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SOME ORGANIC DERIVATIVES OF LEAD AND GERMANIUM.

by

Keith A.Hooton, B.Sc.

A Thesis

Submitted for the Degree of Doctor of Philosophy

in the University of Durham.

August 1963.

The work described in this thesis was carried

out in the Durham Colleges in the University

of Durham between September 1960 and August

1963. 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:

"Mesityl and Phenyl Derivatives of Lead."

J.Chem.Soc., 4405,(1961),with F.Glockling and D.Kingston.

"Triphenylgermyl Complexes of Copper, Silver and Gold."

J.Chem.Soc., 2658,(1962), with F.Glockling.

"Hexa-aryldigermanes."

J.Chem.Soc., 3509,(1962), with F.Glockling.

"Organogermanium Polymers."

J.Chem.Soc., 1849,(1963), with F.Glockling.

"Organogermanium-Phosphorus Compounds."

Proc. Chem. Soc., 146,(1963), with F.Glockling.

ABSTRACT of thesis submitted by K.A.HOOTON of University

College, Durham, for the degree of Doctor of Philosophy, entitled:

"Some Organic Derivatives of Lead and Germanium."   JULY 1963.

This thesis describes a study into the reactions of organic and

inorganic halides of germanium and lead with organo-lithium and Grignard

reagents, and also an investigation into the formation of compounds

containing germanium σ bonded to transition metals. Such compounds had not

previously been described.

Triphenylgermyl-triphenylphosphinegold(1), $Ph_3Ge-AuPPh_3$, and similar

copper and silver compounds were prepared by reacting triphenylgermyl-lithium

with the corresponding tertiary phosphine – metal halide complex.

1,2-Dibromoethane cleaved the metal – metal bond to give ethylene,

bromotriphenylgermane and the corresponding metal halide – phosphine complex;

and phenyl-lithium gave the unstable salt, lithium bis(triphenylgermyl)aurate(1)

etherate, $Li^+\left[(Ph_3Ge)_2Au\right]^-.4Et_2O$, which was converted into the more stable

tetraethylammonium salt.

Germanium(11)iodide reacted with phenyl-lithium to give, not

diphenylgermanium(11), but yellow to red polymeric materials, intermediate in

composition between PhGe and Ph_2Ge, containing Ph_3Ge, Ph_2Ge, PhGe and Ge

groupings. A reaction path involving "metal – halogen" exchange reactions

is put forward. Tetraphenylgermane and triphenylgermane were also isolated

from these reactions. Triphenylgermyl-lithium reacted with germanium(11)iodide

to give the lithium salt, lithium tris(triphenylgermyl)germane.

In contrast, lead(11)bromide reacted with mesitylmagnesium bromide to

give solutions involving the equilibrium:

$$Ms_2Pb + MsMgBr \rightleftharpoons Ms_3PbMgBr, \qquad Ms = 1,3,5 - (CH_3)_3C_6H_2.$$

This equilibrium could be displaced by carbonation, as shown by bromination studies.

The formation of digermanes, (R_6Ge_2), from the interaction of germanium(IV)chloride with Grignard reagents has been suggested to involve germanium(II)chloride as intermediate. In this work, however, the formation of digermanes has been shown to involve the germyl-Grignard reagent, R_3GeMgX. This may be formed predominantly by the reaction between the halide R_3GeX and the magnesium metal remaining from the Grignard preparation, though in cases of sterically hindered Grignard reagents the exchange reaction

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

can occur.

The reactions of lithium diphenylphosphide with germanium(IV)chloride and organogermanium halides, $(R_nGeX_{4-n}, n = 1,2,3)$, and properties of the germanium - phosphorus bond in the resulting compounds are also described.

CONTENTS

SUMMARY

PART A. Triphenylgermyl Complexes of Copper, Silver, and Gold.

A novel type of compound has been prepared by the reaction of triphenylgermyl-lithium, Ph_3GeLi, with the tertiary phosphine complexes of $Cu(1)Cl$, $Ag(1)I$, and $Au(1)Cl$ in 1,2-dimethoxyethane. These compounds, $(R_3P)_nM-GePh_3$, where M = the transition metal, contain a metal-metal σ bond. The copper and silver compounds were unstable, and pure compounds could be obtained only when triphenylphosphine was the ligand and when n = 3; decomposition was rapid on exposure to the atmosphere. The gold compound, $Ph_3PAuGePh_3$, was, in contrast, stable to air and water, and considerably more so than the monomeric trimethylphosphine complex.

The Ge-M bond in these complexes was readily cleaved by 1,2-dibromoethane to give bromotriphenylgermane, ethylene and the corresponding tertiary phosphine-metal bromide complex.

Phenyl-lithium cleaved the Au-Ge bond in $Ph_3PAuGePh_3$ to give triphenylphosphinomonophenylgold(1) and the very unstable salt, lithium-bis(triphenylgermyl)aurate(1) etherate, $Li^+ \left[(GePh_3)_2Au \right]^-$. $4Et_2O$, which, on reaction with tetraethylammonium iodide, gave the corresponding unsolvated salt $Et_4N^+ \left[(GePh_3)_2Au \right]^-$.

PART B. <u>Hexa-aryldigermanes</u>.

Hexa-aryldigermanes, $Ar_3Ge-GeAr_3$, formed in the reaction between aryl-Grignard reagents and germanium(lV)chloride, are considered to be produced by a coupling reaction between the halide, R_3GeX, and the "germyl-Grignard reagent", R_3GeMgX. The latter reagent is formed essentially by reaction of the free magnesium which remains unreacted after the preparation of the normal Grignard reagent, RMgX, with R_3GeX. However, in cases involving a sterically hindered R group, such as <u>o</u>- or <u>m</u>-tolyl, it can be produced by the exchange reaction:

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

The presence of "germyl-Grignard reagents" in such reactions was shown by the isolation of the corresponding hydrides, R_3GeH, after hydrolysis, and the acid $R_3GeCOOH$ after carbonation with subsequent hydrolysis.

Thus the reaction between phenyl- or <u>p</u>-tolyl-magnesium bromide and germanium(lV)chloride, in the absence of free magnesium, afforded only the tetrasubstituted monogermane, R_4Ge; the digermane, R_6Ge_2, was the principle product in the presence of free magnesium.

<u>m</u>-Tolylmagnesium bromide behaved in a similar way, but gave, in the absence of magnesium, some 6% of $(\underline{m}\text{-tolyl})_6Ge_2$. <u>o</u>-Tolylmagnesium bromide gave only the digermane, both in the presence, and in the absence of free magnesium.

The formation of hexa-aryldisilanes was found to proceed in an analogous manner.

PART C. Phenylgermanium Polymers.

The reaction between a 2:1 molar ratio of phenyl-lithium and germanium(11)iodide in ether gave, after prolonged refluxing, not di-phenylgermanium(11) as expected, but yellow to red polymeric materials (M = 800-1500), intermediate in composition between diphenylgermanium(11) and phenylgermanium (PhGe). Some tetraphenylgermane was also isolated.

Hydrolysis of the reaction mixtures involving excess phenyl-lithium led to the isolation of similar products together with triphenylgermane (Ph_3GeH).

The yellow to red polymers were oxygen and halogen free, stable to high temperatures (360°), and to hydrolysis, though varied in their reactivity towards oxygen.

The reaction of the yellow polymer with bromine under mild conditions, followed by treatment of the mixed bromides with ethylmagnesium bromide, and isolation of the products suggested the presence of Ph_3Ge, Ph_2Ge, PhGe, and Ge groups in the polymer.

To account for the products containing all degrees of phenylation, the reaction is considered to involve "metal-halogen" exchange reactions of the type:

$$PhGeI + PhLi \longrightarrow PhGeLi + PhI.$$

Tetraphenylgermane is produced by the interaction of iodobenzene and triphenylgermyl-lithium:
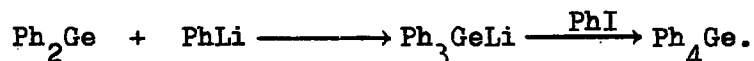
$$Ph_2Ge + PhLi \longrightarrow Ph_3GeLi \xrightarrow{PhI} Ph_4Ge.$$

Triphenylgermyl-lithium reacted with germanium(11)iodide in 1,2-dimethoxyethane to give, after hydrolysis, tris(triphenylgermyl)germane,

$(Ph_3Ge)_3GeH$, which was readily metalated by $\underline{n}$-butyl-lithium to give the lithium salt $(Ph_3Ge)_3GeLi$.

PART E. <u>Organo-Germylphosphines</u>.

Although compounds are known in which germanium is bonded both to carbon and to nitrogen, the analogous phosphorus compounds had not previously been prepared, though Et_3SnPPh_2 (158) and $Si(PEt_2)_4$ (166) are known. This work was undertaken with the aim of preparing such compounds. Triethylgermyldiphenylphosphine, Et_3GePPh_2, was prepared by the inter-action of bromotriethylgermane and lithium diphenylphosphide in tetrahydrofuran, and the reactivity of the germanium – phosphorus bond towards various reagents was studied. Probably of greatest interest was the oxidation with dry oxygen to the ester triethylgermyldiphenyl-phosphonate, $Et_3Ge-O-P(O)Ph_2$.

The reaction of the series of halides Ph_nGeX_{4-n}, n = 0,1,2,3, X = Cl, Br, with lithium diphenylphosphide was carried out in an attempt to prepare the analogous diphenylphosphino derivatives. Although this was not in itself completely successful, a most interesting trend in the mode of reaction was observed. While bromotriphenylgermane gave the expected triphenylgermyldiphenylphosphine, Ph_3GePPh_2, a well crystalline solid, germanium(1V)chloride gave, not <u>tetrakis</u>(diphenylphosphino)germane, but a red amorphous polymer of approximate composition $(Ph_2PGe)_n$, n = 3, together with tetraphenyldiphosphine. A similar polymer, of approximate composition $(PhGePPh_2)_n$, n = 2, was obtained together with tetraphenyl-diphosphine from tribromophenylgermane. Dibromodiphenylgermane was somewhat intermediate in behaviour, giving <u>bis</u>(diphenylphosphino)diphenyl-germane, $(Ph_2P)_2GePh_2$, as the main product but some tetraphenyldiphosphine was also isolated. Possible mechanisms for these reactions are discussed.

PART E. <u>Dimesityl-lead(11)</u>.

The reaction between mesitylmagnesium bromide and lead(11)bromide in tetrahydrofuran at $-30°$ was studied with the primary aim of isolating dimesityl-lead(11). Evidence was obtained which suggested that the reaction involved the final equilibrium stage (2), similar to that previously postulated for reactions involving phenyl-lithium or phenylmagnesium bromide and lead(11)halides.

$$PbBr_2 + 2MsMgBr \longrightarrow Ms_2Pb + 2MgBr_2 \quad \ldots\ldots(1)$$

$$Ms_2Pb + MsMgBr \rightleftharpoons Ms_3PbMgBr \quad \ldots\ldots\ldots(2)$$

$$Ms = 1,3,5-(CH_3)_3C_6H_2.$$
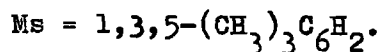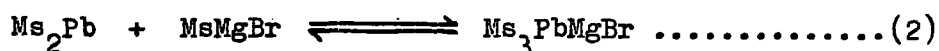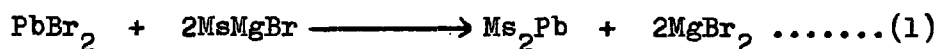
The equilibrium could be displaced in favour of dimesityl-lead(11) by reaction with carbon dioxide, which caused an intensification of the red colour. Bromination of these carbonated solutions led to the isolation of dimesityl-lead dibromide, whilst bromination without carbonation gave trimesityl-lead bromide.

Attempts to isolate pure dimesityl-lead from the carbonated reaction mixtures were unsuccessful due to the presence of inorganic salt etherates and the ease of hydrolysis of lead-carbon bonds.

INTRODUCTION

This introduction is concerned with a general review of organo-germanium chemistry, together with a more detailed account of aspects particularly relevant to the work carried out by the author in preparation for this thesis.

A. General Characteristics of the Group 1Vb Elements.

All the elements of Group 1Vb form a large number of organic derivatives. Compounds of the type R_4M, (R = alkyl or aryl, M = Ge, Sn, or Pb), differ from the fully alkylated or arylated derivatives of elements in the adjacent groups in their relatively low chemical reactivity. For example, tetramethylstannane is stable on exposure to the atmosphere whereas both trimethylindium and trimethylstibine inflame in the air. The high reactivity of Group 111 organic compounds may be attributed mainly to their vacant orbital and electron deficient character. The high reactivity of the trivalent organic compounds of Group V elements is due to their unsaturated character, and to the presence of a "lone pair" of electrons. The alkyls and aryls of Group 1Vb elements behave as saturated compounds, and the elements show no tendency to expand their co-valency above four, unless they are bonded to strongly electro-negative atoms or groups, e.g. $(NH_4)_2SnCl_6$.

As regards the stability of compounds of the type R_4M, (R = alkyl, aryl; M = Ge, Sn, Pb), there is a decrease in the thermal and chemical stability as the atomic weight of the central metal atom increases. For example, both Et_4C and Et_4Si undergo atomic chlorination with the retention of the "metal"-carbon bonds. Tetraethylgermane is easily broken down to Et_3GeCl, Et_4Sn reacts rapidly and care is required to

stop the reaction after the first substitution. Tetraethyl-lead is
broken down completely under comparable conditions.

A unique feature of the organic compounds of the Group lVb elements
is the wide occurrence of metal-metal bonds; although these are present
in the metal itself there are comparatively few examples of its occurr-
ence in chemical compounds outside this group, noteworthy examples being
the mercurous ion and the carbonyl $Mn_2(CO)_{10}$. The stability of the
metal-metal bonds in the organic compounds of Group lVb elements in-
creases towards the top of the Group. There are also many examples of
compounds containing mixed metal-metal bonds, and a considerable amount
of work has been carried out on these compounds.

Despite the fact that inorganic compounds of the divalent metals
are well known and stable,there is but limited evidence for the charact-
erization of the analogous organic compounds, with the exception of
some tin compounds.

B. <u>Organic Chemistry of Germanium</u>.

The organic chemistry of germanium has been reviewed by Johnson(1) in
1951, who described some 230 compounds, and by Rijkens(2) in 1960, and
for aspects of the chemistry not described below, these reviews are
recommended. The time between these reviews saw a large increase in the
number of compounds described in the literature, however, these belonged
largely to known classes and were synthesised by known reactions. The
most interesting developments have been the work on the addition of part-
ially substituted monogermanes to olefinic and acetylenic systems,
including the preparation and reactions of organogermanes containing

unsaturated centres, together with the preparation and uses of alkali metal compounds.

(1) THE SIMPLE GERMANES. Ge_nH_{2n+2}.

Monogermane, GeH_4, was first prepared in small amounts and impure by Voegelen(3) in 1902. Paneth(4) prepared a pure sample by the action of mineral acid on a germanium-zinc or germanium-magnesium alloy. It was not until 1924 that monogermane was prepared in reasonable amounts, together with some di- and tri-germane (Ge_2H_6 and Ge_3H_8),by the treatment of magnesium germanide with acid(5). Recent methods for the preparation of monogermane include the reduction of germanium(lV)chloride with lithium aluminium hydride(6,7) or with sodium borohydride(8), the latter reagent being more efficient, giving yields of 80%.

The series of hydrides of germanium has been extended by Amberger(9), who prepared tetragermane (Ge_4H_{10}), and pentagermane (Ge_5H_{12}), along with the lower members, by the reaction between a magnesium-germanium alloy and 10% aqueous hydrochloric acid.

The higher germanes are less stable thermally compared to the lower members:

GeH_4, b.p =-90°, decomposes at 350°/760mm.

Ge_5H_{12}, b.p = 20°/10^{-5}mm.Hg, decomposes at 100°/760mm.

The products of thermal decomposition of the higher germanes are mainly monogermanes and germanoethylene $(GeH_2)_x$. Complete breakdown to the elements occurs above 350°.

Decomposition of monogermane by a silent electrical discharge has been studied under a variety of conditions by Drake and Jolly(10).

Among the products were _iso_-tetragermane, _neo_-pentagermane and _iso_-penta-germane, together with the normal germanes, the series being extended to nonogermane. Separation was effected by gas-liquid chromotography and identification by vapour pressure, I-R spectra, mass spectra and proton magnetic spectra measurements.

The hydride $(GeH_2)_x$ has been prepared by a variety of methods (11, 12, 13), for example:

$$CaGe + 2HCl \longrightarrow CaCl_2 + GeH_2 \longrightarrow (GeH_2)_x.$$
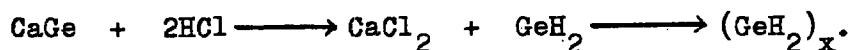
$(GeH_2)_x$ has a low volatility and low solubility and explodes in the air. Bromination with bromine in hydrogen chloride gives germanium(1V)bromide and hydrogen bromide. Hydrolysis proceeds according to the scheme:

$$(GeH_2)_x \xrightarrow{H_2O} (HGeOH)_x \underset{dil.KOH}{\overset{aq.HCl}{\longleftrightarrow}} (HGeCl)_x.$$
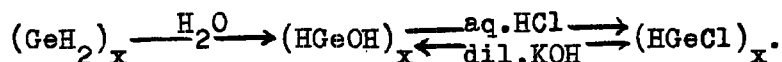
Heating with aqueous hydrochloric acid gives a mixture of higher hydrides and hydrogen, and prolonged heating with potassium hydroxide solution gives K_2GeO_2, hydrogen and monogermane.

A quantitative reaction for the preparation of germanoethylene was investigated by Glarum(14).

$$NaGeH_3 + PhBr \longrightarrow NaBr + PhH + (GeH_2)_x.$$
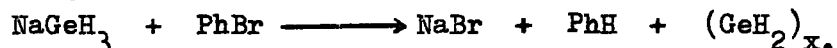
Germanoethylene is stable in liquid ammonia, though removal of the ammonia at -33° causes the decomposition to monogermane and germano-acetylene, GeH, the latter compound decomposes to the elements at 180°.

(2) THE SUBSTITUTED GERMANES.

a) The substituted monogermanes, R_4Ge.

The first compound of the type R_4Ge was prepared by Winkler(15) in 1887 by the reaction:

$$GeCl_4 + 2ZnEt_2 \longrightarrow 2ZnCl_2 + Et_4Ge.$$

This method is now obselete, though an adaptation has been used(16)
for the preparation of o-, m-, and p-tolylgermanes by reacting the appro-
priate Grignard reagent with zinc chloride, followed by the reaction with
germanium(1V)chloride. The standard reaction between a germanium(1V)
halide and a Grignard reagent has been extensively used for the synthesis
of both alkyl- and aryl-monogermanes in ether or ether/toluene solution
(17,18,19). The reaction proceeds via the intermediates $RGeX_3$, R_2GeX_2
and R_3GeX, and, in certain cases, in which the reaction is slow, the
conditions can be adjusted to give a principle yield of a given inter-
mediate. The use of alkyl- or aryl-lithium reagent often gives improved
yields over those obtained using the corresponding Grignard reagent(20).
It has been reported(21) that the addition of triphenylgermane in ether
to ethereal phenyl-lithium results in the formation of tetraphenylgermane,
whereas the addition of phenyl-lithium to triphenylgermane leads to the
formation of hexaphenyldigermane. This reaction has been studied further
by Gilman and co-workers(22), who also used alkyl-lithium reagents. In
most cases they reported a rapid reaction giving high yields of tri-
phenylgermyl-lithium. It was also reported that triphenylgermyl-lithium
reacts slowly with triphenylgermane to give hexaphenyldigermane.

Coupling reactions of the Würtz type have been used to prepare
both alkyl- and aryl- substituted monogermanes:

$$GeCl_4 + 4PhBr + 8Na \xrightarrow{\text{ether}} Ph_4Ge + 4NaCl + 4NaBr.$$
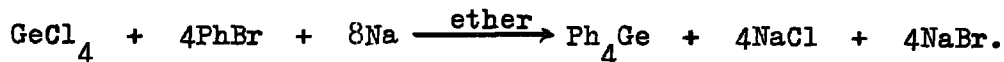
The reaction is vigourous and cannot be used to prepare the intermediate
aryl- or alkyl-halogermanes(19).

The preparation of tetraethylgermane has recently been described by the interaction of triethylaluminium and germanium(1V)chloride in the presence of sodium chloride,yields of 89% were reported(23).

The reaction between trialkyl- or triaryl-monogermanes and a compound containing an olefinic or acetylenic carbon-carbon bond can be used to prepare fully substituted organo-monogermanes. For example, Gilman prepared octadecyltriphenylgermane by the reaction:

$$Ph_3GeH \ + \ CH_2=CH(CH)_{15}CH_3 \longrightarrow CH_3(CH_2)_{17}Ph_3Ge.$$
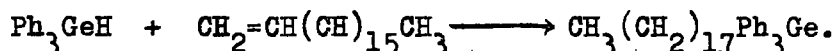
The reaction is catalysed by benzoyl peroxide or ultra-violet radiation (24). A similar reaction occurs with 1-octene and cyclohexene(25). A far more useful application of this reaction is the formation of fully substituted monogermanes in which one of the groups attached to the central germanium atom is either unsaturated or contains a reactive centre; the Ge-H bond in tri-n-butylgermane adds across an acetylenic carbon-carbon bond(26):

$$n\text{-}Bu_3GeH \ + \ HC{\equiv}CCR_2OH \longrightarrow n\text{-}Bu_3GeCH=CHCR_2OH$$
$$R=H,Me.$$
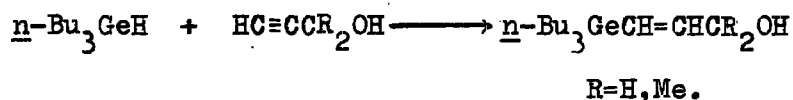
the reaction is catalysed with chloroplatinic acid. A similar reaction occurs with α-substituted olefines(27):

$$R_3GeH \ + \ CH_2=CHY \longrightarrow R_3GeCH_2CH_2Y$$
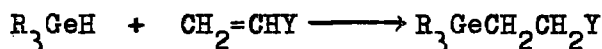
R = alkyl,

Y = -CN, -COOH, -COOR, without catalyst,

Y = $-CH_2OH$, benzoyl peroxide catalyst,

Y = -CHO, Pt + hydroquinone catalyst.

This type of reaction can also be carried out using a tetra-alkylgermane,

one group of which is unsaturated, and a compound containing an active
hydrogen atom:

$$Et_3GeCH=CH_2 \ + \ HSCH_2COOH \longrightarrow Et_3GeCH_2CH_2SCH_2COOH,$$

and $\quad Et_3GeCH_2CH=CH_2 \ + \ HSCH_2CH_2OH \longrightarrow Et_3GeCH_2CH_2CH_2SCH_2CH_2OH, (28,29).$
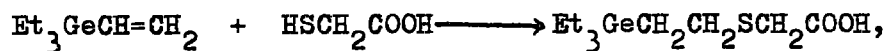
Germyl-lithium and potassium compounds react with olefins in a way
similar to triphenylgermane, to give, after hydrolysis, the corresponding
tetra-substituted monogermane:

$$Ph_3GeLi \ + \ Ph_2C=CH_2 \longrightarrow Ph_2CHCH_2GePh_3, \ (24).$$

A similar reaction occurs with octadecene-1, but no reaction appears
to take place with trans-stilbene, octene-1 or cyclohexene(24).

Ketones react in a similar manner:

$$Ph_3GeK \ + \ Ph_2C=O \longrightarrow Ph_3GeC(OH)Ph_2, \ (30,31).$$
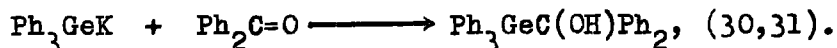
Properties of fully substituted monogermanes.

Compounds of the type R_4Ge, where R is either an alkyl or aryl group,
are very stable chemically and thermally. The lower alkyls are volatile
liquids: Me_4Ge, b.p 43.4°; Et_4Ge, b.p 162.5°. The aryl compounds are
crystalline solids and melt without decomposition, Ph_4Ge, m.p 235°;
$(PhCH_2)_4Ge$, m.p 110°. Mixed alkyl-aryl compounds have intermediate
properties, Et_3GePh, b.p 116/13 mm; Et_2GePh_2, b.p 316°; $EtGePh_3$, m.p 78°.

Tetraethylgermane undergoes bromination to give bromotriethylgermane,
$BrGeEt_3$ using bromine in ethyl bromide(122,32). Halogen halides are less
effective halogenating reagents, only HF gives the corresponding halide
R_3GeF, (R = Me, Et), in reasonable yields(33). Direct substitution of
a further ethyl group to give dibromodiethylgermane, Br_2GeEt_2, does not
occur.

Tetraphenylgermane can be brominated to bromotriphenylgermane, Ph_3GeBr, using bromine in carbon tetrachloride solution after refluxing for 7 hrs(17), or more effectively by using 1,2-dibromoethane as solvent at room temperature(34). Unlike tetraethylgermane, tetraphenylgermane can be further substituted to give dibromodiphenylgermane, Ph_2GeBr_2, in high yield by refluxing with bromine in 1,2-dibromoethane(35). Simons(36) carried out bromination reactions, using bromine or hydrogen bromide, with various fully substituted arylmonogermanes and obtained the following relative rates of reaction:

$$p\text{-tolyl-} \rangle \underline{m}\text{-tolyl-} \rangle \text{ phenyl-} \rangle \text{benzyl-.}$$
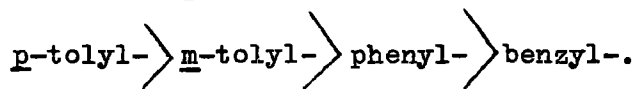
Lesbre and Mazerolles(37,29) prepared a series of mixed tetra-alkyl-germanes. In cleavage reactions of these compounds the lighter radicals were split off in preference to heavier ones, however, phenyl groups were more easily cleaved than alkyl groups. An example of the selective cleavage was shown by Flood(38), who prepared dibromodiethylgermane by the reaction scheme:

$$Ph_2GeBr_2 \ + \ 2EtMgBr \longrightarrow Ph_2GeEt_2 \xrightarrow{Br_2} Et_2GeBr_2.$$
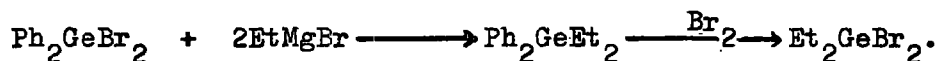
The attempted cleavage of R_4Ge (R=alkyl) with alkali metals in 1,2-dimethoxyethane or tetrahydrofuran has been carried out(39,40), but in no cases was evidence for the formation of the corresponding trialkylgermanium-alkali metal compound, R_3GeM (M=Li,K), obtained, starting material being recovered. Tetraphenylgermane can be readily cleaved to give Ph_3GeM (M=Li,Na) under a variety of conditions, by sodium in liquid ammonia(17), or by lithium in 1,2-dimethoxyethane(30). Further cleavage to give Ph_2GeNa_2 has been postulated, using sodium in liquid

ammonia, to explain the formation of red coloured solutions(17).

b) <u>The substituted higher germanes</u>.

Completely substituted derivatives of the higher germanes of the type $R_3Ge(R_2Ge)_nGeR_3$, n=0,1,2...., are more difficult to prepare than the fully substituted monogermanes, and are more reactive chemically.

Hexaphenyldigermane, Ph_6Ge_2, was first prepared by Morgan and Drew in 1925, who reacted bromotriphenylgermane with sodium in boiling xylene(18):

$$Ph_3GeBr + 2Na \longrightarrow Ph_6Ge_2.$$
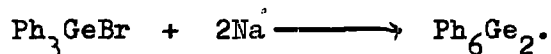
Bromotriethylgermane does not react under similar conditions, but does so at higher temperatures(32). This reaction presumably proceeds via the formation of the alkali metal compound, R_3GeNa.

