than in $Bu^i{}_4Ge$), 639m, 610w.. (s = strong, m = medium, w = weak, sh = shoulder).

The number of bands expected for the Ge-Ge stretch in the Raman spectrum of a polygermane can be calculated, and this has been used in the identification of the germanes themselves (Section 3:2). An attempt to identify the structure of $Me_{10}Ge_4$, obtained in the preparative work, from its Raman spectrum failed because of insufficient material. No Ge-Ge stretching vibrations were visible. Two bands ascribed (by comparison with the spectrum of Me_6Ge_2[148]) to δ(Ge-Me) were seen at approximately 150 and 170 cm^{-1}.

4:2 Ultraviolet Spectra

The ultraviolet spectra of Me_6Ge_2, Et_6Ge_2 and $Bu^i{}_6Ge_2$ all had a maximum at about 204 mμ., and the value of the extinction coefficient increased along the series (Table 6). The $Bu^i{}_6Ge_2$ maximum shifted slightly to higher wavelength with increasing concentration, but became unsymmetrical.

Table 6. Absorption Maxima of Organodigermanes

Compound	Maximum, mμ	Extinction Coefficient(log)
Me_6Ge_2	204	3·67
Et_6Ge_2	204	3·80
$Bu^i{}_6Ge_2$	204	4·24

Mixtures of $Me_{12}Ge_5$ and $Me_{18}Ge_8$ and of $Me_{12}Ge_5$, $Me_{14}Ge_6$ and $Me_{16}Ge_7$ had a broad asymmetrical band with its maximum at 208 mμ.

At very high concentrations, Me_4Ge, Et_4Ge and $Bu^i{}_4Ge$ have maxima visible at 201, 201 and 203 mμ respectively. The extinction coefficient was measured for the ethyl compound, and found to be very small (ϵ = 0·61). This is the region in which hydrocarbons begin to absorb weakly, so the band in organogermanes may be associated with the organic part of the molecule.

4:3 Proton Magnetic Resonance Spectra

Many of the methylpolygermanes isolated in the preparative work could be identified only partially from their mass spectra. For instance, the compound formulated as $Me_{10}Ge_4$ could have been either of the two possible isomers, or a mixture of both (although v.p.c. strongly suggested a single compound). The p.m.r. spectra obtained at 60 mc. were often suggestive of a particular isomer, but the instrument was operating near the limit of its resolution, and the samples available were usually so weak (1-5% solutions in benzene) that the noise level reduced the spectrum to a relatively featureless envelope. The use of a 220 mc. spectrometer overcame all these difficulties.

Although 'H-^{73}Ge coupling has been described in liquid Me_4Ge (Section 3:4), it was not observed in the present study. Coupling of the type 'H-C-Ge-C-H' and 'H-C-Ge-Ge-C-H' did not occur (this possibility was eliminated by examining the compounds at 100 and 220 mc.), although H'-Ge-C-H' and 'H-Ge-Ge-H' coupling are known (Section 3:4), and H'-Sn-C-C-H' coupling has been reported.[188] As a result the spectra were exceptionally simple, and even mixtures of isomers gave spectra which could be interpreted. The magnitude of the chemical shift was indicative of the methyl proton environment (Me_3Ge, Me_2Ge or MeGe) but since it was very sensitive to the structure of the molecule as a whole, it was not so useful for identifying a proton type as was relative peak area.

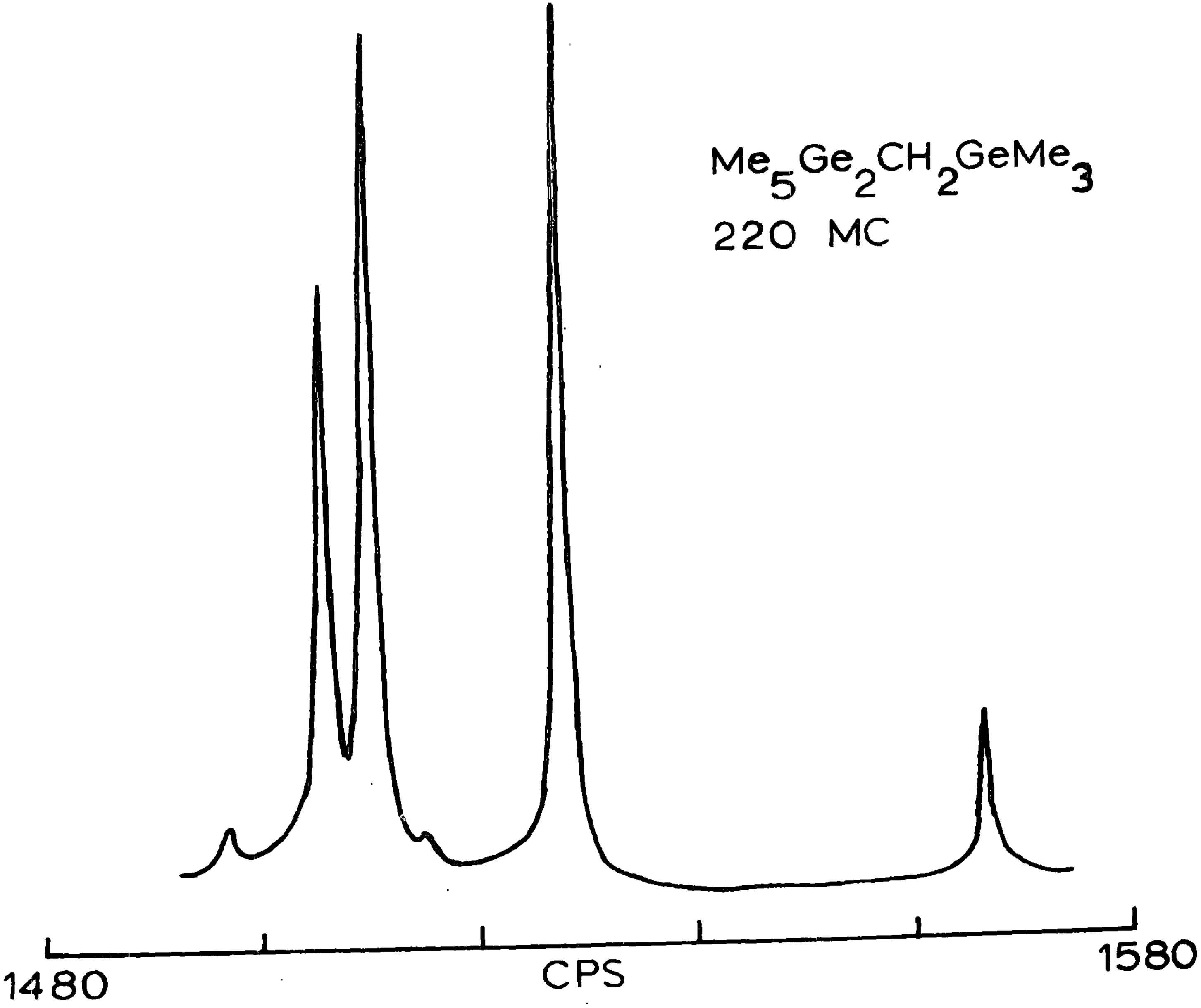
The p.m.r. spectra of Me_4Ge and Me_6Ge_2 were run for comparison purposes. Both gave single, sharp peaks as expected. The chemical shifts in p.p.m. upfield from benzene (solvent and internal standard, τ = 2·734 ± 0·003)[189] are given in Table 7.

Table 7. Chemical Shifts in Methylpolygermanes Relative to C_6H_6

Compound	Me_3Ge	Me_2Ge	MeGe	$GeCH_2$	CH_3(Et)
Me_4Ge	7·023				
Me_6Ge_2	6·886				
$Me_5Ge_2CH_2GeMe_3$	6·945 6·864	6·845		7·145	
$(Me_3Ge)_3GeMe$	6·768		6·691		
$(Me_3Ge)_2Ge(Me)GeMe_2Et$	6·750	6·795	6·709	6·209	6·036
$(Me_3Ge)_4Ge$	6·895				
$(Me_3Ge)_2GeMeGe_2Me_5$	6·759 6·800	6·677	6·686		
$Me(GeMe_2)_5Me$	6·817	6·731 6·718			
$(Me_3Ge)_2GeEtGe_2Me_5$	6·797 6·754	6·713			
$Me_{12}Ge_5$ + $Me_{18}Ge_8$	6·727 6·645				
$Me_{14}Ge_6$ mixture	6·814 6·801 6·759 6·756 6·752	6·710 6·708 6·699	6·669 6·663 6·652		

$Me_3Ge(Me)_2GeCH_2GeMe_3$ was characterised completely from its mass spectrum, but the p.m.r. spectrum (Figure 2) provided useful

Figure 2

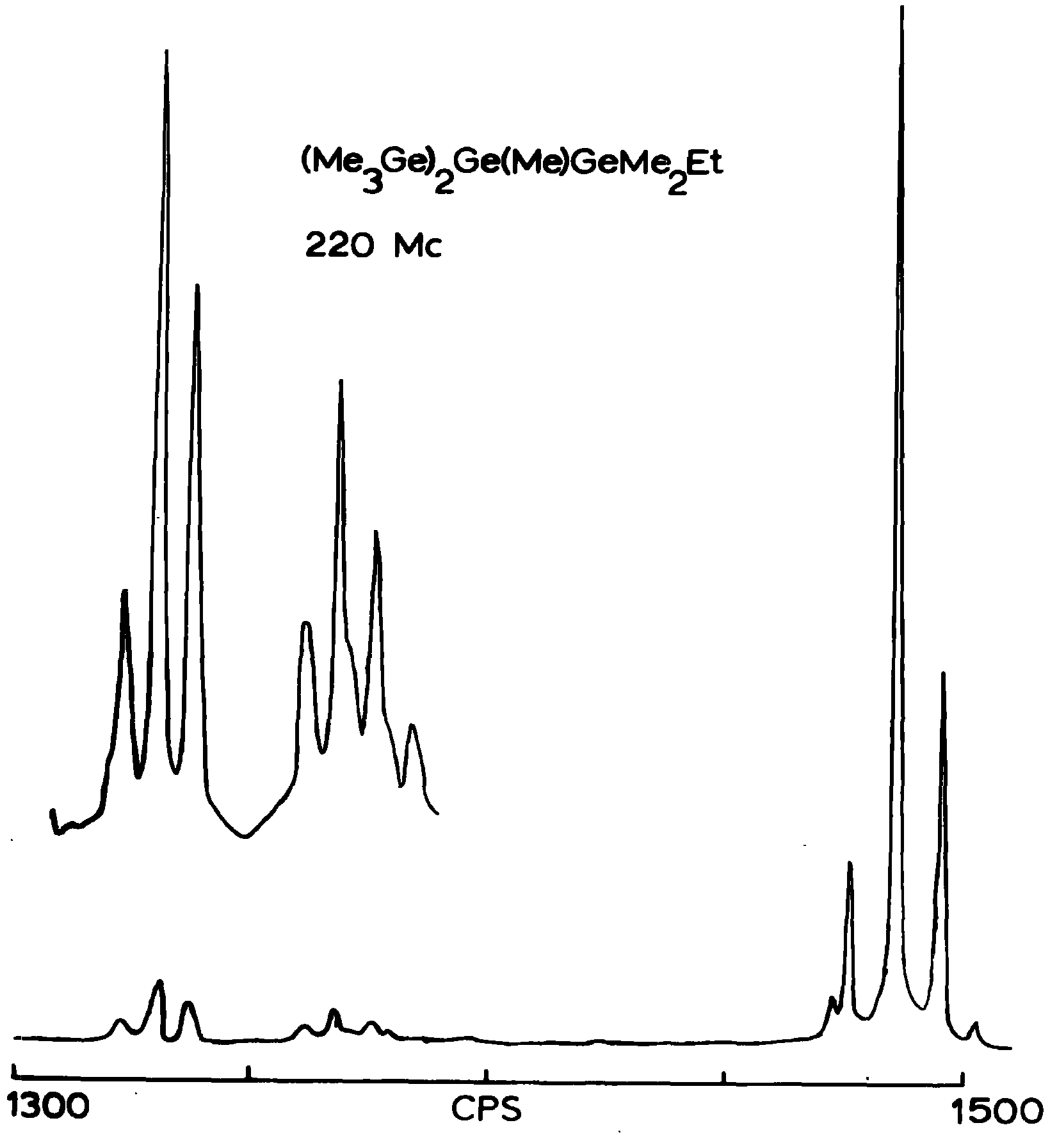


confirmation of it. The extremely high chemical shift of the Ge-CH_2-Ge protons (relative area, A = 2) has been noted also in the compound $Me_3GeCH_2GeMe_3$, but the CH_2 protons in $Me_3GeCH_2CH_2GeMe_3$ are shifted to low field.[169] (Table 3). The $GeMe_2$ protons were easily distinguished (A = 6), but the two Me_3Ge resonances could not be identified unambiguously, both having the same area (A = 9).

The spectrum of $Me_{10}Ge_4$ showed quite clearly that it was in fact $(Me_3Ge)_3GeMe$, having two resonances of relative areas 9:1. Me_9EtGe_4 had the same germanium skeleton, the relative areas of the three Ge-Me resonances (6:2:1) showing that the ethyl group replaces one of the Me_3Ge methyls, (Figure 3). The Ge-CH_2 protons of the ethyl group are well down-field, and the CH_3 protons of the ethyl group are lower still. This is the reverse of the order in hydrocarbons, but is normal for ethyl groups bonded to germanium. The fine structure of the triplet and quartet were well resolved, the coupling constant being 7·4 c.p.s. The chemical shifts were close enough for the beginnings of a second order spectrum, the triplet and quartet sloping towards one another.

As expected, the spectrum of $(Me_3Ge)_4Ge$ was a single sharp peak. The one other isomer obtained pure proved to be $(Me_3Ge)_2GeMeGe(Me_2)GeMe_3$. In this compound the two Me_3Ge resonances could be assigned as they had different areas (A = 6,3). The GeMe and $GeMe_2$ resonances were not well enough separated for individual integration, but their sum was as expected (A = 3), and visual inspection indicated a 1:2 ratio of the peaks.

Figure 3



A mixture of this compound with the linear isomer was also obtained. Because the spectrum was that of a mixture and complicated by overlapping, accurate integration was not possible, but visual inspection showed the peaks to be present in approximately the right ratios for a 3 to 2 mixture of linear to branched isomers.

$Me_{11}EtGe_5$ was rather weak for accurate integration, but visual inspection strongly indicated the structure $Me_3GeGe(Me)_2GeEt(GeMe_3)_2$. The ethyl resonance was swamped by noise.

The mixture of $(Me_3Ge)_4Ge$ and $(Me_3Ge)_6Ge_2$ showed two sharp peaks. The resonance assigned to $(Me_3Ge)_4Ge$ was 0·17 c.p.s. lower than that found for the pure compound, but the strengths of the solutions were different, and solvent effects (generally pronounced in benzene) could have produced this shift. The relative areas of the two peaks corresponded to a 2 to 1 mixture of $(Me_3Ge)_4Ge$ and $(Me_3Ge)_6Ge_2$.

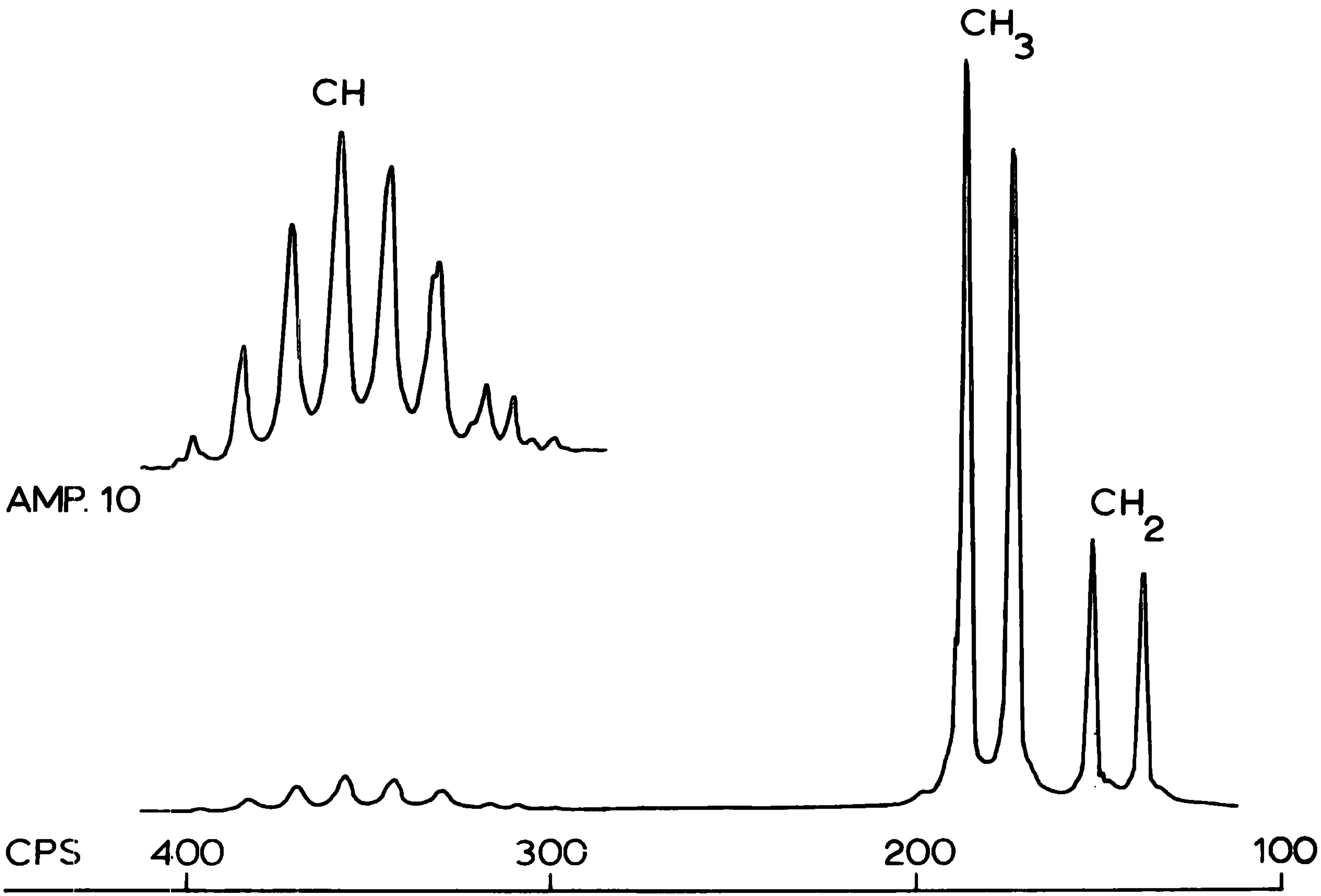
The spectrum of the $Me_{14}Ge_6$ compound was complex, but compatible with a mixture of $Me(GeMe_2)_3GeMe(GeMe_3)_2$, $(Me_5Ge_2)_2GeMeGeMe_3$, $((Me_3Ge)_2GeMe)_2$ and $Me(GeMe_2)_6Me$.

Discussion of relative chemical shifts must be generously laced with caution. The differences are slight, and the samples were not all run at the same concentration (because of the minute amounts available), so that solvent effects could be important. It is probably safe to make comparisons within a molecule, but extension to other molecules is less sound.

The chemical shift of the protons in tetramethylgermane is very high, and this can be ascribed to the greater electronegativity of carbon compared with germanium. Electron density withdrawn from the Ge-C bond towards carbon reinforces the shielding of the protons. In hexamethyldigermane, it would appear that the available charge density per methyl group is greater, and therefore the shielding should be greater. However, the shielding depends not only on the overall charge density, but also on the symmetry of charge distribution. This in turn is related to the symmetry of the molecule as a whole, and the higher the symmetry, the greater the shielding effect. The symmetry in Me_6Ge_2 is less than that of Me_4Ge, and this outweighs the inductive effect, and the resultant shift is down-field. A similar argument can be used to account for the fact that in most of the molecules examined the up-field shift decreases in the order $Me_3Ge > Me_2Ge > MeGe$. In $Me_5Ge_2CH_2GeMe_3$, the $GeCH_2Ge$ protons are shifted up-field, and here the inductive effect must predominate. In the compound $(Me_3Ge)_2Ge(Me)GeMe_2Et$, the two methyl groups attached to the germanium with the ethyl resonate at higher field than the Me_3Ge groups. Here, the smaller inductive withdrawal of electron density by the ethyl group must more than compensate for the loss of symmetry. In $(Me_3Ge)_4Ge$, the resonance is at higher field than in Me_6Ge_2, because of the greater symmetry of the former. It is lower than in Me_4Ge, but then the local symmetry in $(Me_3Ge)_4Ge$ is lower. In $(Me_3Ge)_2GeMeGe_2Me_5$, the $GeMe_3$ attached to $GeMe_2$ gave a signal at higher field than those attached to GeMe. In this particular compound the GeMe proton resonance is at higher field than the Me_2Ge proton resonance. No explanation is offered for these observations. In the linear compound $Me(GeMe_2)_5Me$, the central Me_2Ge group gave a resonance at higher field than the flanking Me_2Ge groups. This is contrary to the analogous silicon compound.[190]

The 100 mc. p.m.r. spectrum of Bu^i_4Ge (Figure 4) in carbon tetrachloride at 33° showed a doublet (τ8·55) due to methylene protons (J_{CH_2-CH} = 14·3 c.p.s.) and a doublet (τ8·20) due to methyl protons (J_{CH_3-CH} = 13·0 c.p.s.). The ratio of the peak areas of the latter to the former was 3·0. Because of the closeness of the J_{CH_2-CH} and J_{CH-CH_3} values, the methyne proton should show nine peaks at the resolution used, and eight rather broad peaks (mean separation 13·6 c.p.s.) were clearly visible (τ6·43). The ratio of methyl proton peak area to methyne was 5·2 (expected value 6).

Figure 4



100 MC PMR Spectrum of Bu^i_4Ge (downfield from TMS).

4:4 Electron Impact Spectrometry

When the present study of the mass spectra of organogermanes was begun, very little was known about the fragmentation of Group IV organometallic compounds. Low resolution studies of tetramethylgermane[174] and the fragmentation of the germanes Et_3GeR, ($R = C\vdots CCH:CH_2$, $C\vdots CCH:CHCH_3$, $C\vdots CC(Me):CH_2$)[191] had been reported. Mass spectrometry had helped establish molecular formulae in some instances (Section 3:5). The investigation of organo-silanes, -stannanes and -plumbanes had only just begun.[192]

One of the difficulties encountered in mass spectroscopic studies of germanium, tin and lead compounds, is the large number of isotopes of appreciable abundance which each has. This problem was avoided in studies of GeH_4, Ge_2H_6 and Ge_3H_8 (Section 3:5) by preparing the compounds from isotopically pure ^{74}Ge. This approach is not normally practicable. In the early study of Me_4Ge[174] (by time-of-flight mass spectrometry) overlapping patterns of ions were analysed by trial and error construction of the observed pattern from assumed components. This is tedious and by no means fool-proof. The tedium can be removed to some extent by the use of computers, and the spectrum of 1,1-germanacyclopentane-d_2 has been reduced to the monoisotopic (^{70}Ge) spectrum to illustrate a program for this.[193] The program requires that the decomposition modes of the compounds considered are known, and it can deal only with fairly simple cases, without consuming an inordinate amount of time.

The commercial availability of high resolution mass spectrometers first made possible detailed and reliable studies of the spectra of compounds containing a polyisotopic element. The remaining problem, calculation of mass and abundance data for combinations of more than one polyisotopic element has been dealt with adequately, only in the last few years. These combinations must be evaluated even when studies are confined to low resolution spectra. For Ge_2 the most abundant peak does not correspond to $(^{74}Ge)_2$ but to a triplet ($^{70}Ge^{76}Ge$, $^{72}Ge^{74}Ge$, $^{73}Ge^{73}Ge$) which could be resolved at mass 146 under optimum high resolution conditions, but at low resolution (1:1000) appears as a single peak, $^{146}Ge_2$ with a relative abundance equal to the sum of the relative abundances of each of the three contributing combinations. In practice, the masses of ions actually observed are normally large enough to prevent separation of the $^{146}Ge_2$ peak into its three components even at high resolution. As a result, an average value must be taken in calculating precise masses, and this corresponds to the weighted arithmatic mean of the isotope combinations involved.[13] Simple combinations, for example GeCl, can be worked out by hand, but some combinations, like Ge_7, are more conveniently calculated by computer. Programs have been written to calculate both relative abundances and precise masses, for a wide range of combinations.[194]

4:4:1 Analysis of the Spectra

A variety of known compounds was investigated under high resolution to provide a reliable picture of fragmentation processes in organogermanes. The compounds examined were R_4Ge (R = H, Me, Et, Bu^i, Ph, $PhCH_2$ and p-Tolyl), R'_3GeR'' (R' = Ph and R'' = Et, H; R' = $PhCH_2$ and R'' = Et), R_6Ge_2 (R = Bu^i, $PhCH_2$), $(PhCH_2)_2GeMe_2$, Ph_6Ge_2O and Me_3GeCl. These studies were supplemented by complete low resolution investigations of $(o,m\text{-Tolyl})_4Ge$, Ph_3GeX (X = Me, $PhCH_2$, Cl, Br and I), R_6Ge_2 (R = Et, Ph, m-Tolyl), $(PhCH_2)_3GeH$, Me_3GeH and $GeCl_4$. Significant points were noted from the spectra of $Bu^n{}_4Ge$, Ph_2GeEt_2, $PhGeEt_3$, Ph_3GeBu^n, Ph_3GeSMe, Ph_2GeD_2, $(PhCH_2)_3GeD$, Me_6Ge_2, $MeGeCl_3$, Et_3GeX (X = H, Cl, Br), R_6Ge_2O (R = Me, Et, $PhCH_2$), $(Me_2GeO)_{3,4}$, $(p\text{-Tolyl})_3GeCO_2H$, $(o,p\text{-Tolyl})_6Ge_2$ and $(PhCH_2)_3GeMe$.

The general background thus obtained, mass spectrometry proved invaluable in the characterisation of Et_3GeBu^n, $Et_5Ge_2C_6H_{13}$, Me_5Ge_2Et, Me_5Ge_2Pr, $Bu^i{}_5Ge_2I$, Me_8Ge_3, $Me_5Ge_2CH_2GeMe_3$, Et_8Ge_3 and $Bu^i{}_8Ge_3$ and the partial characterisation of $(Me_3Ge)_3GeMe$, $(Me_3Ge)_2GeMeGeMe_2Et$, Me_9Ge_4Pr, $Me_8Ge_4Et_2$, $Me_{10}Ge_4CH_2$, several dodecamethylpentagermanes including $(Me_3Ge)_4Ge$ and $(Me_3Ge)_2GeMeGe_2Me_5$, $Me_{11}Ge_5Et$, $Me_{14}Ge_6$, $Me_{18}Ge_8$ and $Bu^i{}_7Ge_3I$. This in turn has provided additional information on the fragmentation modes of organogermanes.