The addition of phenyl-lithium to triphenylgermane giving hexa-phenyldigermane

$$Ph_3GeH + PhLi \longrightarrow Ph_6Ge_2 +$$
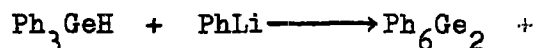
has been described(21,22), see also page 11 of this thesis. This reaction presumably involves hydrogen-metal exchange and formation of lithium hydride:

$$Ph_3GeH + PhLi \longrightarrow C_6H_6 + Ph_3GeLi$$
$$Ph_3GeH + Ph_3GeLi \longrightarrow Ph_6Ge_2 + LiH.$$
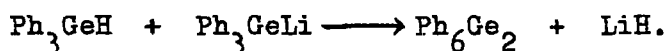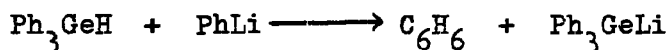
The reaction between germanium(1V)chloride and an excess of phenylmagnesium bromide has been described as a method of preparing tetraphenylgermane. However hexaphenyldigermane is also produced under the conditions generally employed. The yield of the digermane has been reported to be lowered by increasing the temperature of reflux(35).

Part B of this thesis is concerned with an investigation of this and related reactions.

The only substituted trigermane known is octaphenyltrigermane(43), Ph_8Ge_3, which is prepared by the reaction of triphenylgermylsodium with dichlorodiphenylgermane in benzene. No substituted higher germane has as yet been prepared, though note should be made of $(Ph_2Ge)_4$ which will be discussed later.

Properties of fully substituted di- and tri-germanes.

The strength of the germanium-germanium bond is less than that of the germanium-carbon bond. Thus, as may be expected, cleavage reactions generally involve rupture of the metal-metal link.

Hexaphenyldigermane is a high melting, micro-crystalline solid, m.p $335°$, whereas hexaethyldigermane melts at $90°$.

Cleavage of the metal-metal bond in R_6Ge_2 (R=alkyl or aryl) with alkali metals occurs easily and this reaction will be discussed later, (page 26). The expected products, R_3GeBr, are obtained on bromination (17,32).

Octaphenyltrigermane, m.p $247°$, is readily brominated by bromine in carbon tetrachloride at room temperature to give bromotriphenylgermane and dibromodiphenylgermane(42;43).

c) The partially substituted monogermanes.

Partially substituted monogermanes of the type R_nGeH_{4-n} are known for values of n=1,2 and 3. Preparation is most conveniently effected by the reduction of the corresponding halide with lithium aluminium hydride in refluxing ether(35,44,45,27,46,47).

$$R_nGeX_{4-n} + LiAlH_4 \longrightarrow R_nGeH_{4-n}.$$
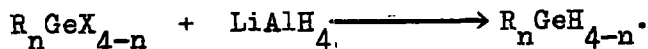
Cleavage of the Ge-C bond in the reduction of trichloro-$\underline{n}$-propylgermane

has been reported to occur above 70°, among the products are monogermane

and germanium metal(45).

Germylsodium reacts with alkyl halides in liquid ammonia to give

monoalkylgermanes; methyl-, ethyl- and $\underline{n}$-propyl-germane were prepared

by this method(48):

$$NaGeH_3 + MeX \longrightarrow MeGeH_3 + NaX \quad (X=halogen).$$
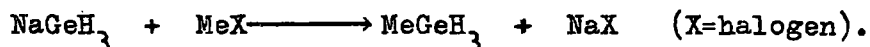
Recently Anderson(50) prepared the first organo germanium compound

containing both hydrogen and a halogen atom attached to the central

germanium atom. Compounds of the type $BuGeH_2X$ and Bu_2GeHX, $(X=Cl,Br,I)$,

were prepared by the reaction of $BuGeH_3$ and Bu_2GeH_2 with deficiencies

of the corresponding mercuric halide.

Properties of partially substituted monogermanes

The partially substituted monogermanes are comparatively air stable,

the alkyls are gases or low boiling liquids, the aryls high boiling

liquids or solids; $MeGeH_3$, b.p -23°; Ph_2GeH_2, b.p 93°/1mm, Ph_3GeH, which

exists in two forms, α, m.p 47°; β, m.p 27°.

The hydrogen atoms bonded to germanium are very easily removed by

bromine in ether at 0°C(35):

$$Ph_2GeH_2 + 2Br_2 \longrightarrow Ph_2GeBr_2 + 2HBr,$$

or by alkali metals in ethylamine:

$$Et-\underline{iso}-AmGeH_2 \xrightarrow{\text{Li}} Et-\underline{iso}-AmGeHLi + \tfrac{1}{2}H_2.$$
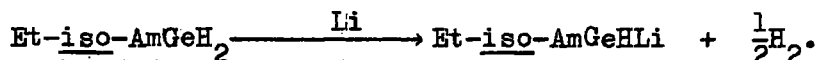
Sodium reacts similarly in liquid ammonia, though less effectively(49).

Triethylgermane is rather a strong reducing agent(44), reducing

platinum, palladium, gold and mercury salts to the corresponding metal, and cupric compounds are reduced to cuprous. Perfluoroacetic acid reacts to give the ester $Et_3GeOCOCF_3$, and hydrogen; however trichloro-, tri-bromo-, and tri-iodo-acetic acid give the corresponding triethylhalo-germane and acetic acid. Acetic acid fails to react under similar conditions(51). It is of interest that triethylstannane does react with acetic acid.

Triphenylgermane reacts with alcoholic potassium hydroxide with the evolution of hydrogen, whereas tri-n-hexylgermane does not(52).

The addition of trialkyl- and triaryl-monogermanes to olefinic or acetylenic systems has been discussed(page 12)but further applications of this reaction will be described here. The addition of di-n-butyl-germane to phenylacetylene proceeds according to the equation:

$$\underline{n}\text{-Bu}_2GeH_2 + PhC{\equiv}CH \longrightarrow \underline{n}\text{-Bu}_2GeHCH{=}CHPh.$$
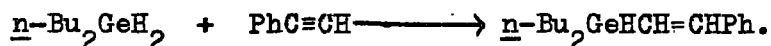
With non-terminal acetylenes the expected products are generally obtained, though in lower yields:

$$Et_3GeH + RC{\equiv}CR \longrightarrow Et_3GeCR{=}CHR, \quad R{=}HOCMe_2, (26).$$
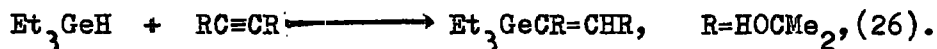
As would be expected further addition, involving two molecules of the germane, can occur:

$$2Et_3GeH + HC{\equiv}CH \longrightarrow Et_3GeCH_2CH_2GeEt_3, (26).$$
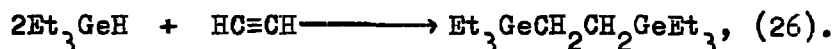
Triphenylgermane also adds across an olefinic system in compounds of the type $CH_2{=}CHCH_2MPh_3$, where M=Si (53), or Ge (24), to give $Ph_3GeCH_2CH_2CH_2MPh_3$. No reaction appears to occur for M=Sn (54). The reactions are catalysed by benzoyl peroxide or ultra-violet radiation.

Gilman and Gerow(22) reported a pronounced difference in the mode

of reaction of organo-lithium compounds with triphenylsilane and triphenyl-germane. The respective reactions are:

$$Ph_3SiH + RLi \longrightarrow Ph_3SiR + LiH,$$
$$Ph_3GeH + RLi \longrightarrow Ph_3GeLi + RH.$$

Triphenylgermane resembles triphenylmethane in this reaction, the cause of this difference in behaviour is not known. The reaction involving n-butyl-lithium and triphenylgermane in ether solution is instantaneous at room temperature and gives quantitative yields of triphenylgermyl-lithium. The reaction with phenyl-lithium affords an 80% yield of triphenylgermyl-lithium after 5mins at room temperature, whereas that of methyl-lithium requires a reflux period of 24hrs to give a comparable yield. Grignard reagents do not react under these conditions, however, the use of tetrahydrofuran as solvent promotes the reaction(55):

$$Ph_3GeH + allylMgCl \longrightarrow Ph_3GeMgCl + allylH,$$

which is discussed further on page 30 of this thesis.

3) THE ORGANOHALOGERMANES.

The complete series of organohalogermanes; R_3GeX, R_2GeX_2, $RGeX_3$, R = alkyl- or aryl-, X = F,Cl,Br,I; are known. The stability to hydrolysis is generally in the order(32):

$$F \rangle Cl \rangle Br \rangle I.$$
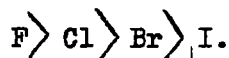
The direct halogenation of substituted monogermanes or digermanes as a means of preparing organohalogermanes, usually of the type R_3GeX and R_2GeX_2 (X = halogen), has been described (page 13,16), and it is the preferred method for the preparation of these compounds.

By careful control of the conditions, the reaction between

germanium(1V)chloride and a Grignard reagent can yield as major product

the required organohalogermane, though separation of the mixed product

is often difficult(52).If the organic group R is sufficiently bulky

so that substitution beyond R_3GeX is sterically hindered, then higher

yields than is usual can be obtained of this intermediate.The reaction

between germanium(1V)chloride and an excess of 1-naphthylmagnesium

bromide gives no tetra-1-naphthylgermane; bromotri-1-naphthylgermane

is the main product(56). Similarly bromotri-_iso_-propylgermane does not

undergo further substitution under normal conditions(29,57). No steric

hindrance was observed in the preparation of tetra-_iso_-butylgermane,

yields of 70-80% being obtained(29,37).

The direct reaction between germanium metal and alkyl- or aryl-

halides proceeds at temperatures greater than 320°, in the presence of

copper as catalyst, to yield di- and tri-halo-organogermanes(58):

$$MeCl + Ge \longrightarrow Cl_2GeMe_2 + Cl_3GeMe,$$

$$EtCl + Ge \longrightarrow Et_2GeCl_2 + EtGeCl_3,$$

$$PhCl + Ge \longrightarrow Ph_2GeCl_2.$$
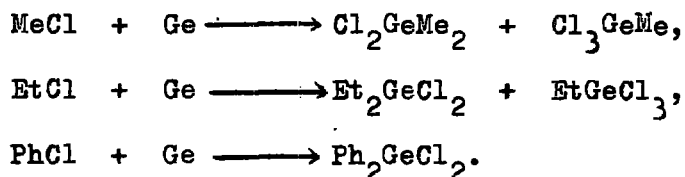
This method is of limited applicability because of the high temperature

involved which tends to cause dehydrohalogenation.

Two somewhat obscure reactions have been reported involving ger-

manium halides(59,60):

$$CsCl + GeCl_2 \longrightarrow CsGeCl_3 \xrightarrow{EtI} EtGeCl_3,$$

$$3GeCl_4 + Ph_4Ge \xrightarrow[210-290°]{sealed\ tube} 4GePhCl_3$$
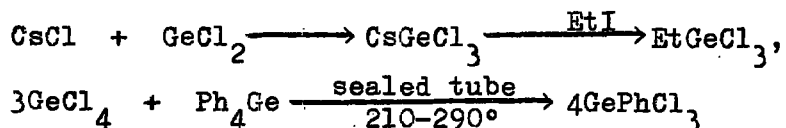
Trichlorogermane Cl_3GeH adds to olefinic double bonds under a

variety of conditions to yield the trihalo-organogermane,benzoyl peroxide

(29,61) and chloroplatinic acid(62) have been used as catalysts:

$$Cl_3GeH + H_2C=CH(CH_2)_3CH_3 \longrightarrow Cl_3Ge(CH_2)_5CH_3.$$
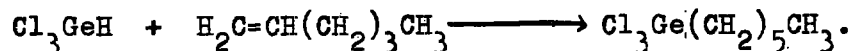
Riemschneider and co-workers synthesised several compounds of this type by heating the reaction partners in sealed tubes at 85° in the absence of catalysts, e.g. $Cl_3Ge(CH_2)_3CHClCH_3$. Trichlorogermane adds at room temperature to an unactivated olefinic bond, for example, ethylene to yield trichloroethylgermane.

Mixtures of organohalogermanes are often very difficult to separate by distillation, and it is often more convenient to hydrolyse to the corresponding oxide or anhydride, which are more readily separated. Reconversion to the desired halide can be effected by treatment with the appropriate halogen acid(42). Alternatively, tribromophenylgermane and dibromodiphenylgermane can be separated by conversion to the parent germanes, with lithium aluminium hydride, which are readily fractionated and rehalogenated(35).

Properties of organohalogermanes.

Organohalogermanes are high boiling liquids, (Et_3GeCl, b.p 176°/760mm; $EtGeBr_3$, b.p 200°/763mm; $PhGeBr_3$, b.p 120°/13mm.); or solids, (Ph_3GeBr, m.p 138.5°; Ph_3GeCl, m.p 116°); and can generally be distilled without change, the iodides are the least stable thermally and some decomposition does occur on heating:

$$EtGeI_3 \xrightarrow{\text{T}>350°} GeI_4 + \text{unidentified gas, (63)}.$$
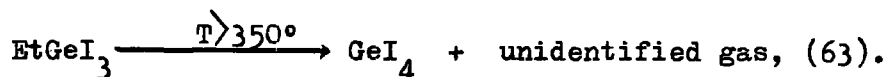
The halides are stable to dry air, though slow hydrolysis occurs in moist air; hydrolysis being more easily effected by either an aqueous or alcoholic solution of sodium hydroxide:

$$R_3GeX \longrightarrow \left[R_3GeOH\right] \rightleftharpoons (R_3Ge)_2O.$$

$$R_2GeX_2 \longrightarrow \left[R_2Ge(OH)_2\right] \rightleftharpoons R_2GeO.$$

$$RGeX_3 \longrightarrow \left[RGe(OH)_3\right] \rightleftharpoons \left[RGeOOH\right] \rightleftharpoons (RGeO)_2O.$$
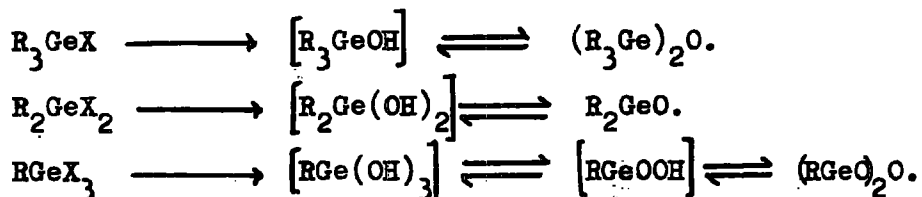
R = alkyl or aryl, X = halogen.

The isolated product of hydrolysis is usually the oxide or the acid anhydride. The rate of hydrolysis increases from R_3GeX to $RGeX_3$. It appears as though the monofunctional hydroxides split off water by a bimolecular mechanism, thus, in cases where the organic group R is sufficiently bulky, this process is sterically hindered, and the intermediate germanol, R_3GeOH, can be isolated. Examples are triphenylgermanol, and tri-_iso_-propylgermanol(57).

From the hydrolysis of dibromodiphenylgermane, Morgan and Drew(18) isolated what was thought to be trianhydro-_tetrakis_-diphenylgermanediol, $HO(GePh_2O)_3GePh_2OH$, m.p 149° and tetrameric diphenylgermanium oxide, $(Ph_2GeO)_4$, m.p 218°. Kraus and Brown obtained a white powder with an indefinite melting point from the hydrolysis of dichlorodiphenylgermane with ammonium hydroxide in ethanol(42). This work was repeated by Zeiss (65) who hydrolysed dibromodiphenylgermane with water and obtained an insoluble, polymeric oxide with m.p 230–295°. Treatment with boiling acetic acid gave the tetrameric oxide, m.p 219–221°, presumably identical to that obtained by Morgan and Drew. The structure of this compound is suggested to be:
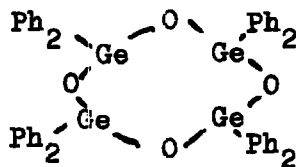
Strong absorption was observed at 860 and 818 cm^{-1} in the infrared

spectrum of the tetramer (Ge-O stretch). Hydrolysis of dibromodiphenyl-

germane with caustic soda gave a micro-crystalline oxide, m.p 290-95°,

which gave di-iododiphenylgermane on treatment with hydriodic acid.

Hydrolysis of this iodide with water gave the trimeric oxide $(Ph_2GeO)_3$,

m.p 147-49°. This compound is probable identical to the diol obtained by

Morgan and Drew. No O-H stretch was observed in the infrared spectrum.

Treatment of the trimer with acetic acid gave the tetramer (m.p 218°)

and with ethanol was formed the polymeric oxide, m.p 230-295°.

The ammonolysis of organohalogermanes has been extensively studied.

When bromotrimethylgermane is dissolved in benzene and dry ammonia

passed into the solution, a crystalline precipitate of ammonium bromide

appears. Evaporation of the solvent gives, as residue, a compound believed

to be an amine. Condensing ammonia onto bromotriethylgermane leads to the

formation of bis-(triethylgermyl)amine, $(Et_3Ge)_2NH$, as a colourless

liquid which reacts vigorously with water to give bis-(triethylgermyl)

oxide, $(Et_3Ge)_2O$, (32).

Dibromodiethylgermane also undergoes ammonlysis with liquid ammonia

to give diethylgermanium imine, Et_2GeNH, which is a high boiling liquid,

probably tetrameric(38).

Tri-iodo- or tri-bromo- ethylgermane is similarly ammonolysed by

liquid ammonia to give the nitride, EtGeN, which is soluble in liquid

ammonia and undergoes hydrolysis to give the anhydride $(EtGeO)_2O$, (66).

Ammonolysis of bromotriphenylgermane with liquid ammonia gives the

completely substituted compound <u>tris</u>-(triphenylgermyl)amine, $(Ph_3Ge)_3N$,
(17); however under less vigorous conditions, bubbling ammonia gas into
a solution of bromotriphenylgermane, triphenylgermylamine is obtained,
Ph_3GeNH_2, (17,67). Condensation of this compound, with elimination of
ammonia proceeds readily to give the secondary amine, $(Ph_3Ge)_2NH$, which
undergoes further condensation to give the nitride $(Ph_3Ge)_3N$. Complete
conversion to the nitride can be effected by heating to 200°, followed
by evacuation. Treatment of triphenylgermylamine with hydrogen chloride
gives chlorotriphenylgermane.

Diphenylgermanium imine, Ph_2GeNH, a colourless liquid, soluble in
organic solvents and very susceptible to hydrolysis, is prepared by the
ammonolysis of dihalodiphenylgermanes with liquid ammonia. Dichlorodiphenyl-
germane dissolves in ethylamine without ammonoylsis occuring(42).

If compounds of the type R_3GeX do not ammonolyse in ethylamine,
then reductions with alkali metals can be carried out in this solvent:

$$R_3GeX + 2Li \longrightarrow 2LiX + R_6Ge_2.$$

It is preferable to use fluoro-organogermanes which, in general, are
stable in ethylamine, e.g. Et_3GeF.

In 1936 Schwarz and Schmeisser(68) reacted trichlorophenylgermane
with metallic potassium in refluxing xylene. They isolated a compound
which had the empirical formula PhGe, which was reported to be unaffect-
ed by oxygen. Molecular weight measurements indicated a degree of
association of six in freezing benzene. Two alternative structures were
put forward:

1)   -Ge=Ge-Ge=Ge-Ge=Ge-
     Ph Ph Ph Ph Ph Ph

11)

```
          Ph
          Ge
         /  \
    PhGe      GePh
     |          |
    PhGe      GePh
         \  /
          Ge
          Ph
```

The authors preferred structure (1), though no indications as to methods of chain termination were given. Oxidation of phenylgermanium was effected by passing air through a refluxing xylene solution, the product being $Ge_6Ph_6O_3$, the structure of which was suggested to be:

```
       O       O.      O       O
      / \     / \     / \     / \
....Ge-Ge-Ge-Ge-Ge-Ge-Ge-Ge......
    .   .   .   .   .   .   .   .
    Ph  Ph  Ph  Ph  Ph  Ph  Ph  Ph
```
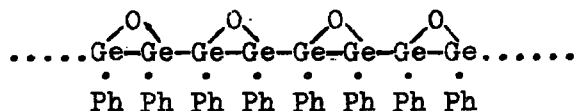
Bromination of phenylgermanium in carbon tetrachloride solution leads to the absorption of eight equivalents of bromine.

This reaction has been studied further by Zeiss and Metlesics(69). After many attempts to avoid excessive as well as incomplete reaction, it was possible to stop the dehalogenation at a stage when the solution did not undergo any colour change on exposure to the air. From this was obtained a compound which had a Ge:Ph ratio of 1:1. However the material contained from between 5-10% of oxygen, showing strong Ge-O absorption in the region of $800-900cm^{-1}$. The molecular weight ranged from 805-1280, corresponding to 8-10 (PhGe) units. Bromination of this material suggested that it was essentially the same as that of Schwarz and Schmeisser, taking up 1.3 to 1.4 atoms of bromine per (PhGe) unit. The products of bromination included sym-tetrabromodiphenyldigermane, $PhBr_2Ge-GeBr_2Ph$, dibromodiphenylgermane, tribromophenylgermane, and,

after hydrolysis, germanoic acid and phenylgermanoic acid. It was shown

that sym-tetrabromodiphenyldigermane decomposes on heating to give

tribromophenylgermane. The authors thus suggest that the polymer contains

$PhGe-$, Ph_2Ge-, $PhGeO-$, and $Ge-O$ units.

4) GERMANIUM-ALKALI METAL COMPOUNDS.

Compounds of the type R_3GeM, R = alkyl- or aryl-, M = Li,Na,K, are

all known, with the exception of $(alkyl)_3GeNa$.

The early methods of preparation involved cleavage of substituted

digermanes with alkali metals in liquidammonia or ethylamine(32):

$$Et_6Ge_2 \xrightarrow{\text{Li in } EtNH_2} Et_3GeLi,$$
$$Et_6Ge_2 \xrightarrow{\text{K in liq. } NH_3} Et_3GeK.$$
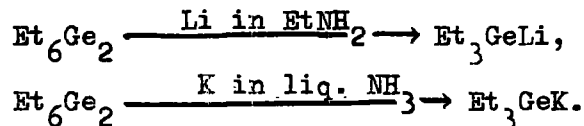
Triethylgermyl-lithium is completely ammonolysed in liquid ammonia:

$$Et_3GeLi + NH_3 \longrightarrow Et_3GeH + LiNH_2.$$

Phenyl-germanium bonds are cleaved, under the same conditions,

with much greater ease than alkyl-germanium bonds:

$$Ph_6Ge_2 (\text{or } Ph_4Ge) \xrightarrow{\text{Na in liq.} NH_3} Ph_3GeNa, \quad (17).$$
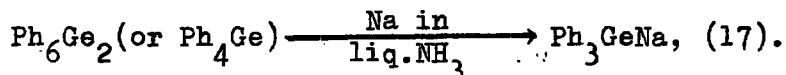
No appreciable cleavage of tetraethylgermane, or hexaethyldigermane,

with sodium in liquid ammonia has been observed.

Gilman and co-workers introduced the use of ethereal solvents,

1,2-dimethoxyethane and tetrahydrofuran being the most successful, for

the cleavage of both fully substituted mono- and di-germanes with

alkali metals. Both tetraphenylgermane(30) and hexaphenyldigermane(70)

are readily cleaved by lithium in 1,2-dimethoxyethane, to give approx-

imately 70% yield of triphenylgermyl-lithium. Similarly triphenylgermyl-

potassium is prepared by cleavage of hexaphenyldigermane using a 1:5

Na-K alloy in ether, with a trace of tetrahydrofuran(70).

Bromotriphenylgermane reacts with lithium in tetrahydrofuran to give a 50% yield of the corresponding lithium compound, characterised by the addition of chlorotriethylsilane. The amount of hexaphenyldigermane obtained was not reported(71).

The most efficient method for the preparation of triphenylgermyl-lithium is by the hydrogen-metal exchange reaction:

$$Ph_3GeH \; + \; RLi \xrightarrow{\text{ether}} Ph_3GeLi \xrightarrow[\text{2. } H_2O]{\text{1. } CO_2} Ph_3GeCOOH.$$
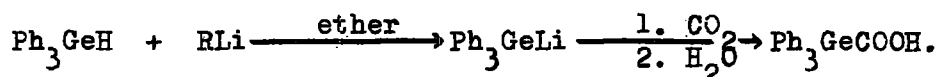
A rapid and quantitative reaction occurs using n-BuLi at room temperature. Methyl-lithium requires a reflux period of 24hrs to effect an 80% conversion. Phenyl-lithium also reacts rapidly in ether at room temperature to give, after carbonation, an 80% yield of triphenylgermyl carboxylic acid(22).

Properties of germanium-alkali metal compounds.

Dilute solutions of triphenylgermylsodium in liquid ammonia are yellow while more concentrated ones are orange. Triphenylgermylsodium can be crystallised from liquid ammonia with three molecules of solvent of crystallisation. Solutions of triphenylgermyl-lithium in 1,2-dimethoxy-ethane are red-brown in colour, the solvent is slowly cleaved and the reagent should be prepared as required. Triphenylgermyl-lithium is stable in diethyl ether. In the cleavage of tetraphenylgermane by lithium metal, no product resulting from the reaction of phenyl-lithium has been detected after subsequent reaction.

Hydrolysis of these compounds give the corresponding germane:

$$R_3GeM \; + \; H_2O \longrightarrow R_3GeH \; + \; MOH.$$

R = alkyl or aryl, M = Li,Na,K.

Oxidation of triphenylgermylsodium has been reported to proceed:

$$Ph_3GeNa + (0) \longrightarrow Ph_3GeONa, (17).$$

Carbonation of a solution of triphenylgermyl-lithium gives, as shown above, triphenylgermyl carboxylic acid. Triphenylgermyl carboxylic acid melts at 203-220° with evolution of carbon monoxide(64).

Triphenylgermyl-lithium reacts slowly with triphenylgermane:

$$Ph_3GeLi + Ph_3GeH \xrightarrow[\text{reflux.}]{\text{ether at}} Ph_6Ge_2 + LiH,$$
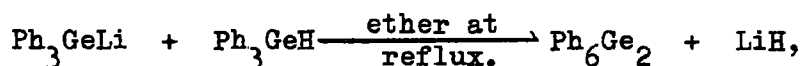
a 10% yield of hexaphenyldigermane being obtained(22).