For compounds studied at high resolution every ion was identified by mass measurements (Section 2:2:1) (1:10,000) on at least one isotope combination, the agreement with the calculated value being better than six parts per million. The actual figures are not reproduced here because of the space this would require.

For non-overlapping patterns relative ion abundances were calculated from measured peak heights in the low resolution spectrum (run at constant monitor current). In comparing the abundances of ions containing polyisotopic elements with those containing only monoisotopic elements, contributions from each isotope combination must be summed. For example, a spectrum showing three peaks of relative height 2:1:1 due to $^{127}I^+$, $^{81}Br^+$ and $^{79}Br^+$ corresponds to a 1:1 ratio of I^+ to Br^+ (Abundances, ^{81}Br = 49%, ^{79}Br = 51%). Even with carbon, where the ^{13}C isotope has an abundance of only 1%[195] a correction must be made, since this abundance is approximately additive. With 18 carbon atoms present, 18% of the ions will contain a ^{13}C atom. Thus the abundance of ions containing large numbers of carbon atoms will be underestimated unless the ^{13}C contribution is added. A similar correction can be made to allow for ions containing two ^{13}C atoms, and this correction was judged significant for ions containing more than ten carbon atoms.

These considerations become especially important for elements like germanium (or bromine) where there are a number of isotopes whose relative abundances are appreciable (^{70}Ge, 20•56; ^{72}Ge, 27•42; ^{73}Ge, 7•79; ^{74}Ge, 36•47; ^{76}Ge, 7•76%).[13] If the abundances of ions containing one germanium atom are to be compared with those of ions containing none or more than one, it is imperative that the contributions of all the germanium isotope or isotope combinations are summed. Failure to do this leads to a very misleading picture of ion abundances. In the reported spectrum[196] of $(C_6F_5)_4Ge$, the ion $(C_6F_4)_2^+$ is described as the base peak. Although it is the largest peak in the spectrum, it is <u>not</u> the most abundant ion, both $(C_6F_5)_4Ge^{+\cdot}$ and $(C_6F_5)_3Ge^+$ being more abundant. Subsequent discussion of the spectrum made it clear that the author had not realised the significance of the distinction. Mass and abundance data for Ge, Ge_2, Ge_3 and Ge_4 combinations have been published[13] and that for Ge_5, Ge_6 and Ge_7 was calculated using the same programs.[194]

In many cases ion patterns overlap. In the spectrum of Me_4Ge six different ions having only one carbon atom were detected ($GeCH_5^+$, $GeCH_4^{+\cdot}$, $GeCH_3^+$, $GeCH_2^{+\cdot}$, $GeCH^+$ and $GeC^{+\cdot}$) and these form a complicated pattern in the low resolution spectrum. The abundance of each ion relative to the others was calculated from the abundance ratios of pairs or triads of ions as measured from their collector currents at high resolution on suitable mass numbers (e.g. $^{72}GeCH_5^+$ and $^{74}GeCH_3^+$ can be compared at m/e 89, and the ratio obtained corrected for the isotope abundance). The particular mass numbers chosen were selected so that the abundances of species being compared were similar. Having obtained the abundances of all the monocarbon species relative to each other they can be related to abundances of GeC_2, GeC_3 and GeC_4 species by measuring the height of one particular peak of the pattern in the low resolution spectrum. For this pattern the most prominent peak occurred at m/e = 89. This peak has contributions from eight species ($^{72}GeCH_5^+$, $^{73}GeCH_4^{+\bullet}$, $^{72}Ge^{13}CH_4^{+\bullet}$, $^{74}GeCH_3^+$, $^{73}Ge^{13}CH_3^+$, $^{74}Ge^{13}CH_2^{+\bullet}$, $^{76}GeCH^+$ and $^{76}Ge^{13}C^{+\bullet}$). The largest of these is $^{74}GeCH_3^+$. Its % contribution to the actual peak height can be calculated by allowing for the contributions from the other seven species. Thus the abundance of this species can be related to the abundance of GeC_2 etc. species in the spectrum, and from it so can the abundances of the other GeC species. Correction for ^{13}C will then give the abundances of the GeC, GeC_2 etc. ions in the spectrum.

Fortunately, not all cases are as complicated as that considered above, and it is sometimes possible to use a simpler approach. In triphenylgermyl compounds, the ion Ph_3Ge^+ is usually accompanied by the minor ions $Ph_2GeC_6H_4^+$ and $GeC_{18}H_{13}^+$. The abundances of these are most conveniently obtained by measuring the heights of the peaks corresponding to the ^{70}Ge containing species. Thus measurement of the peak at m/e = 299 gives the abundance of the $^{70}GeC_{18}H_{13}^+$ species which, after correction for ^{13}C and $^{13}C_2$ contributions and for contributions from the other four germanium isotopes, gives the abundance of the $GeC_{18}H_{13}^+$ ion directly. The peak at m/e = 300, besides the contribution from $^{70}GeC_{18}H_{14}^+$ has a contribution from $^{70}GeC_{17}{}^{13}CH_{13}^+$, and this must first be calculated and subtratced. The residue is treated as before to give the abundance of the $GeC_{18}H_{14}^+$ ion. The peak at m/e = 301 has contributions from $^{70}GeC_{17}{}^{13}CH_{14}^+$ and $^{72}GeC_{18}H_{13}^+$ as well as $^{70}GeC_{18}H_{15}^+$, and these must be allowed for. It often happened that a particular problem was most easily solved by a judicious combination of the collector current measurements and selected peak heights from the low resolution spectrum.

Having obtained figures for the relative abundance of each ion in the spectrum, these relative abundances were summed, and the abundance of each ion was expressed as a percentage of this sum. Calculation of abundances of ions obtained from Me_4Ge, from two spectra run on different occasions gave essentially the same values. Collector current ratios were also reproducible and ion abundance ratios calculated from collector current ratios of different isotopic species (e.g. $^{74}GeCH_5{}^+/{}^{76}GeCH_3{}^+$ and $^{72}GeCH_5{}^+/{}^{74}GeCH_3{}^+$) were in good agreement. The abundance of hydrocarbon ions was low, and so although these were ignored, the individual ion abundances presented do approximate to the percentage of the ion current carried.

The reason for ignoring hydrocarbon ions was three-fold. Firstly, the decomposition of hydrocarbon ions in the mass spectrometer has been thoroughly studied already;[195] secondly, they carry only a small fraction of the ion current, and so are not normally an important feature of the spectrum; thirdly, the operating conditions of a mass spectrometer are such that there is nearly always a background of hydrocarbon ions present. The labour of subtracting this background from the ions present on a sample spectrum would not be justified by the small amount of additional information obtained. In the spectrum of

$Bu^i{}_4Ge$ there appeared to be a much higher proportion of hydrocarbon ions than usual, and calculation showed that the % ion current carried by non-germanium containing species was 16% ($C_4H_9{}^+$ being most important) compared with 1% in Me_4Ge (no allowance made for background). A recent study[197] reported that hydrocarbon ions are present to the extent of 3% in Me_4Ge, 3% in Et_4Ge, 7% in Pr_4Ge, 15% in $Bu^n{}_4Ge$, 22% in $(C_5H_{11})_4Ge$ and 23% in $(C_6H_{13})_4Ge$. The reason for the low abundance of hydrocarbon ions is the greater electronegativity of carbon and hydrogen relative to the metal, which means that when a positive ion decomposes the charge is likely to remain with the metal-containing fragment.

4:4:2 Metastable Ions

Diffuse "metastable" peaks of low abundance often appear in low resolution mass spectra, usually at non-integral masses. These result from the decomposition of ions in the field-free region between the magnetic and electrostatic analysers, (in a double focussing instrument) and for a transition

$$m_1{}^+ \longrightarrow m_2{}^+ + (m_1-m_2)$$

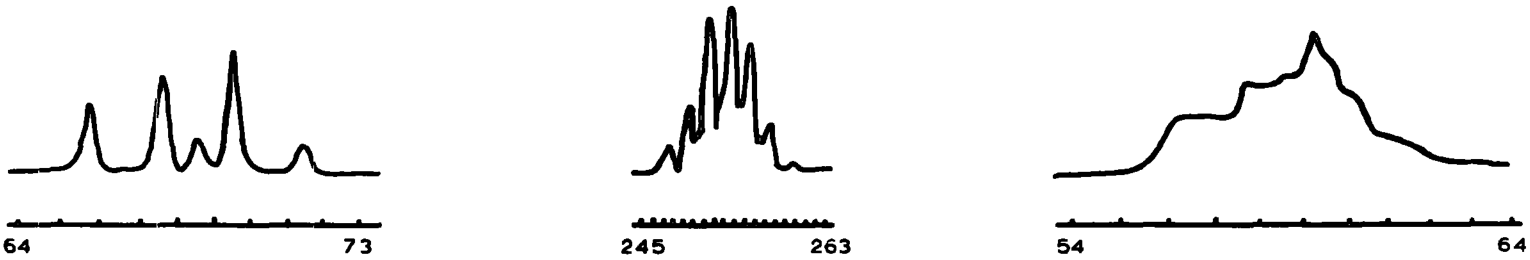
if there is no internal energy release the apparent mass of the metastable peak m^* is given by[195]

$$m^* = \frac{m_2{}^2}{m_1}$$

Metastable peaks are not always symmetrical.[198] When an ion containing a polyisotopic element decomposes to another ion containing this element, a pattern of metastable peaks corresponding to the isotope pattern of the element is obtained. Thus if a transition $Me_3Ge^+ \longrightarrow MeGeH_2^+ + C_2H_4$ gives rise to a metastable, there will be five peaks visible in the low resolution spectrum (Figure 5(a)). A similar state of affairs obtains for the elimination of an organic fragment from a Ge_2 containing ion (Figure 5(b)). Clearly recognisable patterns of this type are most usually caused by the elimination of a neutral organic radical or molecule. If m_1 is of high mass or if the neutral fragment (m_1-m_2) eliminated is large, individual peaks coalesce. If the neutral fragment itself contains germanium, then different but characteristic metastable patterns are produced. These patterns can be calculated by considering the decomposition of all possible isotope combinations. In most cases, all the transitions fall under a single envelope, and the maximum of this envelope is not usually coincident with the m/e value obtained by substituting the most abundant isotope combination in the usual formula. Four examples encountered in the present work are shown in Figure 5 (c,d,e,f).

The experimental values of m^* (apparent mass of the metastable ion) quoted are those for the most abundant germanium isotope or combination of isotopes, and agreed with the calculated values to $\pm$ 0·1 mass unit (except at very high m/e values. The % agreement was always better than 0·5%). The presence of a metastable peak corresponding to a given

Figure 5



$Me_3Ge^+ \longrightarrow MeGeH_2^+ + C_2H_4$

(a)

$Et_5Ge_2O^+ \longrightarrow Et_4Ge_2(H)O^+ + C_2H_4$

(b)

$Me_5Ge_2O^+ \longrightarrow Me_3Ge^+ + Me_2GeO$

(c)


$(m\text{-tolyl})_6Ge_2^{+\cdot} \longrightarrow (m\text{-tolyl})_3Ge^+ + (m\text{-tolyl})_3Ge^\cdot$

(d)

$Ph_3GeCl^{+\cdot} \longrightarrow Ph_2^{+\cdot} + PhGeCl$

(e)

$GeC_7H_7^+ \longrightarrow C_7H_7^+ + Ge$

(f)

process does not necessarily mean that this process occurs as a single step.[199]

4:4:3 General Features

As with organostannanes[192] decomposition of the molecular (odd-electron) ions occurs mainly by elimination of an odd-electron (radical) fragment giving even-electron ions. The bond broken is nearly always a Ge-X bond and this can be ascribed to the low Ge-X bond strengths compared to C-C and C-H, causing Ge-X bonds to break in preference to bonds within the hydrocarbon moiety. The even-electron ions thus formed most frequently decompose by elimination of even-electron (molecular) fragments. Decomposition routes leading to odd-electron fragment ions are usually much less favourable, although some processes of this type such as $R_3GeH^{+\bullet} \longrightarrow R_2Ge^{+\bullet} + RH$ give ions of high abundance. The decomposition modes of organogermanes are discussed as far as possible in terms of the types of bond cleavage involved. Peculiarities of individual compounds are then discussed. Comparisons with tin compounds are all based on data for tin compounds appearing in the literature.[192]

4:4:4 Molecular Ions

The abundance of molecular ions was commonly in the range 0·1-4%. Exceptionally abundant molecular ions were shown by $GeCl_4$ (16·9%) and $(m\text{-Tolyl})_6Ge_2$ (11·6%). In tetraphenylgermane the molecular ion was some 20 times more abundant than in tetraphenyltin, although the Ph_3M^+

abundances were almost identical; this may be a reflection of the greater Ph-Ge bond strength. In Ph_3GeCl the molecular ion was about five times as abundant as the Ph_3Ge^+ ion whereas in the bromide, Ph_3GeBr, the molecular ion was relatively much weaker, and was not detected in the iodide. This effect is again a reflection of the Ge-X bond strengths. Other compounds showing molecular ions of extremely low abundance were GeH_4 and $(Et_3Ge)_2O$. In $(Me_3Ge)_2O$, $(Me_2GeO)_{3,4}$, $(PhCH_2)_6Ge_2$ and $(PhCH_2)_6Ge_2O$ the molecular ions could not be detected. Low intensity molecular ions were reported for $(Pr^i{}_2GeO)_3$.[13] The generally low abundance of molecular ions in Group IVb organo-compounds as a whole is compatible with removal of an electron from an M-C bond on ionisation. It does appear that with unsymmetrical compounds the weakest bond is the same as in the molecule, and this is the bond most susceptible to cleavage.

4:4:5 Radical Elimination by Ge-X Bond Cleavage

This is a dominant process for all odd-electron ions and is frequently metastable supported (Table 8). It must also occur with some even-electron ions although only one metastable-supported example has been found viz., the elimination of a methyl radical from Ph_2GeMe^+ derived from methyltriphenylgermane. In contrast to tin compounds the only triphenylgermyl halide showing a metastable peak for elimination of $X^{\cdot}$ from the molecular ion was the bromide. Methyl radical elimination from $Me_3GeCl^{+\cdot}$ gave unusually sharp metastable peaks; Et_3GeCl and

Table 8. Metastable Supported Ge-X Bond Cleavages

	m^*
$\mathrm{Me_4Ge^{+\bullet} \longrightarrow Me_3Ge^{+} + Me^{\bullet}}$	105·7
$\mathrm{Et_4Ge^{+\bullet} \longrightarrow Et_3Ge^{+} + Et^{\bullet}}$	136·4
$\mathrm{Bu^{i}{}_4Ge^{+\bullet} \longrightarrow Bu^{i}{}_3Ge^{+} + C_4H_9{}^{\bullet}}$	198·8
$\mathrm{(PhCH_2)_4Ge^{+\bullet} \longrightarrow (PhCH_2)_3Ge^{+} + PhCH_2{}^{\bullet}}$	275·0
$\mathrm{Et_3GeBu^{+\bullet} \longrightarrow Et_2GeBu^{+} + Et^{\bullet}}$	163·9
$\mathrm{Ph_3GeMe^{+\bullet} \longrightarrow Ph_3Ge^{+} + Me^{\bullet}}$	290·6
$\mathrm{Ph_3GeEt^{+\bullet} \longrightarrow Ph_3Ge^{+} + Et^{\bullet}}$	278·5
$\mathrm{PhGeEt_3{}^{+\bullet} \longrightarrow PhGeEt_2{}^{+} + Et^{\bullet}}$	183·5
$\mathrm{(PhCH_2)_3GeEt^{+\bullet} \longrightarrow (PhCH_2)_2GeEt^{+} + PhCH_2{}^{\bullet}}$	216·0
$\mathrm{(PhCH_2)_3GeMe^{+\bullet} \longrightarrow (PhCH_2)_2GeMe^{+} + PhCH_2{}^{\bullet}}$	202·9
$\mathrm{(PhCH_2)_2GeMe_2{}^{+\bullet} \longrightarrow PhCH_2GeMe_2{}^{+} + PhCH_2{}^{\bullet}}$	133·0
$\mathrm{(PhCH_2)_3GeH^{+\bullet} \longrightarrow (PhCH_2)_2GeH^{+} + PhCH_2{}^{\bullet}}$	189·8
$\mathrm{(PhCH_2)_3GeD^{+\bullet} \longrightarrow (PhCH_2)_2GeD^{+} + PhCH_2{}^{\bullet}}$	190·7
$\mathrm{Ph_2GeMe^{+} \longrightarrow Ph_2Ge^{+\bullet} + Me^{\bullet}}$	214·0
$\mathrm{(p\text{-}Tolyl)_2Ge^{+\bullet} \longrightarrow C_{14}H_{13}{}^{+} + GeH^{\bullet}}$	128·0
$\mathrm{Me_3GeCl^{+\bullet} \longrightarrow Me_2GeCl^{+} + Me^{\bullet}}$	125·5
$\mathrm{Et_3Ge^{35}Cl^{+\bullet} \longrightarrow Et_2Ge^{35}Cl + Et^{\bullet}}$	142·3
$\mathrm{Et_3Ge^{79}Br^{+\bullet} \longrightarrow Et_2Ge^{79}Br^{+} + Et^{\bullet}}$	185·5
$\mathrm{Ph_3Ge^{81}Br^{+\bullet} \longrightarrow Ph_3Ge^{+} + {}^{81}Br^{\bullet}}$	241·1
$\mathrm{PhGeCl^{+\bullet} \longrightarrow GeCl^{+} + Ph^{\bullet}}$	63·9
$\mathrm{Ph_3GeSMe^{+\bullet} \longrightarrow Ph_3Ge^{+} + SMe^{\bullet}}$	264·3

Table 8 (contd.)

	m^*
$Et_6Ge_2^{+\bullet} \longrightarrow Et_5Ge_2^{+} + Et^{\bullet}$	264·6
$Bu^i_6Ge_2^{+\bullet} \longrightarrow Bu^i_5Ge_2^{+} + C_4H_9^{\bullet}$	380·5
$Ph_6Ge_2^{+\bullet} \longrightarrow Ph_3Ge^{+} + Ph_3Ge^{\bullet}$	152-153
$(m\text{-},p\text{-}Tolyl)_6Ge_2^{+\bullet} \longrightarrow (m\text{-},p\text{-}Tolyl)_3Ge^{+} + (m\text{-},p\text{-}Tolyl)_3Ge^{\bullet}$	173·5
$Me_5EtGe_2^{+\bullet} \longrightarrow Me_5Ge_2^{+} + Et^{\bullet}$	195·4
$\searrow Me_4EtGe_2^{+} + Me^{\bullet}$	220·9
$Et_5(C_6H_{13})Ge_2^{+\bullet} \longrightarrow Et_4(C_6H_{13})Ge_2^{+} + Et^{\bullet}$	320·2
$Et_8Ge_3^{+\bullet} \longrightarrow Et_7Ge_3^{+} + Et^{\bullet}$	393·9
$(Me_3Ge)_3GeMe^{+\bullet} \longrightarrow Me_9Ge_4^{+} + Me^{\bullet}$	411
$\searrow (Me_3Ge)_2GeMe^{+} + Me_3Ge^{\bullet}$	236
$(Me_3Ge)_2Ge(Me)GeMe_2Et^{+\bullet} \longrightarrow (Me_3Ge)_2Ge(Me)GeMe_2^{+} + Et^{\bullet}$	397·9
$Me_9PrGe_4^{+\bullet} \longrightarrow Me_9Ge_4^{+} + Pr^{\bullet}$	386·0
$(Me_3Ge)_4Ge^{+\bullet} \longrightarrow (Me_3Ge)_3GeGeMe_2^{+} + Me^{\bullet}$	514·4
$Me_8Ge_4^{+\bullet} \longrightarrow Me_7Ge_4^{+} + Me^{\bullet}$	380·5
$(Me_3Ge)_2Ge(Et)Ge_2Me_5^{+\bullet} \longrightarrow (Me_3Ge)_2GeGe_2Me_5^{+} + Et^{\bullet}$	501
$Bu^i_5Ge_2I^{+\bullet} \longrightarrow Bu^i_4Ge_2I^{+} + Bu^{\bullet}$	450

and Et_3GeBr both showed $Et^{\bullet}$ elimination. Unsymmetrical germanes of the types A_3GeB and A_2GeB_2 always gave ions corresponding to cleavage of both A-Ge and B-Ge bonds, though the abundances of the product ions varied greatly. For example, in the mass spectrum of trimethylgermane the ion Me_2GeH^+ is some five times as abundant as Me_3Ge^+, and in the spectrum of trimethylchlorogermane the ion Me_2GeCl^+ is twice as abundant as Me_3Ge^+. Even more striking examples are provided by some phenyl- and benzyl-germanes [Ph_3GeEt(Ph_3Ge^+ = 64%; Ph_2GeEt^+ = 0·8%) and $(PhCH_2)_3GeEt$(($PhCH_2)_3Ge^+$ = 0·8%; $(PhCH_2)_2GeEt^+$ = 40%)]. Differences of this type may result from differences in A-Ge and B-Ge bond strengths in the molecular ion, but the resultant ions will usually be able to decompose by different routes so that conclusions concerning relative bond strengths may well be invalid. The effect of Ge-halogen bond strengths is shown quite plainly in the mass spectra of triphenylhalogermanes Ph_3GeCl, Ph_3GeBr and Ph_3GeI where the relative abundances of first cleavage products are: $Ph_2GeCl^+ > Ph_3Ge^+$; $Ph_3Ge^+ > Ph_2GeBr^+$; $Ph_3Ge^+ \gg Ph_2GeI^+$. By contrast, triphenylbromostannane showed the reverse abundance, $Ph_2SnBr^+ > Ph_3Sn^+$. In the mass spectra of Et_3GeCl and Et_3GeBr, the most abundant ions are Et_2GeX^+.

Germyl radicals are produced from the molecular ions of digermanes, $R_6Ge_2^{+\bullet} \longrightarrow R_3Ge^+ + R_3Ge^\bullet$, the extent to which this decomposition occurs is dependent on the R group. No such metastables have been seen for alkyl digermanes, and it seems likely that rupture of the Ge-Ge bond in these does not occur until the $R_5Ge_2^+$ ion is reached, as with hexabenzyldigermane where the elimination of a diradical (or neutral molecule) is seen.

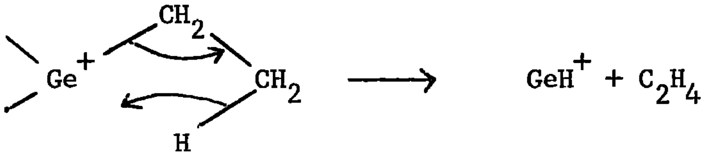
$$(PhCH_2)_3Ge\cdot Ge(CH_2Ph)_2^+ \longrightarrow (PhCH_2)_3Ge^+ + (PhCH_2)_2Ge^{\bullet\bullet}$$

This type of degradation is very common for the methylpolygermanes.

4:4:6 Alkene Elimination by Ge-C Bond Cleavage

Examination of the mass spectra of ethyltin compounds, Et_nSnPh_{4-n} (n = 1-4), showed that ethylene elimination is a favoured process of low-activation energy which only occurs from even-electron ions.[192] This is equally true of all the ethylgermanium compounds examined (although reported spectra[200,201] of germanacyclopentanes show C_2H_4 loss from the molecular ion). For each ethyl group cleaved in this way a germanium-hydrogen bond is formed ($EtGe^+ \longrightarrow C_2H_4 + GeH^+$) and these transitions are commonly metastable-supported. (Table 9). Hexaethyldigermoxane and octaethyltrigermane in particular show impressive successions of ethylene-elimination reactions, including one involving doubly-charged ions.

A mechanism has previously been proposed for ethylene elimination from Et-Sn groups,[192] and ethylgermane ions probably decompose by the



same mechanism, but ethylene elimination also occurs from Me_3Ge^+ and from several Me_2GeX^+ ions. This may involve primary rearrangement to an ethyl germanium hydride ion followed by ethylene elimination.

$$-GeMe_2^+ \longrightarrow -GeHEt^+ \longrightarrow -GeH_2^+ + C_2H_4$$

Table 9. Metastable Supported Alkene-Elimination.

Compound		m^*
Et_4Ge Et_6Ge_2 Et_6Ge_2O Et_8Ge_3 Et_3GeBu	$Et_3Ge^+ \longrightarrow Et_2GeH^+ + C_2H_4$	110·0
	$Et_2GeH^+ \longrightarrow EtGeH_2^+ + C_2H_4$	83·0
	$EtGe^+ \longrightarrow GeH^+ + C_2H_4$	54·6
Et_6Ge_2 Et_8Ge_3	$Et_5Ge_2^+ \longrightarrow Et_4Ge_2H^+ + C_2H_4$	237·7
	$Et_4Ge_2H^+ \longrightarrow Et_3Ge_2H_2^+ + C_2H_4$	210·0
	$Et_3Ge_2H_2^+ \longrightarrow Et_2Ge_2H_3^+ + C_2H_4$	182·3
	$Et_2Ge_2H_3^+ \longrightarrow EtGe_2H_4^+ + C_2H_4$	154·8
Et_8Ge_3	$Et_7Ge_3^+ \longrightarrow Et_6Ge_3H^+ + C_2H_4$	366·9
	$Et_6Ge_3H^+ \longrightarrow Et_5Ge_3H_2^+ + C_2H_4$	339·0
	$Et_5Ge_3H_2^+ \longrightarrow Et_4Ge_3H_3^+ + C_2H_4$	311·1
	$Et_4Ge_3H_3^+ \longrightarrow Et_3Ge_3H_4^+ + C_2H_4$	283·3
	$Et_3Ge_3H_4^+ \longrightarrow Et_2Ge_3H_5^+ + C_2H_4$	255·5
Et_6Ge_2O	$Et_5Ge_2O^+ \longrightarrow Et_4Ge_2(H)O^+ + C_2H_4$	253·7
	$Et_4Ge_2(H)O^+ \longrightarrow Et_3Ge_2(H)_2O^+ + C_2H_4$	225·9
	$Et_3Ge_2O^+ \longrightarrow Et_2Ge_2(H)O^+ + C_2H_4$	196·1
	$Et_2GeOH^+ \longrightarrow EtGe(H)OH^+ + C_2H_4$	98·3
	$EtGe(H)OH^+ \longrightarrow H_2GeOH^+ + C_2H_4$	71·5
	$Et_4Ge_2O^{2+} \longrightarrow Et_3Ge_2(H)O^{2+} + C_2H_4$	112·4

Table 9 (contd.)