As expected, triphenylgermyl-lithium reacts with organic and inorganic halides. With organic halides or dihalides the expected products are usually obtained, 1,2-dimethoxyethane being the solvent of choice in most cases(72). The reactionsinvolving metal halides often proceed less cleanly due to halogen-metal exchange and subsequent coupling reactions. For example triphenylgermylpotassium and chlorotriphenylsilane react to give all three possible products(73,74):

$$Ph_3GeK + Ph_3SiCl \longrightarrow Ph_3Ge-SiPh_3,$$

$$Ph_3GeK + Ph_3SiCl \longrightarrow Ph_3GeCl + Ph_3SiK,$$

$$Ph_3GeCl + Ph_3GeK \longrightarrow Ph_6Ge_2,$$

$$Ph_3SiCl + Ph_3SiK \longrightarrow Ph_6Si_2.$$
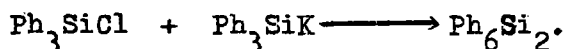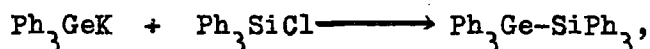
As has already been discussed, triphenylgermyl-lithium adds to olefinic double bonds and to carbonyl groups to give, after hydrolysis, the fully substituted monogermane,(page 13). However, with the methyl ester of triphenylgermyl carboxylic acid, $Ph_3GeCOOMe$, or diethyl carbonate, an immediate reaction occurs with the evolution of carbon

monoxide, the reaction being carried out in 1,2-dimethoxyethane(30).
The supposed mechanism is:

$$Ph_3Ge^- \; + \; O=C(OEt)_2 \longrightarrow Ph_3GeCOOEt \; + \; EtO^-,$$

$$Ph_3GeCOOEt \; + \; Ph_3Ge^- \longrightarrow Ph_3Ge\ldots\underset{\underset{Ph_3}{\mid}}{Ge}\ldots\underset{\underset{O}{\parallel}}{C}\ldots OEt,$$

$$Ph_3Ge\ldots\underset{\underset{Ph_3}{\mid}}{Ge}\ldots\underset{\underset{O}{\parallel}}{C}\ldots OEt \longrightarrow Ph_6Ge_2 \; + \; CO \; + \; EtO^-.$$
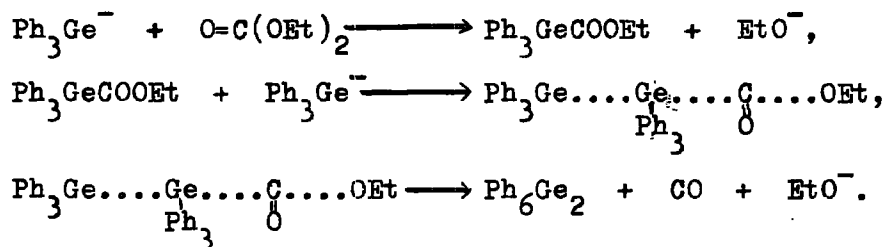
An interesting reaction occurs with azoxybenzene,(or azobenzene, which is produced in this reaction), leading to the formation of a substituted hydrazine(75):

$$Ph_3GeLi \; + \; Ph-N=\overset{\overset{O}{\uparrow}}{N}-Ph \longrightarrow \left[\underset{\underset{Li}{}}{PhN=NPh}\right] \; + \; Ph_3GeOLi,$$

$$Ph_3GeLi \; + \; \left[PhN=NPh\right] \longrightarrow Ph-\underset{\underset{GePh_3}{}}{N}-\overset{}{N}-Ph \xrightarrow{H_2O} Ph-\underset{\underset{GePh_3}{}}{N}=\overset{\overset{H}{}}{N}Ph \; .$$
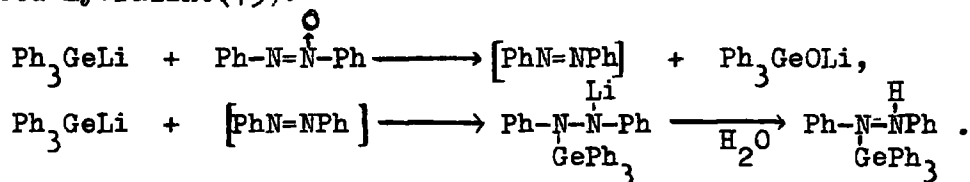
Triphenylgermyl-lithium undergoes a metal-hydrogen exchange reaction with fluorene(76):

 + Ph₃GeLi ⟶ + Ph₃GeH.
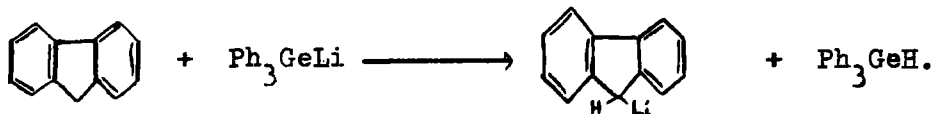
Characterisation of 9-fluoryl-lithium was effected by carbonation, isolating the corresponding acid. Some hexaphenyldigermane also was isolated, presumably formed by the reaction between triphenylgermyl-lithium and triphenylgermane,(see page 11 & 15).

c) GROUP 1V METAL-GRIGNARD REAGENTS

Germyl-Grignard reagents of the type R_3GeMgX, R = aryl-, have been postulated recently as intermediates in certain reactions, and Gilman and co-workers have obtained substantial evidence for the existence of such compounds.

The exchange reaction:

$$\underline{n}\text{-BuLi} \quad + \quad Ph_3GeH \longrightarrow Ph_3GeLi,$$
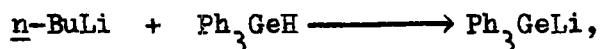
has been described (page 27), and Gilman and co-workers attempted the similar reaction:

$$CH_2=CHCH_2MgCl \quad + \quad Ph_3GeH \longrightarrow Ph_3GeMgCl \quad + \quad CH_2=CHCH_3,$$

in ether, however no reaction was observed(55). In contrast, the use of tetrahydrofuran as solvent promotes the reaction, and triphenylgermyl carboxylic acid was isolated after carbonation of the reaction mixture. Also isolated was 4-hydroxybutyltriphenylgermane, formed by the cleavage reaction:

$$Ph_3GeMgCl \quad + \quad \underset{CH_2\diagdown_0\diagup CH_2}{\overset{CH_2----CH_2}{|\qquad|}} \longrightarrow Ph_3GeCH_2CH_2CH_2CH_2OMgBr$$

$$(\underline{A})$$

$$(\underline{A}) \xrightarrow{\quad H_2O \quad} Ph_3Ge(CH_2)_4OH.$$
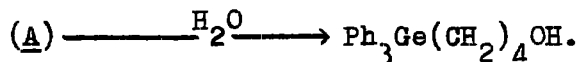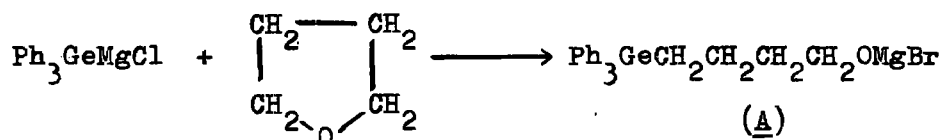
Higher yields of the cleavage product of the solvent were obtained after prolonged refluxing of the reaction mixture. Both allylmagnesium bromide and phenylmagnesium bromide gave, under conditions designed to furnish triphenylgermyl carboxylic acid, only the cleavage product. $\underline{n}$-Butyl-magnesium bromide was reported not to react at all.

From the reaction of vinylmagnesium bromide and germanium(1V)chloride, Seyferth isolated both tetravinylgermane and hexavinyldigermane(77). The reaction scheme :

$$GeCl_4 \quad + \quad 2.CH_2=CHMgBr \longrightarrow GeCl_2 \quad + \quad CH_2=CH.CH=CH_2 \quad + \quad 2MgClBr,$$

$$GeCl_2 \quad + \quad 2.CH_2=CHMgBr \longrightarrow (CH_2=CH)_2Ge \quad + 2MgClBr,$$

$$(CH_2=CH)_2Ge + \quad CH_2=CHMgBr \longrightarrow (CH_2=CH)_3GeMgBr,$$

$$(CH_2=CH)_3GeMgBr \quad + \quad (CH_2=CH)_3GeCl \longrightarrow (CH_2=CH)_6Ge_2,$$
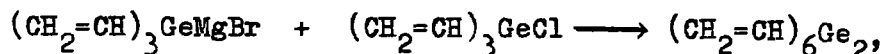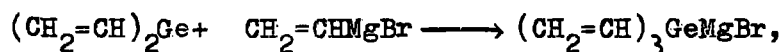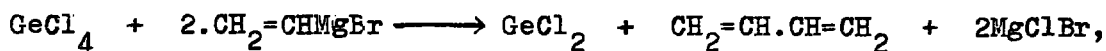
was proposed. The author points out that the scheme is attractive because:

1). The reduction of a metal halide to a lower valency by a Grignard
reagent is well known, quoting as example the formation of
bis-arene complexes of Cr(0) from chromium(111)chloride and
phenylmagnesium bromide.

2). The addition of an organometallic reagent to an organogermanium(11)
compound has been reported(78,79).

In Part C of this thesis it is shown that the reaction of phenyl-lithium
with germanium(11)iodide is more complex than is indicated by the equation:

$$GeI_2 + 3PhLi \longrightarrow Ph_3GeLi,$$
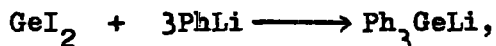
though this equation represents one of the reactions which does occur in
this system.

The substituted digermane, $(CH_2=CH)_6Ge_2$, thus results from the
interaction of chlorotrivinylgermane and trivinylgermylmagnesium bromide;
and the monogermane, $(CH_2=CH)_4Ge$, from normal substitution.

In his review(2), Rijkens suggests that the coupling mechanism for
the production of substituted digermanes may proceed via a Grignard
exchange reaction of the type:

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

followed by interaction with R_3GeX'. In support he quotes the work of
Mazerolles(29), who isolated tri-iso-propylgermane from the reaction of
germanium(1V)chloride with iso-propylmagnesium bromide. The formation
of tetra-iso-propylgermane is sterically hindered, alkylation not pro-
ceeding beyond chlorotri-iso-propylgermane, and the trisubstituted mono-
germane could result from the hydrolysis of tri-iso-propylgermyl magnesium
halide, $(iso-Pr)_3GeMgX$.

Selin and West carried out the reaction of chlorotriphenylsilane with various Grignard reagents, for example cyclohexylmagnesium bromide, and obtained high yields of hexaphenyldisilane(80), also isolated was ᴄ cyclohexane and cyclohexene. The mechanism:

$$\text{C}_6\text{H}_{11}\text{MgBr} + \text{HCl} \longrightarrow \text{C}_6\text{H}_{12} + \text{MgBrCl,}$$
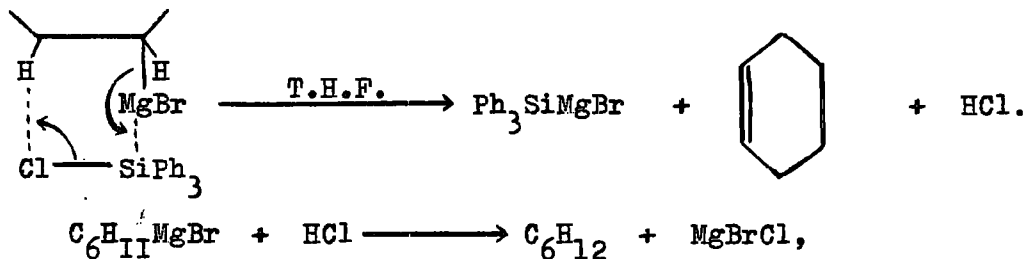
was suggested, the disilane resulting from the reaction of the "silyl Grignard" reagent with unreacted chlorotriphenylsilane:

$$\text{Ph}_3\text{SiMgBr} + \text{Ph}_3\text{SiCl} \longrightarrow \text{Ph}_3\text{SiSiPh}_3 + \text{MgBrCl.}$$

It was reported that chlorotrimethylsilane was not coupled with phenyl-magnesium bromide after 24hr at reflux, however mixtures of chloro-trimethylsilane and triphenylchlorosilane gave triphenylsilyl-trimethyl-silane in 14% yield under similar conditions, presumably formed by the interaction of triphenylsilyl magnesium bromide and chlorotrimethylsilane. The authors suggested that aryl- groups were required to stabilize the "silyl-Grignard" reagent. It was reported that experiments were carried out which showed that triphenylsilane was not involved. A modified interpretation of these reactions is presented in Part B of this thesis.

In 1933 Kipping and co-workers(81) reacted trichlorophenylsilane with cyclohexylmagnesium bromide and obtained, after hydrolysis, dicyclohexylphenylsilane. The reaction scheme which was proposed involved the formation of a "silyl-Grignard" reagent as intermediate:

$$\text{PhSiCl}_3 + 2\text{C}_6\text{H}_{11}\text{MgBr} \longrightarrow (\text{C}_6\text{H}_{11})_2\text{PhSiCl,}$$

$$(C_6H_{11})_2PhSiCl + C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2PhSiMgBr + C_6H_{11}Cl.$$

$$(C_6H_{11})_2PhSiMgBr + H_2O \longrightarrow (C_6H_{11})_2PhSiH + MgBr(OH).$$
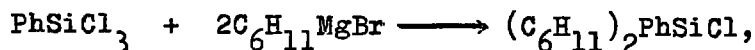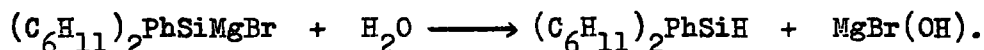
This reaction was repeated later by Nebergall and co-workers(82) who isolated dicyclohexylphenylsilane both before and after hydrolysis. Also isolated was cyclohexene, which led the authors to propose the reaction path:

$$PhSiCl_3 + 2C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2PhSiCl \xrightarrow{C_6H_{11}MgBr} \bigcirc$$
$$+ (C_6H_{11})_2PhSiH.$$
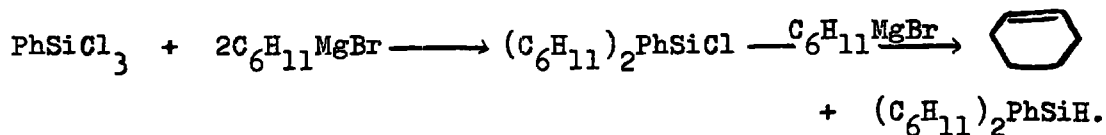
It was reported that a high temperature, 160°, favoursthe reduction reaction.

The reaction of triarylchlorosilanes with alkali metals and with magnesium in tetrahydrofuran have been studied(71,83). The metals Li, K, Rb, and Cs gave the corresponding silyl-metallic compound, the reaction was proposed to proceed:

$$Ph_3SiCl + 2Li \longrightarrow Ph_3SiLi + LiCl,$$

$$Ph_3SiLi + Ph_3SiCl \longrightarrow Ph_3SiSiPh_3 + LiCl,$$

$$Ph_6Si_2 + 2Li \longrightarrow Ph_3SiLi.$$
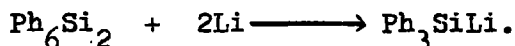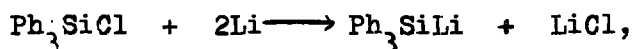
However, in the case of magnesium or sodium, the disilane was the isolated product, the metal failing to cleave the silicon-silicon bond:

$$Ph_3SiCl + Mg \longrightarrow Ph_3SiMgCl,$$

$$Ph_3SiMgCl + Ph_3SiCl \longrightarrow Ph_6Si_2.$$
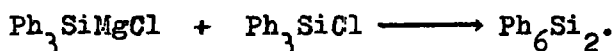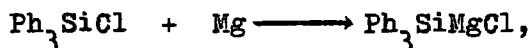
It thus appears as though coupling to form a disilane occurs by the reaction of a triarylhalosilane and a "silyl Grignard" reagent; the latter probably being formed by either the reaction of magnesium or a Grignard reagent of the normal type, with the triarylhalosilane.

An interesting reaction in the organo chemistry of tin has been reported(84). The interaction of magnesium metal and chlorotriphenyltin in tetrahydrofuran gave a non-isolable compound bis(triphenylstannyl) magnesium, $(Ph_3Sn)_2Mg$. The initial reaction was suggested to be:

$$Ph_3SnCl \ + \ Mg \longrightarrow Ph_3SnSnPh_3 \ + \ MgCl_2.$$
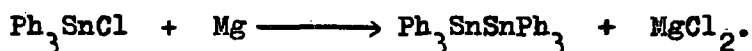
At this stage a negative Gilman Colour Test was obtained. The precipitate of hexaphenylditin then gradually redissolved to give a green-grey solution and a positive Colour Test:

$$Ph_6Sn_2 \ + \ Mg \longrightarrow (Ph_3Sn)_2Mg.$$

Reacting preformed hexaphenylditin with magnesium in tetrahydrofuran gave the same compound, which affords triphenyltin hydride on hydrolysis and hexaphenylditin on carbonation.

The reaction between lead(ll) bromide and phenylmagnesium bromide in tetrahydrofuran at -40° gives, as intermediate, diphenyl-lead(ll), which is involved in the following equilibrium with triphenyl-lead magnesium bromide:

$$PbPh_2 \ + \ PhMgBr \rightleftharpoons Ph_3PbMgBr, \ (85).$$

This reaction will be discussed in Part E of this thesis.

D). COMPOUNDS CONTAINING "METAL-METAL" BONDS.

Compounds of the type $R_3M-M'R_3$, R = alkyl or aryl, M,M' = C,Si,Ge,Sn,Pb, have been known for a number of years.

Kraus and Nelson(86) prepared triethylsilyltriphenylgermane, $Ph_3GeSiEt_3$, by the reaction of triphenylgermylsodium with bromotriethyl-silane. It is a crystalline solid, m.p 93°, and is soluble in benzene. Gilman and co-workers prepared a series of such compounds by the general

reaction(87,64,70,73,74,88):

$$Ph_3MM' + Ph_3MX \text{ (or } Ph_3MCOOR) \longrightarrow Ph_3M-MPh_3$$
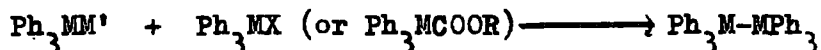
$$M' = \text{alkali metal, } X = \text{halogen,}$$

$$M = Si, Ge, Sn; R = \text{alkyl-.}$$

The general chemical properties of these compounds were described on page 16 of this thesis, it should be noted here that these compounds do not dissociate into free radicals as does hexaphenylethane.

There are however but few examples of compounds containing a Group 1Vb metal bonded directly to a metal of a different group.

Gilman studied the reaction of triphenylsilyl-lithium with various metal halides, e.g. mercury(11)chloride, silver chloride, aluminium chloride, tin(11)chloride and iron(11)chloride. The only product isolated was hexaphenyldisilane together with the free metal:

$$Ph_3SiLi + HgCl_2 \longrightarrow [Ph_3SiHgCl] \longrightarrow Ph_3SiCl + Hg,$$
$$Ph_3SiCl + Ph_3SiLi \longrightarrow Ph_6Si_2 + LiCl.$$
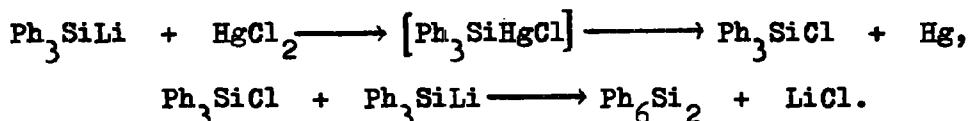
On no occasion was the unstable intermediate isolated.

A compound which was suggested to be <u>tris</u>(triphenylgermyl)boron, $(Ph_3Ge)_3B$, was obtained by reacting triphenylgermyl-lithium with boron trichloride(72). Recently, Seyferth carried out a similar reaction between triphenylgermyl-lithium and triphenylboron, the initial product was proposed to be lithium triphenylgermyl-triphenylborate,(1), though this material could not be purified and isolated. Characterisation was effected however by the addition of tetramethylammonium iodide in alcohol solution. An immediate reaction occurred to give a crystalline, stable product(11):

$$Ph_3GeLi + Ph_3B \longrightarrow Li^+ \left[Ph_3Ge.BPh_3\right]^- \xrightarrow{Me_4NI} Me_4N^+ \left[Ph_3Ge.BPh_3\right]^-.$$
$$(1) \hspace{4cm} (11)$$
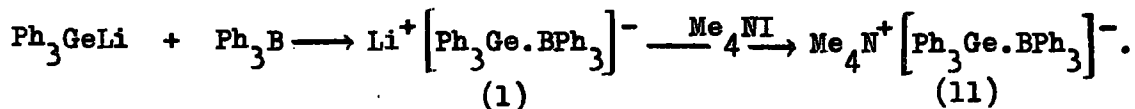
The analogous silicon compound was also prepared.

Part A of this thesis is concerned with an investigation into the formation of compounds containing germanium bonded directly to the metals of Group 1b.

Some information is being obtained concerning compounds containing a Group 1Vb metal bonded to transition metals. The compound, π-cyclo-pentadienyldicarbonyl σ-trimethylsilyliron, $(\pi-C_5H_5)Fe(CO)_2(\sigma-SiMe_3)$, has been known for some time(125). It was prepared by the reaction (1):

$$C_5H_5Fe(CO)_2Na \ + \ Me_3SiCl \longrightarrow C_5H_5Fe(CO)_2(\sigma-SiMe_3); \quad (1).$$
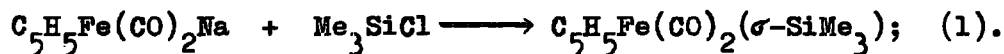
The compound is stable up to 200° and presumably contains a silicon-iron σ bond.

Very recently Gorsich[126] reported the preparation of a series of compounds containing tin and lead bonded to manganese. The general reaction was:

$$R_{4-n}SnCl_n \ + \ nNaMn(CO)_5 \xrightarrow{\text{T.H.F.}} R_{4-n}Sn\left[Mn(CO)_5\right]_n \ + \ NaCl.$$

$$R = \text{alkyl or aryl}$$

$$n = 1,2.$$
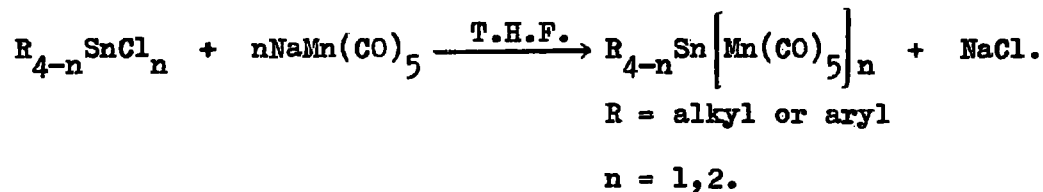
Similar lead compounds were also prepared and π-cyclopentadienyldicarbonyl-σ-triphenylstannyliron, $C_5H_5Fe(CO)_2SnPh_3$, was prepared by reaction (1) for comparison purposes.

Carbonyl groups in $Ph_3SnMn(CO)_5$ were readily displaced by tertiary phosphines or arsines:

$$Ph_3SnMn(CO)_5 \ + \ Ph_3P \longrightarrow Ph_3SnMn(CO)_4PPh_3 \ + \ CO.$$
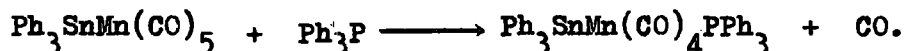
Somewhat surprisingly, halogenation failed to cleave the metal-metal bond, the tin-phenyl bonds being cleaved in preference:

$$Ph_3SnMn(CO)_5 + 3Cl_2 \longrightarrow Cl_3SnMn(CO)_5 + 3PhCl.$$
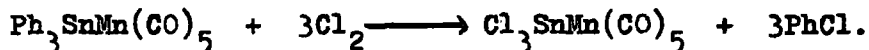
The analogous germanium compounds, $Mn(CO)_5GePh_3$ and $C_5H_5Fe(CO)_2GePh_3$ were prepared simultaneously by Seyferth and co-workers(127).

E). <u>Organo Derivatives of Germanium(11), Tin(11) and Lead(11).</u>

The electronic configuration of the Group 1Vb metals is ns^2, np^2. In the four co-valent state there is a tetrahedral, sp^3, configuration of groups about the central metal atom. For the di-valent state, however, there is some doubt as to the configuration. It is unlikely that a straight-forward p bonding of the metal in the ground state occurs. Such compounds would thus have a bond angle of 90°, with a "lone pair" of electrons in the s orbital and a vacant p orbital, as shown in figure i.
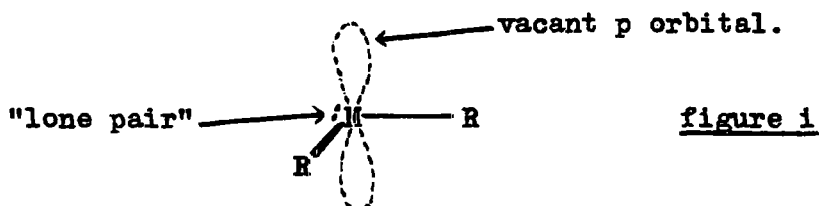
figure i

Electron diffraction data on tin(11)chloride in the vapour phase shows that the bond angle is greater than 90°, and it is probable that sp^2 hybridization is involved, the structure is shown in figure ii.

figure ii
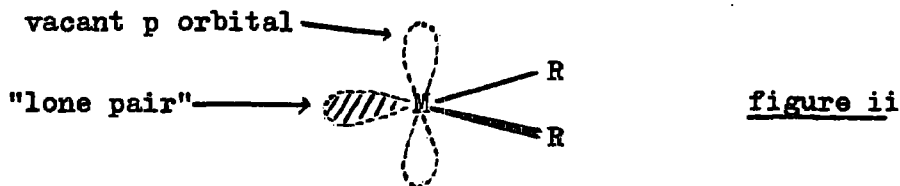
This structure involves a "lone pair" of electrons in a sp^2 hybridized orbital and a vacant p orbital at right angles to the plane of the molecule.

1). GERMANIUM(11).

The isolation of an organogermanium(11) compound has, as yet,

probably not been effected.

In an attempt to prepare diphenylgermanium(11), Ph_2Ge, Kraus and Brown(43) reacted dichlorodiphenylgermane with a sodium dispersion in refluxing xylene. The principle product was a polymeric material which could not be purified. There was obtained, however, a very low (about 10%) yield of a colourless crystalline material which was empirically Ph_2Ge. Molecular weight measurements however indicated the tetramer $(Ph_2Ge)_4$, which may have the cyclic structure:

$$Ph_2Ge \text{------} GePh_2$$
$$| \qquad\qquad |$$
$$Ph_2Ge \text{------} GePh_2$$
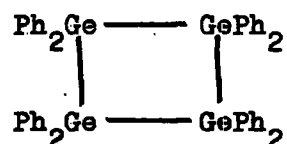
The reaction of germanium(11)iodide with phenyl-lithium in ether has been reported to be slow(79), requiring several days at reflux for 3 mole equivalents of phenyl-lithium to be absorbed. Treatment of the red-brown reaction mixture with benzylchloride followed by hydrolysis, led to the isolation of diphenylgermanium(11), together with trace amounts of tetraphenylgermane. No molecular weight, analytical data or experimental details were reported.

Jacobs(78) attempted to prepare organogermanium(11) compounds by the reaction of germanium(11)iodide with diethylmercury, di-n-butylmercury, n-butyl-lithium, ethyl-lithium, di-n-butylzinc and di-iso-butylzinc. The only organogermanium compound isolated was $n-Bu_4Ge_2I_2$, the probable structure of which is $Bu_2IGe-GeIBu_2$, from the reaction using $n-Bu_2Hg$. Mercury metal was also formed in this reaction. Ethyl-lithium reacted slowly, n-butyl-lithium reacted more quickly though no product was obtained.

The author suggested that any R_2Ge compound formed would complex with unreacted organo lithium reagent to give the complex R_3GeLi, with similar solubility properties to those of lithium iodide also produced in the reaction. However, hydrolysis of the reaction mixtures should have revealed the presence of any R_3GeLi compounds. A reaction was observed with the zinc alkyls, but attempted distillation of the reaction mixtures led to complete decomposition.

Gilman(76) obtained evidence that the equilibrium:

$$Ph_2Ge \ + \ PhLi \rightleftharpoons Ph_3GeLi$$
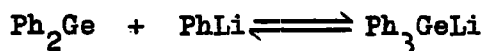
if it existed, must lie to the right, as carbonation of solutions of triphenylgermyl-lithium gave, not benzoic acid, but triphenylgermyl-carboxylic acid, $Ph_3GeCOOH$. Bromination gave hexaphenyldigermane and bromotriphenylgermane, and not dibromodiphenylgermane:

$$Ph_2Ge \ + \ PhLi \rightleftharpoons Ph_3GeLi \xrightarrow{Br_2} Ph_3GeBr \xrightarrow{Ph_3GeLi} Ph_6Ge_2.$$
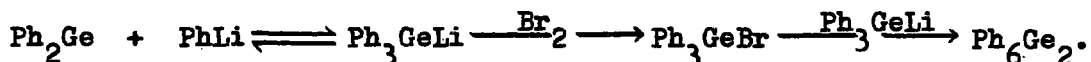
II).TIN(11).

Unlike germanium and lead there are several organo-tin(11) compounds described in the literature. Even so, there are associated with them some unusual and unexplained properties.

The first report of an organo-tin(11) compound was by Löwig(93) in 1852, who prepared diethyltin(11) by the reaction:

$$\begin{array}{l} Na-Sn \ + \ EtI \longrightarrow Et_2Sn \ + \ Et_3SnI \ + \ Et_6Sn_2. \\ alloy \end{array}$$
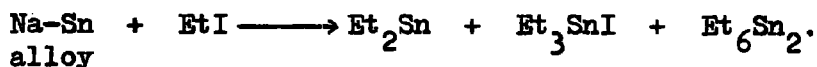
This reaction has been used by several workers to prepare corresponding alkyl compounds(94,95,96). The reaction probably involves the following steps(96):

$$2NaSn \ + \ 2RCl \longrightarrow R_2Sn \ + \ 2NaCl \ + \ Sn,$$

$$R_2Sn + RCl \longrightarrow R_3SnCl,$$

$$2R_2Sn \longrightarrow R_4Sn + Sn.$$
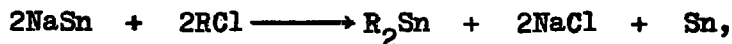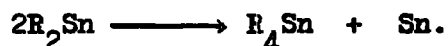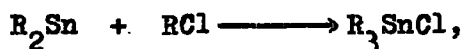
The distannane obtained by Löwig is presumably an intermediate decomposition product of R_2Sn to R_4Sn.