Compound		m^*
Bu^nGeEt_3	$BuGeEt_2^+ \rightarrow GeC_6H_{15}^+ + C_2H_4$	137·1
	$BuGeEt_2^+ \rightarrow GeC_4H_{11}^+ + C_4H_8$	93·6
$Et_5Ge_2C_6H_{13}$	$Et_4Ge_2C_6H_{13}^+ \rightarrow Ge_2C_{12}H_{29}^+ + C_2H_4$	293·3
	$Et_4Ge_2C_6H_{13}^+ \rightarrow Et_4Ge_2H^+ + C_6H_{12}$	199·3
	$Et_3Ge_2C_6H_{13}(H)^+ \longrightarrow Et_2Ge_2C_6H_{13}(H_2)^+ + C_2H_4$	265·5
$EtMe_5Ge_2$ $EtMe_9Ge_4$	$EtMe_4Ge_2^+ \longrightarrow Me_4Ge_2H^+ + C_2H_4$	182·3
Me_9EtGe_4	$EtMe_8Ge_4^+ \longrightarrow Me_8Ge_4H^+ + C_2H_4$	384·8
	$EtMe_6Ge_3^+ \longrightarrow Me_6Ge_3H^+ + C_2H_4$	283·3
$Me_8Et_2Ge_4$	$EtMe_8Ge_4^+ \longrightarrow Me_8Ge_4H^+ + C_2H_4$	384·8
	$Et_2Me_7Ge_4^+ \longrightarrow Me_7EtGe_4H^+ + C_2H_4$	398·7
	$EtMe_7Ge_4H^+ \longrightarrow Me_7Ge_4H_2^+ + C_2H_4$	370·8
	$EtMe_6Ge_3^+ \longrightarrow Me_6Ge_3H^+ + C_2H_4$	283·3
	$Et_2Me_5Ge_3^+ \longrightarrow Me_5EtGe_3H^+ + C_2H_4$	297·0
	$EtMe_5Ge_3H^+ \longrightarrow Me_5Ge_3H_2^+ + C_2H_4$	269·4
$PrMe_9Ge_4$	$PrMe_8Ge_4^+ \longrightarrow Me_8Ge_4H^+ + C_3H_6$	373
	$PrMe_6Ge_3^+ \longrightarrow Me_6Ge_3H^+ + C_3H_6$	272
$Me_{11}EtGe_5$	$Me_{10}EtGe_5^+ \longrightarrow Me_{10}Ge_5H^+ + C_2H_4$	488
	$Me_8Ge_4Et^+ \longrightarrow Me_8Ge_4H^+ + C_2H_4$	384·8

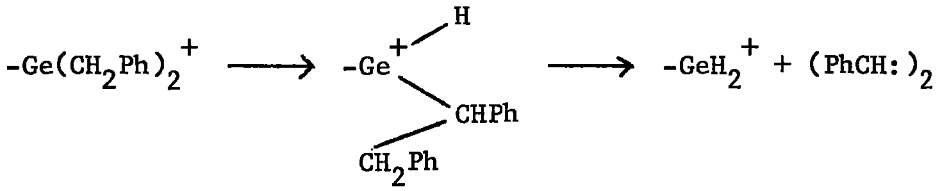
Table 9 (contd.)

Compound		m^*
$\mathrm{Et_3GeH}$	$\mathrm{Et_2GeH^+ \longrightarrow EtGeH_2^+ + C_2H_4}$	82·9
$\mathrm{Et_3GeCl}$	$\mathrm{Et_2GeCl^+ \longrightarrow EtGe(H)Cl^+ + C_2H_4}$	115·7
$\mathrm{Et_3GeBr}$	$\mathrm{Et_2GeBr^+ \longrightarrow EtGe(H)Br^+ + C_2H_4}$	158·7
$\mathrm{Ph_3GeEt}$ $\mathrm{Ph_2GeEt_2}$	$\mathrm{Ph_2GeEt^+ \longrightarrow Ph_2GeH^+ + C_2H_4}$	204·1
$\mathrm{Ph_2GeEt_2}$ $\mathrm{PhGeEt_3}$	$\mathrm{PhGeEt_2^+ \longrightarrow PhGe(H)Et^+ + C_2H_4}$	156·6
	$\mathrm{PhGe(H)Et^+ \longrightarrow PhGeH_2^+ + C_2H_4}$	129·2
$\mathrm{(PhCH_2)_3GeEt}$	$\mathrm{(PhCH_2)_2GeEt^+ \longrightarrow (PhCH_2)_2GeH^+ + C_2H_4}$	231·8
Almost all compounds containing the $\mathrm{Me_3Ge}$ group.	$\mathrm{Me_3Ge^+ \longrightarrow MeGeH_2^+ + C_2H_4}$	69·6
$\mathrm{Me_3GeH}$	$\mathrm{Me_2GeH^+ \longrightarrow GeH_3^+ + C_2H_4}$	56·4
$\mathrm{Me_3GeCl}$	$\mathrm{Me_2GeCl^+ \longrightarrow H_2GeCl^+ + C_2H_4}$	88·6
$\mathrm{(Me_3Ge)_2O}$	$\mathrm{Ge_2C_5H_{13}^+ \longrightarrow Me_3Ge_2^+ + C_2H_4}$	166·7
$\mathrm{(PhCH_2)_2GeMe_2}$	$\mathrm{PhCH_2GeMe_2^+ \longrightarrow PhCH_2GeH_2^+ + C_2H_4}$	143·0
$\mathrm{Bu^i_4Ge}$ $\mathrm{Bu^i_6Ge_2}$	$\mathrm{Bu^i_3Ge^+ \longrightarrow Bu^i_2GeH^+ + C_4H_8}$	145·8
	$\mathrm{Bu^i_2GeH^+ \longrightarrow Bu^iGeH_2^+ + C_4H_8}$	93·5
$\mathrm{Bu^i_6Ge_2}$	$\mathrm{Bu^i_5Ge_2^+ \longrightarrow Bu^i_4GeH^+ + C_4H_8}$	326·2
	$\mathrm{Bu^i_4Ge_2H^+ \longrightarrow Bu^i_3Ge_2H_2^+ + C_4H_8}$	271·3
	$\mathrm{Bu^i_3Ge_2H_2^+ \longrightarrow Bu^i_2Ge_2H_3^+ + C_4H_8}$	216·8
	$\mathrm{Bu^i_2Ge_2H_3^+ \longrightarrow Bu^iGe_2H_4^+ + C_4H_8}$	162·9

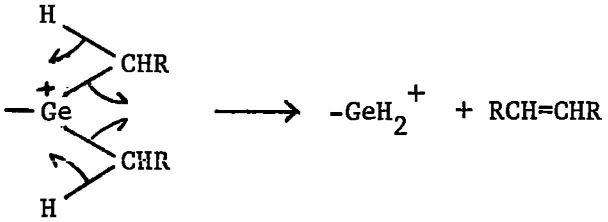
Table 9 (contd.)

Compound		m^*
$Bu^i_5Ge_2I$	$Bu^i_4Ge_2I^+ \longrightarrow Bu^i_3Ge_2(H)I^+ + C_4H_8$	395·2
	$Bu^i_3Ge_2(H)I^+ \longrightarrow Bu^i_2Ge_2(H)_2I^+ + C_4H_8$	340·0
	$Bu^i_4Ge_2^{+\bullet} \longrightarrow Bu^i_3Ge_2(H)^{+\bullet} + C_4H_8$	270·4
$(PhCH_2)_4Ge$ $(PhCH_2)_6Ge_2$ $(PhCH_2)_6Ge_2O$	$(PhCH_2)_3Ge^+ \longrightarrow PhCH_2GeH_2^+ + (PhCH:)_2$	80·4

The elimination of stilbene, observed in the spectra of tetrabenzylgermane and hexabenzyldigermane, from the tribenzylgermyl ion could be analogous:



Alternatively, methyl and benzyl compounds may eliminate alkene by a concerted cleavage of two Ge-C bonds:



where R = H and Ph, respectively, and half arrows indicate transfer of one electron.

The elimination of C_2H_4 from $Ge_2C_5H_{13}^+$ in the spectrum of hexamethyldigermoxane need not lead to Ge-H bonds:

$$Me_5Ge_2O^+ \xrightarrow{-H_2O} Ge_2Me_3(CH_2)_2^+ \longrightarrow Ge_2Me_3^+ + C_2H_4$$

Hexaisobutyldigermane shows extensive alkene elimination rather than fission of the Ge-Ge bond and 46% of the ion current is carried by Ge_2-containing ions. Similar observations have been made for isopropylgermanes.[9]

4:4:7 Molecule Elimination by Cleavage of Two Ge-X Bonds

A number of odd- and even-electron ions undergo metastable-confirmed transitions in which a neutral molecule is eliminated by cleavage of two bonds to germanium (Table 10).

This type of reaction is most common for even-electron ions. For reactions of the type $R_2GeH^+ \longrightarrow RGe^+ + RH$, it is almost certainly the Ge-H hydrogen which is eliminated, since in $(PhCH_2)_3GeD$, there is a metastable supported elimination of monodeuteriotoluene from the ion $(PhCH_2)_2GeD^+$ and also from the molecular ion.

The elimination of R_1R_2 from odd-electron ions is one of the few types of metastable confirmed processes leading to odd-electron ions of high abundance. The elimination of R_2 from $R_4Ge^{+\bullet}$ gives metastable peaks only for the phenyl, m-, and p-tolyl compounds, and for these compounds the $R_2Ge^{+\bullet}$ ions are of high abundance. In (o-tolyl)$_4$Ge, the transition does not occur and the (o-tolyl)$_2Ge^{+\bullet}$ ion is of low

Table 10.

Metastable-supported cleavage of two Ge–X bonds

Compound		m^*
	$Et_3GeH^{+\cdot} \longrightarrow EtGe^{+\cdot} + C_2H_6$	107·6
	$(PhCH_2)_3GeH^{+\cdot} \longrightarrow (PhCH_2)_2Ge^{+\cdot} + PhCH_3$	188·3
	$(PhCH_2)_3GeD^{+\cdot} \longrightarrow (PhCH_2)_2Ge^{+\cdot} + C_7H_7D$	187·8
	$Ph_4Ge^{+\cdot} \longrightarrow Ph_2Ge^{+\cdot} + Ph_2$	136·1
	$(m\text{-}, p\text{-}Tolyl)_4Ge^{+\cdot} \longrightarrow (m\text{-}, p\text{-}Tolyl)_2Ge^{+\cdot} + C_{14}H_{14}$	149·6
	$Ph_3GeCl^{+\cdot} \longrightarrow Ph_2^{+\cdot} + PhGeCl$	70·1
	$Ph_3GeBr^{+\cdot} \longrightarrow Ph_2^{+\cdot} + PhGeBr$	61·9
	$(Ph_3Ge)_2O^{+\cdot} \longrightarrow Ge_2C_{36}H_{28}^{+\cdot} + H_2O$	588·7
GeH_4	$GeH_2^{+\cdot} \longrightarrow Ge^{+\cdot} + H_2$	72·1
Et_4Ge Et_3GeH Et_6Ge_2	$EtGeH_2^{+} \longrightarrow EtGe^{+} + H_2$	101·1
Ph_3GeEt	$PhGeH_2^{+} \longrightarrow PhGe^{+} + H_2$	148·9
Me_3GeH	$Me_2GeH^{+} \longrightarrow MeGe^{+} + CH_4$	75·4
Me_3GeCl	$Me_2Ge^{35}Cl^{+} \longrightarrow Ge^{35}Cl^{+} + C_2H_6$	85·4
	$Me_2Ge^{35}Cl^{+} \longrightarrow MeGe^{+} + Me^{35}Cl$	56·9
$(Me_3Ge)_2O$	$Me_3GeOGeMe_2^{+} \longrightarrow Ge_2C_5H_{13}^{+} + H_2O$	202·4
Ph_3GeR $R = Et, Bu, Ph, I, PhCH_2,$ Ph_3Ge, Ph_3GeO	$Ph_3Ge^{+} \longrightarrow PhGe^{+} + Ph_2$	74·8
Ph_3GeCl	$Ph_2Ge^{35}Cl^{+} \longrightarrow PhGe^{+} + Ph^{35}Cl$	86·7
	$Ph_2Ge^{35}Cl^{+} \longrightarrow Ge^{35}Cl^{+} + Ph_2$	45·2
Ph_3GeBr	$Ph_2GeBr^{+} \longrightarrow PhGe^{+} + PhBr$	74·1
$(o\text{-}, m\text{-}, p\text{-}Tolyl)_4Ge$ $(o\text{-}, m\text{-}Tolyl)_6Ge_2$ $(p\text{-}Tolyl)_3GeCO_2H$	$(Tolyl)_3Ge^{+} \longrightarrow (Tolyl)Ge^{+} + C_{14}H_{14}$	78·5
Ph_3GeR ($R = H, Et, Bu$), Ph_2GeEt_2	$Ph_2GeH^{+} \longrightarrow PhGe^{+} + C_6H_6$	99·6
$PhGeEt_3$	$PhGeH_2^{+} \longrightarrow GeH^{+} + C_6H_6$	36·7
Ph_2GeD_2	$PhGeD^{+\cdot} \longrightarrow Ge^{+\cdot} + PhD$	35·8
$(PhCH_2)_3GeR$, $R = H, Et$	$(PhCH_2)_2GeH^{+} \longrightarrow PhCH_2Ge^{+} + PhCH_3$	105·9
$(PhCH_2)_3GeD$	$(PhCH_2)_2GeD^{+} \longrightarrow PhCH_2Ge^{+} + C_7H_7D$	105·5
$(PhCH_2)_3GeMe$	$(PhCH_2)_2GeMe^{+} \longrightarrow PhCH_2Ge^{+} + PhEt$	100·4
	$(PhCH_2)_2GeMe^{+} \longrightarrow MeGe^{+} + (PhCH_2)_2$	29·2
$(PhCH_2)_2GeMe_2$	$PhCH_2GeMe_2^{+} \longrightarrow MeGe^{+} + PhEt$	40·6
$(o\text{-}, m\text{-}Tolyl)_4Ge$ $(o\text{-}, m\text{-}, p\text{-}Tolyl)_6Ge_2$ $(p\text{-}Tolyl)_3GeCO_2H$	$GeC_{14}H_{13}^{+} \longrightarrow C_{14}H_{11}^{+} + GeH_2$	125·7

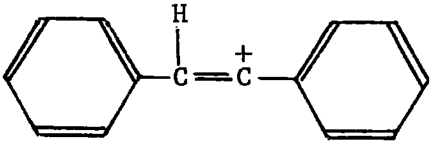
abundance. Triphenylchloro- and triphenylbromo-germanes provide one of the few examples of a reaction in which a neutral germanium-containing species is eliminated. Most of the tolyl-germanes show a similar transition in which GeH_2 is eliminated leaving the ion $C_{14}H_{11}^{+}$, but p-tolylgermanes also eliminate the $GeH^{\bullet}$ radical.

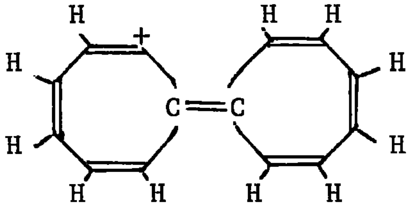
$$Ph_3GeX^{+\bullet} \longrightarrow Ph_2^{+\bullet} + PhGeX$$

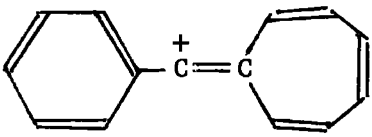
$$GeC_{14}H_{13}^{+} \longrightarrow C_{14}H_{11}^{+} + GeH_2$$

$$GeC_{14}H_{14}^{+\bullet} \longrightarrow C_{14}H_{13}^{+} + GeH^{\bullet}$$

The $C_{14}H_{11}^{+}$ ion presumably has an extensively delocalised structure and there are several possibilities







A similar elimination has been observed[202] in $\pi C_5H_5(CO)_2(Ph_3P)MoGeR_3$:

$$\pi C_5H_5(CO)_2(Ph_3P)MoGeH_2^{+} \longrightarrow \pi C_5H_5(CO)_2(Ph_3P)MoH^{+} + GeH^{\bullet}$$

In the tetra-alkylgermanes the abundance of $R_2Ge^{+\bullet}$ is always extremely low, and only in the spectra of trimethyl- and triethyl-germanes is the odd-electron ion $R_2Ge^{+\bullet}$ of high abundance, and here it is derived by methane or ethane elimination from the molecular ion. Similarly, in tribenzylgermane, $(PhCH_2)_2Ge^{+\bullet}$ although of low abundance, is formed by toluene elimination from the molecular ion, and it is reasonable to suppose that the high abundance (31·5%) of the ion $Ph_2Ge^{+\cdot}$ in the spectrum of triphenylgermane is due to the same type of elimination:

$$Ph_3GeH^{+\cdot} \longrightarrow Ph_2Ge^{+\cdot} + C_6H_6$$

An interesting case, not strictly in this category, is the elimination of water from hexaphenyldigermoxane where the resulting ion may have a Ge-Ge bond.

$$Ph_3GeOGePh_3^{+\cdot} \longrightarrow Ge_2C_{36}H_{28}^{+\cdot} + H_2O$$

4:4:8 Molecule Elimination by Cleavage of One Ge-X Bond

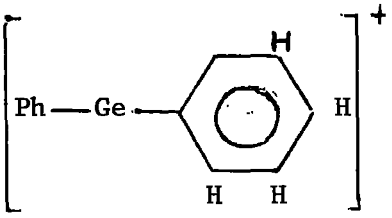
Whereas even-electron alkylgermanium ions decompose largely by elimination of alkene, analogous arylgermanium ions commonly eliminate the aromatic hydrocarbon. For example, a wide range of triphenylgermyl compounds, Ph_3GeR (R = H, Me, Et, Bu, Ph, $PhCH_2$, $GePh_3$, $OGePh_3$, SMe, Br or I) show ions corresponding to elimination of benzene from the Ph_3Ge^+ ion whilst hexaphenyldigermoxane shows three additional metastable-supported processes for benzene elimination one of which occurs for an odd-electron ion (Table 11). Benzyl- and tolyl-germanes likewise show transitions involving elimination of toluene. The structure of the even-electron ions formed by benzene elimination from Ph_3Ge^+ and related species is not clear. They may be formulated as two-co-ordinate or three-co-ordinate ions.

Table 11. Metastable Supported Cleavage of One Ge-X Bond

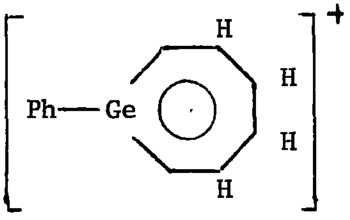
Compound		m^*
Ph_4Ge, most Ph_3GeR	$Ph_3Ge^+ \longrightarrow PhGeC_6H_4^+ + C_6H_6$	168·9
$(Ph_3Ge)_2O$	$Ph_5Ge_2O^+ \longrightarrow Ph_3(C_6H_4)Ge_2O^+ + C_6H_6$	402·0
	$Ph_4Ge_2O^{+\cdot} \longrightarrow Ph_2(C_6H_4)Ge_2O^{+\cdot} + C_6H_6$	326·9
	$Ph_4Ge_2O^{2+} \longrightarrow Ph_2(C_6H_4)Ge_2O^{2+} + C_6H_6$	163·5
$(PhCH_2)_4Ge$ $(PhCH_2)_6Ge_2$ $(PhCH_2)_6Ge_2O$	$(PhCH_2)_3Ge^+ \longrightarrow C_{14}H_{13}Ge^+ + PhCH_3$	187·4
$(PhCH_2)_6Ge_2$	$(PhCH_2)_5Ge_2^+ \longrightarrow (PhCH_2)_3Ge_2C_7H_6^+ + PhCH_3$	431·0
$(PhCH_2)_6Ge_2O$	$(PhCH_2)_5Ge_2O^+ \longrightarrow (PhCH_2)_3Ge_2OC_7H_6^+ + PhCH_3$	447·0
(o-,m-,p-Tolyl)$_4$Ge (o-,m-Tolyl)$_6$Ge$_2$ (p-Tolyl)$_3$GeCO$_2$H	$(Tolyl)_3Ge^+ \longrightarrow C_{14}H_{13}Ge^+ + PhCH_3$	187·4
Me_3GeCl	$Me_2GeCl^+ \longrightarrow MeGeCH_2^+ + HCl$	76·3
Ph_3GeCl	$Ph_2GeCl^+ \longrightarrow PhGeC_6H_4^+ + HCl$	196·0
$(PhCH_2)_6Ge_2$	$(PhCH_2)_5Ge_2^+ \longrightarrow (PhCH_2)_3Ge^+ + (PhCH_2)_2Ge$	200·0
$EtMe_9Ge_4$, $Me_{10}Ge_4$	$Me_5Ge_2^+ \longrightarrow Me_3Ge^+ + Me_2Ge$	63·5
$EtMe_9Ge_4$	$EtGe_2Me_4^+ \longrightarrow EtGeMe_2^+ + Me_2Ge$	75·3
$Me_5Ge_2CH_2GeMe_3$	$Me_5(GeCH_2Ge)^+ \longrightarrow Me_3Ge^+ + Me_2GeCH_2$	59·9
	$Me_7(GeCH_2Ge)^+ \longrightarrow Me_5(GeCH_2Ge)^+ + Me_2Ge$	164·8
$EtMe_9Ge_4$, $Me_{10}Ge_4$	$Me_7Ge_3^+ \longrightarrow Me_5Ge_2^+ + Me_2Ge$	151·0

Table 11. (contd.)

Compound		m^*
Me_9Ge_4R (R = Me,Et,Pr), $(Me_3Ge)_4Ge$	$Me_9Ge_4^+ \longrightarrow Me_7Ge_3^+ + Me_2Ge$	245-6
$(Me_3Ge)_4Ge$	$Me_{11}Ge_5^+ \longrightarrow Me_9Ge_4^+ + Me_2Ge$	342·0
$Me_{16}Ge_7$	$Me_{13}Ge_6^+ \longrightarrow Me_{11}Ge_5^+ + Me_2Ge$	443·0
$(Me_3Ge)_2O$	$Me_3GeOGeMe_2^+ \longrightarrow Me_3Ge^+ + OGeMe_2$	59·2
$(Me_2GeO)_4$	$Me_7Ge_4O_4^+ \longrightarrow Me_5Ge_3O_3^+ + OGeMe_2$	231·0
$(PhCH_2)_6Ge_2O$	$(PhCH_2)_3Ge_2O^+ \longrightarrow (PhCH_2)_3Ge^+ + GeO$	276·0
Most benzyl- and tolyl-germanes	$GeC_7H_7^+ \longrightarrow C_7H_7^+ + Ge$	50·2
$(p\text{-Tolyl})_3GeCO_2H$	$(p\text{-Tolyl})_2GeOH^+ \longrightarrow C_{14}H_{13}Ge^+ + H_2O$	238·2

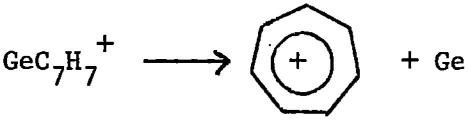


or



There is even more uncertainty about the structure of ions obtained by toluene elimination from benzyl- or tolyl-germanes since hydrogen may be abstracted from a methylene or methyl group, or from an adjacent aromatic ring.

Elimination of hydrogen chloride is observed from the ions Me_2GeCl^+ and Ph_2GeCl^+. Benzyl- and tolyl-germanes show a metastable transition due to elimination of germanium from the ion $GeC_7H_7^+$, with probable formation of the tropylium ion:



This is understandable since the ionisation potential[203] of the benzyl radical (7·7 eV) is less than that of germanium (7·9 eV), whereas for phenyl (9·9 eV) the reverse is true; hence the transition $PhGe^+ \longrightarrow Ph^+ + Ge$ is not observed.

4:4:9 Decompositions Not Necessarily Involving the Ge-X Bonds

The fragmentation of organo-germanes and -stannanes shows clearly that even-electron ions are the dominant species; these are usually three- or one-co-ordinate. In this section are discussed transitions which do not necessarily involve a change in the number of groups directly bonded to germanium.

Molecular ions are the most common four-co-ordinate species and loss of a hydrogen atom or methyl group can convert these into even-electron ions, although no metastable peaks for these transitions have been observed

$$Ph_4Ge^{+\bullet} \longrightarrow Ph_3GeC_6H_4^+ + H^\bullet$$

$$(PhCH_2)_4Ge^{+\bullet} \longrightarrow (PhCH_2)_3GeC_7H_6^+ + H^\bullet$$

$$(\text{m- or p-Tolyl})_4Ge^{+\bullet} \longrightarrow (\text{Tolyl})_3GeC_7H_6^+ + H^\bullet$$

$$(\text{p-Tolyl})_3GeCO_2H^{+\bullet} \longrightarrow C_{22}H_{21}GeO_2^+ + H^\bullet$$

Tetraphenyltin has a similar ion, but for the germanes the doubly charged ions $Ph_3GeC_6H_4^{2+\bullet}$ and $(p\text{-Tolyl})_3GeC_7H_6^{2+\bullet}$ are also observed. The ion $C_{22}H_{21}GeO_2^+$ could be $(p\text{-Tolyl})_2(C_7H_6)GeCO_2H^+$ or $(p\text{-Tolyl})_3GeCO_2^+$, but judging by its abundance compared with e.g. $(p\text{-Tolyl})_3GeC_7H_6^+$, the second formulation is more likely. $(p\text{-Tolyl})_3GeOH^+$ also occurs in the spectrum. A variety of tolyl-germanes show low abundance four-co-ordinate ions corresponding to elimination of a methyl radical, but these, like $H^\bullet$ eliminations, do not give observable metastable transitions

$$(m\text{-},p\text{-Tolyl})_4Ge^{+\bullet} \longrightarrow (Tolyl)_3GeC_6H_4^+ + CH_3^\bullet$$

$$(o\text{-Tolyl})_6Ge_2^{+\bullet} \longrightarrow (o\text{-Tolyl})_5Ge_2C_6H_4^+ + CH_3^\bullet$$

Analogous eliminations from presumably two-co-ordinate species do give metastable ions:

$$(Tolyl)_2Ge^{+\bullet} \longrightarrow (Tolyl)GeC_6H_4^+ + Me^\bullet$$

$$(m\text{-Tolyl})GeC_7H_6^+ \longrightarrow GeC_{13}H_{10}^{+\bullet} + Me^\bullet$$

The only indisputably two co-ordinate ions observed were $GeH_2^{+\bullet}$ and $GeCl_2^{+\bullet}$. For most other ions a variety of structures are possible (Section 4:4:8).