A much used method for the preparation of both alkyl- or aryl-tin(11) compounds has been the Grignard synthesis:

$$RMgX + SnCl_2 \xrightarrow[\text{or benzene/ether}]{\text{ether, T.H.F.}} R_2Sn.$$
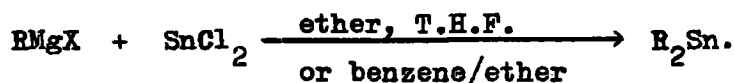
Diethyltin(11)(97), diphenyltin(11)(98), dicyclohexyltin(11)(99) and diphenathyl-9-tin(11)(100) have been prepared by this method. Diphenyltin(11) prepared by this method is initially monomeric in freezing benzene but slowly polymerises.

Organo-lithium reagents can be used instead of Grignard reagents, but there is a tendancy for the reaction:

$$R_2Sn + RLi \longrightarrow R_3SnLi,$$
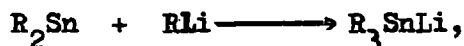
to occur(101). Diphenyltin(11) prepared by these methods is a bright yellow non-crystalline solid, and can only be purified by precipitation from chloroform solution with methanol.

The reduction of a dihalo-organo-tin compound with zinc,

$$Et_2SnCl_2 + Zn \longrightarrow Et_2Sn + ZnCl_2, \quad (102);$$
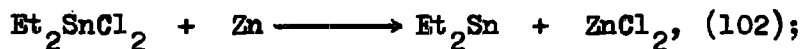
or better with sodium in liquid ammonia(103,104),

$$R_2SnX_2 + 2Na \longrightarrow R_2Sn + 2NaX,$$

has been used to prepare organo-tin(11) compounds. With excess sodium in the second reaction further reaction can occur to give R_2SnNa_2. Diphenyltin(11), even when freshly prepared by this method is polymeric.

The decomposition of diphenylstannane was found to proceed at room

temperature according to the equation:

$$Ph_2SnH_2 \longrightarrow Ph_2Sn + H_2,$$

Diphenyltin prepared by this method is monomeric(103). The tin hydride was prepared by the reduction of dichlorodiphenyltin with sodium in liquid ammonia:

$$Ph_2SnCl_2 + 4Na \longrightarrow Ph_2SnNa_2 + 2NaCl \xrightarrow{2NH_4Br} Ph_2SnH_2.$$

The bulk of the ammonia was allowed to evaporate and ether was added, evolution of hydrogen occurred and the solution turned yellow, from which was isolated diphenyltin(11).

Sawyer and co-workers(105) prepared several modifications of diphenyltin(11) by the decomposition of diphenylstannane in the presence of various reagents, for example diethylamine and methanol. The stannane was isolated in a pure form by the lithium aluminium hydride reduction of dichlorodiphenyltin, and low temperature crystallization. All the decompositions and interconversions were carried out at room temperature. The following system was established:

$$Ph_2SnCl_2 + LiAlH_4 \xrightarrow{\text{ether}} Ph_2SnH_2 \xrightarrow{\text{diethylamine}} (Ph_2Sn)_n$$

$$n=8$$

Modification A

Methanol

$$(Ph_2Sn)_n$$

$$n=6$$

Dimethyl-

Formamide

Modification B

$$SnCl_2 + 2PhLi \longrightarrow (Ph_2Sn)_n \xrightarrow[\text{Slow.}]{\text{Dimethyl-Formamide,}} (Ph_2Sn).$$

$$n=8$$

Modification C

$$\text{Modification B} \xrightarrow{\text{Dimethyl-Formamide.}} \text{Modification C}$$

Modification C was a colourless crystalline material which could be recrystallised from toluene, with solvent of crystallisation.

Similar results have been obtained by Neumann and König(106) who proposed cyclic structures for the products obtained by decomposition of diphenylstannane in dimethyl-formamide or pyridine. The following scheme was suggested:

$$Ph_2SnH_2 \xrightarrow[\text{at } 20°.]{\text{Dimethyl-Formamide}} 5H_2 + (I)$$

(I)

$$Ph_2SnH_2 \xrightarrow{\text{Methanol}} H-(Ph_2Sn)_6-H$$

$$\xrightarrow{\text{Pyridine}}$$

Pyridine at 20°.

(II)

Compounds I and II were obtained as crystalline materials from toluene, but containing solvent of crystallization, which could be removed by heating under vacuum. These compounds, as formulated, are Sn(1V) and not Sn(11) compounds. These authors also report that diphenyl-tin, prepared by the reaction of phenyl-lithium with tin(11)chloride, is not homogeneous and contains Ph_3Sn-, and $PhSn-$ groups in addition to Ph_2Sn- groups.

Properties of Organo-Tin(11) Compounds.

Alkyl- and aryl-tin(11) compounds, with the exception of bis(cyclo-pentadienyl)tin(11) (107), are deeply coloured in the range yellow to red. Solutions in benzene or chloroform are similarly coloured.

Diphenyltin(11), when freshly prepared by the Grignard method is mono-meric in freezing benzene but slowly polymerises with time to n $\rangle$ 5. This polymerisation was studied by Jensen and Clauson-Kaas(108), who reported that at all stages of the polymerisation diphenyltin(11) is diamagnetic and has a dipole moment of approximately 1 Debye. The actual mechanism of polymerisation is in some doubt(108,109).

Oxidation and halogenation, to give the corresponding tin(1V) com-pound proceeds rapidly:

$$2R_2Sn + O_2 \longrightarrow 2R_2SnO,$$

$$R_2Sn + X_2 \longrightarrow R_2SnX_2, \quad (98,99,102,103).$$
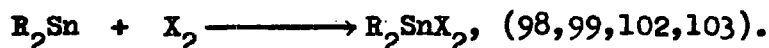
Diethyltin(11) is similarly oxidized by mercury(11) compounds(110):

$$Et_2Sn + HgCl_2(Ph_2) \longrightarrow Et_2SnCl_2(Ph_2) + Hg.$$

Dimethyltin(11) undergoes an interesting reaction with sodium in liquid ammonia(104), the ultimate product is dimethylstannylene-disodium:

$$Me_2Sn + 2Na \longrightarrow Me_2\underset{Na}{Sn}\text{---}\underset{Na}{Sn}Me_2 \xrightarrow{2Na} 2Me_2SnNa_2.$$
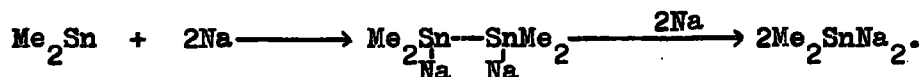
It was observed that dimethyltin(11) reacted with the product:

$$Me_2Sn + Me_2SnNa_2 \longrightarrow Me_2NaSn\text{-}SnNaMe_2$$

The addition of three mole equivalents of an organo lithium compound to stannous chloride gives the lithio-compound, R_3SnLi:

$$SnCl_2 + 2RLi \longrightarrow R_2Sn + 2LiCl,$$

$$R_2Sn + RLi \longrightarrow R_3SnLi.$$
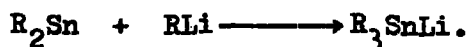
It has been suggested that the second stage of the reaction involves the equilibrium:

$$R_2Sn + RLi \rightleftharpoons R_3SnLi.$$
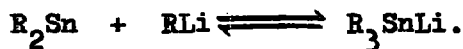
The evidence for this is based upon the reactions of solutions of R_3SnLi. All the results, however, are not completely compatible, but it is evident that the position of equilibrium can be displaced by the reagent used to give, as isolated products, compounds resulting from R_2Sn and RLi, or, alternatively R_3SnLi. Thus bromination of triphenylstannyl-lithium results in the displacement of the equilibrium in favour of diphenyltin(11) and phenyl-lithium, dibromodiphenyltin being isolated:

$$Ph_3SnLi \rightleftharpoons Ph_2Sn + PhLi \xrightarrow{Br_2} Ph_2SnBr_2, \quad (111).$$
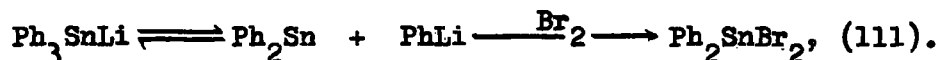
Carbonation, on the other hand, gave no benzoic acid, but lithium oxalate and hexaphenylditin(112,113,114).

$$2Ph_3SnLi + 2CO_2 \longrightarrow Ph_6Sn_2 + Li_2C_2O_4.$$

By contrast, the reaction of tri-n-butylstannyl-lithium with carbon dioxide indicates an equilibrium involving di-n-butyltin(11) and n-butyl-lithium(115):

$$\underline{n}\text{-Bu}_3SnLi \rightleftharpoons \underline{n}\text{-Bu}_2Sn + \underline{n}\text{-BuLi} \xrightarrow{CO_2} \underline{n}\text{-Bu}_2CO + \underline{n}\text{-BuCOOH}.$$

The reaction with chlorotrimethylsilane also suggests an equilibrium:

$$\underline{n}\text{-Bu}_3SnLi \rightleftharpoons \underline{n}\text{-Bu}_2Sn + \underline{n}\text{-BuLi} \xrightarrow{Me_3SiCl} \underline{n}\text{-BuMe}_3Si.$$
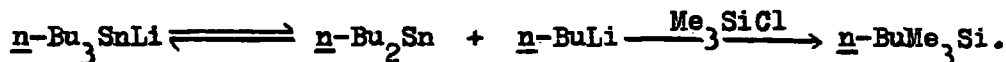
However, it was also reported that n-butyl iodide and iodobenzene react with tri-n-butyl-lithium in the normal way(115):

$$\underline{n}\text{-Bu}_3SnLi + \underline{n}\text{-Bu(Ph)}I \longrightarrow \underline{n}\text{-Bu}_3Sn\text{-}\underline{n}\text{-Bu(Ph)}.$$
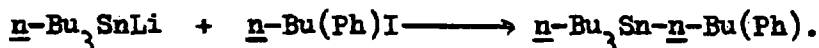
III).LEAD(11).

The first report of an organo-lead(11) compound was in 1922, when

Krause and Reissaus reported the preparation of diphenyl-lead(11) and di-o-tolyl-lead(11):

$$2PhMgBr + PbCl_2 \xrightarrow{\text{ether, 2°C}} Ph_2Pb + 2MgClBr.$$
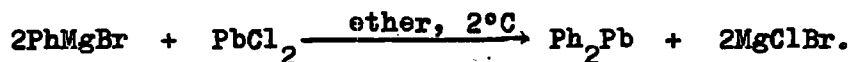
The authors reported a 4% yield of diphenyl-lead(11), which they described as a blood red amorphous solid, stable to water, though rapidly attacked by oxygen. The diphenyl-lead(11) decomposed from 100° and appeared to be monomeric in freezing benzene.

Since then, all attempts to repeat this work have met with failure (108,118), Krause and Reissaus themselves reported difficulty in duplicating their results. The bulk of the lead recovered from this reaction was in the form of tetraphenyl-lead, hexaphenyldilead and lead metal. Decreasing the temperature of the reaction below 0°, in an attempt to reduce decomposition, causes the reaction to proceeed at a negligible rate. Using ethereal phenyl-lithium instead of the corresponding Grignard reagent the reaction can be carried out at -10°, giving a bright yellow solution, in contrast to the reported colour of diphenyl-lead(11), without the separation of metallic lead. However attempts to isolate diphenyl-lead(11) from such reactions were unsuccessful(119).

Refluxing an ether/benzene solution resulting from the reaction of a Grignard reagent and lead(11)chloride, which presumably contains R_2Pb, causes the rapid production of lead metal, the reaction can be represented as:

$$3R_2Pb \longrightarrow R_6Pb_2 + Pb.$$
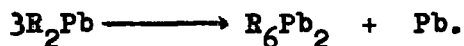
Continued refluxing often results in further decomposition with the formation of a R_4Pb compound:

$$2R_6Pb_2 \longrightarrow 3R_4Pb + Pb.$$
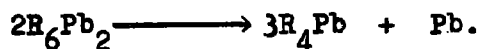
This reaction is the preferred method of preparation of R_6Pb_2 and R_4Pb

compounds(120). Brief refluxing of the reaction mixture resulting from

the interaction of phenyl-lithium and lead(11)chloride leads to the isolat-

ion of good yields of hexaphenyldilead(119).

The actual mechanisms of these decompositions are unkown.

The reaction between Pb(11)halides and phenyl-lithium in ether has

been proposed to involve the equilibrium:

$$Ph_2Pb + PhLi \rightleftharpoons Ph_3PbLi,$$
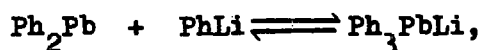
similar to that already discussed for the germanium and tin analogues.

The evidence for the presence of such an equilibrium was based on the

appearance of a positive Gilman colour test when more than 2.8 mole

equivalents of phenyl-lithium were used per mole of lead(11)chloride(119).

Hydrolysis of such solutions gave no diphenyl-lead, but a heavy precipitate

and a red-yellow ether solution. Furthermore Gilman(119) reported that

the yellow solutions resulting from the interaction of 2 mole equivalents

of phenyl-lithium with lead(11)chloride deposited lead rapidly on warming,

whereas similar solutions involving 3 mole equivalents of phenyl-lithium

were stable. This presumably implies that the equilibrium, under these

conditions ,lies to the right.

In contrast to ether, the use of tetrahydrofuran as solvent greatly

facilitates the reaction between phenyl-lithium and lead(11)halides, the

reaction being rapid at -40°, giving, using 2 or 3 mole equivalents of

phenyl-lithium, yellow-green solutions, without the separation of lead

metal(85). Hydrolysis of these solutions gave, as Gilman observed(119),

a copious yellow precipitate of lead oxide bromide, $\left[3PbO,PbBr_2\cdot(1-3H_2O)\cdot\right]$,
together with a trace of hexaphenyldilead. This behaviour is compatible
with the equilibrium suggested by Gilman and co-workers, but also implies
that diphenyl-lead(11) is highly susceptible to hydrolysis:

$$Ph_3PbLi \rightleftharpoons PbPh_2 + PhLi \xrightarrow{H_2O} LiOH + C_6H_6 + Pb(OH)_2\cdot$$
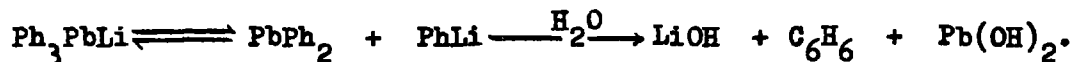
It was reported that $Pb(OH)_2$ reacts with $MgBr_2$ in tetrahydrofuran to
give, after hydrolysis, a basic lead bromide.

The isolation of small quantities of hexaphenyldilead without the
production of lead metal may be accounted for by hydrolysis of undissociat-
ed triphenyl-lead lithium, followed by decomposition of the hydride:

$$Ph_3PbLi \xrightarrow{H_2O} Ph_3PbH \left\langle \begin{array}{l} \rightarrow Ph_6Pb_2 + H_2 \quad (A) \\ \xrightarrow{O_2} Ph_6Pb_2 + H_2O \quad (B). \end{array} \right.$$
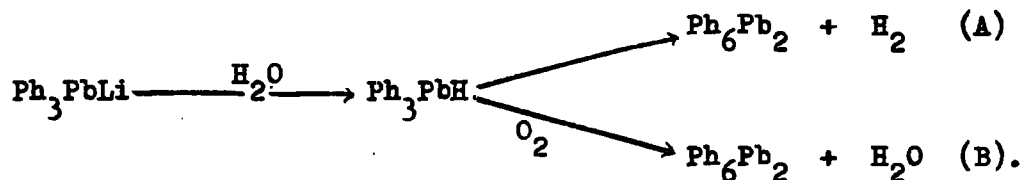
From the hydrolysis of triphenyl-lead lithium it was shown that no hydro-
gen was obtained, and appreciable yields of hexaphenyldilead were obtained
only in the presence of air, suggesting route (B).

The reaction between equi-molar amounts of phenyl-lithium and lead(11)
bromide in tetrahydrofuran(85), caused solution of only part of the lead
(11)bromide. Treating the organic solution with benzyl chloride led to
the isolation of benzyltriphenyl-lead. The authors suggest that the initial
reaction:

$$PbBr_2 + PhLi \longrightarrow PbPhBr,$$
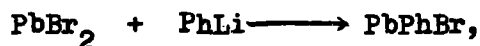
is slow, and that phenyl-lead(11)bromide reacts rapidly to give diphenyl-
lead(11), which is postulated, even under these conditions, to be in
equilibrium with triphenyl-lead lithium:

$$Ph_2Pb \; + \; PhLi \rightleftharpoons Ph_3PbLi \xrightarrow{\;PhCH_2Cl\;} Ph_3PbCH_2Ph.$$

This behaviour is in contrast to that reported by Gilman(119) who found that carbonation of reaction mixtures resulting from the interaction of lead(11)chloride with 2 equivalents of phenyl-lithium in ether, gave no benzoic acid, whereas using 2.6 or 3 equivalents moderate yields of benzoic acid were obtained. This was suggested to show that the equilibrium only came into operation when complete conversion to diphenyl-lead had occurred.

The reaction between lead(11)bromide and phenyl- or mesityl-magnesium bromide in tetrahydrofuran was reported to behave essentiallyin the same manner, except that a more distinct change of colour was observed. The reaction mixture changes from yellow to red-brown as 1 to 3 mole equivalents of Grignard reagent are added. Hydrolysis of these solutions gave no diphenyl- or dimesityl-lead(11), the bulk of the lead being recovered as the basic bromide, together with traces of hexaphenyldilead and tetramesityl-lead respectively.

Part E of this thesis is concerned with the reaction of mesityl-magnesium bromide with lead(11)bromide.

$\underline{Bis}$(cyclopentadienyl)lead(11), $(C_5H_5)_2Pb$, has been prepared recently by the reaction of cyclopentadienylsodium, C_5H_5Na, with lead(11)chloride in liquid ammonia(128), or with lead(11)nitrate(129). It is described as a yellow diamagnetic solid (m.p 132-135°), insoluble in water but soluble in organic solvents. Fischer and Grubert(129) report that it is not a "sandwich" molecule but contains homopolar bonds and is thus an authentic organo-lead(11) compound.

F). Compounds of the Type $(SiR_2)_n$.

In 1921 Kipping and Sands(130) reacted dichlorodiphenylsilane with sodium in refluxing xylene and obtained the following products, all of which were empirically Ph_2Si, though varied in their degree of polymerisation:

COMPOUND A. This material crystallized out from the reaction mixture during the reaction and was sparingly soluble in toluene. No molecular weight data were obtained because of its insolubility. This compound underwent a rapid reaction with iodine, indicating unsaturation, to give $Si_4Ph_8I_2$ and the structure of compound A was suggested to be

....$SiPh_2$.$SiPh_2$.$SiPh_2$.$SiPh_2$....
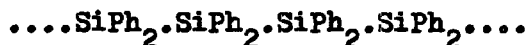
containing trivalent terminal silicon atoms to account for the unsaturated nature. Compound A was attacked by boiling nitrobenzene to give the oxide $Si_4Ph_8O_2$, whereas the monomeric iodide afforded the monomeric oxide, $Ph_2\overline{Si.Ph_2}Si-O-SiPh_2$.$SiPh_2$,on hydrolysis.

COMPOUND B. This material was tetrameric in benzene and was unattacked by iodine, and is thus "saturated". It was suggested that it was most likely to be octaphenylcyclotetrasilane:

$$
\begin{array}{ccc}
Ph_2Si & \!\!\!\!-\!\!\!\!- & SiPh_2 \\
| & & | \\
Ph_2Si & \!\!\!\!-\!\!\!\!- & SiPh_2
\end{array}
$$
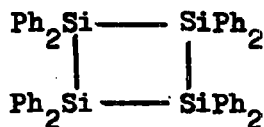
This compound should be compared to the germanium analogue(page 38).

The majority of the silicon was recovered in the form of a polymeric resin of high molecular weight (1500), corresponding to approximately 8 Ph_2Si units. This material was attacked but slowly by bromine, inferring a very low degree of unsaturation.

The reaction of dichlorodimethylsilane with sodium in benzene has been reported to give as a crystalline product, the hexamer $(SiMe_2)_6$, presumably of cyclic structure. Again the bulk of the silicon was recovered in a highly polymeric form, $(SiMe_2)_{55}$. The reaction was carried out in an autoclave(131).

G). <u>Nitrogen and Phosphorus containing compounds of Silicon, Germanium, Tin and Lead.</u>

1) <u>Silicon.</u>

   a) <u>ORGANO-SILYLAMINES.</u>

Organo-silylamines, in which an organo-silane is linked co-valently to nitrogen have been known for a number of years, e.g $(Me_3Si)_2NH$ and Me_3SiNEt_2 (143,144,145).

A common method of preparation is the direct interaction of the organo-silyl halide and the appropiate amine in ether, benzene or carbon tetrachloride solution.

$$2Me_3SiCl + 3NH_3 \longrightarrow (Me_3Si)_2NH + 2NH_4Cl.$$
$$Me_3SiCl + 2NHEt_2 \longrightarrow Me_3SiNEt_2 + Et_2NH_2Cl. \quad (143,144,145).$$
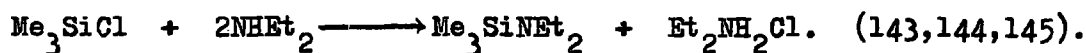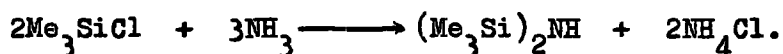
Trimethylsilylamine, Me_3SiNH_2, is an intermediate in the first reaction, but it rapidly condenses with the elimination of ammonia to give hexamethyldisilazane, $(Me_3Si)_2NH$. As one would expect, increasing the size of the organic group on either the silicon or the nitrogen atom tends to reduce the ease with which this elimination reaction can occur, thus:

$$\underline{n}-Pr_3SiCl + NH_3 \longrightarrow \underline{n}-Pr_3SiNH_2 + NH_4Cl.$$
$$Me_3SiCl + PhNH_2 \longrightarrow Me_3SiNHPh + PhNH_3Cl. \quad (145).$$
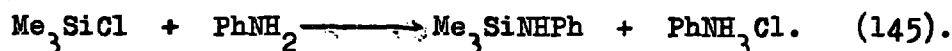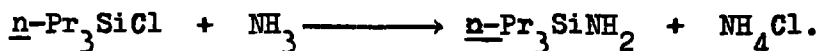
The reaction between R_3SiX and an amine is reversible, and usually

the amine hydrochloride can be removed by filtration, thus displacing the equilibrium. If, however, the reaction solution is heated,then it is possible to effect reversal of the reaction by distilling off the amine or the organo–silyl halide(145,146).

Dialkylsilyl halides react with amines to give the initial product $(alkyl)_2Si(NR'R'')_2$, R',R'', = alkyl or H. This can then condense to give cyclic polymeric products, as indicated by the reaction of dichlorodimethylsilane with ammonia(147):

hexamethylcyclotri-
silazane.

octamethylcyclotetra-
silazane.
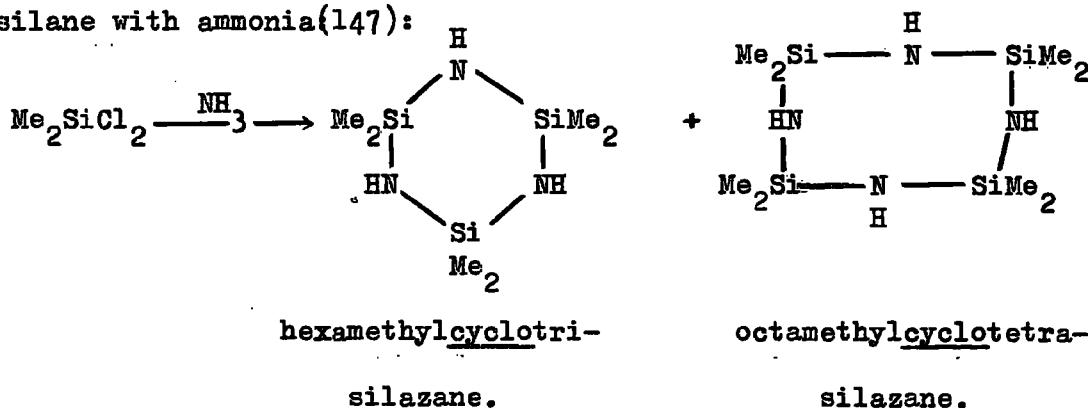
Large organic groups attached to either the silicon or the nitrogen atom again reduces the possibility of polymer formation. Thus dichloro-dimethylsilane and methylamine give essentially $Me_2Si(NHMe)_2$ (148).

The reaction of metal amides with either silanes or halosilanes has been used to prepare silylamines and silazanes:

$$2Ph_3SiH + NH_3 \xrightarrow{\text{NaNH}_2} (Ph_3Si)_2NH + 2H_2 \quad (149).$$

$$Ph_3SiCl + LiNBu^n_2 \xrightarrow{\text{Et}_2O} Ph_3SiNBu^n_2 + LiCl \quad (150).$$
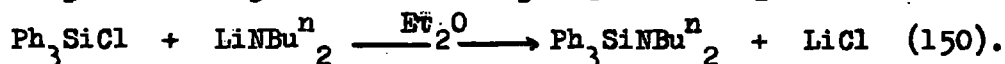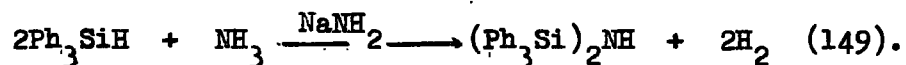
The replacement of an amino group attached to silicon by one containing larger organic groups can be effected by heating the reactants together:

$$Et_3SiNH_2 + RNH_2 \longrightarrow Et_3SiNHR + NH_3, \quad R = Bu^n, Ph. \quad (151).$$
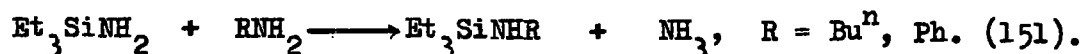
Properties of Organo-Silylamines.

Organo-silylamines are thermally stable liquids or solids,
$(Me_2SiNH)_4$, b.p 225°; $EtSi(NHPh)_3$, b.p 381°, $(Me_2SiNPh)_3$, m.p 250°.

The silicon-nitrogen bond is readily attacked by water or alcohol
to give the parent amine and the silanol (or alkoxy compound):

$$Et_3SiNH_2 + H_2O \longrightarrow Et_3SiOH + NH_3 \qquad (152),$$

$$\underline{n}-Pr_3SiNHPr^n + MeOH \longrightarrow \underline{n}-Pr_3SiOMe + H_2NPr^n \quad (153).$$
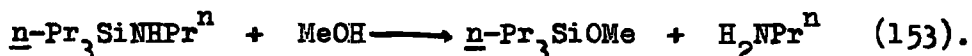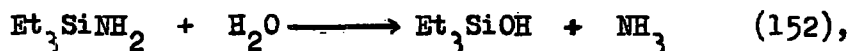
However, in some cases the silylamines appear to be unattacked by water
or alkali, because of their low solubilities. Addition of sufficient
methanol to effect solution usually results in rapid hydrolysis, e.g
hexamethyldisilazane(144).

Halogen acids cleave the silicon-nitrogen bond:

$$EtSi(NHPh)_3 + 6HI \longrightarrow EtSiI_3 + 3NH_3PhI \quad (154),$$
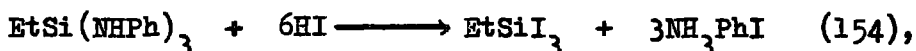
as also does hydrogen sulphide or hydrogen cyanide:

$$3Et_3SiNH_2 + 2H_2S \longrightarrow Et_3SiSH + (Et_3Si)_2S + 3NH_3 \quad (154),$$

$$(Me_3Si)_2NH + 3HCN \longrightarrow 2Me_3SiNC + NH_4CN \qquad (155).$$

The reaction between carbon dioxide or carbon disulphide and organo-
silylamines proceeds rapidly at room temperature to give silyl dialkyl-
carbamates or thiocarbamates:

$$Me_3SiNEt_2 + CX_2 \longrightarrow Me_3Si-X-\underset{X}{\overset{}{C}}-NEt_2, \qquad X = O,S.$$
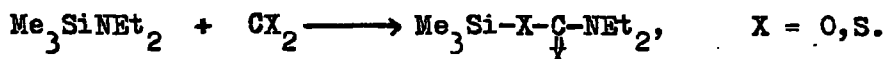
Traces of free amine are essential for the reaction to proceed, and the
mechanism:

$$CX_2 + HNEt_2 \longrightarrow HX\underset{X}{\overset{\shortparallel}{C}}NEt_2 ,$$

$$HX\underset{X}{\overset{\shortparallel}{C}}NEt_2 + Me_3SiNEt_2 \longrightarrow Me_3SiX\underset{X}{\overset{\shortparallel}{C}}NEt_2 + Et_2NH,$$
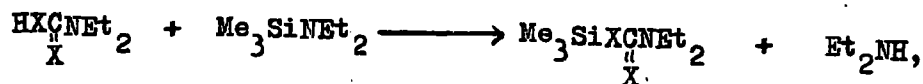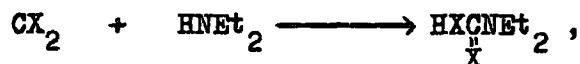
has been proposed(156).