Metastable confirmed elimination reactions involving three- and one-co-ordinate ions which do not necessarily involve the atoms directly bonded to germanium are shown in Table 12. These are all even-electron transitions with formation of H_2, C_6H_6 or C_2H_2, but in no case can a

Table 12

Metastable transitions without Ge–X bond cleavage

Compound		m^*
$Bu^t_6Ge_2$ Bu^t_4Ge	$Bu^t_2GeH^+ \longrightarrow Bu^tGe(H)Me^+ + C_3H_6$	114·3
	$Bu^tGeH_2^+ \longrightarrow EtGeH_2^+ + C_2H_4$	82·8
	$Bu^tGeH_2^+ \longrightarrow MeGeH_2^+ + C_3H_6$	62·3
$Bu^t_6Ge_2$	$Bu^tGe_2H_4^+ \longrightarrow MeGe_2H_4^+ + C_3H_6$	131·4
Ph_3GeMe	$Ph_2GeMe^+ \longrightarrow C_{13}H_{11}Ge^+ + H_2$	239·0
$(PhCH_2)_4Ge$ $(PhCH_2)_6Ge_2$	$(PhCH_2)_3Ge^+ \longrightarrow C_{15}H_{15}Ge^+ + C_6H_6$	208·5
$(PhCH_2)_3GeMe$	$(PhCH_2)_2GeMe^+ \longrightarrow C_9H_{11}Ge^+ + C_6H_6$	137·4
$(PhCH_2)_3GeR$ $R = Et, PhCH_2, Ge(CH_2Ph)_3$	$(PhCH_2)_3Ge^+ \longrightarrow C_{21}H_{19}Ge^+ + H_2$	343·0
Ph_3GeR $R = Me, Ph, Cl, I, PhCH_2, H, Et, GePh_3$	$PhGeC_6H_4^+ \longrightarrow PhGeC_4H_2^+ + C_2H_2$	178·0
Ph_3GeR $(R = H, Et, Ph, OGePh_3, GePh_3)$	$PhGeC_4H_2^+ \longrightarrow PhGeC_2^+ + C_2H_2$	152·5
(*o*-, *m*-, *p*-Tolyl)$_4$Ge (*o*-Tolyl)$_6$Ge$_2$ $(PhCH_2)_4Ge$	$C_{14}H_{13}Ge^+ \longrightarrow C_{14}H_{11}Ge^+ + H_2$	251·0
Ph_3GeI Ph_3GeCH_2Ph	$PhGe^+ \longrightarrow C_6H_3Ge^+ + H_2$	147·0
$Ph_3GeR, Ph_2GeEt_2, PhGeEt_3$ (R = all groups studied)	$PhGe^+ \longrightarrow C_4H_3Ge^+ + C_2H_2$	103·4
Most benzyl- and tolyl-germanes	$C_7H_7Ge^+ \longrightarrow C_5H_5Ge^+ + C_2H_2$	117·1
(*m*-, *p*-Tolyl)$_4$Ge (*p*-Tolyl)$_3$GeCO$_2$H	$(Tolyl)_2Ge^{+\cdot} \longrightarrow$ (*m*-Tolyl)$GeC_6H_4^+ + Me^\cdot$	226·9
(*m*-Tolyl)$_4$Ge	(*m*-Tolyl)$GeC_7H_6^+ \longrightarrow GeC_{13}H_{10}^{+\cdot} + Me^\cdot$	226·0
	$Et_4Ge_2(C_6H_{13})^+ \longrightarrow Ge_2Et_5^+ + C_4H_8$	244·0

unique structure be assigned to the product ions. In addition to the transitions in Table 12 many other organogermanes show ions which are most readily accounted for by similar H_2-elimination processes, but because of their proximity to the ions themselves, the metastable peaks are not easily discerned. Although germanium compounds appear to give more ions due to H or H_2 loss than analogous tin compounds, comparison of the Ge and Sn isotope patterns suggest that their presence would be much more obvious in the Ge compounds.

Isobutylgermanes, in addition to eliminating C_4H_8 and forming Ge-H ions, also show fragmentation of isobutyl groups with the formation of ethylene and propene, and $Et_5Ge_2(C_6H_{13})$ shows elimination of butene. This has also been noted for the isopropyl group, which gives C_2H_4 elimination as well as C_3H_6.[13] Similarly, aryl-germanium ions degrade partly by successive elimination of alkyne. This fragmentation is most pronounced with the $PhGe^+$ ion and is shown by all the triphenylgermyl compounds examined. It is a high activation energy process which is absent at 20 eV.

$$PhGe^+ \xrightarrow{-C_2H_2} C_4H_3Ge^+ \xrightarrow{-C_2H_2} C_2HGe^+$$

There is also metastable confirmation for acetylene elimination from $PhGeC_6H_4^+$ and $PhGeC_4H_2^+$. Benzyl- and tolyl-germanes all show high abundance ions of composition $GeC_7H_7^+$ which commonly have a strong metastable peak corresponding to elimination of acetylene, and there is evidence that this process continues

$$GeC_7H_7^+ \xrightarrow{-C_2H_2} GeC_5H_5^+ \xrightarrow{-C_2H_2} GeC_3H_3^+$$

The ion $GeC_{12}H_{11}^+$ in the spectra of tolylgermanes could arise by acetylene elimination from $(Tolyl)GeC_7H_6^+$.

Other series of ions may arise by an initial hydrogen loss from an abundant ion, followed by acetylene elimination, or by loss of H from each ion in the parent series, e.g.

$$\begin{tikzcd}
\mathrm{GeC_7H_7}^{+} \arrow[r] \arrow[d, dashed] & \mathrm{GeC_5H_5}^{+} \arrow[r] \arrow[d, dashed] & \mathrm{GeC_3H_3}^{+} \arrow[d, dashed] \\
\mathrm{GeC_7H_6}^{+\bullet} \arrow[r] & \mathrm{GeC_5H_4}^{+\bullet} \arrow[r] & \mathrm{GeC_3H_2}^{+\bullet}
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{GeC_6H_5}^{+} \arrow[r] \arrow[d, dashed] & \mathrm{GeC_4H_3}^{+} \arrow[r] \arrow[d, dashed] & \mathrm{GeC_2H}^{+} \\
\mathrm{GeC_6H_4}^{+\bullet} \arrow[r] & \mathrm{GeC_4H_2}^{+\bullet} &
\end{tikzcd}$$

4:4:10 Methylene Elimination Reactions

These processes, first observed with tin,[192] leave the co-ordination of the germanium ions unchanged. Many ethylgermanes show low abundance ions which are difficult to account for except by methylene elimination from ethyl-Ge groups. The ion $MeGeH_2^+$, which occurs in the

$$Et_3Ge^+ \longrightarrow Et_2GeCH_3^+ + CH_2$$

spectrum of tetraethylgermane may arise in the same way, but it could also be formed by successive ethylene loss from $Et_2GeCH_3^+$, although the intermediate ion $EtGe(H)CH_3^+$ is not observed.

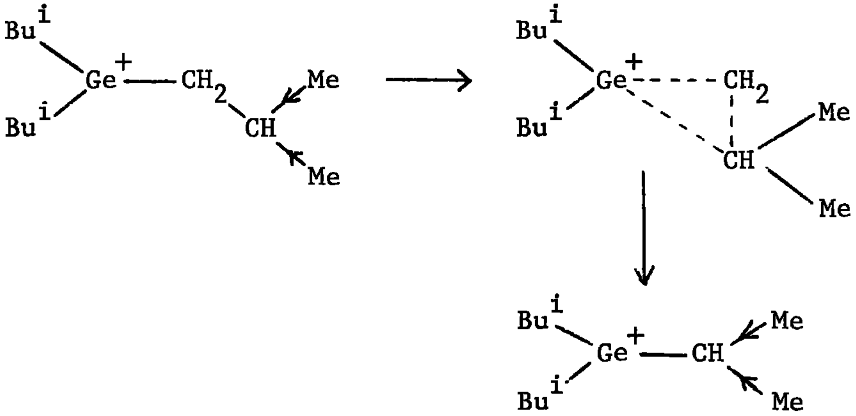
$$EtGeH_2^+ \longrightarrow MeGeH_2^+ + CH_2$$

$$Et_2GeCH_3^+ \longrightarrow EtGeH(CH_3)^+ \longrightarrow MeGeH_2^+$$

The mass spectrum of tetramethylgermane contains the ion Me_2GeH^+ which is most readily explained by a methylene elimination reaction.

$$Me_3Ge^+ \longrightarrow Me_2GeH^+ + CH_2$$

Similar processes probably account for the ions Ph_2GeMe^+ (from Ph_3GeEt), $(PhCH_2)_2GeMe^+$ (from $(PhCH_2)_3GeEt$), $Bu^i_2GeC_3H_7^+$ (from Bu^i_4Ge and $Bu^i_6Ge_2$, but not present in Bu^n_4Ge) and $(p\text{-Tolyl})_2GePh^+$, (from $(p\text{-Tolyl})_4Ge$). The difference between Bu^i_4Ge and Bu^n_4Ge may arise from a difference in the delocalisation gained. For the formation of $Bu^i_2GePr^+$:



Thus by elimination of CH_2, the delocalisation of the positive charge on the metal can be increased. The increased delocalisation going from $Bu^n_3Ge^+$ to $Bu^n_2GePr^{n+}$ is very much less, so the ion $Bu^n_2GePr^{n+}$ is not seen in the spectrum of Bu^n_4Ge.

Certain ions in the spectra of phenyl-, benzyl-, and tolyl-germanes are difficult to explain except by the elimination of C_6H_4 and C_7H_6 fragments, which may have benzyne structures. Some examples are given below.

$$(p\text{-tolyl})_3Ge^+ \longrightarrow (p\text{-tolyl})_2GeH^+ + C_7H_6$$

$$GeC_7H_7^+ \longrightarrow GeH^+ + C_7H_6$$

$$GeC_6H_4^{+\bullet} \longrightarrow Ge^{+\bullet} + C_6H_4$$

$$(PhCH_2)_2GeEt^+ \longrightarrow (PhCH_2)GeEtH^+ + C_7H_6$$

$$PhGe^+ \longrightarrow GeH^+ + C_6H_4$$

$$(PhCH_2)GeMe_2^+ \longrightarrow Me_2GeH^+ + C_7H_6$$

4:4:11 Individual Compounds

In this section peculiarities of particular compounds or groups of compounds are discussed. In the fragmentation diagrams solid arrows are used to denote elimination of even-electron fragments and broken arrows to denote elimination of odd-electron fragments. Metastable transitions are indicated by insertion of the neutral fragment against the arrow. Ion abundances are shown under the formulae. For some of the higher polygermanes, accurate abundances were not calculated because of the labour involved, and the difficulty of obtaining constant monitor sweeps over wide mass ranges, for compounds of low volatility. In such cases, relative abundances are reported as high (h), medium (m) or low (l), and this indicates the important fragmentation routes. For simplicity of representation, only one mode of formation of a given ion is shown, unless there is good reason to think that more than one process is important. The structure assigned to an ion is in all cases the most probable, but not necessarily the only one.

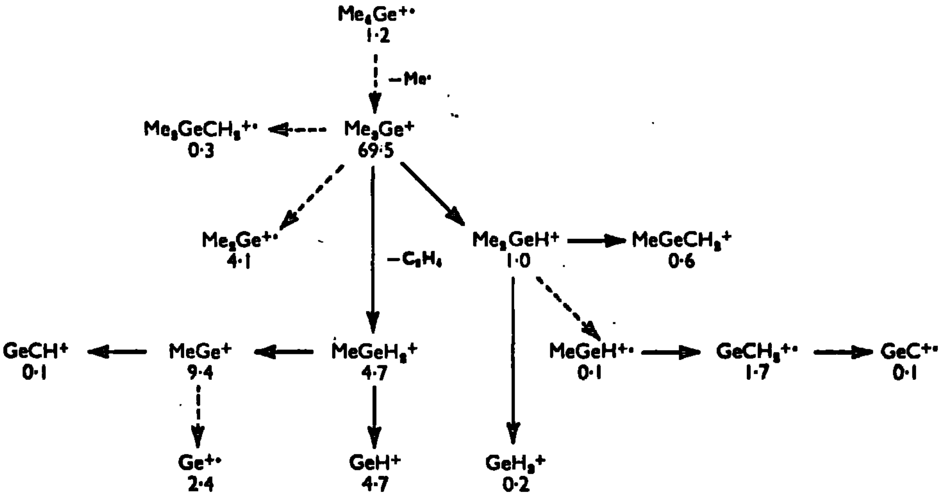
$\underline{GeH_4}$. Features not noted in previous studies (Section 3:4) are the occurrence of three doubly charged ions (GeH_2^{2+}, $GeH^{2+\bullet}$, and Ge^{2+}) and rhe metastable transition, $GeH_2^{+\bullet} \longrightarrow Ge^{+\bullet} + H_2$. Metastable peaks and doubly charged ions are particularly dependent on the design and operating conditions of the spectrometer. Abundances found were: $GeH_4^{+\bullet} < 0{\cdot}1$, GeH_3^{+} 36·2, $GeH_2^{+\bullet}$ 36·8, GeH_2^{2+} 0·3, GeH^{+} 7·9, $GeH^{2+\bullet}$ 2·8, $Ge^{+\bullet}$ 13·8, and Ge^{2+} 2·2%. These agree well with previous reports.

$\underline{GeCl_4}$. $GeCl_4^{+\bullet}$ 16·9, $GeCl_3^{+}$ 73·1, $GeCl_3^{2+\bullet}$ 0·6, $GeCl_2^{+\bullet}$ 1·3, $GeCl^{+}$ 6·4, $GeCl^{2+\bullet}$ 0·5, and $Ge^{+\bullet}$ 1·2%. Some of these details have since been reported by other authors.[204]

$\underline{Me_4Ge}$. (Scheme 1). Not all of the ions reported by earlier workers[174] were found. This illustrates the dangers of using only low resolution spectra, together with the method of synthesizing observed patterns from ions assumed to be there. Small errors in measurement can easily delude one into accepting the presence of an ion which is really absent, in order to make the pattern fit. The only sure test of the presence of an ion is a precise mass measurement. The high abundance of $Me_2Ge^{+\bullet}$ (4·1%) is probably due to difficulty of alkene elimination compared with higher alkyl compounds. A recent report of this spectrum[205] suggests the presence of other metastables, (e.g. $GeCH_5^{+} \longrightarrow GeCH_3^{+} + H_2$) but careful re-examination of the spectra could not confirm these.

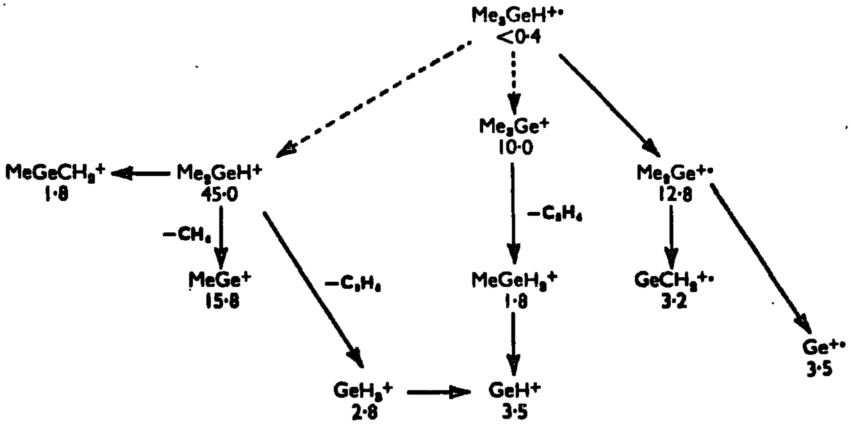
$\underline{Me_3GeH}$. (Scheme 2).

Me_4Ge.



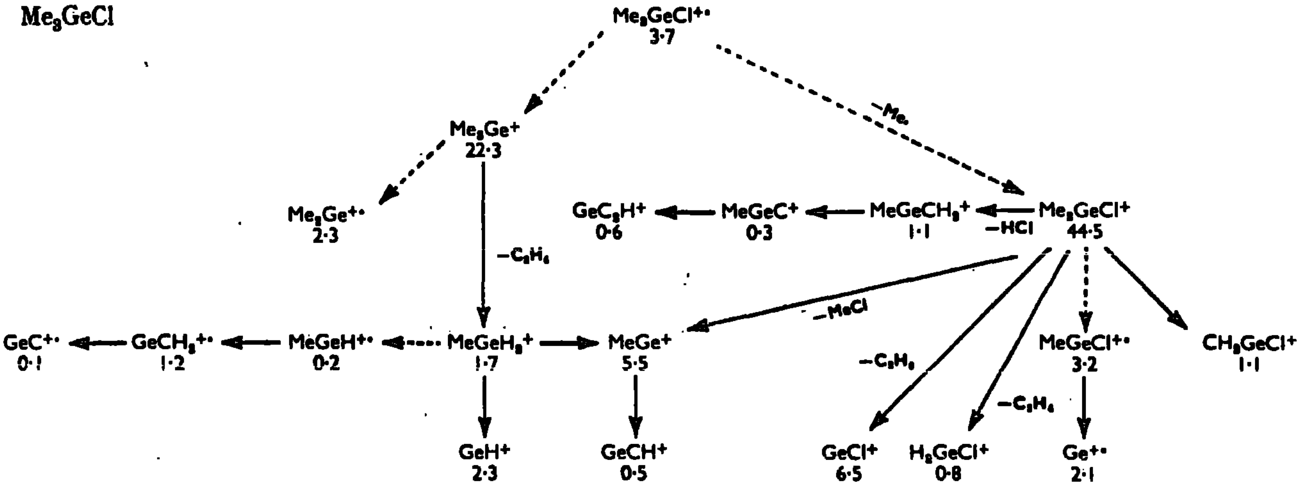
SCHEME 1

Me_3GeH.



SCHEME 2

Me_3GeCl



SCHEME 3

Me_3GeCl. (Scheme 3).

$MeGeCl_3$. The order of abundance of the major ions is $MeGeCl_2^{+} > GeCl_3^{+}, GeCl^{+} > MeGeCl_3^{+\cdot} > Ge^{+\cdot} > MeGeCl^{+\cdot} > GeCl_2^{+\cdot}$. The high abundance of ions containing Cl in this and other chlorine compounds suggests that the electronegative chlorine atom exerts a powerful stabilising effect.

Et_4Ge. (Scheme 4). Unlike Et_4Sn, the germane has Et_2GeH^{+} as the most abundant ion and the ratio R_2GeH^{+}/R_3Ge^{+} is even greater when R = Bu^{i}, than it is when R = Et. Comparison of the tetraethyl compounds of germanium, tin and lead shows that the proportion of hydride ions increases with the strength of the metal-hydrogen bond.

Table 13. Hydride Ion Abundances in MEt_4 at 70 eV, Relative to M^{+}

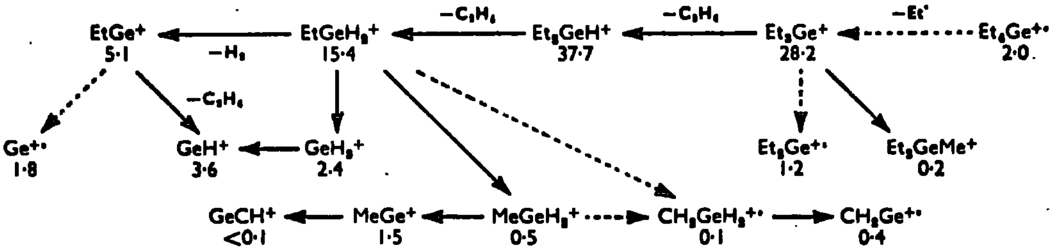
	M^{+}	MH^{+}	MH_3^{+}	$(MH^{+} + MH_3^{+})$
$PbEt_4$	1	0·9	0	0·9
$SnEt_4$	1	2·5	0·3	2·8
$GeEt_4$	1	2·0	1·3	3·3

Et_4Ge, unlike Et_4Sn, shows the $Et_2M^{+\cdot}$ ion.

Et_3GeH. The order of abundance of the main ions is: $EtGeH_2^{+} > Et_2GeH^{+} > Et_2Ge^{+\cdot} > GeH^{+} > EtGe^{+} > Ge^{+\cdot} > Et_3Ge^{+} > Et_3GeH^{+\cdot}$.

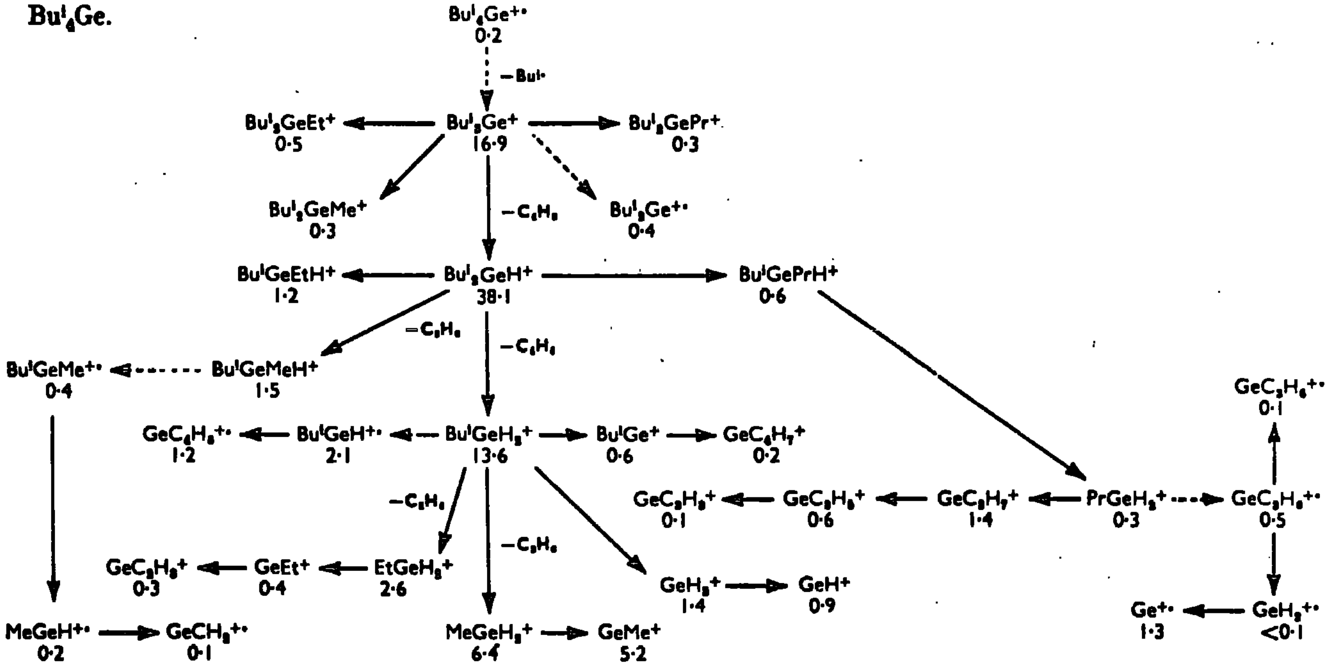
Bu^{i}_4Ge. (Scheme 5). Although the ions in the scheme are written as though they contain isobutyl groups, this is not necessarily so, but in the absence of any evidence to the contrary it is the simplest assumption.

Et_4Ge.



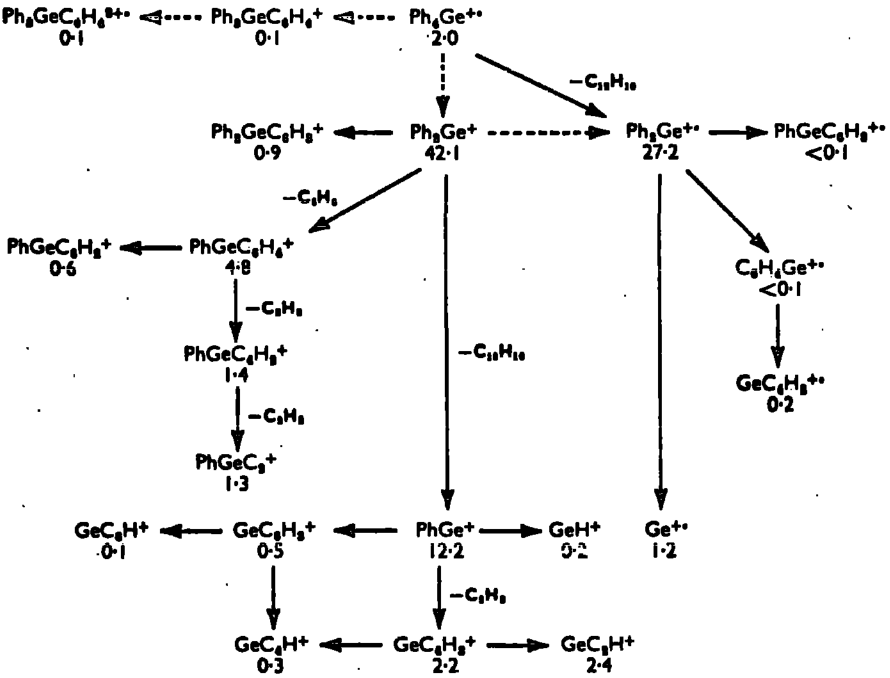
SCHEME 4

Bu^t_4Ge.



SCHEME 5

Ph_4Ge.



SCHEME 6

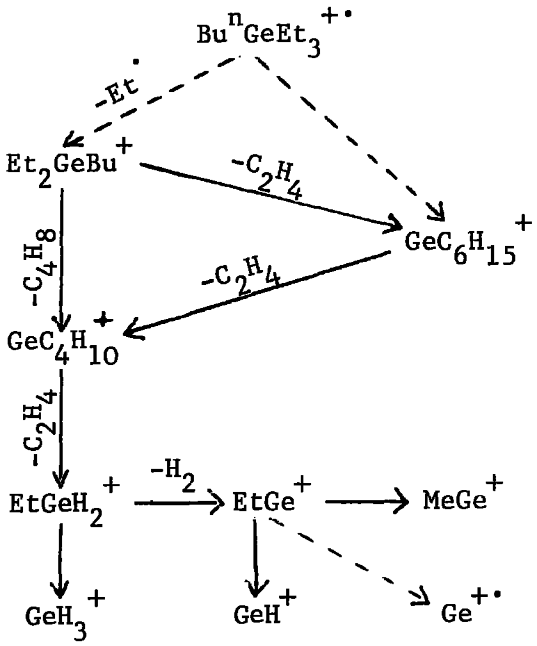
$Bu^n{}_4Ge$. This has been studied at low resolution[197] since the completion of the work on $Bu^i{}_4Ge$. It shows no significant differences, but fewer metastables were identified. The mass spectrum of $Pr^i{}_4Ge$ has also been published.[13]

Ph_4Ge. (Scheme 6). Comparison of ion abundances with tetraphenyltin shows that whereas $Ph_2Sn^{+\cdot}/PhSn^{+} \sim 1$ with germanium $Ph_2Ge^{+\cdot}/PhGe^{+} \sim 2$. There is also a vast difference between the M^+ abundances (Ge^+, 1·3%; Sn^+, 18·6%). These figures indicate that the reaction $Ph_2M^{+\cdot} \longrightarrow M^{+\cdot} + Ph_2$ is much less energetically favourable for germanium than for tin, reflecting the greater Ge-C bond strength.

Et_3GeBu^n. (Scheme 7). This was not a known compound but was first identified by its fragmentation pattern. Infrared spectrum and C/H analysis later confirmed it. An important diagnostic feature is the butene elimination. Several ions cannot have even tentative structures assigned e.g. $GeC_6H_{15}{}^+$ is probably a mixture of $GeEt_3{}^+$ formed by $Bu^\cdot$ elimination from the molecular ion, and $BuGeEtH^+$ formed by ethylene elimination from Et_2GeBu^+.

Ph_3GeH. (Scheme 8). Comparison with the spectrum of tetraphenylgermane shows that benzene elimination is a major process leading to $Ph_2Ge^{+\cdot}$, $PhGe^+$, and $PhGeC_6H_4{}^+$.

Et_3GeBu^n



SCHEME 7

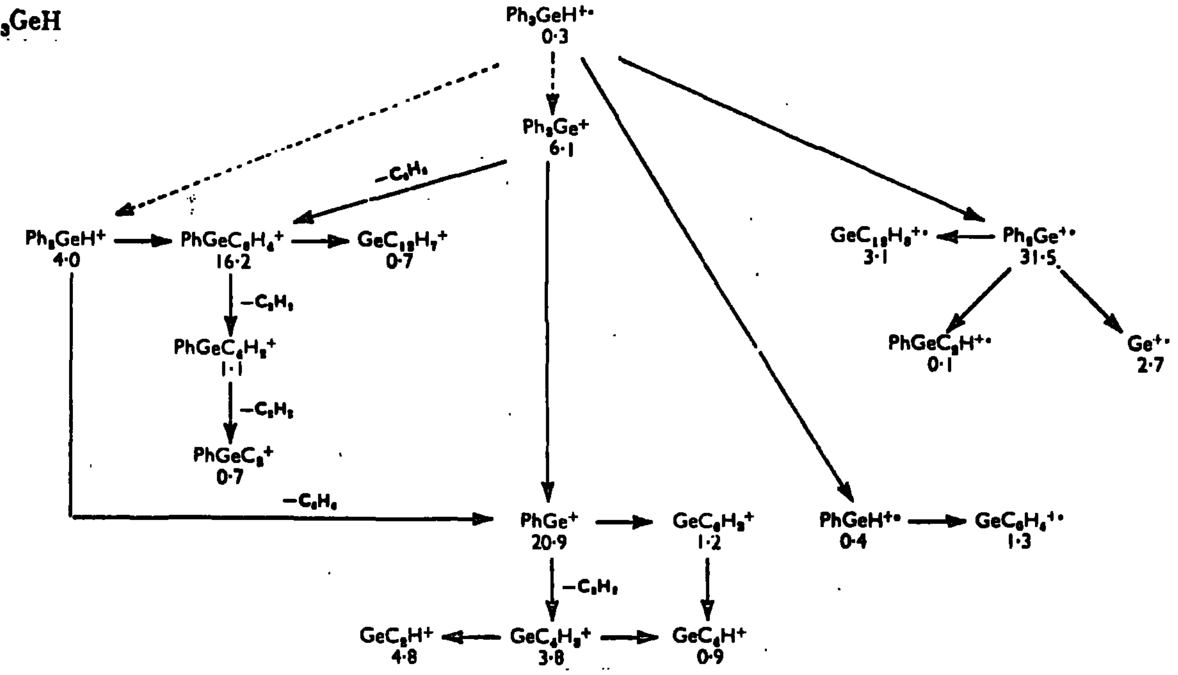
Ph_3GeCl. (Scheme 9). Both Ph_3GeCl and Ph_3GeBr show elimination of PhGeX from $Ph_3GeX^{+\bullet}$ to give $Ph_2^{+\bullet}$ in much higher abundance than in other phenylgermanes. The chloride was the only compound examined which showed a metastable peak for the elimination of $Ph^\bullet$. The molecular ion $Ph_3GeCl^{+\bullet}$ was much more abundant (10%) than in Ph_3SnCl (1%), and MX^+ ions were in general much less abundant for germanium than for tin.

Ph_3GeBr. (Scheme 10).

Ph_3GeI. (Scheme 11).

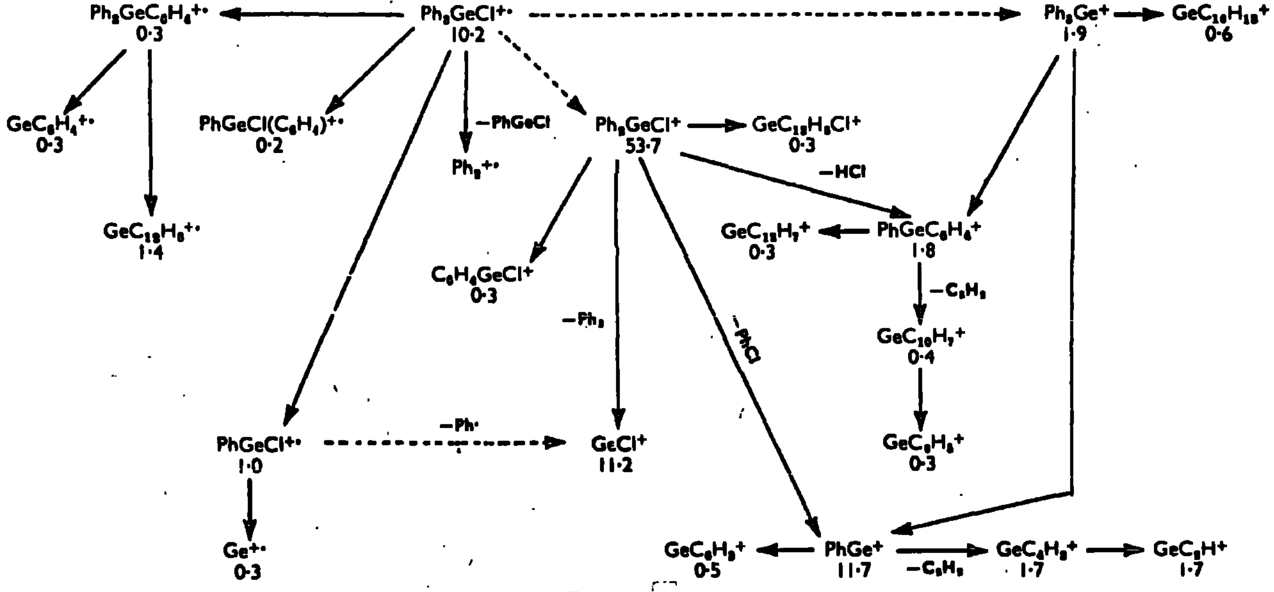
Ph_3GeMe. (Scheme 12).

Ph_3GeH



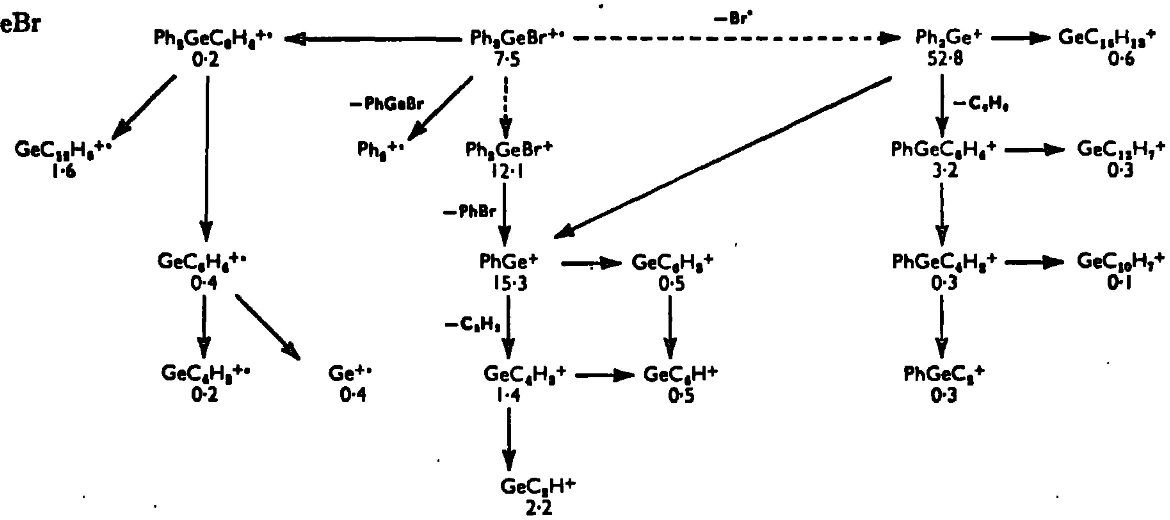
SCHEME 8

Ph_3GeCl



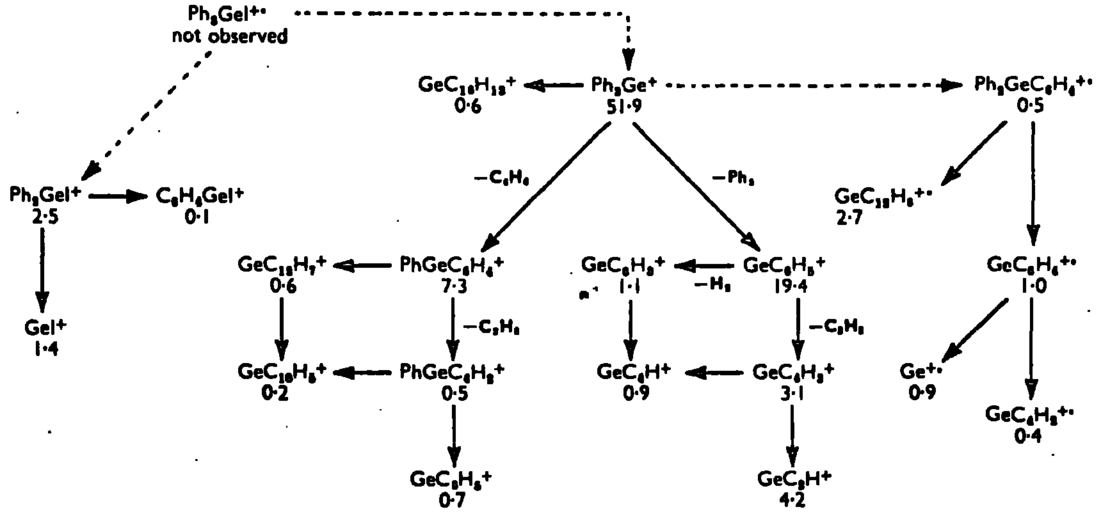
SCHEME 9

Ph_3GeBr



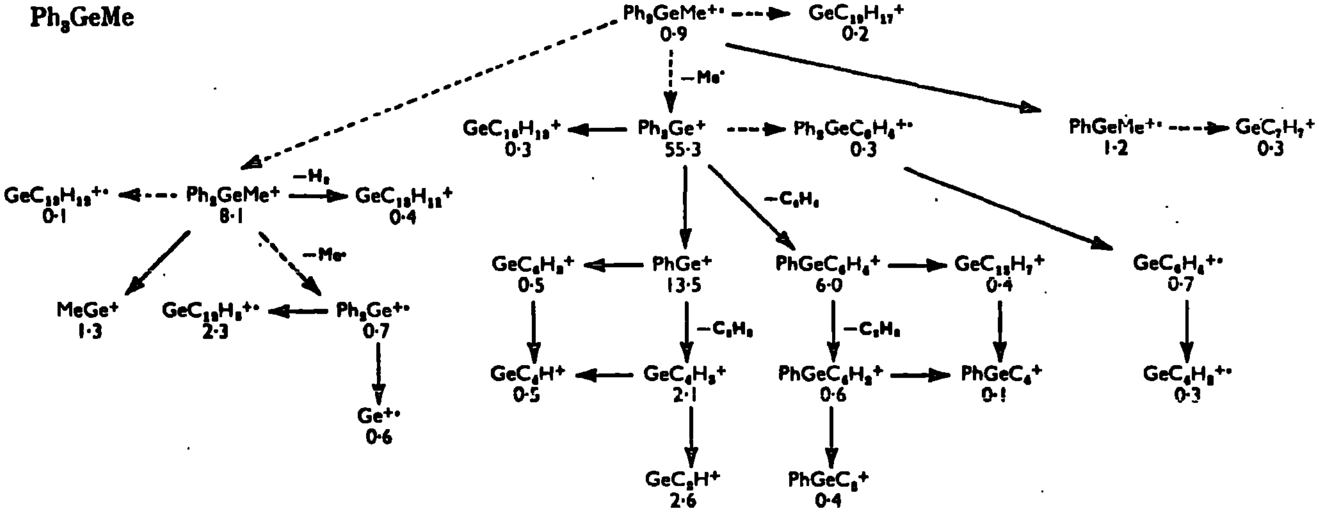
SCHEME 10

Ph_3GeI



SCHEME 11

Ph_3GeMe



SCHEME 12

Ph_3GeEt, (Scheme 13), Ph_2GeEt_2, and $PhGeEt_3$. In general these resemble the corresponding tin compounds except for the lower abundance of $Ge^{+\bullet}$ (Ph_3MEt: $Ge^{+\bullet}$, 0·6 and $Sn^{+\bullet}$, 13·4%) and the greater abundance of $Ph_2Ge^{+\bullet}$. A further difference from tin is the occurrence of doubly charged ions, $Ph_3Ge^{2+\bullet}$ (from Ph_3GeEt), $PhGeEt_2^{2+\bullet}$ and $PhGe(H)Et^{2+\bullet}$ (from $PhGeEt_3$) and $Ph_2GeH^{2+\bullet}$ (from Ph_2GeEt_2).

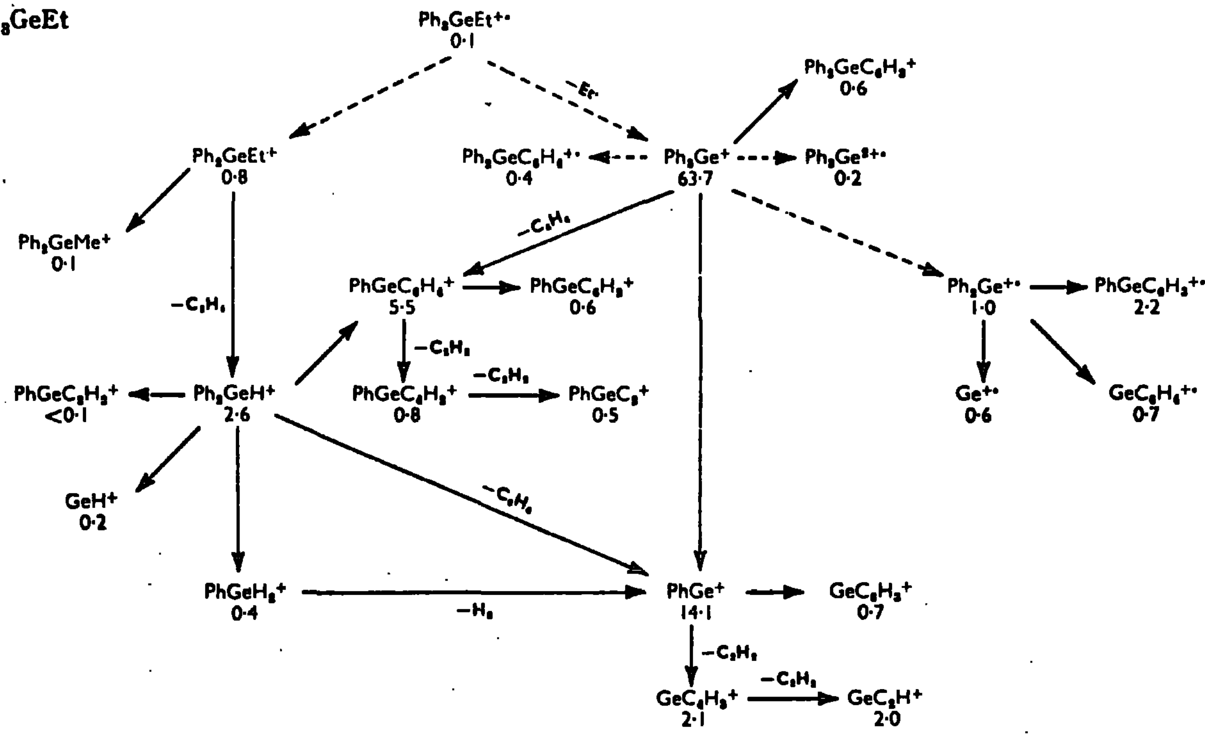
Ph_3GeBu^n. As the molecular weight of the alkyl group in the triphenylalkylgermanes increases, so the number and abundance of ions containing alkyl fragments decreases. In the spectrum of Ph_3GeBu, the only ions not arising from Ph_3Ge^+ are the molecular ion, Ph_2GeBu^+ and Ph_2GeH^+. The doubly charged ion $Ph_3Ge^{2+\bullet}$ was observed.

Ph_3GeCH_2Ph. (Scheme 14).

Tolylgermanes. These illustrate the effect of steric factors on elimination reactions; tetra-m- and -p-tolyl-germanes are strikingly similar in their fragmentation patterns, but the ortho-compound shows many differences. The mass spectrum of tetra-p-tolylgermane resembles that of Ph_4Ge in that $H^\bullet$ loss from the molecular ion gives singly and doubly charged ions, bi-p-tolyl is eliminated from the molecular ion and from the R_3Ge^+ ion and fragmentation of the $GeC_7H_7^+$ ion involves successive elimination of acetylene.

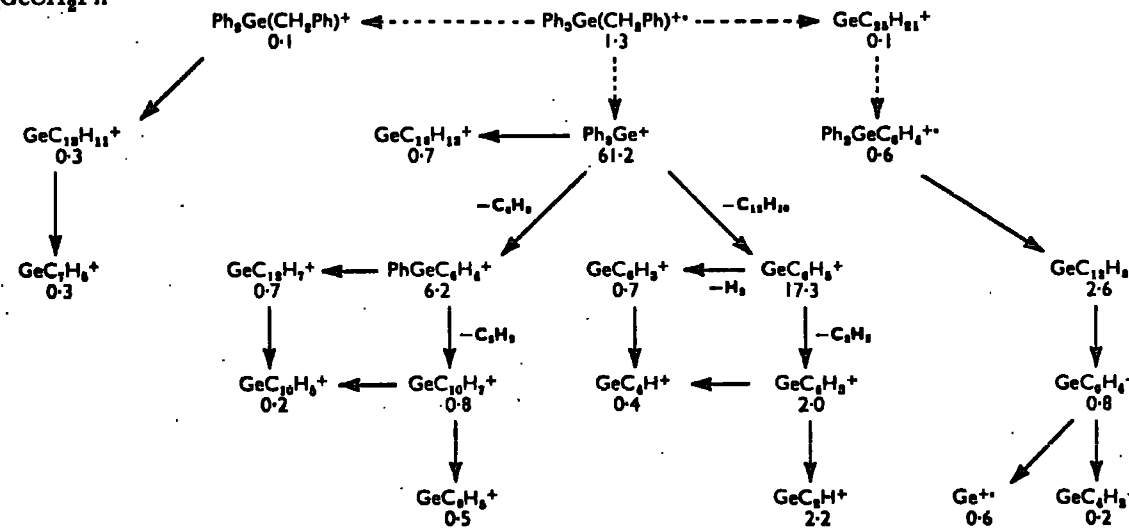
$$GeC_7H_7^+ \longrightarrow GeC_5H_5^+ \longrightarrow GeC_3H_3^+$$

Ph_3GeEt



SCHEME 13

Ph_3GeCH_2Ph



SCHEME 14

Differences from tetraphenylgermane are those expected from the presence of methyl groups. Thus the ions $(p\text{-Tolyl})_3GeC_6H_4^+$ and $(p\text{-Tolyl})GeC_6H_4^+$ are formed by methyl-radical elimination. Tetra-m-tolylgermane differs from tetra-p-tolylgermane in that the doubly charged molecular ion is present rather than the ion $(m\text{-Tolyl})_3GeC_7H_6^{2+\bullet}$

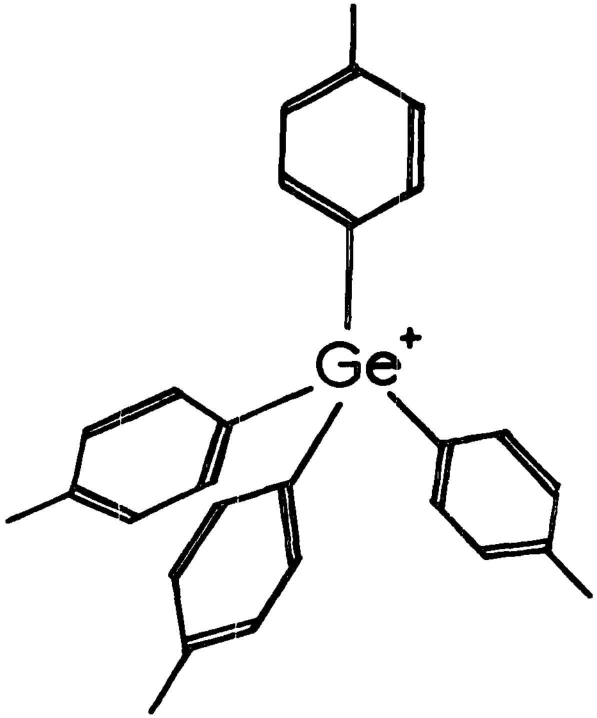
The molecular ion is some six times more abundant in $(p\text{-Tolyl})_4Ge$ than in $(o\text{-Tolyl})_4Ge$ whilst the ion $(\text{Tolyl})_2Ge^{+\bullet}$ which is 26% abundant in the para and 28% in the meta isomers is only 2•5% abundant in the ortho. Since $R_2Ge^{+\bullet}$ is formed by the process $R_4Ge^{+\bullet} \longrightarrow R_2Ge^{+\bullet} + R_2$ this difference is most probably due to ortho methyl groups interfering with C-C bond formation in the o-tolyl case (Figure 6). Whereas $(p\text{-Tolyl})_2Ge^{+\bullet}$ loses a methyl radical forming an even-electron ion $(\text{Tolyl})GeC_6H_4^+$, in the spectrum of tetra-o-tolylgermane this process is insignificant, and the loss of a methyl radical leads to an odd-electron ion.

$$(o\text{-Tolyl})GeC_7H_6^+ \longrightarrow GeC_{13}H_{10}^{+\bullet} + Me^\bullet$$

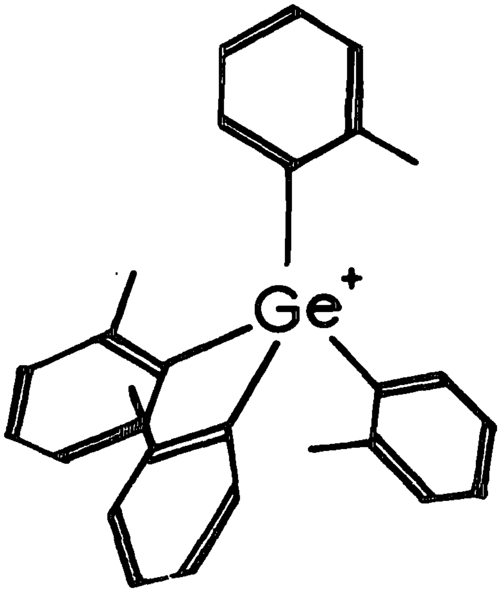
The fact that the meta and para isomers resemble each other and are different from the ortho isomer is consistent with steric rather than electronic effects.

$(o\text{-Tolyl})_4Ge$. (Scheme 15). The presence of $GeC_{15}H_{15}^+$ in $(o\text{-Tolyl})_4Ge$ and not in the meta and para compounds may mean that the o-Tolyl group is readily converted to a benzyl group, since the ion $GeC_{15}H_{15}^+$ is

Figure 6



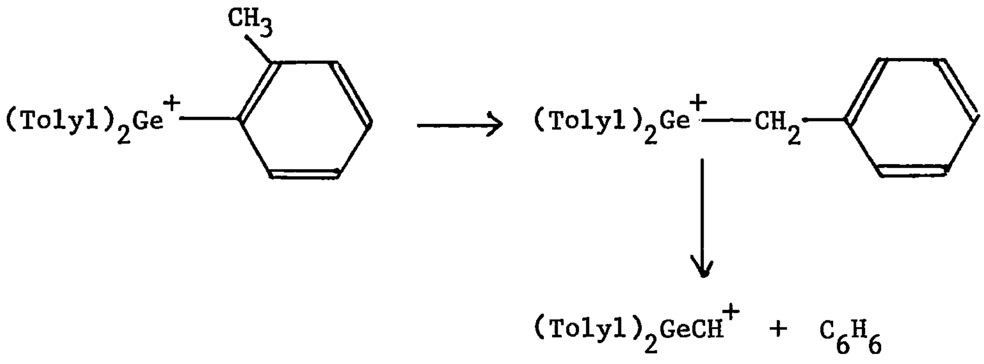
para



ortho

Stereochemistry of molecular ions

formed by benzene elimination from $(PhCH_2)_3Ge^+$ in benzyl compounds.

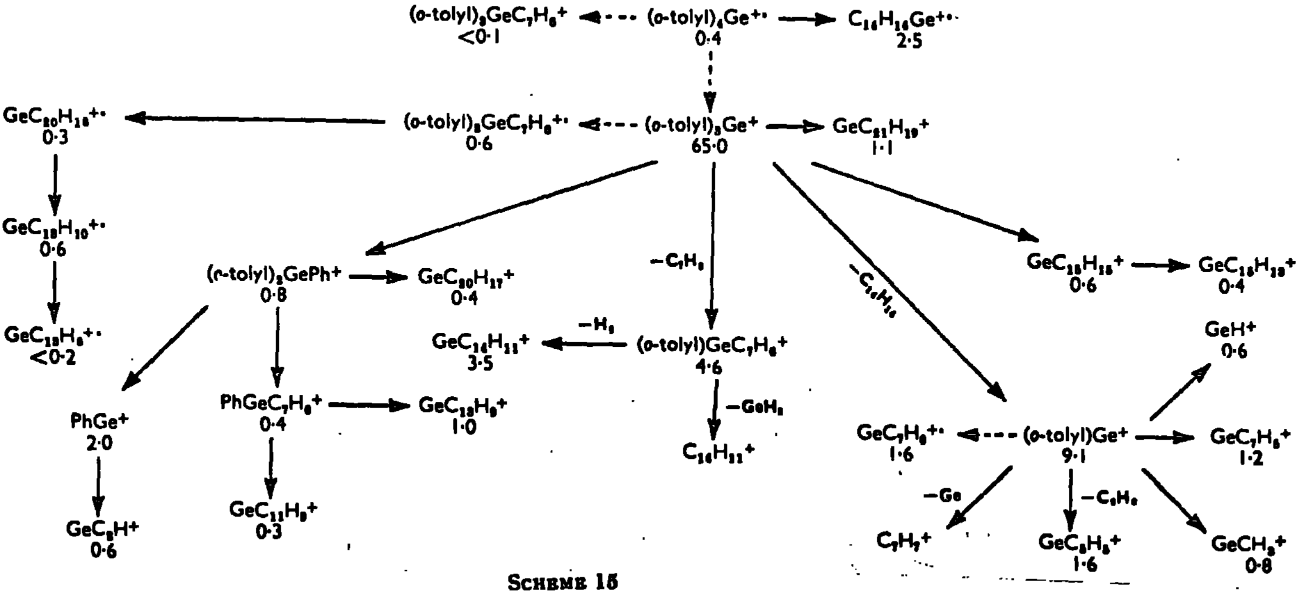


<u>$(m\text{-}Tolyl)_4Ge$.</u> (Scheme 16).

<u>$(p\text{-}Tolyl)_4Ge$.</u> (Scheme 17).