Trimethylsilyldimethylamine gives a 1:1 adduct with methyl iodide, and is presumably trimethylsilyltrimethylammonium iodide, $Me_3SiNMe_3^+I^-$ (157).

b) ORGANO-SILYLPHOSPHINES.

The only organo-silylphosphine known is trimethylsilyldiphenyl-phosphine, $Me_3Si-PPh_2$ (158). It was prepared by the reaction of sodium diphenylphosphide with chlorotrimethylsilane:

$$Me_3SiCl \quad + \quad NaPPh_2 \xrightarrow{\text{ether}} Me_3SiPPh_2.$$
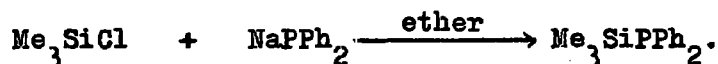
The product was isolated by distillation (b.p $126/10^{-1}$mm.) and under-went rapid hydrolysis with water:

$$Me_3SiPPh_2 \quad + \quad H_2O \longrightarrow Me_3SiOH \quad + \quad Ph_2PH.$$
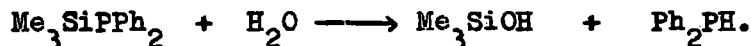
2) Germanium.

a) ORGANO-GERMYLAMINES.

The ammonolysis of organo-germanium halides of the type R_nGeX_{4-n}, X = halogen, n = 1,2,3, havebeen described on page 23 of this thesis.

A study of the reaction of germanium(1V)chloride with amines was made first in 1931 by Thomas and Southwood(159). Ethylamine afforded, as product, a substance of composition $GeCl_4 \cdot 6C_2H_5NH_2$ which was shown to be $Ge(NEt)_2 \cdot 4EtNH_3Cl$. Hydrolysis gave only ethylamine as product amine. In contrast aniline gave a solid of composition $GeCl_4 \cdot 4PhNH_2$, irrespective of which reactant was in excess. Extraction of this material with ether gave insoluble aniline hydrochloride and the soluble compound $Ge(NPhHCl)_2$. The reaction path was postulated to be:

$$GeCl_4 \quad + \quad 8PhNH_2 \longrightarrow Ge(NHPh)_4 \quad + \quad 4PhNH_3Cl.$$

$$Ge(NHPh)_4 \longrightarrow Ge(NPh)_2 \quad + \quad 2PhNH_2.$$

$$Ge(NPh)_2 \quad + \quad 2PhNH_3Cl \longrightarrow Ge(NPhHCl)_2 \quad + \quad 2PhNH_2.$$
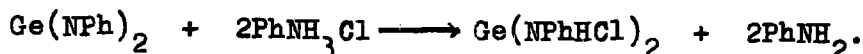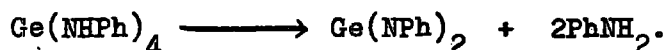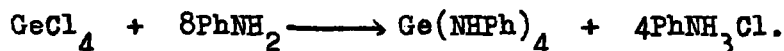
That the reaction involves the intermediate, <u>tetrakis</u>(phenylamino)germane, was suggested by the fact that piperidine gave the isolable product $Ge(NC_5H_{10})_4$ on reaction with germanium(1V)chloride.

Diethylamine was found also to undergo a complicated reaction with germanium(1V)chloride. The initial product, <u>tetrakis</u>(diethylamino)germane, underwent amine elimination, the product isolated was $Ge(NEt_2):NEt.HCl$; the reaction was carried out in ether solution. The reaction path

$$GeCl_4 + 8Et_2NH \longrightarrow 4Et_2NH_2Cl + Ge(NEt_2)_4$$

$$Ge(NEt_2)_4 \longrightarrow Ge(NEt)(NEt_2)_2 + NEt_3$$

$$Ge(NEt_2)_2:NEt + NH_2Et_2Cl \longrightarrow Ge(NEt_2)_2:NEt.HCl.$$
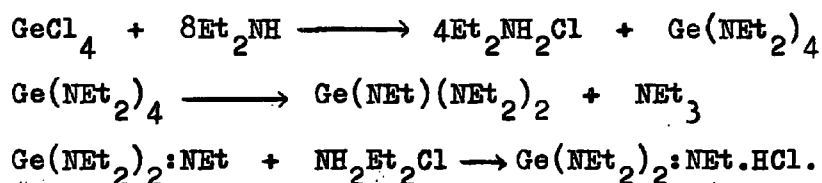
was suggested. Heating the reaction mixture to 85° <u>in vacuo</u> caused the elimination of a further molecule of amine, hydrolysis of the product gave only ethylamine as product amine:

$$Ge(NEt_2)_2:NEt.HCl \longrightarrow EtN:Ge:NEt.HCl + NEt_3$$
$$\downarrow HOH$$
$$EtNH_2.$$
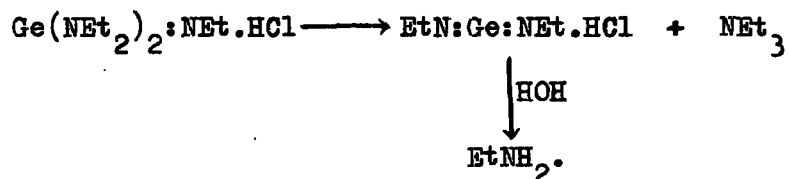
Some tertiary amines form adducts with germanium(1V)chloride, for example (pyridine)$_2$GeCl$_4$ (160), diethylaniline gives no such complex(159).

Trichloroethylgermane reacts with dimethylamine and diethylamine in petrol ether at -40° to give ethyl-<u>tris</u>(dimethylamino)germane and ethyl-<u>tris</u>(diethylamino)germane respectively:

$$EtGeCl_3 + Et_2NH \longrightarrow EtGe(NEt_2)_3 + Et_2NH_2Cl. \quad (161).$$
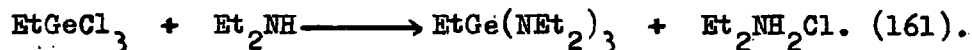
Under similar experimental conditions, the compounds <u>tetrakis</u>(diethylamino) germane and <u>tetrakis</u>(dimethylamino)germane, which had eluded Thomas and Southwood, were also prepared.

Properties of Organo-Germylamines.

As for the silicon analogues the metal-nitrogen bonds in organo-germylamines are rapidly cleaved by water, giving the parent amine and germanol (or germoxane).

Ethyl-tris(diethylamino)germane reacts with hydrogen iodide to give ethyltri-iodogermane and diethylamine(161):

$$EtGe(NEt_2)_3 \ + \ 6HI \longrightarrow EtGeI_3 \ + \ 3EtNH_2I.$$

b) ORGANO-GERMYLPHOSPHINES.

No organo-germylphosphines have been reported, and Part D of this thesis concerns the preparation and reactions of such compounds.

3) Tin.

a) ORGANO-STANNYLAMINES.

Tin(1V)chloride forms adducts with ammonia and amines, e.g $SnCl_4 \cdot 4NH_3$, which are stable and unlike the silicon and germanium analogues do not undergo further reaction with the rupture of tin-chlorine bonds and the formation of tin-nitrogen bonds.

It was not until recently that organo-tin compounds were prepared which contained tin-nitrogen bonds.

Organo-tin halides react with lithium amides to give organo-stannyl-amines (162,163,164). The complete series has been established:

$$R_{4-n}SnCl_n \ + \ nLiR'R''N \longrightarrow R_{4-n}Sn(NR'R'')_n,$$

$$R,R',R'' = alkyl \ or \ aryl$$

$$n = 1,2,3,4.$$
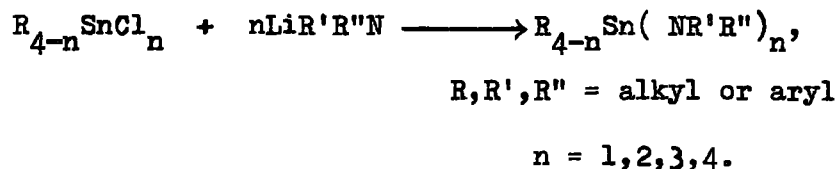
Bromotrimethylstannane has been reported to react with trimethylsilyl-ethylamine to give the corresponding stannylamine(162),

$$Me_3SnBr + EtNHSiMe_3 \xrightarrow{heat} Me_3SnNHEt + Me_3SiBr.$$
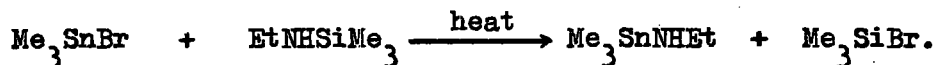
Transamination reactions have been used to prepare stannazanes

$$2Me_3SnNMe_2 + RNH_2 \longrightarrow (Me_3Sn)_2NMe,$$
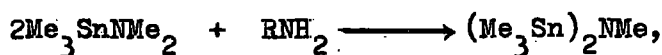
N methyl-hexamethyldistannazane

$$Me_2Sn(NMe_2)_2 + EtNH_2 \longrightarrow$$
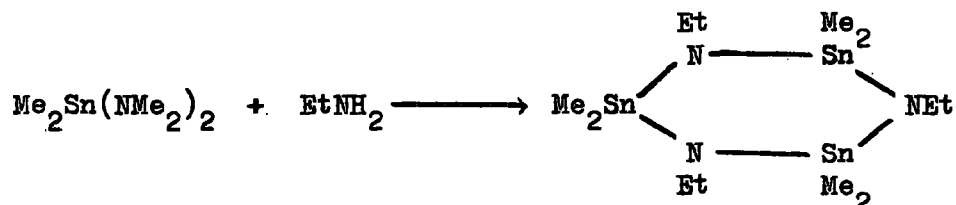
N,N',N" triethyl-hexamethyltristannazane

and <u>tris</u>(trimethylstannyl)amine,(163)

$$Me_3SnNMe_2 + NH_3 \longrightarrow (Me_3Sn)_3N.$$
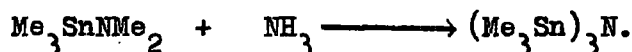
Properties of Organo-Stannylamines

Like the silicon and germanium analogues, stannylamines undergo rapid hydrolysis and are thermally stable.

Trimethylstannyldimethylamine undergoes a reaction, similar to the silicon analogue, with carbon dioxide and carbon disulphide to give a carbamate and thiocarbamate respectively;(163)

$$Me_3SnNMe_2 + CO_2 \longrightarrow Me_3Sn-OCONMe_2,$$

trimethylstannyl-dimethylcarbamate

$$+ CS_2 \longrightarrow Me_3SnSCSNMe_2$$
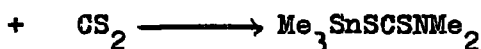
trimethylstannyl-dimethyldithiocarbamate

A similar reaction occurs with phenyl-<u>iso</u>-cyanate (163),

$$Me_3SnNMe_2 + PhNCO \longrightarrow Me_3Sn-\underset{Ph}{N}-\underset{O}{C}NMe_2.$$
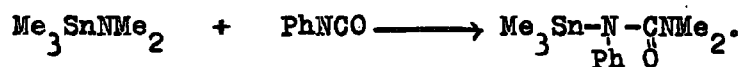
N,N dimethyl-N' phenyl-N' trimethylstannyl-

urea.

b) ORGANO-STANNYLPHOSPHINES.

The only organo-stannylphosphine known is triethylstannyldiphenylphosphine,

b.p 170-172/6mm. It was prepared by the interaction of chlorotriethyl-

stannane and sodium diphenylphosphide(158),

$$Et_3SnCl \ + \ NaPPh_2 \ \longrightarrow \ Et_3SnPPh_2 \ + \ NaCl.$$

4) Lead.

a) ORGANO-PLUMBYLAMINES.

Ammonia and amines react with lead halides to form adducts with retention

of the lead-halogen bonds, e.g $PbCl_4.3C_6H_5NH_2$. No compounds containing

lead-nitrogen bonds have as yet been prepared, and the same applies to

compounds containing lead-phosphorus bonds.

EXPERIMENTAL

PART A.   Triphenylgermyl Complexes of Copper, Silver and Gold.

1) <u>Reaction between triphenylgermyl-lithium and triphenylphosphine-monochlorogold(I)</u>.

To a vigorously stirred suspension of triphenylphosphinemonochloro-gold(I), (6.0g.,0.012 mole), in 1,2-dimethoxyethane,(75 cc.),was added dropwise,triphenylgermyl-lithium,(0.012 mole), in the same solvent,(40 cc.), A dense pale brown solid separated and, after 30 minutes, the reaction mixture was hydrolysed and the crude triphenylgermyl-triphenylphosphine-gold(I) separated. Purification was effected by recrystallisation from boiling benzene, to give colourless plates containing 1 mole of solvent; m.p 185° with complete decomposition. Yield = 5.1 g., 50%.

Found: C,60.8; H,4.7; Au,23.2; Ge,9.0;

$C_{42}H_{36}AuGeP$(i.e. $Ph_3Ge.AuPPh_3.C_6H_6$) requires: C,59.9; H,4.3; Au,23.4; Ge,8.6%.

The benzene of crystallisation was removed by heating <u>in vacuo</u>, 110°/10^{-3}mm.

Found: C_6H_6,9.4;

$C_{42}H_{36}AuGeP$ requires: C_6H_6,9.3%.

Recrystallisation from acetone gave the unsolvated compound as pale green crystals.

Found: C,56.9; H,4.5; Au,25.6;

$C_{36}H_{30}AuGeP$ requires: C,56.7; H,4.0; Au,25.8%.

2) <u>Reaction between triphenylgermyl-lithium and trimethylphosphine-monochlorogold(I)</u>.

To a vigorously stirred suspension of trimethylphosphinemonochloro-gold(I),(3.1 g., 0.01 mole), in 1,2-dimethoxyethane,(75cc.), was added

dropwise,triphenylgermyl-lithium, (0.01 mole), in the same solvent,(40 cc.).

The crude triphenylgermyl-trimethylphosphinegold(I) was removed by

filtration after hydrolysis and recrystallised from warm acetone,(N_2

atmosphere), giving colourless needles which decomposed without melting

at 125-130°. Yield = 3.4 g., 59%.

Found: C,44.7; H,4.1; Au,33.3;

$C_{21}H_{24}AuGeP$ (i.e. $Ph_3Ge.AuPMe_3$) requires: C,43.7; H,4.2; Au,34.2%.

Molecular weight determination,cryoscopically in benzene, gave:

M = 587 at 1.34 wt.%.

$C_{21}H_{24}AuGeP$ requires: M=577.

3) <u>Reaction between triphenylgermyl-lithium and triphenylphosphine-</u>

<u>monoiodosilver(I)</u>.

a) <u>In the presence of excess triphenylphosphine.</u>

To a vigorously stirred suspension of triphenylphosphinemonoiodosilver(I),

(5.0 g., 0.01 mole), in 1,2-dimethoxyethane,(100 cc.), was added triphenyl-

phosphine,(5.24 g., 0.02 mole), followed by triphenylgermyl-lithium,

(0.01 mole), in the same solvent,(40cc.). The resulting heavy brown

precipitate was filtered off under nitrogen and extracted at room tempera-

ture with 1,2-dimethoxyethane,(500cc.), in which it was almost completely

soluble, the residue was grey in colour. Evaporation of the filtrate to

half volume, under vacuum at room temperature, followed by cooling to -30°

overnight,gave triphenylgermyl-<u>tris</u>(triphenylphosphine)silver(I) as very

pale green crystals, m.p 167-170°(dec), containing 2 molecules of solvent

of crystallisation. Yield = 2.7 g., 19.5%.

Found: C,69.3; H,4.9; Ag,7.8;

$C_{80}H_{80}AgGeO_4P_3$ (i.e. $Ph_3Ge.Ag(PPh_3)_3.2C_4H_{10}O_2$) requires: C,69.7; H,5.8; Ag,7.8%.

The solvent of crystallisation was removed by heating the compound at 120° under vacuum and estimated as gas in a vacuum apparatus, characterisation was by infrared spectroscopy.

0.2153 g. compound gave 7.3 N.cc. of 1,2-dimethoxyethane, i.e.

$C_4H_{10}O_2$ = 13.6%,

$C_{80}H_{80}AgGeO_4P_3$ requires: $C_4H_{10}O_2$,13.1%.

Triphenylphosphine was estimated by sublimation under vacuum, (T = 110°; p = 10^{-3}mm.).

0.2153 g. compound gave 0.1304 g. of triphenylphosphine, i.e.

Ph_3P = 57.7%,

$C_{80}H_{80}AgGeO_4P_3$ requires: $C_{18}H_{15}P$,56.6%.

b) In the absence of excess triphenylphosphine.

To a vigorously stirred suspension of triphenylphosphinemonoiodosilver(I), (5 g., 0.01 mole), in 1,2-dimethoxyethane,(100 cc.), was added triphenyl-germyl-lithium,(0.01 mole), in the same solvent,(40 cc.). An exothermic reaction occurred with the production of a copious brown precipitate. After 1 hr the precipitate was removed by filtration under nitrogen and washed with a small volume of solvent, followed by drying under vacuum giving a brown powder,(5.7 g.), insoluble in all common solvents.

To 3.5 g. of this material, suspended in 1,2-dimethoxyethane, (200 cc.) was added triphenylphosphine,(2.6 g., 0.01 mole), and stirred overnight. The reaction mixture was transferred to a Schlenk tube and the unreacted material filtered off,(3.0 g.). Concentration of the pale yellow filtrate

to half volume under vacuum at room temperature, followed by cooling to

−30° gave pale green crystals, m.p 165−170°, identical to the triphenyl-

germyl-<u>tris</u>(triphenylphosphine)silver(1) previously prepared,(0.5 g.).

Found: Ag, 7.85;

$C_{80}H_{80}AgGeO_4P_3$ requires: Ag, 7.8%.

4)<u>Reaction between triphenylgermyl-lithium and triphenylphosphine-</u>

<u>monochlorocopper</u>(1).

a)   <u>In the presence of excess triphenylphosphine.</u>

To a vigorously stirred suspension of triphenylphosphinemonochloro-

copper(1), (3.6 g., 0.01 mole), in 1,2-dimethoxyethane, (100 cc.), was

added triphenylphosphine, (5.24 g., 0.02 mole), followed by triphenyl-

germyl-lithium, (0.01 mole), in the same solvent, (40 cc.), A lustrous

grey precipitate was formed which was removed by filtration under nitrogen.

Recrystallisation from 1,2-dimethoxyethane at room temperature (N_2

atmosphere) of this residue gave triphenylgermyl-<u>tris</u>(triphenylphosphine)

copper(1) in low yield, which was contaminated with traces of lithium

chloride, dec. 130° without melting.

Found: Cu, 5.4;

$C_{72}H_{60}CuGeP_3$ (i.e. $Ph_3Ge.Cu(PPh_3)_3$) requires: Cu, 5.5%.

The infrared spectrum of this compound did not indicate the presence of

solvent of crystallisation. Low yields of this compound were obtained

because of solubility properties similar to those of lithium iodide.

Triphenylgermyl-<u>tris</u>(triphenylphosphine)copper(1) was soluble in benzene,

but decomposition to give a green solution and a brown precipitate

rapidly occurred, even under an atmosphere of nitrogen.

b) <u>In the absence of excess triphenylphosphine.</u>

To a vigorously stirred suspension of triphenylphosphinemonochlorocopper(I),
(3.6g., 0.01 mole), in 1,2-dimethoxyethane,(100 cc.), was added dropwise
a solution of triphenylgermyl-lithium,(0.01 mole), in the same solvent,
(40 cc.). A heavy grey precipitate was formed which was removed by filtra-
tion under nitrogen and dried under vacuum,(6.3 g.). This material fumed
on exposure to the atmosphere,and could not be purified because of its
insolubility in all common solvents.

To 4.0 g; of this material, suspended in 1,2-dimethoxyethane,(50 cc.),
was added triphenylphosphine,(3.4g., 0.0127 mole), After stirring for
5 hrs at room temperature the insoluble material was removed by filtration,
the filtrate, on concentration and cooling, afforded triphenylgermyl-
<u>tris</u>(triphenylphosphine)copper(I),identical to that obtained above, in
small yield.

5) <u>The reaction between the triphenylgermyl- complexes and 1,2-di-
bromoethane.</u>

a) <u>Triphenylgermyl-triphenylphosphinegold(I).</u>

To triphenylgermyl-triphenylphosphinegold(I),(0.318 g., 0.416 mmole),
was added 1,2-dibromoethane,(20 cc.), in a slow stream of nitrogen,and the
reaction mixture slowly stirred with a mercury sealed stirrer. The emergent
gases were passed through two traps, the first at −78° and the second at
liquid air temperature. After 30 mins the reaction was complete, as
shown by complete dissolution of the triphenylgermyl-triphenylphosphine-
gold(I), and the contents of the second trap transferred to a vacuum
apparatus and purrfied by fractional condensation. The ethylene so obtained

was estimated,(7.1 N.cc., 75%), and identified by its infrared spectrum.

The clear, colourless 1,2-dibromoethane solution was evaporated under
vacuum and the residue extracted with hot ethanol, all being soluble.
Colourless needles of triphenylphosphinemonobromogold(I) weredeposited on
cooling; m.p 253-4°(dec). Yield = 0.13 g.,58%.

Found: C,39.5; H,3.1; Au,36.8,

$C_{18}H_{15}AuBrP$ requires: C,40.1; H,2.8; Au,36.6%.

The ethanol filtrate from above was evaporated under vacuum and the
residue sublimed.,(100°/10^{-3}mm), giving bromotriphenylgermane, m.p and
mixed m.p 134-6°.

b) <u>Triphenylgermyl-trimethylphosphinegold(I)</u>.

As described above,triphenylgermyl-trimethylphosphinegold(I),(0.26 g.,
0.452 mmole), gave ethylene,(5.5 N.cc., 55%), bromotriphenylgermane and
trimethylphosphinemonobromogold(I), m.p 214°; yield = 0.08 g., 50%.

Found: Au, 55.2,

C_3H_9AuBrP requires: Au,55.8%.

c) <u>Triphenylgermyl-tris(triphenylphosphine)silver(I) etherate</u>.

Triphenylgermyl-<u>tris</u>(triphenylphosphine)silver(I) etherate, (0.672 g.,
0.485 mmole), gave, in a similar reaction, ethylene,(7.2 N.cc., 66%),
and a clear reaction solution. Removal of the solvent under vacuum afforded
a white residue which, on extraction with petrol ether(40-60°), gave
bromotriphenylgermane m.p 134-136°. The part insoluble in petrol ether
was recrystallised from acetone to give colourless needles of <u>bis</u>(triphenyl
phosphine)monobromosilver(I), $(Ph_3P)_2AgBr$, which loses triphenylphosphine
at 179° with partial melting. Yield = 0.19g, 55%.

Found: C,60.5; H,3.4,

$C_{36}H_{30}AgBrP_2$ requires: C,60.7; H,4.2%.

d) <u>Triphenylgermyl-tris(triphenylphosphine)copper(I)</u>.

In a similar experiment, triphenylgermyl-tris(triphenylphosphine)copper(I),
(0.301 g., 0.263 mmole), gave ethylene,(1.7 N.cc., 29%), and a grey sticky
material as residue, after evaporation of the solvent under vacuum. This
residue was extracted with methanol and the part insoluble in methanol
was recrystallised from <u>n</u>-propanol and gave colourless crystals of <u>tris</u>(
triphenylphosphine)<u>bis</u>(monobromocopper(I)), $(Ph_3P)_3(CuBr)_2$, m.p 236-7°.
Yield = 0.07 g., 51%.

Found: C,59.5; H,4.7; Cu,12.1,

$C_{54}H_{45}Br_2Cu_2P_3$ requires: C,60.4; H,4.2; Cu,11.8%.

The fraction soluble in methanol gave some triphenylphosphine by sublimat-
ion and <u>bis</u>(triphenylgermyl)oxide, m.p 184-5°, by recrystallisation of
the residue from petrol ether(b.p 60-80°); strong Ge-O absorption occured
at 858cm^{-1} in the infrared spectrum.

Found: C,69.4; H,5.5,

$C_{36}H_{30}Ge_2O$ requires: C,69.3; H,4.8%.

The latter compound was presumably formed by hydrolysis of bromotriphenyl-
germane in the working-up process.

6) <u>Reaction between triphenylgermyl-triphenylphosphinegold(I) and</u>

<u>phenyl-lithium</u>.

Phenyl-lithium, (3.38 mmole), in ether was added dropwise to a vigorously
stirred suspension of triphenylgermyl-triphenylphosphinegold(I), (2.1 g.,
2.75 mmole), in ether,(50 cc.), The pale green suspension was slowly

replaced by a pale pink precipitate which, after 1 hr at room temperature, was removed by filtration in a Schlenk tube, washed with ether and dried under vacuum,(1.2 g.). Aerial hydrolysis of this very unstable compound gave lithium hydroxide, gold and hexaphenyldigermane, m.p 340°; its infrared spectrum showed the absence of triphenylphosphine (characteristic absorption at 1443, 541, 498cm^{-1}).

Found: Au,17.3; Li(as LiOH),0.62,

$C_{52}H_{70}AuGe_2LiO_4$ (i.e. Li$^+\left[(Ph_3Ge)_2Au\right]^-$.4Et$_2$O) requires: Au,17.8; Li,0.63%.

An ethanol solution of this ether complex,(0.4 g.), was added to solid tetraethylammonium iodide,(0.2 g.), and the colourless precipitate was removed and recrystallised from warm acetone, giving pale green plates of tetraethylammonium bis(triphenylgermyl)aurate(I), (0.3 g.).

Found: Au,20.8; Ge,15.6; C,56.7; H,5.6,

$C_{44}H_{50}Ge_2AuN$, (i.e. Et$_4$N$^+\left[(Ph_3Ge)_2Au\right]^-$) requires: Au,21.1; Ge,15.5; C,56.7; H,5.4%.

Tetraethylammonium bis(triphenylgermyl)aurate(I) is insoluble in water. It darkens rapidly above 150° and melts with complete decomposition at 195-200°.

The ethereal filtrate from the original reaction was treated with benzyl chloride,(0.36 g., 2.8 mmole), and the solvent removed under vacuum. Extraction of the oily residue with propanol gave triphenyl-phosphinemonophenylgold(I), (0.4 g.,29%), m.p 152°(dec).

Found: Au,36.0,

$C_{24}H_{20}AuP$ requires: Au,36.7%.

No benzyltriphenylgermane was isolated.

7) **The reaction between triphenylgermyl-triphenylphosphinegold(I)**

and triphenylgermyl-lithium.

Triphenylgermyl-lithium,(1.5 mmole), in 1,2-dimethoxyethane,(5 cc.), was added with vigorous stirring to a solution of triphenylgermyl-triphenyl-phosphinegold(I), (1.45 mmole), in the same solvent,(100 cc.). The white solid which separated rapidly was filtered and dried *in vacuo*, (1.3 g.). This complex, $Li^+[(Ph_3Ge)_2Au]^-$. $(CH_3OCH_2CH_2OCH_3)_4$, was rather more stable than the diethylether complex, but still decomposed rapidly on exposure to the atmosphere. The presence of 1,2-dimethoxyethane, and the absence of triphenylphosphine in this compound were established from its infrared spectrum, C-O-C present at $1123cm^{-1}$; the absorptions at 1443, 541, $498cm^{-1}$ characteristic of Ph_3P were absent.

Found: Au,16.5; Ge,11.7; Li,1.0,

$C_{52}H_{70}Ge_2LiO_8$ requires: Au,16.8; Ge,12.4; Li,0.59%.

The excess lithium in the compound is probably due to the presence of lithium methoxide, formed by the cleavage of 1,2-dimethoxyethane by Ph_3GeLi.

The filtrate from the reaction gave, after removal of the solvent under vacuum, and sublimation of the residue, triphenylphosphine,(0.311 g., 82%). The crude 1,2-dimethoxyethane complex gave, on treatment with Et_4NI, tetraethylammonium-bis(triphenylgermyl)aurate(I), identical to the product isolated from the preceeding experiment.

Found: Au,20.7; Ge,15.2%.

PART B. <u>Hexa-aryldigermanes</u>.

1) <u>The reaction between germanium(1V)chloride and phenylmagnesium
bromide in tetrahydrofuran</u>.

Germanium(1V)chloride,(10 g., 0.0467 mole),in tetrahydrofuran,(60 cc.),
was added over 10mins to a filtered solution(grade 4 sintered disc, see
figure I, page 68) of phenylmagnesium bromide prepared from bromobenzene,
(88 g., 0.56 mole), and magnesium,(15.6 g., 0.65 g.atom), in tetrahydro-
furan,(180 cc.). After refluxing for 18hrs the crude tetraphenylgermane
was separated by filtration, without hydrolysis,washed with dilute acetic
acid and recrystallised from toluene, m.p 237-8°. Yield = 15.3 g., 85%.
No hexaphenyldigermane was isolated.

2) <u>The reaction between germanium(1V)chloride and phenylmagnesium
bromide in toluene/ether</u>.

a) <u>Free magnesium present</u>.

Germanium(1V)chloride,(10 g., 0.0467 mole), in toluene,(110 cc.), was
added to a solution of phenylmagnesium bromide, prepared from bromobenzene,
(88 g.,0.56 mole), and magnesium, (15.6g.), in ether, (275 cc.), contain-
ing the unreacted magnesium. After refluxing for 4hrs the crude hexa-
phenyldigermane was removed by filtration, washed with dilute acetic acid
and dried. Recrystallisation from chloroform gave pure hexaphenyldigermane,
m.p 352-354°. Yield = 6.7 g., 49%.

The mother liquors gave, after hydrolysis, some tetraphenylgermane,
m.p 232-5°, <u>ex</u> toluene. Yield = 0.8 g., 4%.

b) In an analogous experiment the Grignard solution was passed through
a grade 4 sintered disc, giving a clear amber solution, to which was

N_2 INLET.

B.34.

SINTERED DISC (porosity 3).

N_2
. OUTLET

RECEIVER.

FIGURE I

added germanium(1V)chloride,(10 g., 0.0467 mole), in toluene,(110 cc.),

After refluxing for 5hrs the reaction mixture was filtered, no hexaphenyl-

digermane was isolated. The filtrate, after hydrolysis, and concentration,

gave tetraphenylgermane (ex toluene), m.p 233-5°. Yield = 12.8 g., 72%.

3) The reaction between benzylmagnesium chloride and germanium(1V)

chloride.

Free magnesium both present and absent.

To benzylmagnesium chloride, prepared from benzyl chloride,(65 g., 0.515

mole), and magnesium,(15 g.), in ether,(330cc.), was added germanium(1V)

chloride,(10 g., 0.0465 mole), in toluene,(100 cc.), either with or with-

out the separation of the excess magnesium metal. The reaction mixture

was refluxed for 8hrs and then hydrolysed with dilute acetic acid.

Separation of the organic layer and treatment in the usual way gave

tetrabenzylgermane, m.p 107-110°, (17.8 g., 88%), in both cases.

4) The reaction between p-tolylmagnesium bromide and germanium(1V)

chloride.

a) Magnesium present

p-Tolymagnesium bromide, from p-bromotoluene,(68 g., 0.4 mole), and

magnesium,(15 g.), in ether,(250 cc.), was treated with germanium(1V)

chloride,(10 g., 0.0465 mole), in toluene,(110 cc.), in the presence of

the unreacted magnesium metal. The reaction mixture was refluxed for 2hrs

and then hydrolysed with dilute acetic acid. The organic layer was separ-

ated, washed, dried and concentrated to low volume; crude hexa-p-tolyl-

digermane was separated by filtration and recrystallised from methylcyclo-

hexane, m.p 345°,(3.4 g.,21.6%). Distillation of the oily residue under

vacuum gave tri-p-tolylgermane,(4.5 g., 28%), b.p 160°/10⁻³mm., m.p 81°
(ex petrol ether, 40-60°).

Found: Ge,21.8,

$C_{21}H_{22}Ge$ requires: Ge,20.9%.

Strong Ge-H stretch occured at 2034cm⁻¹in the infrared spectrum. The resi-
due from the distillation gave some tetra-p-tolylgermane, m.p 224-5°,
which was recrystallised from petrol ether(80-100°).

b) Free magnesium absent.

In an identical reaction, but filtering the Grignard reagent through a
Grade 4 sintered disc prior to use, hydrolysis of the yellow solution,
followed by treatment of the organic layer in the usual way gave tetra-
p-tolylgermane, m.p 222-5°, (10.6., 52%), from petrol ether(80-100°).
Distillation of the mother liquors gave bromotri-p-tolylgermane, b.p
180°/10⁻³mm., m.p 121°(ex petrol ether, 40-60°).

5) The reaction between germanium(1V)chloride and p-tolylmagnesium
   bromide.

To a solution of p-tolylmagnesium bromide, prepared from p-bromotoluene,
(68 g., 0.398 mole), and magnesium,(15 g.), in ether,(280 cc.), containing
the excess magnesium was added germanium(1V)chloride,(10 g., 0.0465 mole),
in toluene,(110 cc.). After refluxing for 2hrs the resulting grey-brown
solution containing much suspended material was poured onto solid carbon
dioxide(N_2 atmosphere), and, after standing for 1hr the reaction mixture
was hydrolysed with water. Acidification of the aqueous layer gave only
p-toluic acid,(32.5 g.), m.p 179° ex petrol ether(80-100). The organic

layer was extracted with sodium hydroxide solution and this extract gave, on acidification, crude tri-p-tolylgermyl carboxylic acid(2.0 g.), from which p-toluic acid was separated by sublimation $(85°/10^{-3})$. The pure tri-p-tolylgermyl carboxylic acid, (0.4 g.), had m.p 141-3° with evolution of carbon dioxide(reduced $PdCl_2$ solution to Pd).

Found: C,67.2; H,5.7; Ge,18.4, equivalent weight,389.

$C_{22}H_{22}GeO_2$ requires: C,67.6; H,5.7; Ge,18.6, equivalent weight,391. The neutral organic layer, on concentration,gave crude hexa-p-tolyldigermane, recrystallised from toluene, m.p 345-50°, yield,3.0 g., 18%. Distillation of the mother liquors gave only 4,4'-dimethylbiphenyl, b.p 140-160°/10^{-3}mm. Extraction of the residue with petrol ether (80-100°) gave colourless crystals of tetra-p-tolylgermane, m.p 227-8°, yield,1 g., 5%.

6) The reaction between m-tolylmagnesium bromide and germanium(1V) chloride.

a) Free magnesium present.

m-Tolylmagnesium bromide, from m-bromotoluene,(68 g., 0.4 mole), and magnesium,(15 g.),in ether,(250 cc.), was treated in the presence of the unreacted magnesium with germanium(1V)chloride,(10 g., 0.0465 mole), in toluene,(110 cc.), and the mixture heated under reflux for 20hr. Hydrolysis of the viscous solution with dilute acetic acid gave, from the organic layer after concentration, crude hexa-m-tolyldigermane,which was recrystall-ised from methylcyclohexane. M.p 177-9°, yield,3.5 g.,21.5%.

Found: C,72.0; H,5.4; Ge,20.9,

$C_{42}H_{42}Ge_2$ requires: C,72.9; H,6.1; Ge,21.0%.

Distillation of the mother liquors gave,after a primary fraction of

3,3'-dimethylbiphenyl, b.p 140-160°/10^{-3}mm; tri-m-tolylgermane, b.p 160-

170°/10^{-3}mm., yield,6.0 g.,36.5%. The infrared spectrum showed strong

Ge—H absorption at 2034cm^{-1}.

Found: C,72.8; H,6.6; Ge,20.8,

$C_{21}H_{22}Ge$ requires: C,72.7; H,6.4; Ge,20.9%.

A higher boiling fraction(ca 210°/10^{-3}mm.) yielded, from petrol ether

(40-60°), tetra-m-tolylgermane, m.p 146-7°, yield,0.4 g.,2%.

b)Free magnesium absent.

In an identical experiment in which the m-tolylmagnesium bromide was fil-

tered prior to use through a Grade 4 sintered disc,was obtained, after

hydrolysis, tetra-m-tolylgermane, m.p 148-9° from petrol ether (40-60°).

Yield, 10.5 g., 52%.

Found: C,76.6; H,6.6,

$C_{28}H_{28}Ge$ requires: C,76.9; H,6.5%.

The material insoluble in petrol ether gave hexa-m-tolyldigermane from

methylcyclohexane, m.p 177-179°, yield, 1.0 g., 6%.

7) The reaction between o-tolylmagnesium bromide and germanium(1V)

chloride

a) Free magnesium present.

To a solution of o-tolylmagnesium bromide, prepared from o-bromotoluene,

(68 g., 0.398 mole), and magnesium,(15 g.), in ether,(275 cc.), containing

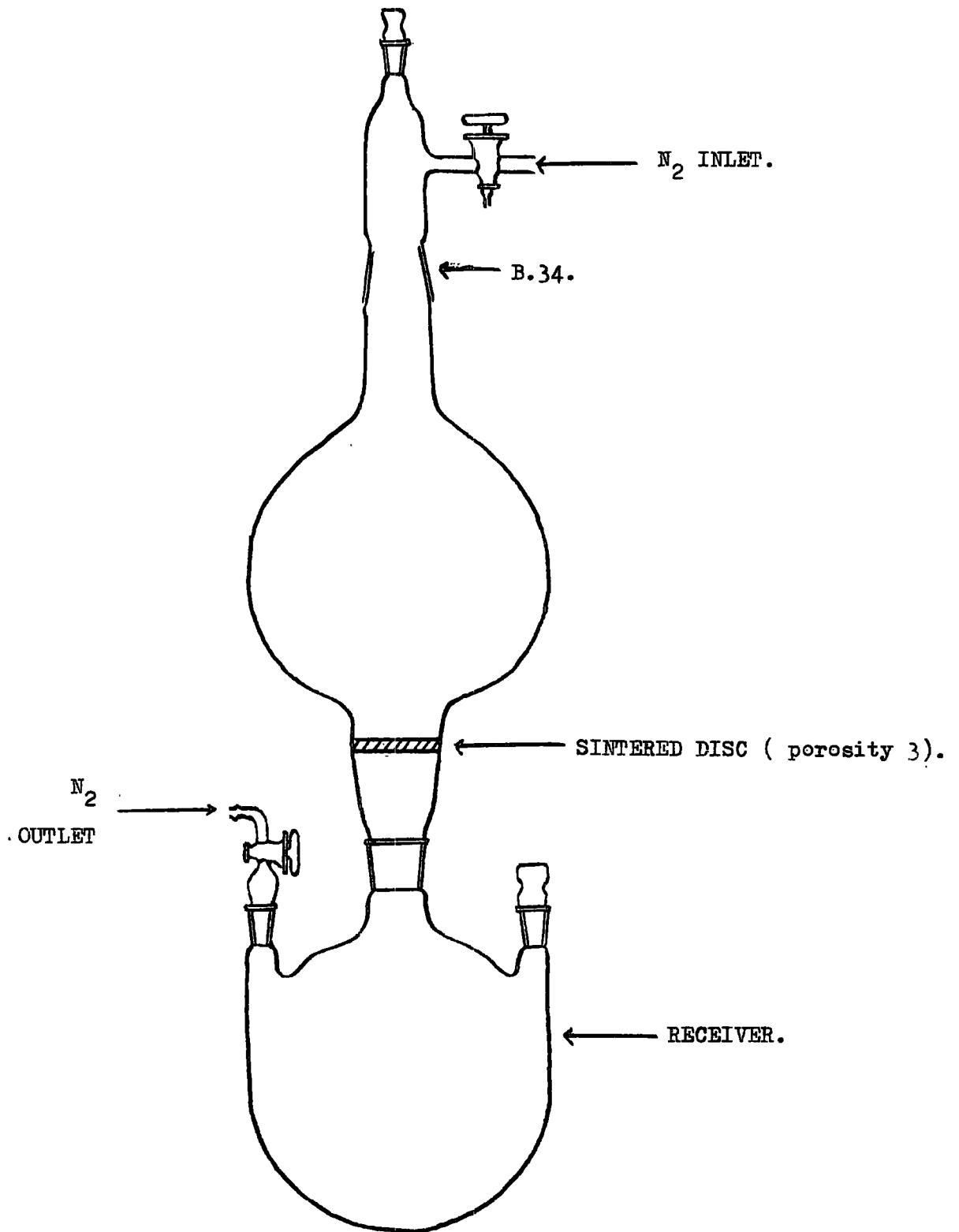the unreacted magnesium, was added germanium(1V)chloride,(10 g., 0.0465

mole), in toluene,(110 cc.). After refluxing for 24hrs. the reaction
mixture was hydrolysed with dilute acetic acid. The organic layer gave
hexa-o-tolyldigermane, which was recrystallised from methylcyclohexane,
m.p 268-70°, yield,3.0 g., 18%.

Found: C,72.7; H,6.7; Ge,21.4,

$C_{42}H_{42}Ge_2$ requires: C,72.9; H,6.1; Ge,21.0%.

Distillation of the mother liquors gave some 2,2'-dimethylbiphenyl, b.p
110/10^{-2}mm., the main fraction being tri-o-tolylgermane, b.p 140-60°/10^{-3}mm.,
which gave feathery needles, m.p 102-3° on recrystallisation from hexane.
Yield = 4.0 g., 24%.

Found: Ge,20.9,

$C_{21}H_{22}Ge$ requires: Ge,20.9%.

The infrared spectrum showed strong Ge-H absorption at 2034 cm^{-1}.

A higher boiling fraction, 180°/10^{-3}mm., consisting of bromotri-o-
tolylgermane,was obtained, m.p 118-20°, ex hexane.

b) Free magnesium absent.

An identical experiment was carried out, but using a filtered solution of
o-tolylmagnesium bromide. From the organic layer was obtained, after
hydrolysis and concentration, crude hexa-o-tolyldigermane, which was
recrystallised from methylcyclohexane, m.p 267-8°. Yield =2.0 g., 13%.
Distillation of the mother liquors gave, after a prerun of 2,2'-dimethyl-
biphenyl, only bromotri-o-tolylgermane, m.p 119-20°, ex hexane. Yield =
4.7 g., 24%.

Found: C,59.7; H,5.2,

$C_{21}H_{21}GeBr$ requires: C,59.2; H,5.0%.

8) <u>The attempted reduction of bromotri-o-tolylgermane.</u>

To bromotri-<u>o</u>-tolylgermane,(3.0 g.), in ether,(60 cc.), and toluene,(10 cc),
was added magnesium,(3 g.), followed by the dropwise addition of dilute
acetic acid. After 2hr the organic layer was separated and from it was
obtained the bromotri-<u>o</u>-tolylgermane unchanged. The infrared spectrum
showed no Ge-H absorption.

9) <u>The reaction between chlorotriphenylsilane and cyclohexylmagnesium
bromide.</u>

a) <u>Free magnesium present</u>.

Chlorotriphenylsilane,(14.7 g., 0.05 mole), which had been redistilled
under vacuum($180°/10^{-3}$mm.), in tetrahydrofuran,(155 cc.), was added to
<u>cyclohexylmagnesium</u> bromide, prepared from <u>cyclohexyl</u> bromide,(16.3 g.,
0.1 mole), and magnesium,(2.9 g.), in tetrahydrofuran,(100 cc.),containing
the unreacted magnesium. The mixture was refluxed for 20 hrs, after which
time a considerable amount of material was out of solution. Filtration
without hydrolysis gave crude hexaphenyldisilane, which was recrystallised
from xylene; m.p 365°, yield, 10 g., 75%.

b) <u>Free magnesium absent</u>.

In an analogous experiment, in which the Grignard reagent was filtered
through a Grade 4 sintered disc, was obtained, after refluxing for 20 hrs,
a clear amber coloured solution. The reaction mixture was hydrolysed with
dilute hydrochloric acid to p.H 6 at 0°. Some hexaphenyldisilane was
separated by filtration and recrystallised from xylene, 1.0 g., 7.8%.

The organic layer was separated, washed and dried, and the solvent removed. Recrystallisation of the residue from ether-hexane gave triphenyl-silanol, m.p 150-1°, yield, 6.0 g.,45%.

PART C Phenylgermanium polymers

1) Reaction between germanium(11)iodide and phenyl-lithium; isolation of Ph$_2$Ge$_2$I.

To a vigorously stirred suspension of germanium(11)iodide,(27.0 g., 0.083 mole), in ether,(100 cc.), was added ethereal phenyl-lithium,(0.279 mole), at -30°C. The resulting deep red solution was stirred for 1hr and then decanted from some red semi-solid material. The latter was washed twice with ether and dried under vacuum. The resulting material was transferred to a Schlenk tube and extracted with benzene,(10 cc.), the filtrate was evaporated to dryness under vacuum, furnishing a red-orange solid,(5.0 g.), which contained iodine and was free from lithium. Decomposition occurred from 198° without melting.

Found: C,32.3; H,2.1; Ge,34.7,

C$_{12}$H$_{10}$Ge$_2$I requires: C,33.8; H,2.4; Ge,34.0%; M,426.4.

Molecular weight determination in freezing benzene showed some association with increase in concentration:

Wt % Solute	M.	n in (Ph$_2$Ge$_2$I)$_n$
1.61	638	1.49
2.15	702	1.65
3.20	793	1.86

A known weight of this material was dissolved in benzene and dry oxygen passed through the solution,resulting in the rapid formation of a heavy yellow precipitate; the benzene was carefully removed under vacuum and the weight of the residue determined.

1.06751 g. material gave 1.10035 g; of oxidized product.

i.e. 0.41 g.atom of oxygen/g.atom of germanium was absorbed.

The product of oxidation showed strong Ge-O absorption in the region of

11.6μ in the infrared spectrum; contained iodine and melted over a range

from 194°.

Found: C,31.3; H,2.3; M(1,2-dibromoethane),3350.

$C_{12}H_{10}Ge_2IO$, i.e. Ph_2Ge_2IO, requires: C,32.6; H,2.3; M,442.

In a similar experiment the reaction mixture was maintained at -25°,

and benzyl chloride,(6.3 g., 0.05 mole), in ether,(40 cc.), was added

and then allowed to warm up to room temperature and heated at reflux for

6hrs. After hydrolysis the orange organic layer was separated and propanol

added, the latter causing the precipitation of a yellow solid which could

not be crystallised, and was purified by dissolving in benzene and pre-

cipitation from solution by the addition of methanol. The pale yellow

solid was filtered off,(9.0 g.), and was free from halogen and oxygen;

m.p 190-200°.

Found: C,53.1;H,4.1; Ge,39.3; M,1049(benzene); 2537(1,2-dibromoethane);

752(nitrobenzene).

C_6H_5Ge requires: C,48.2; H,3.3; Ge,48.5;

$C_{12}H_{10}Ge$ requires: C,63.6; H,4.4; Ge,32.0%.

No benzyltriphenylgermane was isolated, and distillation of the mother

liquors gave diphenylmethane,b.p 124°/10^{-2}mm., 261°/ atmos press., yield,

3.5 g., 0.021 mole.

2) Reaction between germanium(11)iodide and phenyl-lithium; isolation

of tetraphenylgermane.

To a stirred suspension of germanium(ll)iodide,(29.3 g.,0.09 mole), in
ether,(100 cc.), was added phenyl-lithium at room temperature. After 3
days at reflux the reaction mixture was filtered under nitrogen. The
residue was extracted with benzene,(20 cc.), giving a deep red filtrate,
from which was obtained by precipitation with methanol, a deep red-brown
solid,(1.0 g.), which decomposed at 285° without melting.

Found: Ge,49.0; C,43.6; H,3.2; M,(C_6H_6),1508;

C_6H_5Ge requires: Ge,48.5; C,48.2; H,3.3%. M,149.7.

The undissolved material was recrystallised from toluene giving tetra-
phenylgermane,(1.0 g.), m.p 236°.

The original filtrate was hydrolysed and the organic layer concen-
trated by distillation, a further quantity,(1.0 g.), of tetraphenylgermane
crystallised out on cooling. The mother liquors were evaporated to dryness
under vacuum and the residue dissolved in benzene,(10 cc.),from which was
precipitated, by the addition of methanol, a yellow solid,(4.2 g.);
m.p 188-200°.

Found: Ge,39.2; C,52.7; H,3.9;

C_6H_5Ge requires: Ge,48.5; C,48.2; H,3.3;

$C_{12}H_{10}$Ge requires: Ge,32.0; C,63.6; H,4.4%.

Distillation of the mother liquors gave no triphenylgermane; biphenyl,
which sublimed at $90°/10^{-3}$mm., 1 g., being the only material isolated.

   3) <u>Reaction between germanium(ll)iodide and phenyl-lithium: isolation</u>

      <u>of triphenylgermane</u>

To germanium(ll)iodide,(29.3 g.,0.09 mole), suspended in ether,(100 cc.),

was added ethereal phenyl-lithium,(0.36 mole), at room temperature. The
reaction mixture was refluxed for 5 days, followed by filtration under
nitrogen. The residue consisted of tetraphenylgermane,(2.5 g., ex toluene),
with only traces of the red-brown phenylgermanium. The reaction filtrate
was hydrolysed with water and the layers separated, the aqueous layer,
on titration, corresponded to 0.13 mole of phenyl-lithium. The organic
layer was distilled to low volume, and from this was precipitated, by
the careful addition of methanol, a red oil which was separated and
purified by reprecipitation, to give an orange solid,(1.8 g.), m.p 250-70°.

Found: Ge,45.7,

C_6H_5Ge requires: Ge,48.5,

$C_{12}H_{10}Ge$ requires: Ge,32.0%.

Molecular weight determination in freezing benzene showed some association
with increasing concentration:

Wt % Solute.	M.
2.27	1520
3.92	1730
6.2	1922.

Further precipitation from the original solution gave a cream coloured
solid,(2.7 g.), m.p 165-200°.

Found: Ge,36.8,

C_6H_5Ge requires: Ge,48.5,

$C_{12}H_{10}Ge$ requires: Ge,32.0%.

Attempted sublimation of the material gave no sublimate,($190°/10^{-3}$mm.),

both of the above compounds were free from halogen and oxygen. The infra-red spectra (10–15 mg. nujol mull) showed weak Ge–H absorption at $1969 cm^{-1}$.

Further concentration of the mother liquors gave, on cooling, tetraphenyl-germane,(0.5 g.), and distillation of the final solution under vacuum yielded, as main fraction, after a prerun of biphenyl($90°/10^{-3}$mm.,0.9 g.), triphenylgermane, b.p 137–45°/10^{-2}mm., which was recrystallised from methanol to give opalescent flakes, m.p 24°., yield,2.3 g., the infrared spectrum of which showed strong Ge–H absorption at 2030 cm^{-1}.

   4). <u>Bromination Degradation Studies</u>.

a) <u>In chloroform; isolation of bromo-organogermanes</u>.

To 1 g. of yellow polymeric material (found Ge,39.3%) in chloroform,(20cc.), was added astandard solution of bromine in the same solvent,(3.0 g./60cc.), in 2 cc. aliquots, each aliquot being added when the preceeding one had reacted. The reaction mixture was maintained at reflux point for 1 week, after which time 1.1 g.,(0.014 g.atom), of bromine had been absorbed, i.e. 2.58 g.atom of bromine/g.atom of germanium. The solvent was removed under vacuum at room temperature and the liquid residue distilled under vacuum, a main fraction, 1.4 g.,b.p 65–158°/10^{-1}mm., was collected which could not be fractionated and contained germanium and bromine. Extraction of the residue with hexane gave bromotriphenylgermane as fine feathery crystals, m.p 136°, 0.2 g.,

b) <u>In 1,2–dibromoethane; hydrolysis of the mixed bromo–organogermanes</u>.

1.5 g. Of material, identical to that used in a) was brominated in 1,2–di-bromoethane, in a manner identical to that described above. After 1 week at

room temperature 1.84 g. of bromine had been added, though traces of free
bromine remained in solution, i.e. 2.9 g.atom of bromine/g.atom of german-
ium. The reaction mixture was hydrolysed with aqueous sodium hydroxide
(10%), and the organic layer separated. Acidification of the aqueous
layer gave a light buff coloured precipitate which was removed by filtrat-
ion and dried under vacuum,(0.3 g.), m.p 360°.The infrared spectrum showed
strong Ge-O absorption and the presence of phenyl groups.

Found: C,38.4; H,2.8,

$C_6H_5GeO_{1.5}$, i.e. phenylgermanoic anhydride requires: C,41.5; H,2.9%.
No pure compound was obtained from the organic layer.

c). <u>In 1,2-dibromoethane; followed by ethylation.</u>

The room temperature bromination of 3.0 g. of polymer(Ge,39.3%) was carried
out as described above; 2.85 g. of bromine being absorbed after 1 week,
corresponding to 2.33 g.atom of bromine/g.atom of germanium. The reaction
mixture was evaporated at room temperature under vacuum to low bulk(5-10cc),
and the residue added as a benzene solution,(15 cc.),to an ethereal solution
of ethylmagnesium bromide,(0.1 mole),which had been filtered through a
grade 4 sintered disc. The reaction mixture was refluxed for 3hrs and then
hydrolysed with dilute acetic acid. The organic layer was separated, washed,
dried and the ether removed by distillation. Vacuum distillation of the
residue gave the following fractions, the volatile components of which
were characterised by vapour phase chromatography:

FRACTION 1. b.p. 57-63°/50mm., 0.3 g., 1,2-dibromoethane.

FRACTION 2. b.p. 154-56°/45mm., 0.8 g., 1,2-dibromoethane(25%),

tetraethylgermane(trace) and triethylphenylgermane(75%).

FRACTION 3. b.p. 98–138°/0.03mm., 0.4 g., diethyldiphenylgermane(70%); ethyltriphenylgermane(30%) as residue.

FRACTION 4. b.p. 138–176°/0.01mm., 0.5 g., recrystallised from iso-propanol giving ethyltriphenylgermane, m.p 74–6°.
Extraction of the residue from the distillation with boiling propanol gave, on cooling, colourless crystals which were recrystallised from the same solvent, 0.1 g., m.p 122–4°. The infrared spectrum showed both aliphatic and aromatic C–H absorption.

Found: C,64.9; H,6.4; M(camphor)491,

$C_{28}H_{30}Ge_2$, i.e. $Ph_4Ge_2Et_2$ requires: C,65.9; H,5.9%. M,511.
No bromobenzene or ethylbenzene was isolated.

d). Partial bromination in 1,2-dibromoethane.
To 1.3 g. of polymer(Ge,36.8%) in 1,2-dibromoethane,(20 cc.), was added bromine,(0.5 g.). A rapid reaction occurred at room temperature, and was complete after 3hr; i.e. 0.94 g.atom of bromine/g.atom germanium. The resulting solution was evaporated to low bulk under vacuum, and the residue added as a benzene solution,(10 cc.)to ethylmagnesium bromide,(0.1 mole). After 6hr at reflux the reaction mixture was hydrolysed and the organic layer evaporated under vacuum to give a pale yellow oil which could be purified only by precipitation from a benzene solution by the addition of methanol, to give a cream solid,(0.5 g.), m.p 150–200°, the infrared spectrum of which showed both aliphatic and aromatic C–H absorption; and no sublimate was obtained by heating under vacuum$(180°/10^{-3})$.

e) <u>Bromination of hexaphenyldigermane in 1,2-dibromoethane.</u>

To hexaphenyldigermane,(2.0 g., 0.0033 mole), in 1,2-dibromoethane,(20cc.), was added,in a manner identical to that employed for the bromination of the yellow phenylgermanium polymers, bromine,(0.75 g., 0.00469mole), in the same solvent,(4.0 cc.). After 1 week at room temperature free bromine was still present in solution. The bulk of the solvent was removed under vacuum at room temperature, and the residue added as a benzene solution, (15 cc.), to an ethereal solution of ethylmagnesium bromide,(0.1 mole). The reaction mixture was refluxed for 8hrs and worked up in the usual way. Distillation gave the following fractions, the components of which were identified by gas phase chromatography:

FRACTION 1. 1.0 g., b.p 18-40°/3.5mm., ether (trace), benzene (60%), 1,2-dibromoethane(40%), bromobenzene (trace).