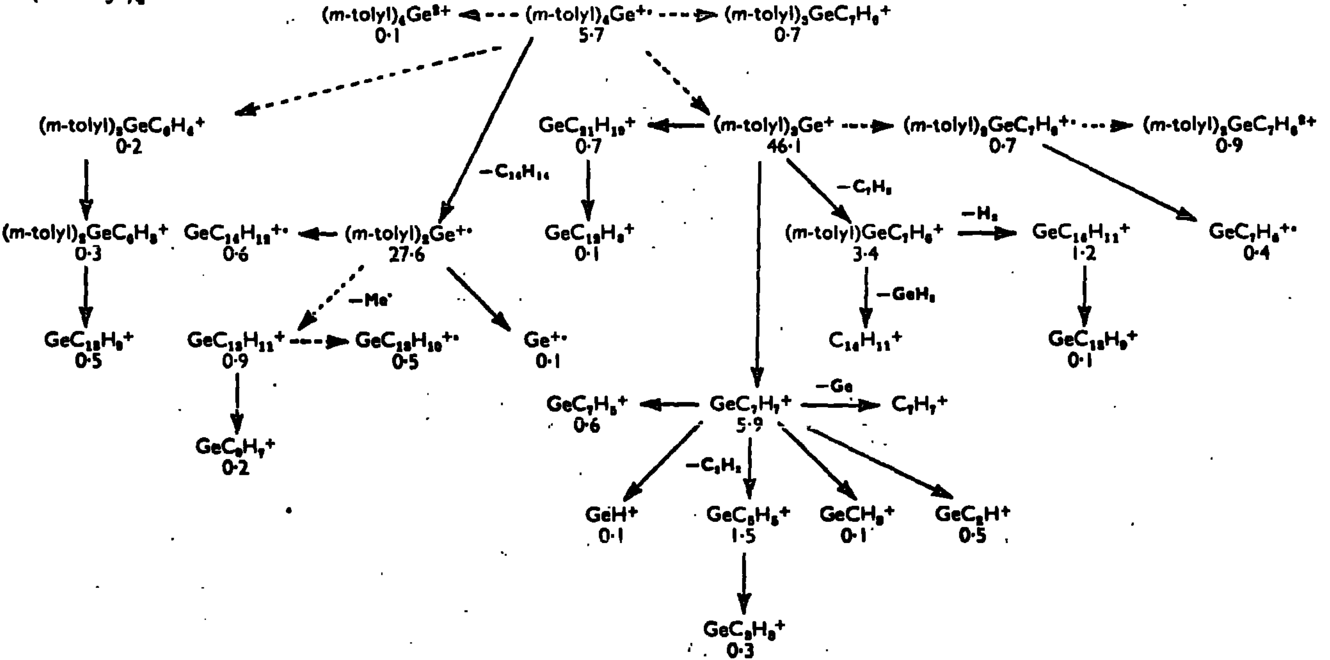
<u>$(p\text{-}Tolyl)_3GeCO_2H$.</u> The ion $(p\text{-}Tolyl)_3GeOH^{+\bullet}$ in this spectrum is probably formed by elimination of CO from the molecular ion, since the acid loses CO when heated to its melting point, and forms the ester $R_3GeOCOGeR_3$. Since no specie above the mass of the molecular ion were observed, loss of CO is probably a true electron impact-induced process. The two doubly charged ions, $(p\text{-}Tolyl)_3Ge^{2+\bullet}$ and $(p\text{-}Tolyl)_2GeC_7H_6{}^{2+}$ are unusual in that the ratio of their abundances (2:1) is far lower than that of the corresponding singly charged species. It is possible that, in addition to the process $R_3Ge^+ \longrightarrow R_3Ge^{2+\bullet}$, elimination of negative ions may contribute to their formation.

(*o*-Tolyl)$_4$Ge



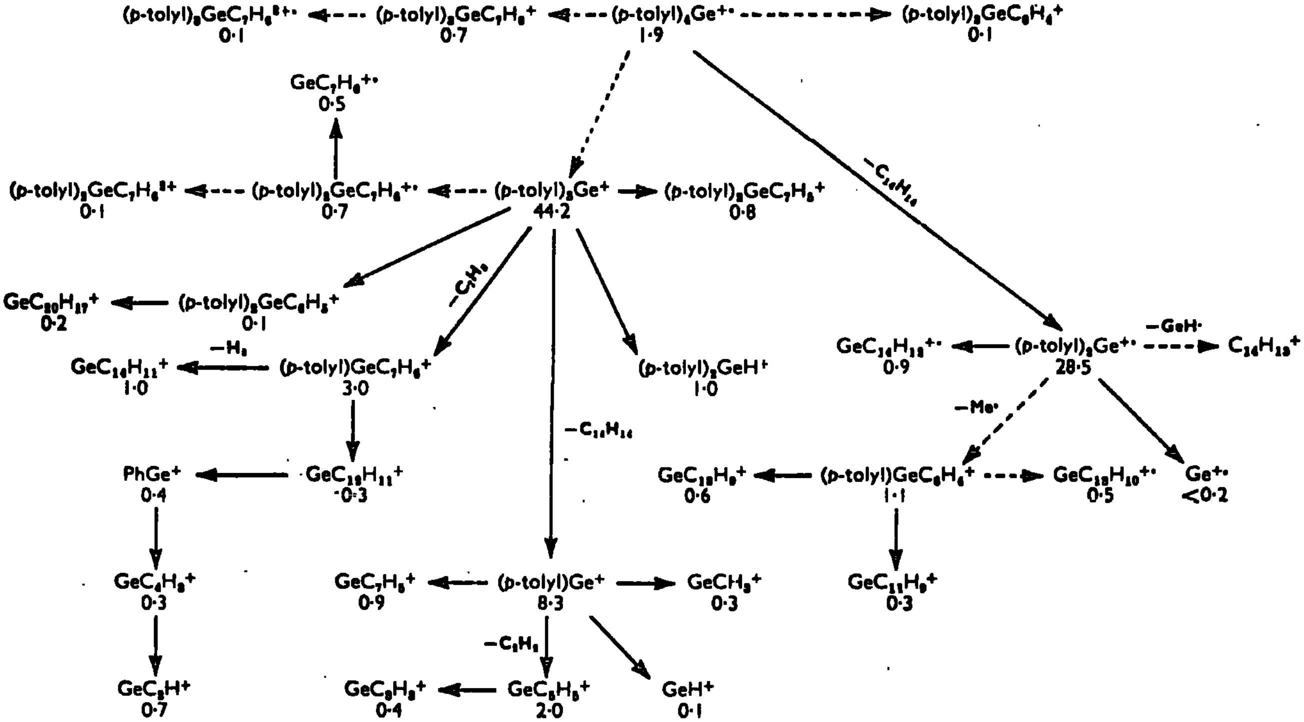
SCHEME 15

(*m*-Tolyl)$_4$Ge



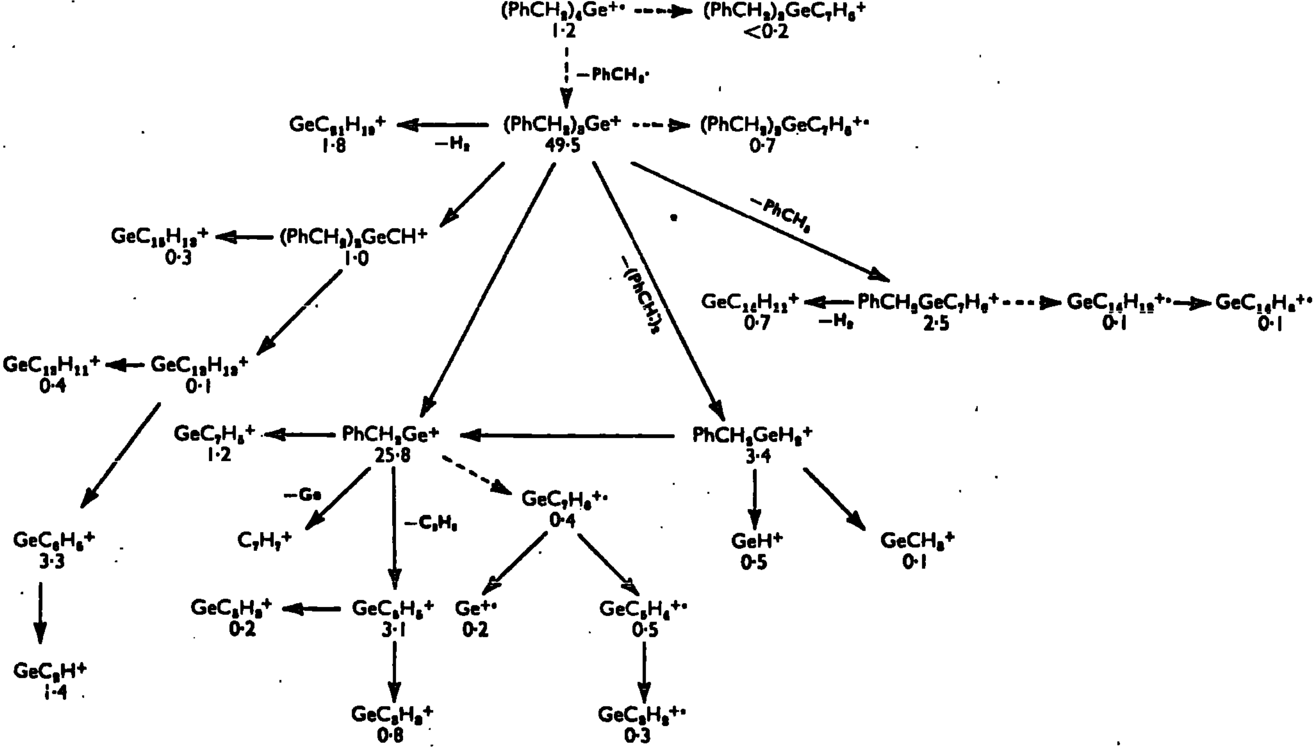
SCHEME 16

$(p\text{-Tolyl})_4Ge$



SCHEME 17

$(PhCH_2)_4Ge$



SCHEME 18

$$\begin{tikzcd}
 & (p\text{-tolyl})_3Ge^{2+\bullet} + OH^- \\
(p\text{-tolyl})_3GeOH^{+\bullet} \arrow[ur] \arrow[dr] & \\
 & (p\text{-tolyl})_2GeC_7H_6^{2+} + H_2O^{-\bullet}
\end{tikzcd}$$

Elimination of negative fragments has been postulated in other systems.[206]

Benzylgermanes. Benzylgermanes are of interest in relation to analogous tolyl compounds since many ions have the same compositions in both cases although they may differ in structure. The formation of some ions, readily explained for benzyl compounds, is extremely difficult to account for in the tolyls, and *vice versa*, suggesting the possibility of an interchange between benzyl- and tolyl-Ge structures in some fragment ions. For example, the ion $GeC_{15}H_{15}^+$ occurs in both series of spectra, but only for the benzyl germanes is its mode of formation clear.

$$(PhCH_2)_3Ge^+ \longrightarrow GeC_{15}H_{15}^+ + C_6H_6$$

The ion $GeC_{13}H_{11}^+$ also occurs in the spectra of both $(PhCH_2)_4Ge$ and $(p\text{-tolyl})_4Ge$ and although its origin is obvious for the tolyl compound, the ion $GeC_{14}H_{14}^{+\bullet}$ (i.e., $(PhCH_2)_2Ge^{+\bullet}$ or an isomer) is absent from tetrabenzylgermane.

$$(p\text{-}MeC_6H_4)_2Ge^{+\bullet} \longrightarrow (p\text{-}MeC_6H_4)GeC_6H_4^+ + Me^\bullet$$

Tetrabenzylgermane resembles the tetra-alkyl-germanes in that the formation of $(PhCH_2)_3Ge^+$ is metastable-supported, and the aliphatic character of the benzyl-Ge bond is most clearly demonstrated by the transition:

$$(PhCH_2)_3Ge^+ \longrightarrow PhCH_2GeH_2^+ + PhCH{=}CHPh$$

It resembles the arylgermanes, however, in that loss of hydrogen from the molecular ion is observed, and elimination of benzene and toluene also occur. The elimination of acetylene is another aryl-type reaction ubiquitous among benzyl compounds.

The presence of $GeC_6H_5^+$ in the spectrum of $(PhCH_2)_4Ge$ is surprising, but after recrystallisation of the compound six times from ethanol and six times from petroleum ether, the spectrum was unchanged. The ion is presumably formed as shown in Scheme 18.

Tribenzylgermanes differ markedly in their fragmentation from triphenylgermanes. In the benzyl compounds molecular ions are more abundant than in Ph_3GeR compounds, and $(PhCH_2)_3Ge^+$ is generally less abundant than $(PhCH_2)_2GeR^+$ whereas the reverse is true for triphenylgermanes.

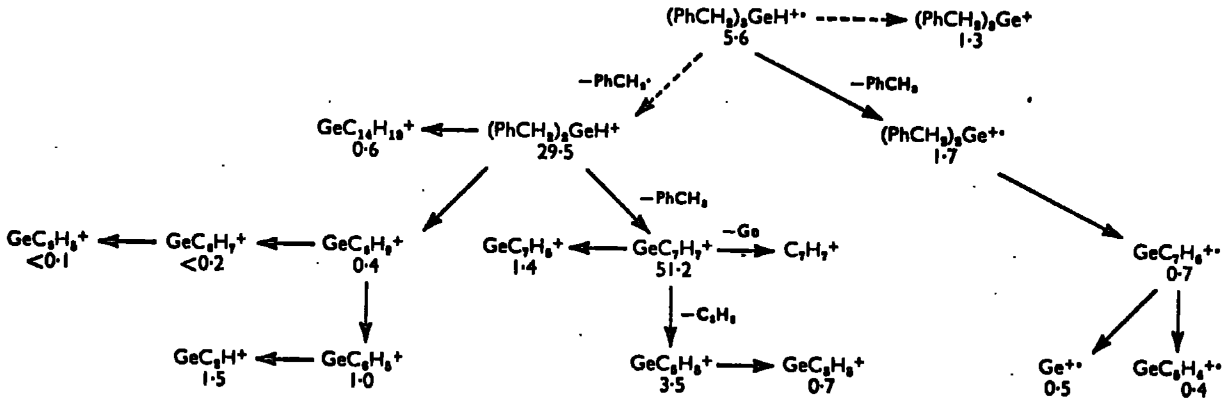
<u>$(PhCH_2)_4Ge$</u>. (Scheme 18).

<u>$(PhCH_2)_3GeH$</u>. (Scheme 19).

<u>$(PhCH_2)_3GeEt$</u>. (Scheme 20).

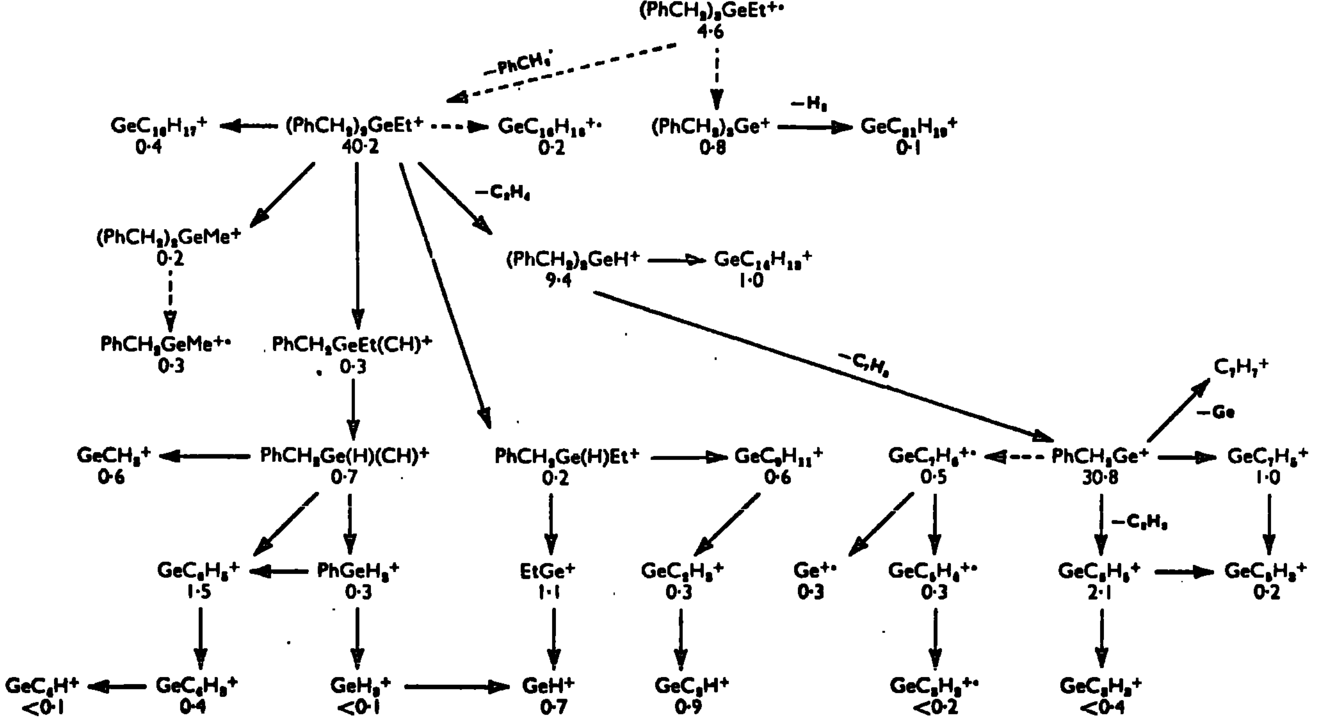
<u>$(PhCH_2)_2GeMe_2$</u>. (Scheme 21).

$(PhCH_2)_3GeH$

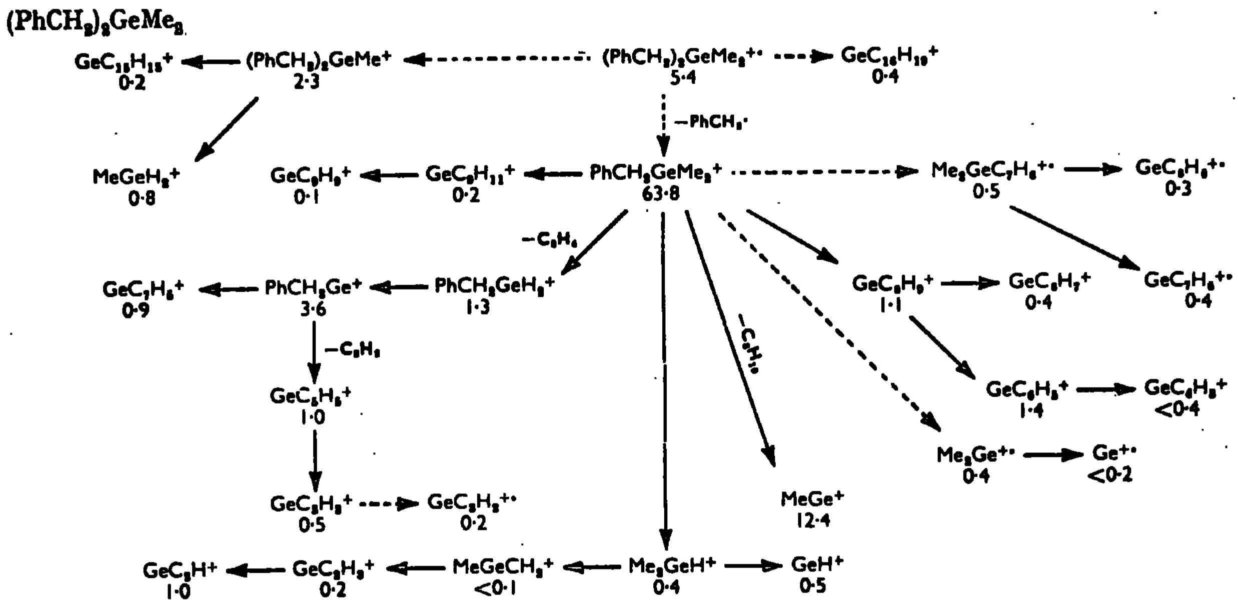


SCHEME 19

$(PhCH_2)_3GeEt$



SCHEME 20



SCHEME 21

<u>Digermanes</u>. Where facile alkene-elimination reactions are possible, as in Et_6Ge_2 and $Bu^i_6Ge_2$ (and $Pr^i_6Ge_2$ [13]), a high proportion of the ion current is carried by digermanium species (79% in Et_6Ge_2 and 46% in $Bu^i_6Ge_2$). However, where this mode of decomposition is not available (Me_6Ge_2 and $(Aryl)_6Ge_2$) monogermanium species predominate, and cleavage of the germanium-germanium bond in the ions $R_6Ge_2^{+\cdot}$ and $R_5Ge_2^+$ must be the process of lowest activation energy. Thus, in hexamethyldigermane loss of a methyl radical from the molecular ion gives $Me_5Ge_2^+$, and these are the only Ge_2 containing ions of appreciable abundance, Me_3Ge^+ being by far the most abundant ion in the spectrum (54%). In Ph_6Ge_2 and the hexatolyldigermanes the molecular ions are the most abundant digermanium species, second only to R_3Ge^+. In $(m\text{-}Tolyl)_6Ge_2$

the molecular ion accounts for 95% of the Ge_2 species, and is one of the most abundant molecular ions found (11·6%). $(p\text{-Tolyl})_6Ge_2$ closely resembles the <u>meta</u> compound, and once again $(o\text{-Tolyl})_6Ge_2$ differs in some minor respects. Hexabenzyldigermane is quite different, in that the molecular ion was not visible, but all the ions $(PhCH_2)_nGe_2^+$ (n = 1-5) were present and carried 39% of the ion current.

An interesting feature in a number of the digermane spectra is the occurrence of ions which can only be explained in terms of transfer of an organic group from one germanium atom to the other, with cleavage of the Ge-Ge bond. Such transformations would obviously

$$Ph_6Ge_2^{+\bullet} \longrightarrow Ph_3GeC_6H_4^+$$

$$(m\text{-},p\text{-Tolyl})_6Ge_2^{+\cdot} \longrightarrow (Tolyl)_3GeC_7H_6^+$$

be more easily studied in compounds of the type $R'_3M'M''R''_3$, and such a study has since been made.[207]

<u>Me_6Ge_2.</u> (Scheme 22).

<u>Et_6Ge_2.</u> (Scheme 23).

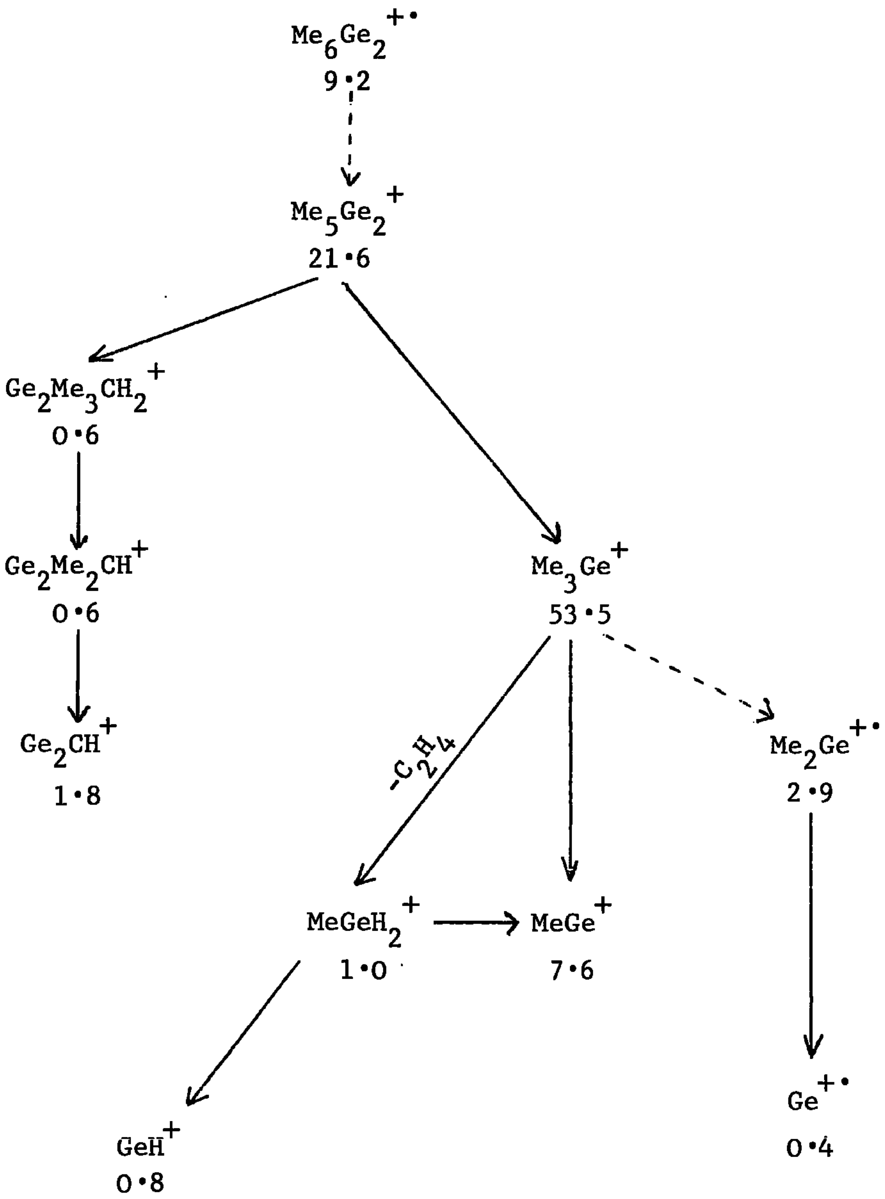
<u>$Bu^i{}_6Ge_2$.</u> (Scheme 24).

<u>Ph_6Ge_2.</u> (Scheme 25).

<u>$(m\text{-Tolyl})_6Ge_2$.</u> (Scheme 26).

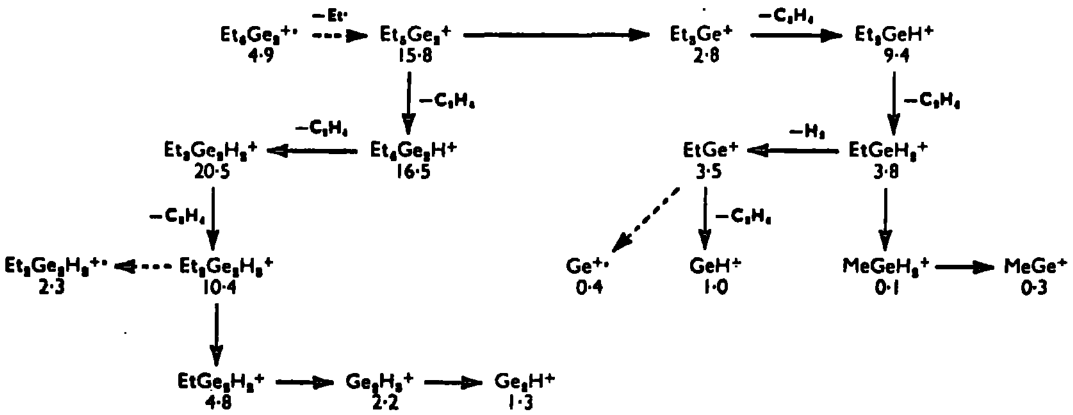
<u>$(PhCH_2)_6Ge_2$.</u> (Scheme 27).