FRACTION 2. 50mgs., b.p 100-138°/0.03mm., diethyldiphenylgermane.

FRACTION 3. 1.5 g., b.p 138-40°/0.03mm., ethyltriphenylgermane, m.p 76-77°(<u>ex iso</u>-propanol), 71%.

5) <u>Thermal decomposition of a phenyl-germanium polymer.</u>

A phenyl-germanium polymer(Ge,45.7%)was heated under vacuum $(10^{-3}$mm.). After 2hr at 360° no appreciable change had occurred; increasing the temperature to 400° caused gradual decomposition to give a pale brown sublimate and a dark coloured residue which was shown by X-ray powder photography to contain free metallic germanium.

"d spacing", observed: 3.3,1.99,1.7,

Ge requires: 3.33,2.0,1.7.

6) <u>The reaction between germanium(ll)iodide and tri-phenylaluminium</u>
<u>etherate</u>.

To triphenylaluminium etherate,(47.3 g., 0.1425 mole), in tetrahydrofuran,
(400 cc.), was added germanium(ll)iodide,(21.1 g., 0.065 mole), and the
reaction mixture was stirred at room temperature overnight. The resulting
red-orange solution was refluxed for 2 days which caused a change to
give a yellow solution with a small amount of pale yellow solid out of
solution. Filtration under nitrogen gave unreacted germanium(ll)iodide,
(1.4 g.), and a bright yellow filtrate; the latter was hydrolysed with
deaerated hydrochloric acid and the organic layer was washed, dried, and
distilled to low bulk; all processes being carried out in an atmosphere
of nitrogen. The final traces of solvent were removed under vacuum, giving
a viscous yellow oil which was dissolved in benzene,(10 cc.). This solution
was added, under nitrogen, to methanol (50 cc.), with vigorous stirring,
which caused the immediate precipitation of a bright yellow solid, which
was filtered off and dried under vacuum. This solid(4.3 g.) decomposed at
210° and contained halogen and oxygen (Ge-O absorption at 11.6μ, broad
and weak).

Found: Ge,34.4; C,33.8; H,2.6; I + O (by difference),29.2,

i.e. Ge:C:H = 1.0 : 5.94 : 5.5.

7) <u>The reaction between germanium(ll)iodide and triphenylgermyl-lith-</u>
<u>ium</u>.

To germanium(ll)iodide,(11.7 g., 0.0358 mole), in 1,2-dimethoxyethane,
was added triphenylgermyl-lithium, prepared from hexaphenyldigermane,

(36.3 g., 0.06 mole), and lithium shot,(6.0 g.), in 1,2-dimethoxyethane, (50 cc.). An immediate exothermic reaction occurred in which the yellow suspension of GeI_2 dissolved to give a deep blood red solution, which was stirred overnight at room temperature. Hydrolysis caused the precipitation of a sticky red-brown material which was removed by filtration in the air, and dried under vacuum. This material was extracted with boiling methylcyclohexane,and the pale red filtrate treated with decolourising charcoal. The filtrate deposited, on cooling, crude tris(triphenylgermyl) germane,(11.9 g., 33.5%.). Some difficulty was encountered in the purification of this compound, because of the existance of two crystal forms, however,after several recrystallisations from methylcyclohexane, a sharp melting, uniformly crystalline, compound(needles) was obtained, m.p 192-4°.

Tris(triphenylgermyl)germane showed absorption at 1953 cm^{-1}(Ge-H stretch), and at 228 cm^{-1} in the far infrared spectrum, the latter being absent in the spectra of tetraphenylgermane and hexaphenyldigermane.

Found: Ge,29.6; C,65.4; H,4.7; M,(benzene),919,

$C_{54}H_{46}Ge_4$ requires: Ge,29.5; C,65.8; H,4.7; M,985.3.

The residue from the methylcyclohexane extraction was extracted with cold benzene,(10 cc.), to give a deep red filtrate which failed to yield any product; rapid decolourisation occurred on exposure to the atmosphere. The benzene insoluble portion was Soxhlet extracted with chloroform to give hexaphenyldigermane, m.p 355°, 6.2 g., 17.3%, and,as residue, unreacted GeI_2,(1.0 g., 8.6%).

The aqueous layer from the hydrolysis of the original reaction mixture

was titrated with standard acid, and contained 0.0266 g.atom of lithium.

8). Bromination of tris(triphenylgermyl)germane.

To tris(triphenylgermyl)germane,(0.685 g., 0.696 mmole), suspended in 1,2-dibromoethane,(20 cc.), was added bromine,(0.485 g., 3.04 mmole),in the same solvent,(7 cc.), in 1 cc. aliquots over a period of 4 days, after which time free bromine was present in the solution. The reaction mixture was concentrated under vacuum at room temperature, and the liquid residue, 10 cc.), treated with ethereal ethylmagnesium bromide,(0.1 mole), After 7 hrs at reflux the reaction mixture was hydrolysed with dilute acetic acid and the organic layer separated, washed, dried, and the ether removed by distillation. The residue was distilled under vacuum, giving, as the only product, ethyltriphenylgermane, b.p 135°/0.03mm., 0.1 g., m.p 76-7,(ex isopropanol).

9) Metalation of tris(triphenylgermyl)germane.

To tris(triphenylgermyl)germane, (4.0 g., 4.05 mmole), suspended in ether, (50 cc.), was added ethereal n-butyl-lithium,(6.0 mmole), An immediate exothermic reaction occurred in which the germane went into solution to give a pale yellow solution, which, towards the end of the reaction deposited a flocculent yellow precipitate of the lithium salt, $(Ph_3Ge)_3GeLi$. After 5 mins at room temperature, methyl iodide,(0.935 g., 6.6 mmole), was added, which caused an immediate decolourisation. The solution was stirred at room temperature for 1hr and, after hydrolysis, crude methyl-tris(triphenylgermyl)germane was separated by filtration. Recrystallisation from methylcyclohexane gave colourless needles, m.p 194-96°., 2.2 g.,

54%). No Ge–H absorption was observed, though the absorption at $228cm^{-1}$ was still evident.

Found: C,66.1; H,4.9; Ge,29.15,

$C_{55}H_{48}Ge_4$ requires: C,66.1; H,4.8; Ge,29.1%.

Removal of solvent from the original ether solution gave a semi-solid material which was recrystallised from methylcyclohexane to give, what appeared to be, n-butylmethyl-bis-(triphenylgermyl)germane, $(Ph_3Ge)_2Ge$--$CH_3(C_4H_9)$, as a colourless crystalline material, (0.2 g.), m.p 187–90°.

Found: C,65.3; H,5.2,

$C_{41}H_{42}Ge_3$ requires: C,65.3; H,5.6%.

Two unidentified compounds were also isolated in small yield; m.p 124–5° and m.p 328–30°. Both compounds showed aromatic and aliphatic C–H stretch in their infrared spectra.

PART D. Organo-Germylphosphines.

1) Reaction between bromotriethylgermane and lithium diphenyl-
phosphide.

To bromotriethylgermane, (31.2g., 0.13 mole), in tetrahydrofuran,
(100 cc), was added a solution of lithium diphenylphosphide, (0.13 mole),
in tetrahydrofuran, (260 cc), at room temperature. An exothermic reaction
occurred with the immediate decolourisation of the cherry-red lithium
diphenylphosphide solution. After complete reaction the solvent was
removed by distillation and the liquid residue fractionated under vacuum.
Triethylgermyldiphenylphosphine was obtained as a colourless liquid,
b.p 146°/10^{-3}mm. Yield = 35.2 g., 79%.

Found: C,62.1; H,7.3; M(benzene),339.

$C_{18}H_{25}GeP$ requires: C,62.9; H,7.3%; M,345.

2) Hydrolysis of triethylgermyldiphenylphosphine.

a) Large scale reaction.

To triethylgermyldiphenylphosphine, (5 g., 0.0145 mole), was added a
10% solution of water in 1,2-dimethoxyethane, containing 2.6 g, water,
(0.145 mole). The solution was kept at room temperature overnight and
the unreacted water was removed with anhydrous magnesium sulphate. The
organic layer was removed and fractionated under vacuum. The following
fractions were collected:

FRACTION 1. b.p 60°/10^{-2}mm., 1.1 g., 45%, consisted of pure hexa-
ethyldigermoxane. The infrared spectrum showed strong Ge-O-Ge absorption
at 851 cm^{-1}.

FRACTION 2. b.p 60-66°/10^{-2}mm., 2.0 g., consisted of hexaethyl-

digermoxane and diphenylphosphine.

FRACTION 3. b.p 100–110°/10^{-2}mm., 0.6 g., 22%, consisted of pure
diphenylphosphine. The infrared spectrum showed strong P–H absorption
at 4.37μ.

b) To 2.7 cc of 9.1% aqueous 1,2-dimethoxyethane,(containing 0.23 g.,
0.0128 mole, of water), was added triethylgermyldiphenylphosphine, (0.43 g,
0.00125 mole), at room temperature. A sample was immediately withdrawn
and placed in an infrared cell (KBr windows, 0.5 mm spacer), and placed
in the infrared spectrometer which had been previously set at 4.3735μ
(P–H stretch). A compensating cell containing the same solvent mixture
was employed to eliminate solvent absorptions. It was found that there
was no increase in the observed absorption at this wavelength with time,
indicating that the limiting time for complete hydrolysis had expired.
A run of the spectrum from 4 to 4.5μ established the presence of P–H
absorption.

3) <u>Oxidation of triethylgermyldiphenylphosphine.</u>
Triethylgermyldiphenylphosphine,(2.1 g., 0.0061 mole), was dissolved
in ether,(50 cc), and dry oxygen (-78° trap) bubbled through the solution
for 20 hrs, after which time the solvent was removed under vacuum and the
viscous liquid residue fractionated. A colourless distillate was obtained,
b.p 160–162°/10^{-3}mm., 0.7 g., the infrared spectrum of which was identical
to that of triethylgermyldiphenylphosphonate, see figure 2 page 90.

Found: C,57.4; H,6.8; M(benzene),381.

$C_{18}H_{25}PO_2Ge$ requires: C,57.3, H,6.6%; M,377.

Some non-volatile residue remained from the distillation which could not
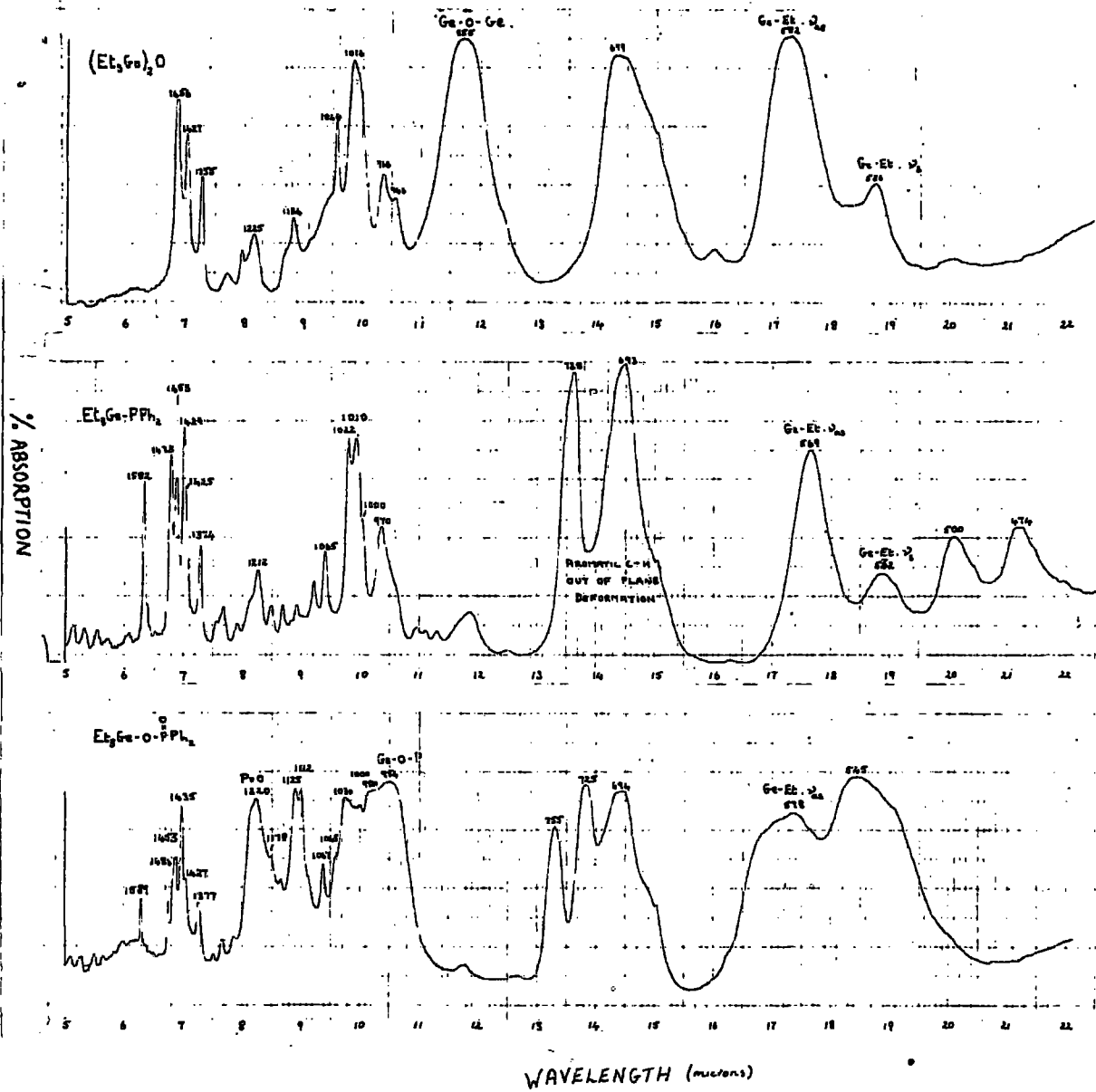
FIGURE 2.

All spectra were recorded in potassium iodide (disc).

be purified.

A sample of triethylgermyldiphenylphosphonate,(0.3 g.), was added to aqueous 1,2-dimethoxyethane,(1.52 cc., containing a 10 fold excess of water), at room temperature. After 1 hr all solvent was removed under vacuum, initially at room temperature and then at 75°, to leave a liquid residue which was heated under vacuum($140°/10^{-3}$mm) and condensed into a cooled 2N flask. The infrared spectrum of the condensate was identical to that of the parent compound in all respects except that O-H stretch was observed at 3431 cm^{-1}.

3) <u>Prolonged hydrolysis of triethylgermyldiphenylphosphonate.</u>
A sample of triethylgermyldiphenylphosphonate was left in contact with an equal volume of water for 6 weeks. The crystals which had slowly formed were then removed by filtration, washed with water and dried in a desiccator, m.p 190-191°. The infrared spectrum was identical to that of diphenylphosphinic acid. The filtrate from above was extracted with ether. The ether was removed on a water bath and the infrared spectrum of the residue indicated it to contain both hexaethyldigermoxane and triethyl-germyldiphenylphosphonate (Ge-O-Ge absorption at 851 cm^{-1}).

5) <u>Preparation of triethylgermyldiphenylphosphonate.</u>
To hexaethyldigermoxane,(0.0259 g., 7.72 10^{-5}mole), in a drawn out B.14 cone, the internal diameter of which was approximately 2mm., was added diphenylphosphinic acid,(0.0508 g., 23.2 10^{-5}mole). A B.14 still head was inserted to facilitate the maintaining of an inert atmosphere. The tube was then heated for three hours at 85°, after which time part of the diphenylphosphinic acid had reacted to give a viscous liquid product.

A sample of this liquid was withdrawn and the infrared spectrum recorded and this is shown in figure 2 page 90. The Ge-O≡Ge absorption at 851 cm^{-1} in hexaethyldigermoxane was absent and the absorption at 956 cm^{-1}, attributed to the system Ge-O-P was apparent. Strong O-H absorption at 3431 cm^{-1} was also observed.

6) <u>Reaction of methyl iodide with triethylgermyldiphenylphosphine.</u>
To triethylgermyldiphenylphosphine,(2.35 g., 6.8 mmole), dissolved in benzene,(40 cc), was added methyl iodide,(0.97 g., 6.8 mmole), and the whole kept at room temperature for 24 hrs.,after which time the white crystalline material,which had slowly developed, was filtered off under nitrogen. This material contained no germanium and was recrystallised from methanol, giving diphenyldimethylphosphonium iodide, m.p 254-255°, yield = 0.6 g., 26%.

Found: I,36.8.

$C_{14}H_{16}PI$ requires: I,37.1%.

In a similar experiment an excess of methyl iodide,(4.56 g., 32.1 mmole), was added to triethylgermyldiphenylphosphine,(2.35 g., 6.8 mmole), in benzene,(25cc), and the reaction mixture maintained at room temperature for three days. Diphenyldimethylphosphonium iodide,(2.0 g., 87%), was removed by filtration. To the filtrate was added an ethereal solution of phenylmagnesium bromide(free from magnesium metal), (0.04 mole), and the reaction mixture refluxed for 10 hrs. Acid hydrolysis followed by treatment of the organic layer in the usual way gave triethylphenylgermane, b.p 100°/3mm., yield = 0.5 g., 31%. Characterisation was by infrared spectrum and vapour phase chromatography.

7) <u>Reaction between triethylgermyldiphenylphosphine and n-butyl-lithium</u>.

To triethylgermyldiphenylphosphine,(5.45 g., 0.0158 mole), in ether, (100 cc), at room temperature, was added ethereal <u>n</u>-butyl-lithium, (0.0158 mole). An immediate reaction occurred with the production of a yellow solution. The solution was cooled in ice for 5 hrs and ethyl bromide (1.8 g., 0.016 mole), was added. Discharge of the colour was immediate and after standing at room temperature overnight the solvent was removed by distillation and the liquid residue fractionated under vacuum.

FRACTION 1. b.p 43°/0.03 mm., 180-185°/760 mm., 1.4 g., 43%. The infrared spectrum was compatible with <u>n</u>-butyltriethylgermane.

FRACTION 2. b.p 90-92°/0.02 mm., 2.1 g., 62%. The infrared spectrum was compatible with ethyldiphenylphosphine and gave ethylmethyldiphenyl-phosphonium iodide on reaction with methyl iodide,(1 g.), in benzene, (25 cc), m.p 184-5° <u>ex</u> methanol.

Found: I,35.7.

$C_{15}H_{18}PI$ requires: I,35.6%.

FRACTION 3. b.p up to 120°/0.02 mm., 0.4 g., 7.3%, consisted mainly of triethylgermyldiphenylphosphine.

8) <u>Reaction between triethylgermyldiphenylphosphine and phenyl-lithium</u>.

To triethylgermyldiphenylphosphine,(5.0 g., 0.0145 mole), in ether, (30 cc), was added ethereal phenyl-lithium,(0.015 mole). A yellow colour rapidly developed, which deepened to red-orange as all of the phenyl-lithium was added. The reaction mixture was refluxed for 1 hr

and ethyl bromide was then added,(1.7 g., 0.0156 mole), which caused immediate discharge of the colour. The solvent was removed by distillation and the residue subjected to vacuum fractionation.

FRACTION 1. b.p 53°/10^{-1}mm., 0.5 g., 14.6%, consisted of triethyl-phenylgermane. Characterisation was by infrared spectrum and vapour phase chromatography.

FRACTION 2. b.p 84°/10^{-2}mm., 0.9 g., 29%, consisted of ethyldiphenyl-phosphine. Characterisation was effected by conversion to ethylmethyl-diphenylphosphonium iodide as above.

FRACTION 3. b.p 138-140°/10^{-2}mm., 2.5 g., 50%. The infrared spectrum was identical to that of triethylgermyldiphenylphosphine.

9) <u>Reaction between triethylgermyldiphenylphosphine and bromine.</u>
To triethylgermyldiphenylphosphine,(4.6 g., 0.01334 mole), in carbon tetra-chloride,(60 cc), was added a standard solution of bromine,(2.13 g., 0.0134 mole), in carbon tetrachloride, the reaction flask being cooled to -20°. Initially the bromine was immediately decolourised, but after the addition of 0.4 mole equivalents a yellow solid began to separate which gradually redissolved after the addition of 0.6 mole equivalents. A sample of this yellow solid was withdrawn from the reaction flask - immediate decolourisation occurred with the formation of hydrogen bromide.

After complete addition of the bromine the solvent was removedby distillation and the residue fractionated under vacuum.

FRACTION 1. b.p 32-40°/10^{-2}mm., 2.2 g., 69%. The fraction consisted of bromotriethylgermane (infrared spectrum, b.p 190°/760mm.).

FRACTION 2. b.p 105°/10^{-2}mm., 2.3 g., 65%. The infrared spectrum was

compatible with bromodiphenylphosphine. This fraction was added, in

ether,(10cc), to phenylmagnesium bromide,(0.012 mole), in the same

solvent∧ the reaction mixture was refluxed for 2hrs. After hydrolysis
   and

with ammonium chloride solution the organic layer was separated and

concentrated, giving triphenylphosphine oxide, 1.7 g., 71 g., m.p and

mixed m.p 153°. The infrared spectrum was identical to that of the authen-

tic compound. The factors responsible for the oxidation of the expected

triphenylphosphine to triphenylphosphine oxide were not known.

10) <u>Reaction between triethylgermyldiphenylphosphine and silver(1)</u>

   <u>iodide</u>.

To silver(1)iodide,(1.48 g., 0.0063 mole), suspended in methyl<u>cyclo</u>-

hexane,(25cc), was added triethylgermyldiphenylphosphine,(2.2 g.,

0.0064 mole), The silver(1)iodide rapidly dissolved to give a pale yellow

solution which was transferred to a Schlenk tube and filtered from traces

of solid material. The solvent was then slowly removed from the filtrate

by pumping at 0°. The colourless prismatic crystals of triethylgermyl-

diphenylphosphinesilver(1)iodide which separated were removed by filtrat-

ion and dried in vacuum. Yield = 2.2 g., 62%, decomposes at 154° melts

at 183°. The infrared spectrum was identical to that of the free phosphine.

Found: AgI,(by treatment with H_2O_2 and gravimetric determination),

   40.0. M(benzene), 2238.

$C_{18}H_{25}$GePAgI requirs: AgI,40.7%. M,580.

Repetition of this reaction employing a 4:1 molar ratio of triethyl-

germyldiphenylphosphine to silver(1)iodide again resulted in the format-

ion of the above 1:1 complex, the unreacted phosphine being recovered.

11) <u>Reaction between diphenylphosphine and bromotriethylgermane.</u>

To bromotriethylgermane,(5.0 g., 0.0209 mole), in tetrahydrofuran, (40 cc.), was added diphenylphosphine,(3.9 g., 0.0209 mole), and pyridine, (1.7 g., 0.021 mole). No apparent reaction occurred and the reaction mixture was kept at reflux for 20 hrs, after which time all solvent was removed by distillation and the liquid residue was fractionated under vacuum. The highest boiling fraction collected was diphenylphosphine, b.p 104°/10^{-2}mm., and no triethylgermyldiphenylphosphine was isolated.

This reaction was repeated in pyridine only, but again none of the desired product was obtained.

12) <u>Reaction between lithium diphenylphosphide and bromotriphenylgermane.</u>

To bromotriphenylgermane,(19.2 g., 0.05 mole), in tetrahydrofuran, (100 cc.), was added dropwise, lithium diphenylphosphide,(0.05 mole.). Immediate decolourisation occurred and the reaction was exothermic. The solvent was then evaporated under vacuum at room temperature and dried finally at 120°/10^{-3}mm., to remove traces of unreacted diphenylphosphine. The colourless residue was extracted with boiling methyl cyclohexane in a Schlenk Tube. The filtrate deposited crude triphenylgermyldiphenyl-phosphine as colourless crystals(needles), 16.3 g., 67%. Recrystallisation from the same solvent gave a pure sample, m.p 154-6° (sealed tube under nitrogen).

Found: C,71.6; H,5.0%, M (benzene),463.

$C_{30}H_{25}GeP$ requires: C,73.8; H,5.1%, M,489.

13) <u>Reaction between triphenylgermyldiphenylphosphine and ethyl</u>

   <u>bromide.</u>

To triphenylgermyldiphenylphosphine,(3.2 g., 0.00655 mole), in

tetrahydrofuran,(50 cc.), was added ethyl bromide,(1.63 g., 0.015mole),

and the reaction mixture was maintained at 40° for two days, after which

time the crystalline material which had separated out was removed by

filtration in a Schlenk tube,(0.6 g., 21%), Recrystallisation from

methanol gave pure diethyldiphenylphosphonium bromide, m.p 195-6°.

   Found: C,58.9; H,6.1,

   $C_{16}H_{20}PBr$ requires: C,59.5; H,6.2%.

The tetrahydrofuran solution from above was evaporated to dryness under

vacuum and the residue extracted with glacial acetic acid, to give

bromotriphenylgermane,(0.7 g., 25 %), m.p 135-6°.

   14) <u>Reaction between dibromodiphenylgermane and lithium diphenyl-</u>

      <u>phosphide.</u>

To dibromodiphenylgermane,(7.6 g., 0.0198 mole), in tetrahydrofuran,(40cc.)

was added lithium diphenylphosphide,(0.04 mole), Immediate decolourisation

occurred until the slight excess of lithium diphenylphosphide had been

added. The solvent was removed at room temperature under vacuum, the

sticky residue was transferred to a Schlenk Tube and heated to $120°/10^{-3}$mm.

Diphenylphosphine was slowly removed and after 2 hrs. tetraphenyldi-

phosphine started to crystallise out of the condensate on the upper parts

of the Schlenk Tube. After 1 day the tetraphenyldiphosphine was removed,

0.7 g., 10%, m.p 118-121°. The infrared spectrum was identical to that

of the known compound.

The residue from the sublimation was extracted with methyl<u>cyclo</u>hexane and the lithium bromide separated by filtration. The filtrate deposited crude <u>bis</u>(diphenylphosphino)diphenylgermane, (3.7 g., 31%), which proved very difficult to purify; three recrystallisations from methyl<u>cyclo</u>hexane were necessary to give a sharp melting compound (needles), m.p 182-185°.

Found: C,71.4; H,5.2; M(benzene), 554,

$C_{36}H_{30}GeP_2$ requires: C,72.4; H,5;1%, M,597.

All attempts to isolate, from the mother liquors, a pure compound associated with the formation of tetraphenyldiphosphine met with failure.

15) <u>Reaction between tribromophenylgermane and lithium diphenyl-phosphide.</u>

To tribromophenylgermane,(9.5 g., 0.0245 mole), in tetrahydrofuran, (75 cc.), was added dropwise a solution of lithium diphenylphosphide, (0.0735 mole), in the same solvent,(80 cc.). Initially the lithium diphenylphosphide was decolourised and the reaction was exothermic. However, after the addition of 0.012 moles a light green colour developed which was replaced by a red colour after the addition of a total of 0.056 moles. This red colour intensified during the addition of the remainder of the lithium diphenylphosphide solution. The reaction mixture was stood overnight and the tetrahydrofuran then removed under vacuum at room temperature, final traces were removed by warming to 50°. The sticky residue was transferred to a Schlenk tube as a benzene slurry.

The benzene was carefully removed under vacuum and some diphenylphosphine was removed by heating for 4 hrs. under vacuum at 120°. No tetraphenyl-diphosphine was obtained at this stage. The residue was extracted three times with methylcyclohexane,(50 cc.), the same solvent was used for each extraction by boiling the solvent off the filtrate through the Schlenk disc onto the residue to be re-extracted. The final pale yellow filtrate deposited a pale yellow powder on cooling to room temperature overnight,(2.1 g.). This solid was 'recrystallised' from methylcyclo-hexane to give an amorphous pale yellow powder, m.p 108–112°, soluble in benzene and intermediate in composition between phenylgermanium,PhGe, and diphenylphosphinophenylgermanium, Ph_2PGePh.

Found: C,57.0; H,4.6; M(benzene),684.

C_6H_5Ge requires: C,48.1; H,3.4; M,149.7.

$C_{18}H_{15}GeP$ requires: C,62.7; H,4.4%,M,344.9.

Extraction of the residue from the methylcyclohexane extraction with benzene,(50 cc.), gave a further 2 g. of the same polymer. The methyl-cyclohexane mother liquors deposited tetraphenyldiphosphine,(3.7 g., 27%),on cooling to −20° overnight. The infrared spectrum was identical to that of the known compound and a sample was sublimed under vacuum at 120° to give pure tetraphenyldiphosphine, m.p 118–120°. The total recovery of material was 45%.