Me_6Ge_2



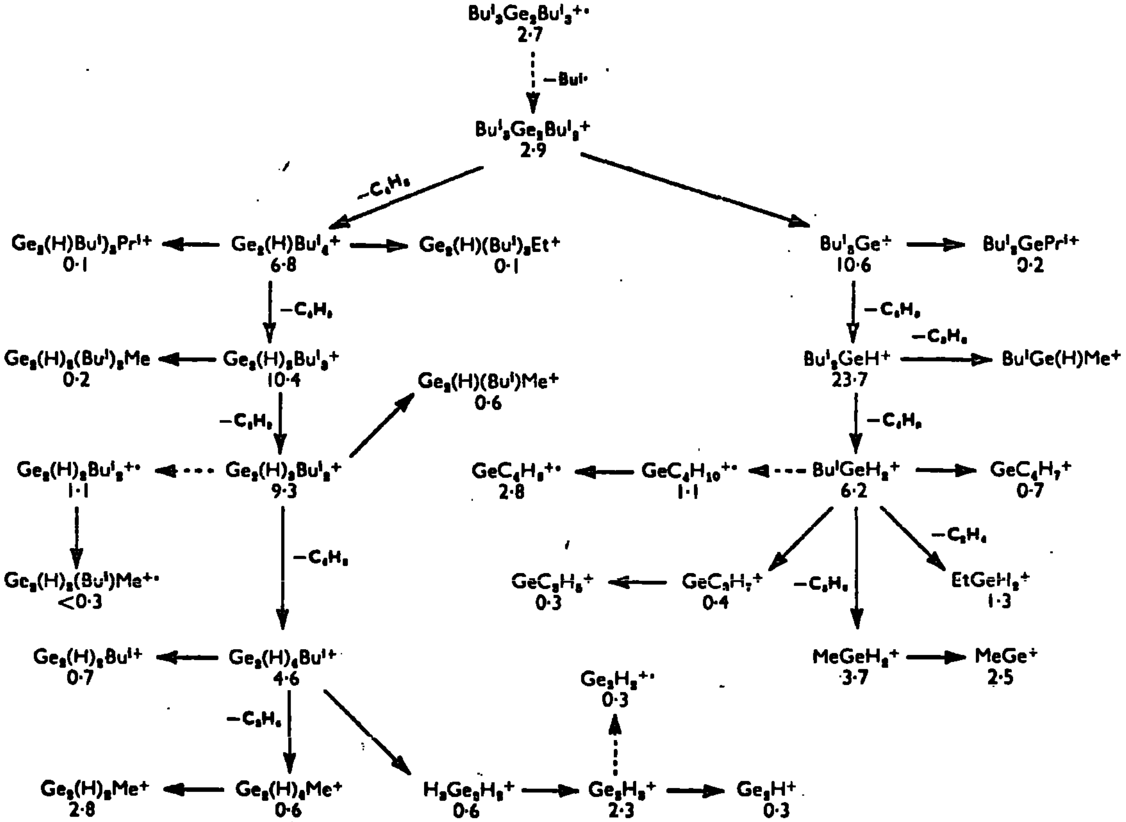
SCHEME 22

Et_6Ge_2



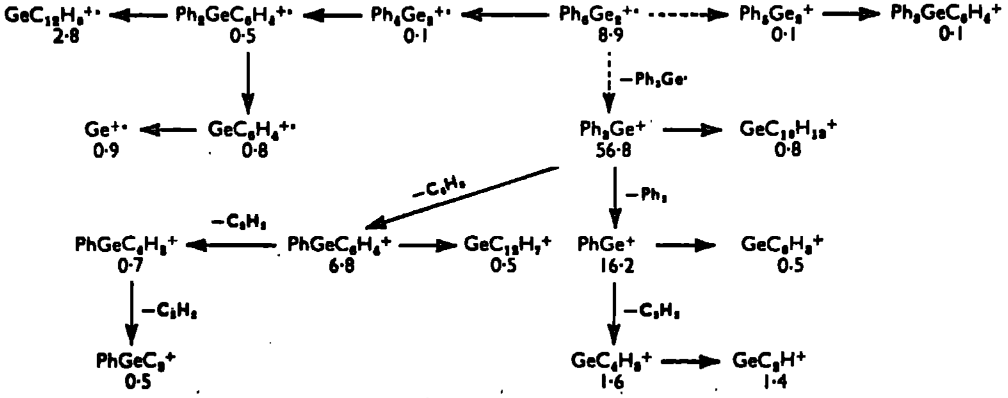
SCHEME 23

$Bu^t_6Ge_2$



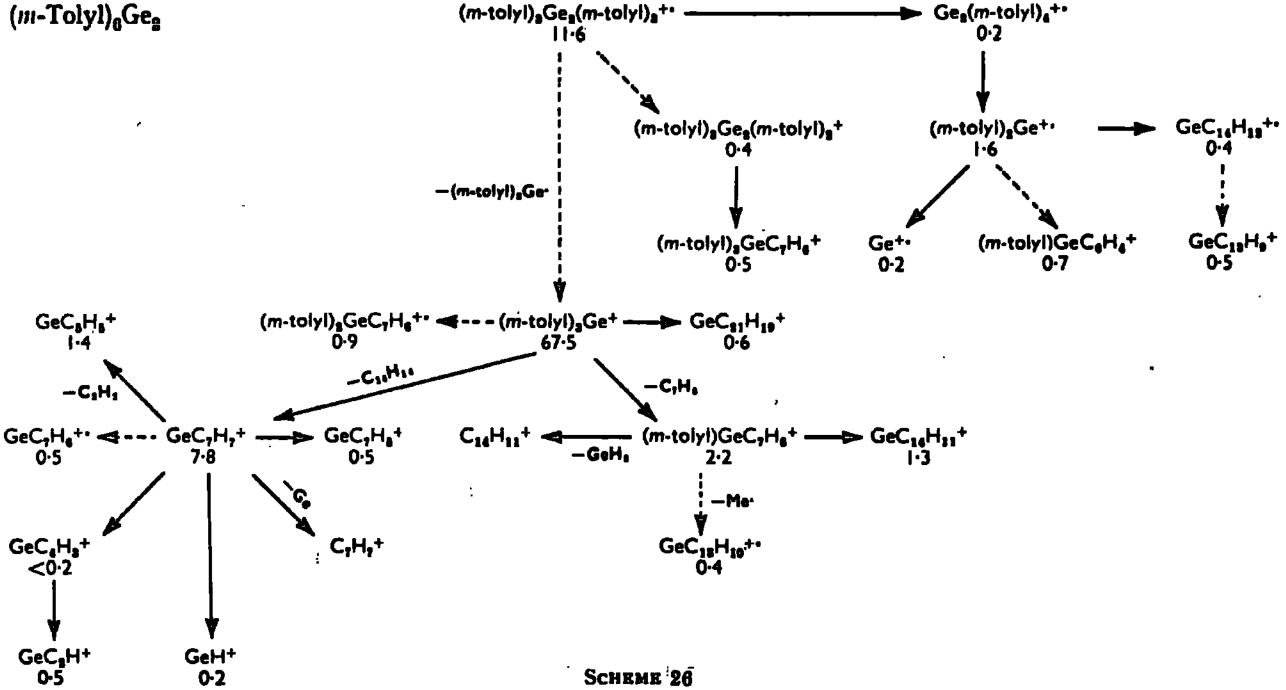
SCHEME 24

Ph_6Ge_2

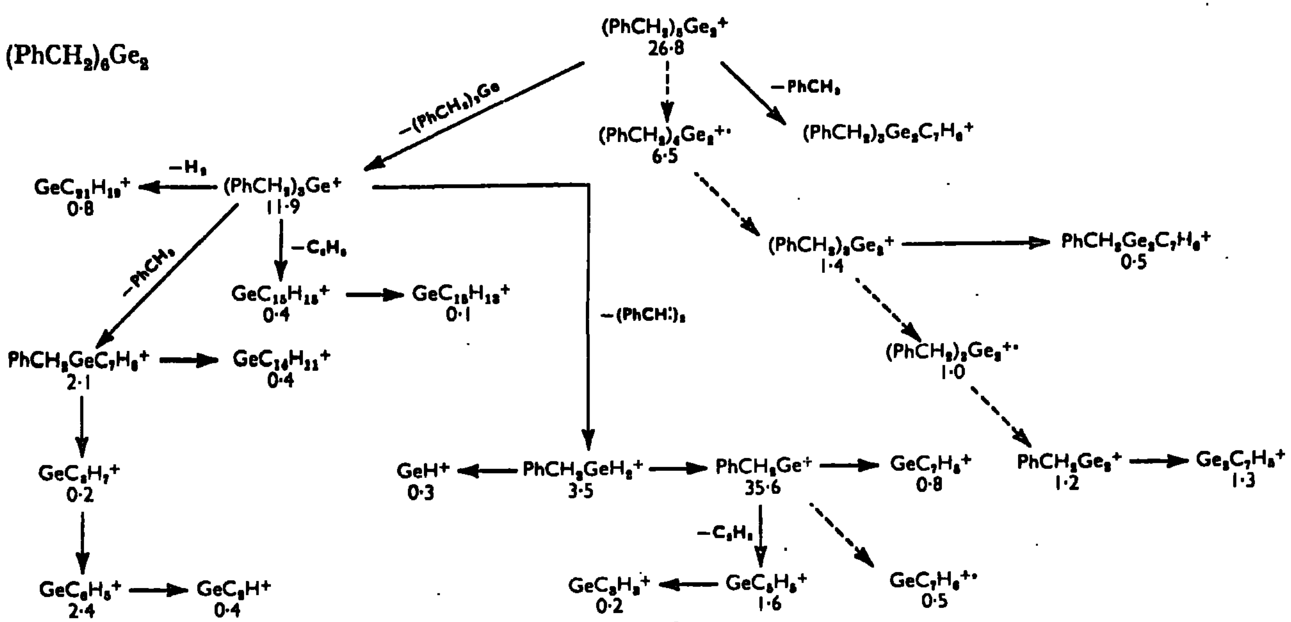


Scheme 25

$(m\text{-Tolyl})_6Ge_2$



Scheme 26



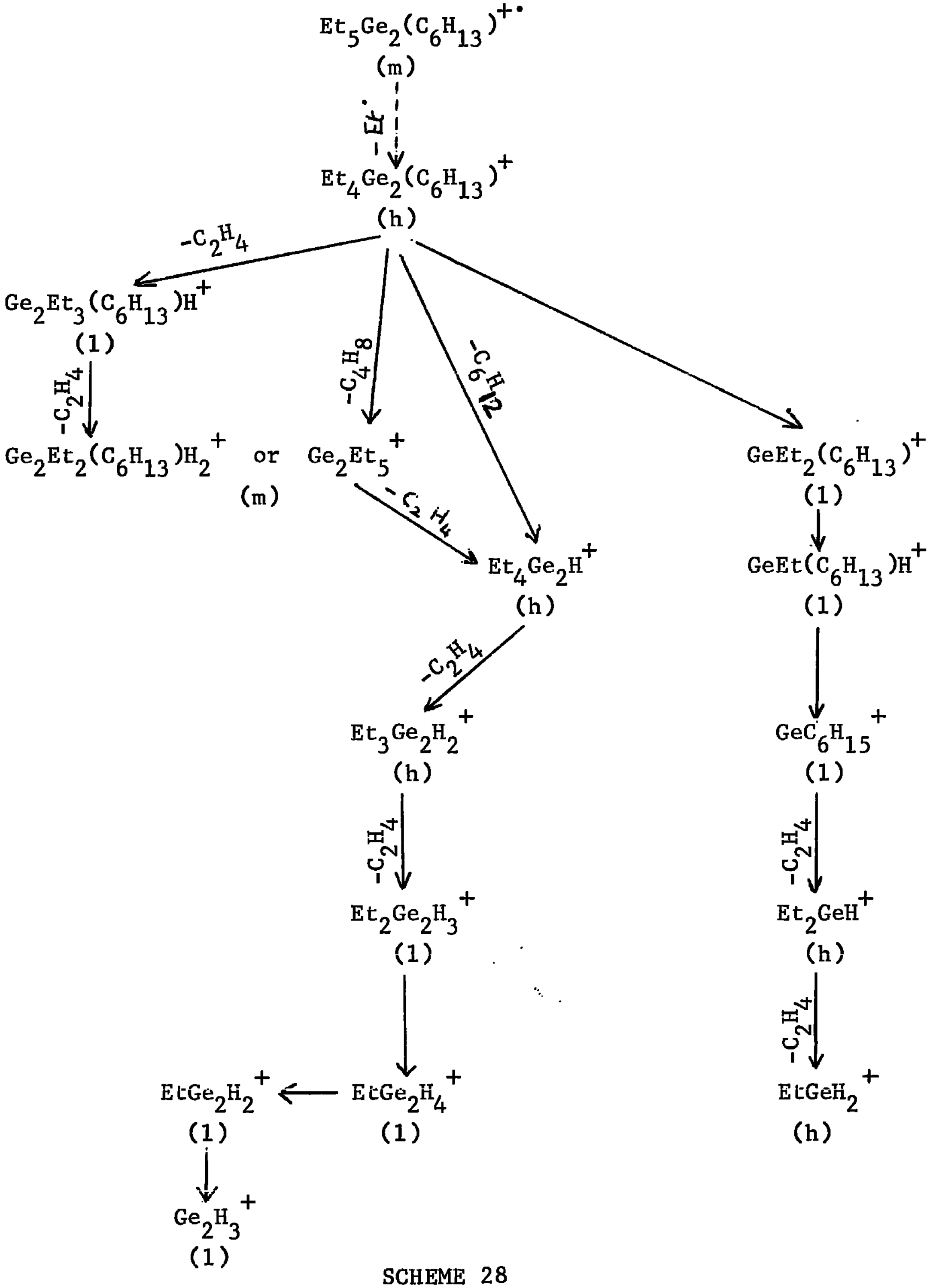
SCHEME 27

$Et_5Ge_2C_6H_{13}$. (Scheme 28). This compound, isolated in the preparative work was identified solely by its mass spectrum. The most important diagnostic feature is the hexene elimination, which rules out any isomeric formulae of the type $Et_4Ge_2Bu_2$.

$Bu^i{}_5Ge_2I$. (Scheme 29). Unlike Ph_3GeI, this compound shows prominent iodine-containing ions. It is unusual in showing an alkene elimination from an odd electron ion, and it seems likely that the ion in question is formed by elimination of isobutyl iodide from the molecular ion.

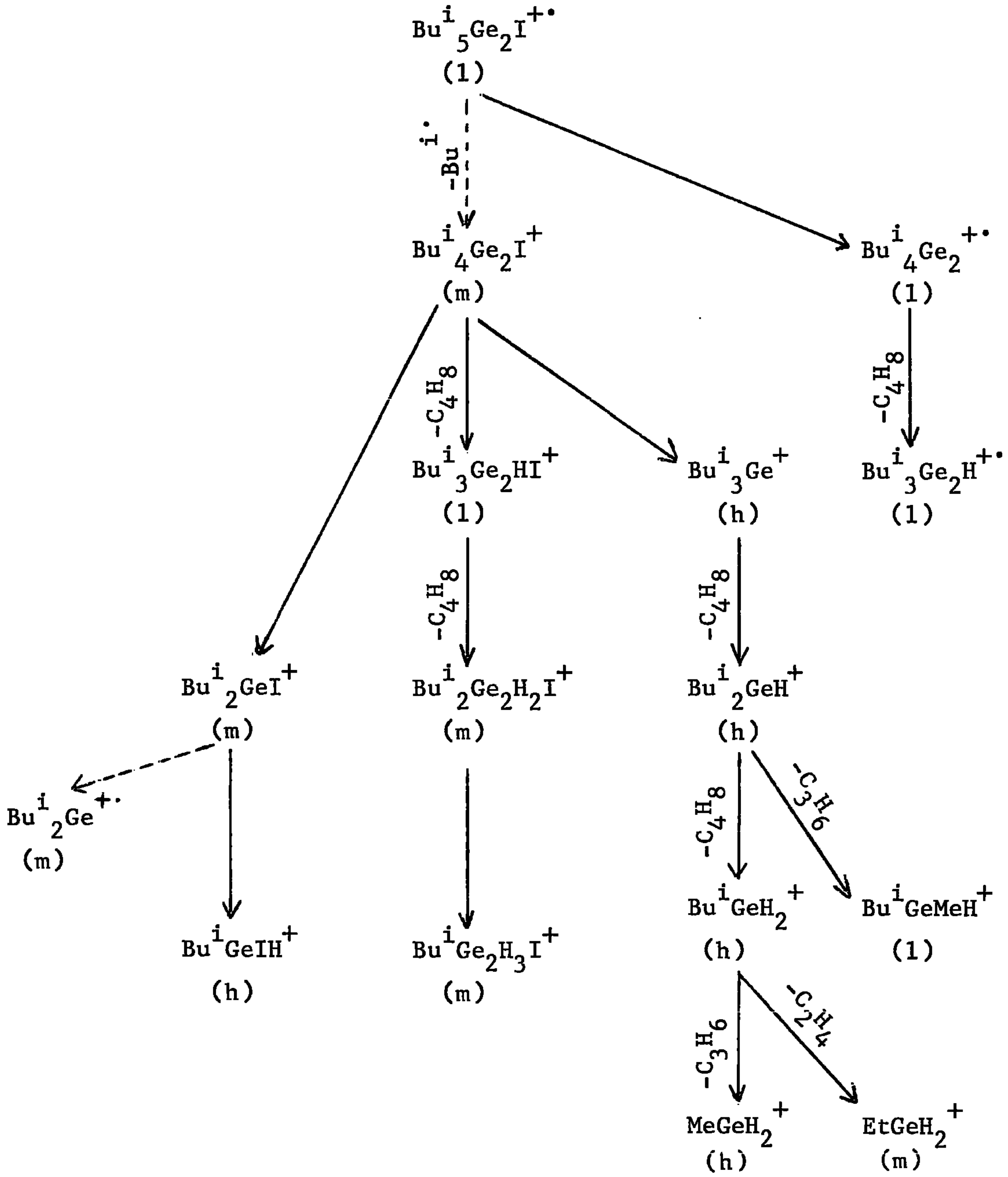
Me_5Ge_2Et and Me_5Ge_2Pr. The mass spectrum of $Ge_2C_7H_{20}$ showed it was definitely Me_5Ge_2Et since metastables for ethyl radical loss and ethylene elimination were observed (Tables 8 and 9). No metastables were observed in the spectrum of $Ge_2C_8H_{22}$, but the fragmentation pattern suggested the propyl compound.

$Et_5Ge_2C_6H_{13}$



SCHEME 28

$Bu^i{}_5Ge_2I$



SCHEME 29

Polygermanes. All the organogermanes with more than two germanium atoms resulted from the preparative work and were very largely characterised by their mass spectra.

From the compounds studied, it was obvious that the difference in fragmentation behaviour between hexamethyl- and hexaethyl-digermanes persists in the series $R_{2n+2}Ge_n$. In octaethyltrigermane, as in the digermane, loss of an ethyl radical from the molecular ion is followed by successive ethylene eliminations, and some H_2 loss, until Ge_3H^+ is reached. Some Ge-Ge bond cleavage must occur at an early stage since $Et_5Ge_2^+$ and fragments are present, but are minor ions. In contrast to this, methylpolygermanes lose a methyl radical, and then Me_2Ge units are eliminated, with some loss of further $Me^\bullet$ radicals as minor pathways. Eventually Me_3Ge^+ is reached, and this fragments in the normal way.

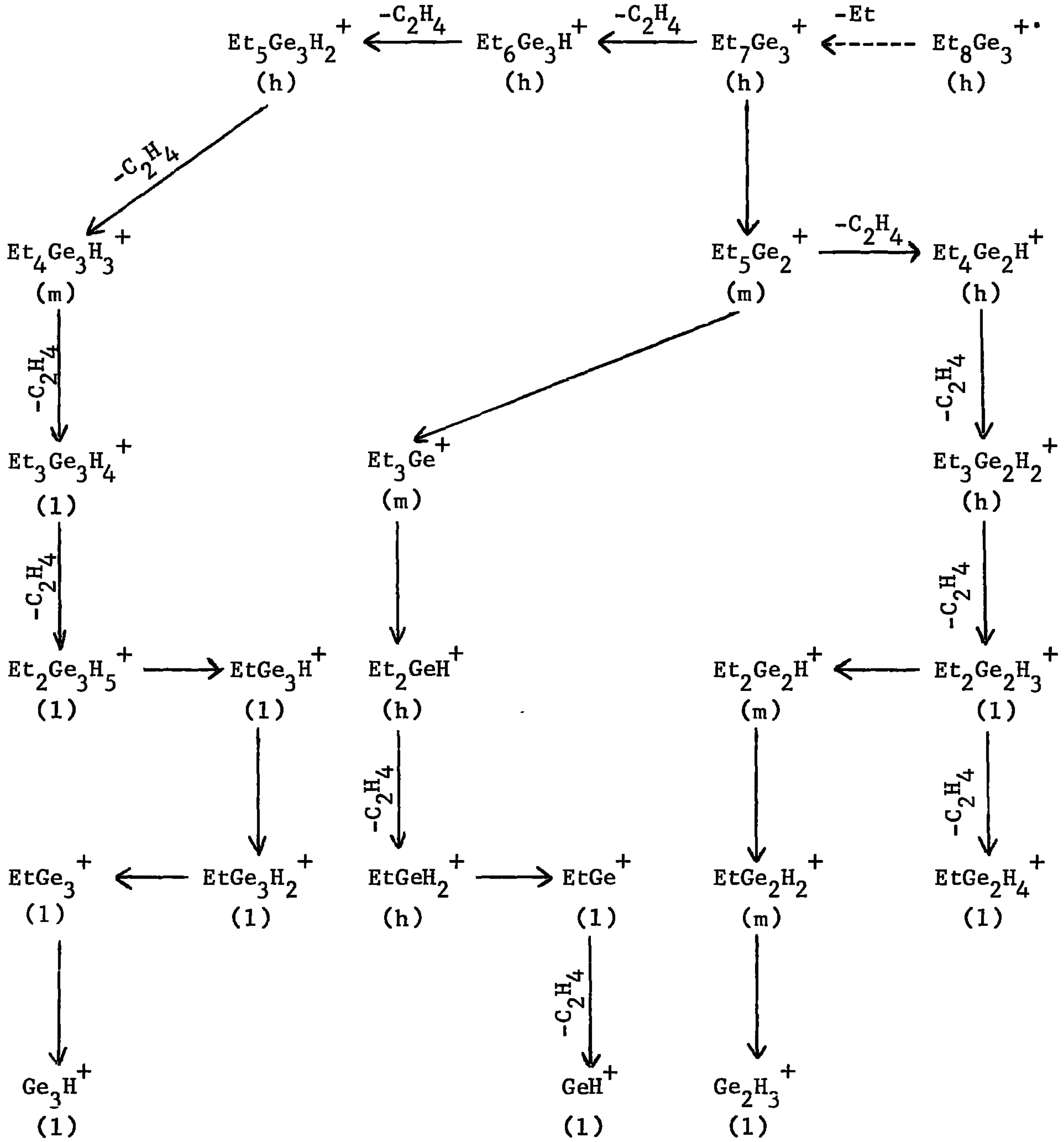
Me_8Ge_3. This is very similar to hexamethyldigermane and the higher methylpolygermanes. The molecular ion loses $Me^\bullet$, then Me_2Ge. Me_3Ge^+ was the most abundant ion.

Et_8Ge_3. (Scheme 30).

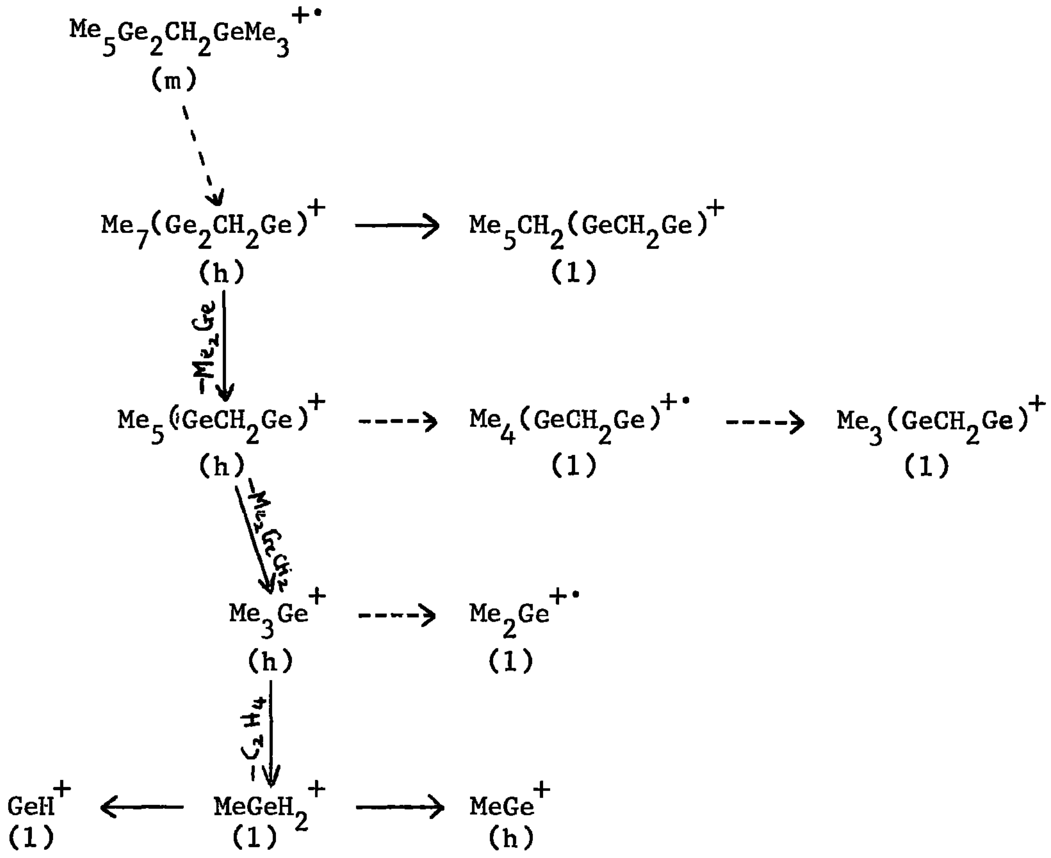
$Bu^i{}_8Ge_3$. This resembled $Bu^i{}_6Ge_2$ in the same way that Et_8Ge_3 resembled Et_6Ge_2.

$Me_5Ge_2CH_2GeMe_3$. (Scheme 31). Compounds, such as Me_9Ge_4Et, show ethyl radical elimination from the molecular ion, and at later stages, ethylene

Et_8Ge_3



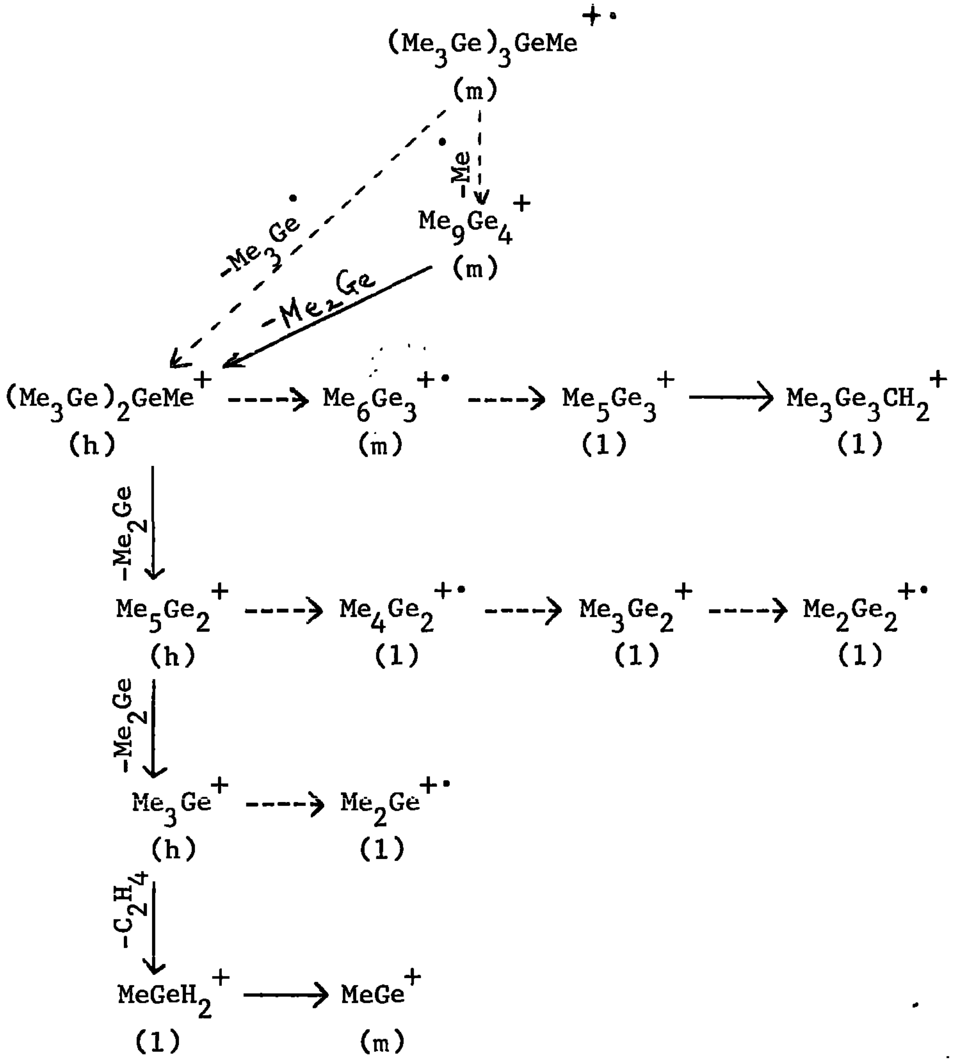
SCHEME 30



SCHEME 31

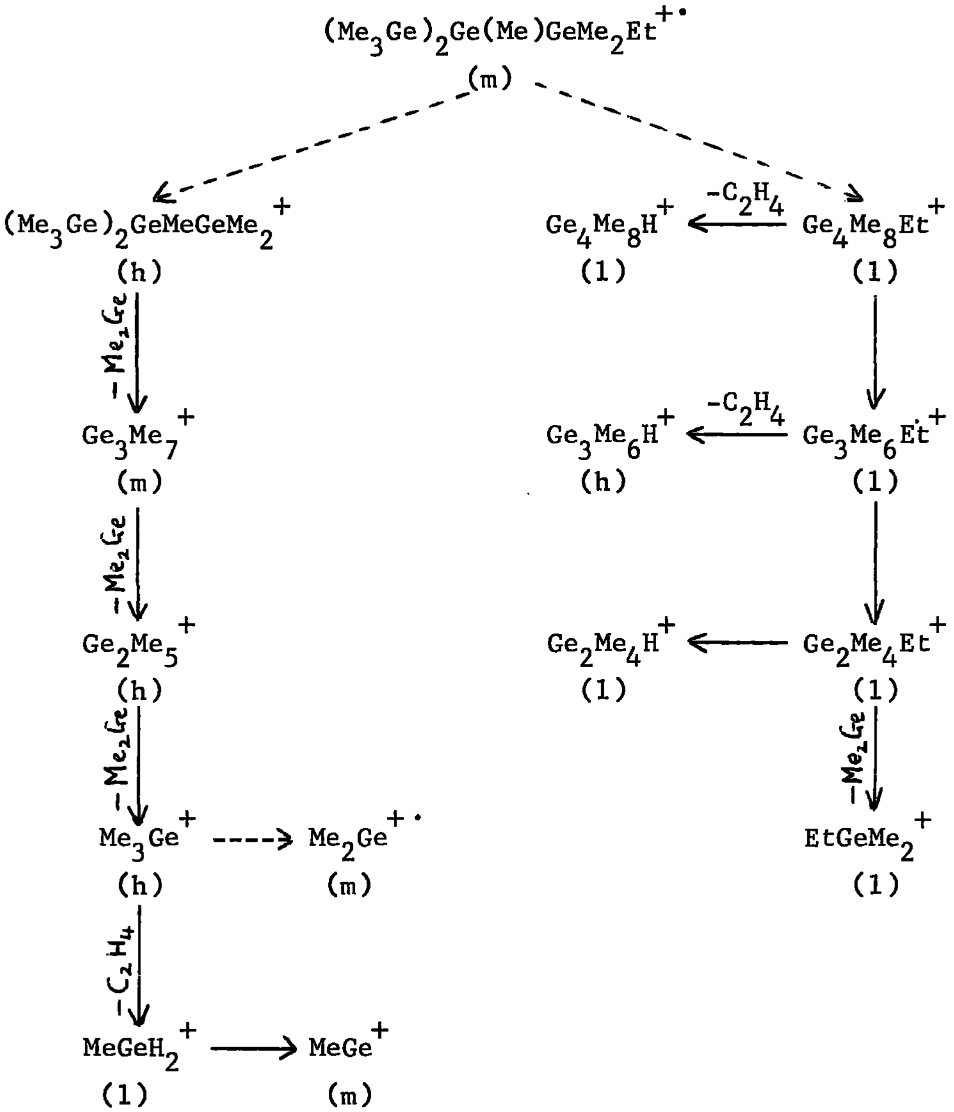
elimination. This compound showed neither, and so must have the structure shown. In addition, after initial methyl and Me_2Ge loss, loss of GeC_3H_8 occurred. Ordinary polymethyl compounds do not show elimination of this fragment, and elimination of EtGeMe has not been observed. Thus GeC_3H_8 is almost certainly Me_2GeCH_2 which is in accord with the proposed structure. (It was afterwards confirmed by its p.m.r. spectrum).

$(Me_3Ge)_3GeMe$. (Scheme 32). It was not possible to say from the mass spectrum alone whether the compound $Me_{10}Ge_4$ had the linear or branched structure. Since it has the formula shown it is obvious that at some stage rearrangement must occur for continued Me_2Ge elimination to be possible, and this is so for many of the compounds discussed subsequently.



SCHEME 32

<u>$(Me_3Ge)_2GeMeGeMe_2Et$</u>. (Scheme 33). The mass spectrum clearly demonstrates that this is Me_9EtGe_4 but it does not reveal the position of the ethyl group nor the configuration of the germanium skeleton.

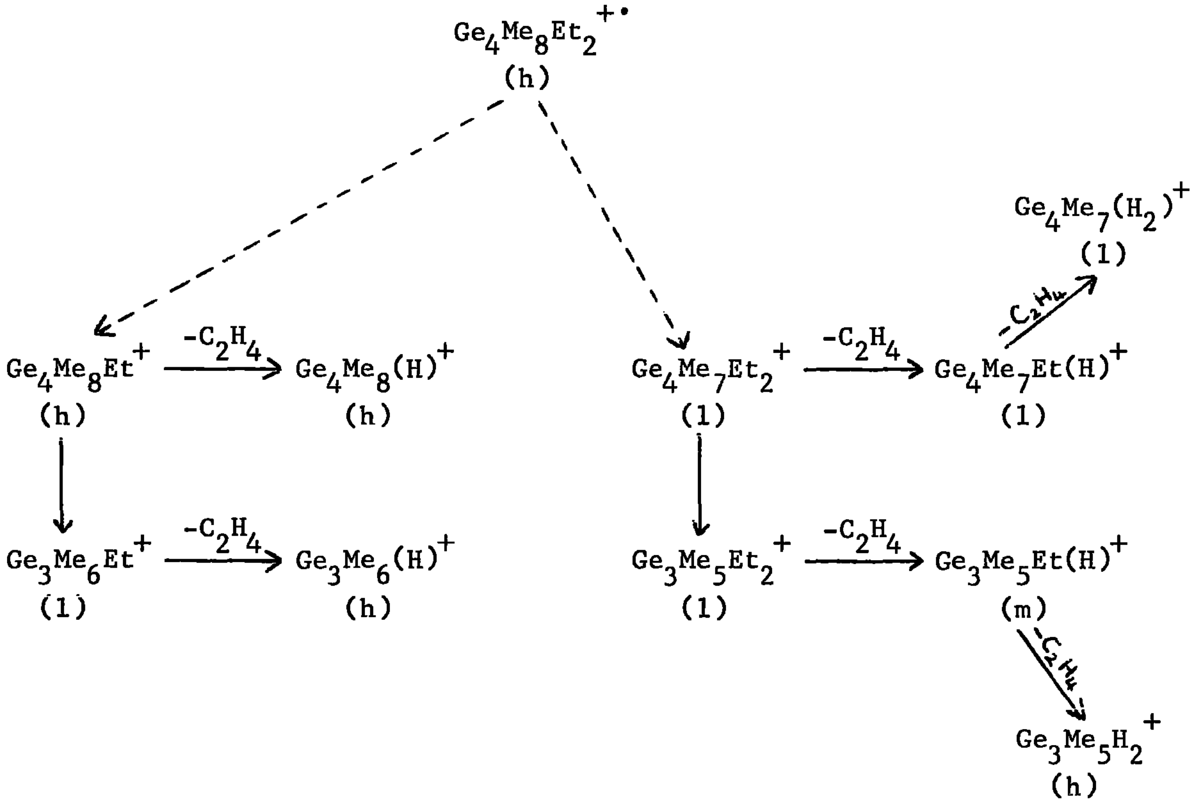


SCHEME 33

Me$_{10}$Ge$_4$CH$_2$. This compound showed no ethylene elimination. The molecular ion lost Me$^•$, and then a Ge-Ge bond was broken. Thus it is not an ethyl compound but contains a Ge-CH$_2$-Ge unit.

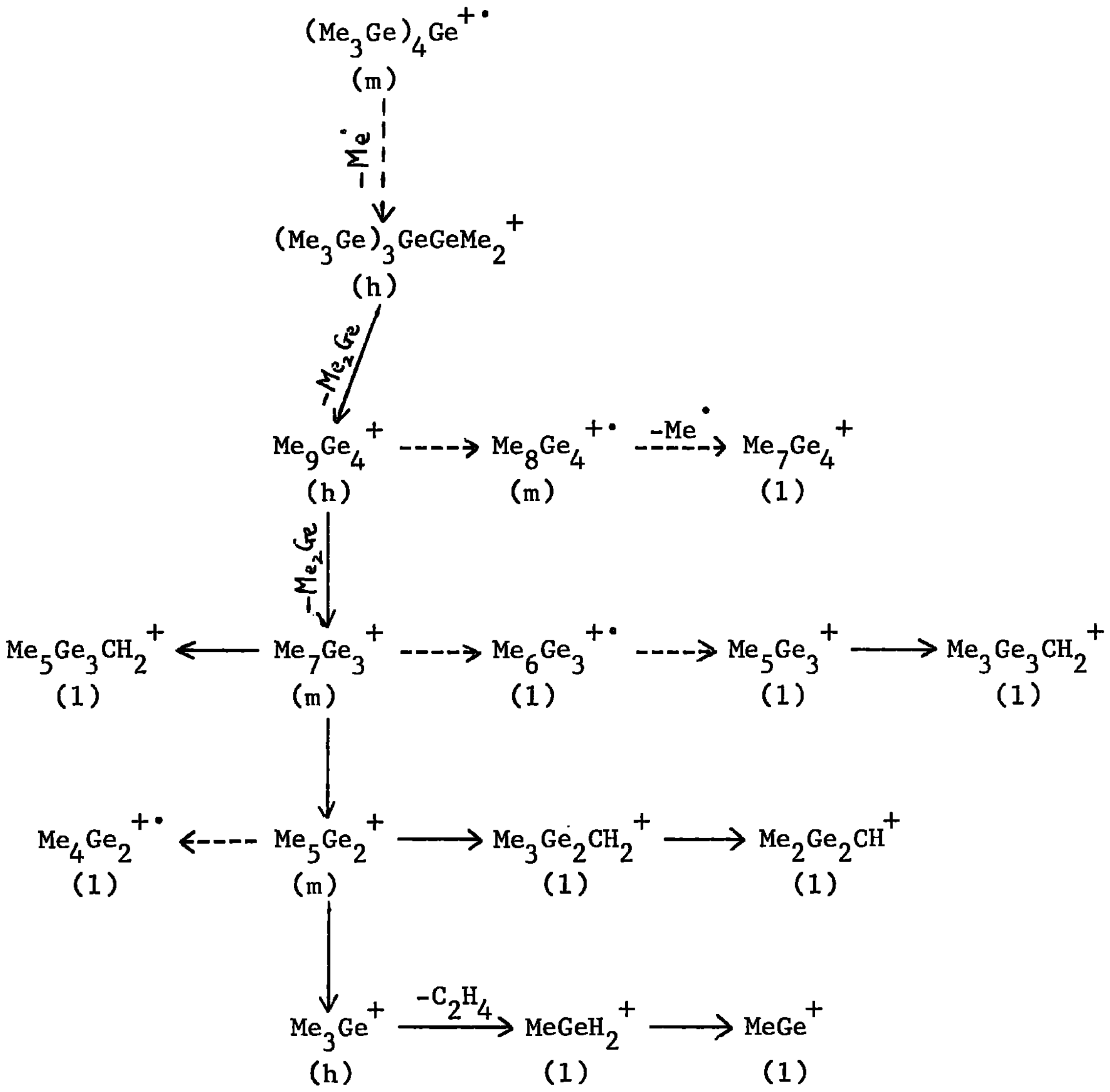
Me$_9$PrGe$_4$. The fragmentation pattern, which includes metastables for initial loss of a propyl radical and propene elimination at later stages, clearly demonstrates that this is a propyl compound, not a compound containing two ethyl groups.

Me$_8$Et$_2$Ge$_4$. (Scheme 34). The fragmentation of this compound, showing numerous ethylene eliminations, is quite different from that of the preceeding compound. (Only the initial fragmentations are shown in the scheme, as these are the most relevant).



SCHEME 34

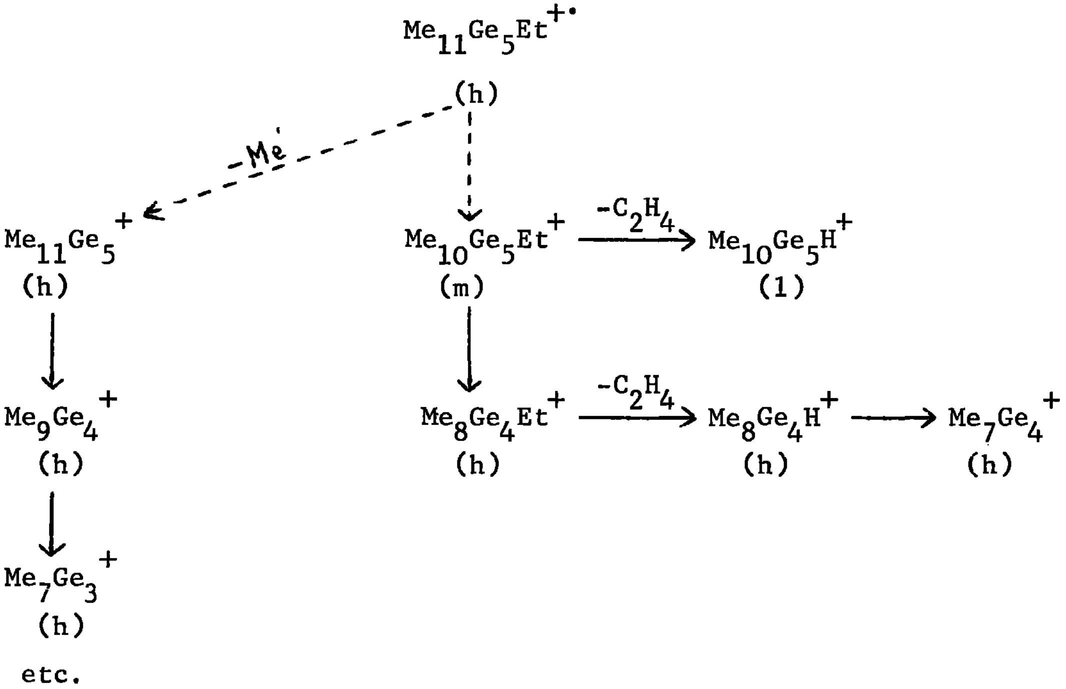
$(Me_3Ge)_4Ge$. (Scheme 35). Once again considerable rearrangement must occur at some stage to permit the continued elimination of Me_2Ge fragments.



SCHEME 35

$(Me_3Ge)_2GeMeGe_2Me_5$. This had approximately the same fragmentation pattern as the symmetrical isomer, but the molecular ion was more abundant than the first fragment ion ($Me_{11}Ge_5^+$). $Me_9Ge_4^+$ was the only significant Ge_4 ion. The spectra of mixtures of other isomers were similar, definitely $Me_{12}Ge_5$ compounds, but no indication of structure apart from this.

$(Me_3Ge)_2Ge(Et)Ge_2Me_5$. (Scheme 36). Only the initial fragmentation is shown, since this is sufficient to demonstrate that the compound is $Me_{11}EtGe_5$.



SCHEME 36

Higher Methylgermanium Oligomers. Although the presence of $Me_{14}Ge_6$, $Me_{16}Ge_7$, $Me_{18}Ge_8$, $Me_{20}Ge_9$ and $Me_{22}Ge_{10}$ was detected in mixtures with the aid of mass spectrometry, no pure isomers were isolated, so it would be inappropriate to discuss their fragmentation in detail. In general, they resembled the lower homologues. With such high molecular weights, spectra tend to "tail-off" and no conclusions were reached about abundances in these compounds. Some interesting features are worth mentioning. The presence of a metastable peak due to

$$Me_{13}Ge_6^{+} \longrightarrow Me_{11}Ge_5^{+} + Me_2Ge$$

and subsequent Me_2Ge eliminations in the spectrum of a mixture of $Me_{16}Ge_7$ isomers indicates that this mode of fragmentation continues to predominate. In $(Me_3Ge)_6Ge_2$ the most abundant ions towards the high mass end of the spectrum are $Me_{18}Ge_8^{+\bullet}$, $Me_{17}Ge_8^{+}$, $Me_{15}Ge_7^{+}$ and $Me_{13}Ge_6^{+}$. Rearrangement must occur at some stage to produce $Me_{13}Ge_6^{+}$.

Germoxanes. In all of the compounds studied, molecular ions are absent or of very low abundance, and loss of R' gives the most abundant ion in the spectrum. Subsequent fragmentation differs markedly for each compound, depending on the nature of the organic groups present. Doubly charged ions are prevalent, presumably because the electronegative oxygen helps to delocalise the extra positive charge.

Methylgermoxanes. Hexamethyldigermoxane shows a number of unusual transitions. Me_2GeO is eliminated as a neutral fragment. Elimination of H_2O from $Me_5Ge_2O^{+}$ leads to an ion which could be a digermane such as

$$\mathrm{Me_3GeOGeMe_3}^{+} \longrightarrow \mathrm{Me_3Ge}^{+} + \mathrm{Me_2GeO}$$

$\mathrm{Me_2(CH)Ge.GeMe_2}^{+}$ or $\mathrm{Me_3Ge.Ge(CH_2)_2}^{+}$, or an ion of the type $\mathrm{Me_2GeCHGeMe_2}^{+}$, but its subsequent decomposition suggests that the methylene structure is most likely. The doubly charged ions $\mathrm{C_4H_{11}Ge_2O}^{2+\bullet}$ and $\mathrm{C_2H_6Ge_2O}^{2+}$

$$\mathrm{Me_5Ge_2O}^{+} \xrightarrow{-\mathrm{H_2O}} \mathrm{Ge_2C_5H_{13}}^{+} \xrightarrow{-\mathrm{C_2H_4}} \mathrm{Me_3Ge_2}^{+}$$

were observed.

No molecular ions were observed for the cyclic oxides $\mathrm{(Me_2GeO)_n}$, $(n = 3,4)$ and this, together with the fact that $\mathrm{Me_2GeO}$ elimination occurs as in the digermoxane:

$$\mathrm{Me_7Ge_4O_4}^{+} \longrightarrow \mathrm{Me_5Ge_3O_3}^{+} + \mathrm{Me_2GeO}$$

leads to uncertainty as to whether the tetramer was ever obtained free from the trimer. In the spectrum of the tetramer, a very intense metastable with its maximum at about $m/e = 430$ corresponds to loss of either $\mathrm{Me}^{\bullet}$ or $\mathrm{CH_4}$ from $\mathrm{Me_7Ge_4O_4}^{+}$. $\mathrm{Me_5Ge_3O_3}^{+}$ probably eliminates $\mathrm{CH_4}$ $(m/e = 310)$.

Hexaethyldigermoxane. Loss of $\mathrm{Et}^{\bullet}$ gives the most abundant ion in the spectrum, $\mathrm{Et_5Ge_2O}^{+}$ and this like other even-electron ethyl-containing ions eliminates ethylene stepwise giving a series of particularly well defined metastables. Two monogermane ions are of especial interest, $\mathrm{C_4H_{11}GeO}^{+}$ and $\mathrm{C_2H_7GeO}^{+}$ since, if they both have three co-ordinate germanium, they may be formed as shown:

$$Et_2GeOGe(H)Et_2^+ \longrightarrow Et_2GeOH^+ + Et_2Ge$$

$$Et_2GeOH^+ \longrightarrow EtGe(H)OH^+ + C_2H_4$$

Two doubly charged ions have one hydrogen less than the corresponding singly charged ions, and a metastable transition indicates the formation of one from the other.

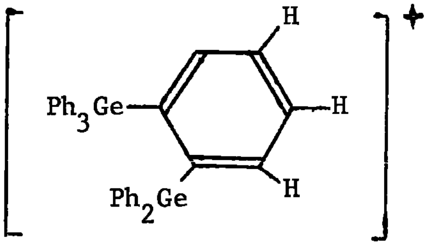
$$Et_4Ge_2O^{2+} \longrightarrow Et_3Ge_2(H)O^{2+} + C_2H_4$$

It may be that the first ion is formed by:

$$Et_5Ge_2O^+ \longrightarrow Et_4Ge_2O^{2+} + Et^-$$

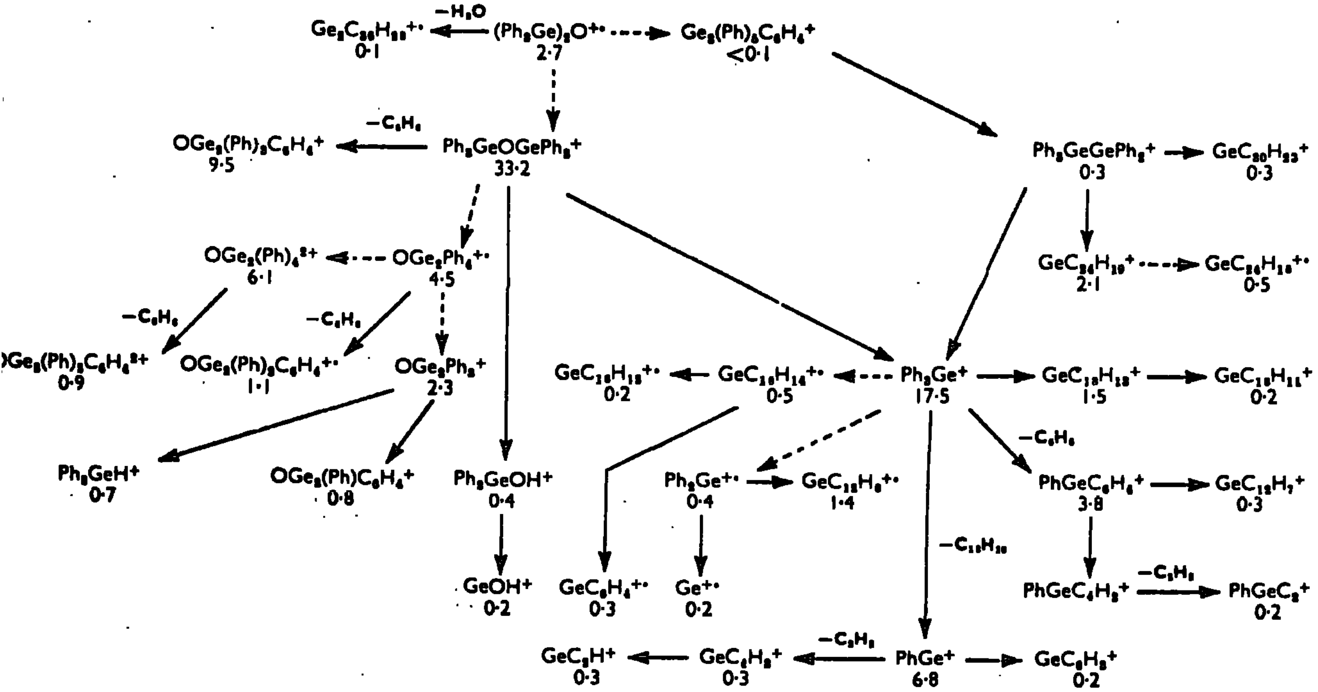
since $Et_4Ge_2O^+$ is absent from the spectrum.

Hexaphenyldigermoxane. (Scheme 37). An important decomposition mode for this compound is benzene elimination, and in one case this gives rise to a metastable confirmed decomposition of a doubly charged ion. The molecular ion loses H_2O, and the resultant ion may have a Ge-Ge bond or a structure of the type



If elimination of Ph_2GeO occurs it could not be observed, since the metastable peak would coincide with that due to the transition $Ph_3Ge^+ \longrightarrow PhGeC_6H_4^+ + C_6H_6$ ($m^* = 168{\cdot}9$) which is prominent in all triphenylgermyl compounds.

$(Ph_3Ge)_2O$



SCHEME 37

$\underline{(PhCH_2)_6Ge_2O}$. As with $(PhCH_2)_6Ge_2$, the molecular ion was not visible. Fragmentation followed normal paths except for the unusual elimination of GeO.

$$(PhCH_2)_3Ge_2O^+ \longrightarrow (PhCH_2)_3Ge^+ + GeO$$

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