16) <u>Reaction between germanium(1V)chloride and lithium diphenyl-phosphide</u>.

To germanium(1V)chloride,(9.4 g., 0.044 mole), in tetrahydrofuran,(100

cc.), was added dropwise, lithium diphenylphosphide,(0.184 mole), in the same solvent. The cherry-red colour of the lithium reagent was discharged immediately until 1.8 mole equivalents had been added; the reaction was exothermic. At this point the reaction mixture rapidly took on a deep red colouration, which intensified as the remainder of the lithium diphenyl-phosphide was added. The reaction mixture was refluxed overnight and then hydrolysed with deaerated water. The organic layer was washed, dried and distilled to low bulk in an atmosphere of nitrogen. The diphenylphosphine, (11.7 g.), remaining from the preparation of the lithium diphenylphosphide and that formed from the hydrolysis of the excess lithium diphenylphosphide was removed under vacuum at 100° and the sticky residue was Soxhlet extracted with methylcyclohexane. The deep red extract deposited a red-brown powder on cooling to room temperature. Traces of tetraphenyldi-phosphine were removed from this solid by heating under vacuum at 125° and the residue was extracted with hot benzene,(30 cc.), in a Schlenk tube. Removal of the solvent from the blood red filtrate gave a red-brown powder with an indefinite melting point, 135-185°, 3.4 g., the composition of which was approximately that of diphenylphosphinogermanium.

Found: C,50.0; H,4.1; Ge,28.5; M,(benzene),817.

$C_{12}H_{10}GeP$ requires: C,55.9; H,3.9; Ge,28.2%;M,257.8.
The methylcyclohexane filtrate from above was cooled to -20° overnight and crude tetraphenyldiphosphine,(17 g., 52%), separated out. Purification of a sample was effected by subliming in vacuum at 120°, m.p 117-120°.

Found: C,76.9; H,5.3,

$C_{24}H_{20}P$ requires: C,77.8; H,5.4%.

A sample of the red phosphine polymer from above was dissolved in benzene and dry oxygen passed through the solution. Rapid decolourisation of the red solution occurred with the simultaneous formation of a bright yellow precipitate. All solvent was carefully removed under vacuum and the increase in weight due to oxidation determined.

0.3386 g. of red polymer gave an increase of 0.0476g.

i.e 1 Ph_2PGe unit absorbs 2.3 g.atoms of oxygen.

This compound melted over the range 120-130° and the infrared spectrum, though confused and ill-defined, showed Ge-O-Ge absorption at 833 cm^{-1} and probably P=O stretch at 1179 cm^{-1} together with Ge-O-P at 980 cm^{-1}. This spectrum was recorded as a nujol mull.

17) <u>Reaction between germanium(1V)chloride and lithium diphenyl-phosphide, 1:2 molar ratio.</u>

To germanium(1V)chloride,(10.1 g., 0.0472 mole), in tetrahydrofuran, (100 cc.), was added lithium diphenylphosphide,(0.086 mole), at which point the first sign of a permanent red colour had developed. The solvent was removed under vacuum at room temperature and the slightly sticky residue was transferred to a Schlenk tube and heated under high vacuum. The yellow solid gradually darkened as the temperature was raised until, at 120°,it was deep red in colour. Some diphenylphosphine distilled off at this temperature, but after 1 day under these conditions no tetra-phenyldiphosphine had crystallised out of the condensate. Increasing the

temperature to 140° caused the condensation of a pale yellow liquid on the upper parts of the Schlenk tube? This solidified to a glass material on cooling and contained chlorine and germanium and is probably trichloro-diphenylphosphinogermane, Ph_2PGeCl_3. The red residue from the sublimation was extracted with benzene,(50 cc.), and filtered from lithium chloride. The filtrate was added, with vigorous stirring, to dry pentane,(400 cc.), under nitrogen and the red-orange oil which was precipitated was separated and dried. The halogen content was determined by titration.

Found: Cl,10.6,

$C_{36}H_{30}P_3GeCl$,i.e $(Ph_2P)_3GeCl$ requires: Cl,5.4,

$C_{24}H_{20}P_2GeCl_2$, i.e $(Ph_2P)_2GeCl_2$ requires: Cl,13.8%.

18) <u>The interaction of tetraphenyldiphosphine and germanium(11)</u>

    <u>iodide.</u>

To germanium(11)iodide,(0.5 g., 1.54mmole), in tetrahydrofuran,(25 cc.), was added tetraphenyldiphosphine,(0.65 g., 1.76mmole). The reaction mixture was refluxed for 2 hrs. and then transferred to a Schlenk tube. All but a small amount of material was in solution and this was removed by filtration. The solvent was removed from the yellow filtrate under vacuum to give, as residue, a yellow oil. A sample of this oil turned red on exposure to the atmosphere, this behaviour is characteristic of phosphine complexes of germanium(11)iodide(167). Tetraphenyldiphosphine, (0.5g.), rapidly sublimed out from this oil on heating at 120° under high vacuum to leave, as residue, a yellow glass material. No attempt was made to obtain quantitative removal of the tetraphenyldiphosphine.

19) <u>Reaction between germanium(1V)chloride and lithium diphenyl-</u>
<u>phosphide (1 : 3 molar ratio) – subsequent reaction with ethyl</u>
<u>bromide and phenylmagnesium bromide.</u>

To germanium(1V)chloride,((8.4 g., 0.039 mole), in tetrahydrofuran,
(50 cc.), was added lithium diphenylphosphide,(0.117 mole), and to the
resulting red reaction mixture was added ethyl bromide,(30 g., 0.27 mole).
The reaction mixture was refluxed gently for 2 days, additional amounts
of ethyl bromide were added from time to time to replace losses due to
evaporation, which caused the discharge of the red colour and the
formation of a small amount of white crystalline material. After filtration,
the filtrate was distilled to half volume and treated with a filtered sol-
ution of phenylmagnesium bromide,(0.5 mole). After refluxing overnight
the reaction mixture was hydrolysed with 2N. sulphuric acid and the
organic layer was separated, washed, dried and distilled, initially at
atmospheric pressure and then under vacuum to remove all solvent and the
bulk of the diphenylphosphine(7.2 g.). The residue was exposed to the air
and extracted with boiling benzene,(100 cc.). This extract deposited
diphenylphosphinic acid ,(4.4 g.), m.p 191–92° (<u>ex</u> meths), on cooling.
The benzene filtrate was then fractionated under vacuum and the following
fractions were collected.

FRACTION 1. B.p 128–138°/10^{-3}mm., weight = 1.1 g.

The infrared spectrum showed that it contained diphenylphosphine and
triphenylphosphine oxide. It was not studied further.

FRACTION 2. B.p 170–220°/10^{-3}mm., weight = 2.7 g.

A viscous pale green liquid which was re-fractionated to give triphenyl-phosphine oxide, m.p 149-151° (ex meths), as the only pure compound isolated.

FRACTION 3. B;p 230-240°/10^{-3}mm., weight = 2.3 g.

A very viscous pale green oil which was re-fractionated, collecting the final cut, b.p 235-240°/10^{-3}mm., the infrared spectrum of this cut showed the following characteristics, compatible with a mixture of symdiethyl-tetraphenyldigermoxane and ethyldiphenylgermyldiphenylphosphonate:

a) both aliphatic and aromatic C-H stretch,

b) P=O absorption at 1219 cm^{-1},

c) Ge-Ph absorption at 1092 cm^{-1},

d) Ge-O-P absorption at 953 cm^{-1},

e) Ge-O-Ge absorption at 842 cm^{-1},

f) Ge-C(Et) stretch (ν_s ?) at 581 cm^{-1}.

The molecular weight of this mixture was determined in freezing benzene.

Found: M, 515,

$C_{28}H_{30}Ge_2O$ requires: M, 528,

$C_{26}H_{25}GePO_2$ requires: M, 473.

All attempts to separate these two compounds met with failure.

20) Reaction between germanium(1V)chloride and lithium diphenyl-phosphide (1 : 1.8 molar ratio) – subsequent reaction with ethyl bromide and phenylmagnesium bromide.

The reaction between germanium(1V)chloride,(8.4 g., 0.039 mole), and lithium diphenylphosphide,(0.0667 mole), in tetrahydrofuran, followed by

treatment with ethyl bromide and phenylmagnesium bromide was carried out as described above. No reaction was observed with ethyl bromide and the resulting reaction mixture was clear and colourless. After acid hydrolysis the organic layer was distilled and gave diphenylphosphine,(5.0 g.). The residue from the distillation was exposed to the air and then extracted with benzene but no diphenylphosphinic acid separated. The benzene extract was fractionated under vacuum and the following fractions were collected.

FRACTION 1. B.p 122–125°/10^{-3}mm., weight = 6.0 g.
This fraction was redistilled, the central fraction b.p 99–105°/10^{-3}, being collected. The infrared spectrum was identical to that of an ethyl-phenylgermane, only one germanium –ethyl stretching frequency (ϑ_s) was observed,at 575 cm^{-1}. This compound contained halogen and the vapour phase chromatogramindicated two components, present in approximately equal amounts, neither of which was diphenyldiethylgermane. It would appear as though it was a mixture of chloroethyldiphenylgermane and bromoethyldiphenylgermane.

Found: C,52.2; H,4.9,

$C_{14}H_{15}GeCl$ requires: C,57.8; H,5.2,

$C_{14}H_{15}GeBr$ requires: C,50.0; H,4.5%.

FRACTION 2. B.p 160–168°/10^{-3}mm., weight = 0.6 g.
The fraction solidified on cooling and was recrystallised from hexane giving triphenylphosphine oxide, m.p 150–151°. The infrared spectrum was identical to that of the known compound.

FRACTION 3. B.p 210–230°/10^{-3}mm., weight = 1.5 g.

The fraction was redistilled to give a main fraction of triphenylphosphine oxide and a small amount of higher boiling material, b.p $220/10^{-3}$ mm., weight = 0.3 g., the infrared spectrum of which indicated that it was a mixture of symtetraphenyldiethyldigermoxane and ethyldiphenylgermyl-diphenylphosphonate, as obtained in the previous experiment.

PART E. Dimesityl-lead.

1) The reaction between mesitylmagnesium bromide and lead(11)bromide.
a) Mesitylmagnesium bromide(0.1mole), in tetrahydrofuran,(100 cc.), was added dropwise to a vigorously stirred suspension of lead(11)bromide, (12.2 g., 0.033 mole), in tetrahydrofuran,(100 cc.), at -30°. The colour changed, through a transient yellow, to a deep blood-red, after the addition of two-thirds of the Grignard reagent; complete addition of the Grignard reagent gave a deep red-brown solution. A positive Gilman Colour Test (Michler's ketone) was obtained after the addition of 2.8 equivalents of mesitylmagnesium bromide. The final reaction mixture was then poured onto solid carbon dioxide,(purified by allowing "drikold" to evaporate through traps maintained at -60° and finally condensing at liquid air temperature), and allowed to stand for 1hr at -30°. The crude reaction mixture was then filtered under nitrogen at -30°, using the apparatus shown in figure I (page 68), in which the receiver and filter were cooled to -30°. The filtrate was then divided into two portions, A and B.

PORTION A was transferred to a 250 cc. 3N flask, cooled to -30°, and a few drops of anhydrous ethanol were added with stirring. Immediate discharge of the blood red colour was observed followed by the production of a copious white precipitate, presumably lead hydroxy bromide.

PORTION B was evaporated under vacuum at -30° to give a red glass which was allowed to decompose at room temperature by exposure to the atmosphere. A grey solid was produced which was Soxhlet extracted with carbon tetrachloride, to give a bright yellow extract, which, on cooling

yielded tetramesityl-lead as a pale yellow powder, m.p 242°(decomp), yield, 1.5g., 7.5%.

Found: C, 62.1; H,6.2; Pb,30.3,

$C_{36}H_{44}Pb$ requires: C,63.2; H,6.5; Pb,30.3%.

The colourless residue(2.0 g.) from the extraction was shown to be a mixture of lead hydroxide bromide and magnesium bromide by X-ray powder photography.

b) The reaction between mesitylmagnesium bromide,(0.1mole), and lead(11) bromide,(12.2 g., 0.033 mole), in tetrahydrofuran, followed by carbonation, was carried out as described in a). The tetrahydrofuran was evaporated, as completely as possible, at -30°, and the red glass residue extracted with methylene chloride,(150 cc.), to give a deep red solution, to which was added sodium dried hexane,(10 cc.), This caused the precipitation of a considerable amount of orange material which was removed by filtration at -30°. Both the residue and the filtrate contained lead, magnesium and halogen. The filtrate was evaporated to half volume and a further quantity, (40 cc.), of hexane added, which caused a slight precipitate to form, which was filtered off, but the residue and filtrate still contained lead, magnesium and halogen. Repetition of this precipitation procedure failed to produce either a filtrate or residue containing organo-lead compounds only.

c) The reaction between mesitylmagnesium bromide,(0.05 mole), and lead(11) bromide,(6.1 g., 0.0165 mole), in tetrahydrofuran,(100 cc.), was carried out as described, and the reaction mixture divided into two portions.

PORTION A was carbonated and, to the resulting deep red solution, was added bromine,(1.0 g., 0.00625 mole), in methylene chloride,(50 cc.), at -45°, the final reaction mixture was bright yellow in colour and gave a negative test for free bromine in solution(starch/KI paper). After hydrolysis the organic layer was quickly removed, washed, dried and evaporated under vacuum, giving a pale yellow material,(1.7 g.) which proved difficult to purify and was thermally unstable in solution, depositing a white inorganic solid($PbBr_2$). However recrystallisation from 50:50 carbon tetrachloride/propanol gave pale yellow crystals of dimesityl-lead dibromide, m.p198-199^c.

Found: C,39.5; H,3.5; Br,25.2,

$C_{18}H_{22}Br_2Pb$ requires: C,35.7; H,3.7; Br,26.4%.

An amount of an organic lead compound,(2.0 g.), was filtered off after the hydrolysis of the reaction mixture.

To PORTION B was added bromine,(0.9 g., 0.0056 mole), in methylene chloride,(50 cc.), at -45°. The final reaction mixture was bright yellow in colour and gave a positive test for the presence of free bromine in solution. The unreacted bromine was removed by hydrolysis with aqueous sodium bicarbonate solution at -45°. At this stage a yellow material, (1.5 g.), was removed by filtration, Soxhlet extraction of this residue with carbon tetrachloride gave, from the pale yellow extract, tetramesityl-lead,(0.2 g.); m.p 240-42°.

The organic layer from the reaction was separated, washed, dried and evaporated under vacuum, to give a pale yellow viscous residue,(2 g.).

Recrystallisation from petrol ether (b.p 60–80°), gave trimesityl-lead bromide, m.p 145–6°, as colourless needles, (0.2 g.).

Found: C,55.6; H,6.0; Br,11.6,

$C_{27}H_{33}BrPb$ requires: C,50.3; H,5.2; Br,12.4%.

2) <u>The reaction between mesityl-lithium and lead(ll)chloride.</u>

To mesityl-lithium,(0.0874 mole), in tetrahydrofuran,(200 cc.), was added solid lead(ll)chloride,(8.14 g., 0.0291 mole), in three portions over a period of 10 mins, at –40°, with vigorous stirring. The reaction mixture turned initially green and then finally red. After stirring for 2 hrs the reaction mixture was carbonated and allowed to stand for 1hr at –30°. The tetrahydrofuran was evaporated at –30° under vacuum, the red glassy residue was extracted with methylene chloride,(75 cc.), and the insoluble material removed by filtration under nitrogen. To the deep red filtrate was added sodium dried hexane,(30 cc.), which caused the separation of two layers; the upper pale orange, and the lower deep red. The lower layer was removed, but all attempts to obtain from this an organo-lead compound free from lithium halide, by partial precipitation by the addition of hexane, met with failure.

PREPARATION OF STARTING MATERIALS.

1). Mesitylmagnesium Bromide.

Bromomesitylene, (19.9 g., 0.1 mole), in tetrahydrofuran, (40 cc.), was added dropwise, over a period of 1 hr, to magnesium turnings, (2.6 g., 0.107 g.atom), in tetrahydrofuran, (50 cc.); the reaction was initiated with a few drops of 1,2-dibromoethane. The final solution was buff in colour, and a yield of approximately 95% (by back titration) was obtained.

Other Grignard reagents were prepared in diethyl ether or tetrahydrofuran in a similar manner.

2). Phenyl-lithium.(123)

Lithium was produced in shot form, which is suitable for reaction, using the apparatus shown in figure 3 page 112. Paraffin oil (b.p 200-30°) was poured into the apparatus to bring the level half way up the creases, the latter cause a downward deflection of the oil when it is stirred, and weighed lumps of lithium metal added.The contents of the flask were then heated with the ring burner until the lithium was molten. Then the burner was turned off and the stirrer at once started. The lithium was rapidly reduced to fine shot and solidified on cooling. As molten lithium reacts rapidly with nitrogen, only a pressure of nitrogen was maintained during the heating proceedure, the lithium being protected by the oil vapour, but this was adjusted to an actual flow as the flask cooled. The oil was then drained off through the tap, together with the corrosion products from the lithium which had settled out. The lithium shot was then washed free from oil with ether (twice), the ether, on which lithium floats,

.112.

N$_2$ INLET.

AIR
CONDENSER, TO
NITROGEN
OUTLET.

CREASED
FLASK.

TANTALUM WIRE
LINKS.

RING BURNER.

1 cm. BORE TAP.
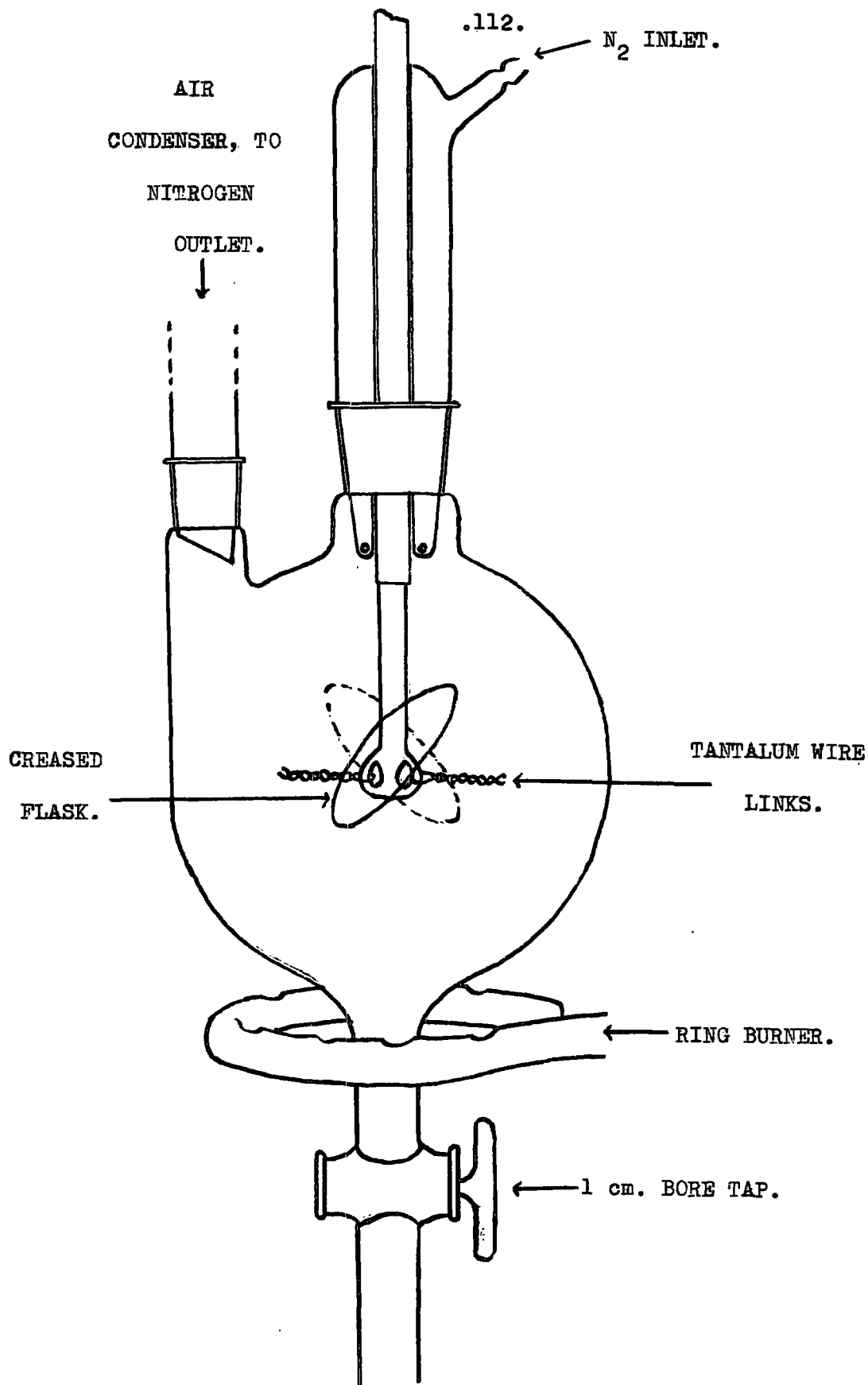
FIGURE 3.

drained off through the tap. The shot was then transferred as an ether

slurry to the reaction flask, through the tap, against a counter current

of nitrogen.

To lithium shot, (1.47g., 0.21 g.atom), in ether,(40 cc.), was added

bromobenzene,(15.7 g., 0.1 mole), in ether,(60 cc.), atarate sufficient

to maintain refluxing of the ether, the reaction was initiated with a

few drops of 1,2-dibromoethane. A yield of 95% of phenyl-lithium (by

titration) was obtained.

3). Mesityl-lithium.

Mesityl-lithium was prepared by the low temperature (-30°) addition of

bromomesitylene, (19.9 g., 0.1 mole), in tetrahydrofuran, (50 cc), to

lithium shot,(1.47 g., 0.21 g.atom), in tetrahydrofuran, (75 cc). The

final solution was deep red-brown in colour, and the yield of mesityl-

lithium approximately 90%. Mesityl-lithium reacts rapidly with tetrahydro-

furan at room temperature and should be used immediately.

4) Germanium(1V)iodide.(134)

Germanium(1V)iodide was prepared in 75% yield by the reaction between

constant boiling hydriodic acid and germanium(1V)oxide. The crude product

was separated from unreacted oxide by sublimation $(100°/10^{-2}mm.)$, giving

red-orange crystals, m.p 145°. Geramnium(1V)iodide was storred in the

dark.

5) Germanium(11)iodide.(135).

Germanium(11)iodide was prepared in 70% yield by the reduction of

germanium(1V)iodide with hypophosphorous acid in the presence of hydriodic

acid. The product was dried, and traces of unreacted germanium(1V)iodide removed, by heating under vacuum, $(110^\circ/10^{-2}mm.)$.

6) <u>Tetraphenylgermane</u> and <u>Hexaphenyldigermane</u>.

For the preparation of these compounds see Part B of this thesis.

7) <u>Tetraethylgermane</u>.

Tetraethylgermane was prepared by the reaction between ethylmagnesium bromide, (0.5mole), in ether,(400 cc), and germanium(1V)chloride,(18.9 g. 0.0885 mole), in benzene, (100 cc), The reaction mixture was refluxed overnight and then hydrolysed with dilute acetic acid. The organic layer was separated, washed, dried and fractionated. Tetraethylgermane had b.p 162°; yield = 10.4 g., 62%.

8) <u>Bromotriethylgermane</u>.

Bromotriethylgermane was prepared by the bromination of tetraethylgermane, (10.35 g., 0.0548 mole), with bromine, (8.85 g., 0.0552 mole), in ethyl-bromide, (10 cc), at 40° (122). The reaction mixture was fractionated, collecting the middle fraction, b.p 186°, of bromotriethylgermane. Yield = 8.0 g., 61%.

9) <u>Triethylphenylgermane</u>.

Triethylphenylgermane was prepared by the reaction of bromotriethylgermane, (8.0 g., 0.0334 mole), in benzene, (15 cc), with phenylmagnesium bromide, (0.1 mole), in ether, (100 cc). The reaction mixture was refluxed for 9 hrs and then hydrolysed with dilute acetic acid. The organic layer was separated in the usual way and fractionated to give triethylphenylgermane, b.p $84-88^\circ/2mm.$, yield = 4.8 g., 61%.

10). Diphenyldibromogermane.

Dibromodiphenylgermane was prepared by the bromination of tetraphenyl-germane, (20 g., 0.0527 mole), with bromine, (17.5 g., 0.11 mole), in 1,2-dibromoethane, (130 cc), the reaction mixture was maintained at the reflux point for 1hr, (136). The 1,2-dibromoethane, bromobenzene and residual bromine were removed by distillation under a pressure of 1mm. The viscous residue was dissolved in ether, (25cc), and added dropwise to lithium aluminium hydride, (7.6 g., 0.21 mole), in ether, (150 cc). After addition, the reaction mixture was refluxed for 2 hrs and the ether replaced by petrol ether (60-70°) by distillation. The lithium aluminium hydride was filtered off under nitrogen and the filtrate fractionated. Diphenylgermane had b.p 93°/1mm., yield = 7.25 g., 60%.

To diphenylgermane, (4.0 g., 0.0175 mole), in chloroform, (50 cc), cooled in an ice bath, was added bromine, (6 g., 0.0375 mole), (21). An immediate reaction occurred, and when traces of free bromine remained in the reaction mixture, the solvent was removed under vacuum and the residue distilled, giving pure dibromodiphenylgermane, b.p 112°/10^{-3}mm., yield= 5.8 g., 86%.

11). Bromotriphenylgermane.(165).

To tetraphenylgermane, (62 g., 0.163 mole), in refluxing 1,2-dibromoethane, (350 cc), was added bromine, (27.1 g.,0.17 mole), and refluxing was main-tained until the reaction flask contained no bromine vapour. The solvent was then removed by distillation and the residue subjected to vacuum distillation. Crude bromotriphenylgermane was collected, b.p 180°/10^{-3}mm.,

and was recrystallised from glacial acetic acid, m.p 136°, yield = 48 g.,
77%.

   12) <u>Tribromophenylgermane.</u>

To germanium(1V)chloride, (32.2 g., 0.15 mole), in ether, (150 cc), at
0° was added, over a period of 4 hrs, phenylmagnesium bromide, (prepared
from 0.18 mole of bromobenzene), in ether, (110 cc), with vigorous stirring.
After standing overnight at room temperature a slurry of lithium aluminium
hydride, (11.5 g., 0.3 mole), in ether, (100 cc), was added from a dropping
funnel at room temperature. The reaction mixture gradually turned yellow-
characteristic of the reaction of germanium(1V)chloride with lithium
aluminium hydride (7). The reaction mixture was refluxed for 3hrs and
then hydrolysed with dilute sulphuric acid, the organic layer was separated
and fractionated through a 30 cm column packed with glass helices. The
fraction b.p 48°/23mm. was phenylgermane, 6.3 g., 27.5%. The infrared
spectrum showed strong Ge-H absorption at 4.85μ. The residue was distilled
under high vacuum and gave diphenylgermane, ($79°/10^{-2}$mm., 4.5 g., 13.2%),
together with triphenylgermane, ($128-136°/10^{-2}$mm., 3.3 g., 7.2%).

   To phenylgermane, (5.6 g., 0.0368 mole), in chloroform, (250 cc),
was added bromine, (17.7 g., 0.111 mole), dropwise at 0°. When the
bromine was no longer rapidly absorbed (after the addition of 6 g.) the
ice bath was removed and the reaction mixture allowed to warm up to room
temperature when the remainder of the bromine was added. After standing
overnight the reaction mixture was refluxed gently for 1 hr and the solvent
removed under vacuum, together with some unreacted bromine. The residue

was then fractionated, collecting tribromophenylgermane, b.p 82-3°/10^{-2}mm., yield = 9.7 g., 68%. This method has not previously been described.

13). Diethyldiphenylgermane

Diethyldiphenylgermane was prepared by the Grignard reaction between dibromodiphenylgermane, (5.8 g., 0.015 mole), in benzene, (10 cc), and ethylmagnesium bromide, (0.1 mole), in ether, (100 cc). The reaction mixture was refluxed for 6 hrs, acid hydrolysis followed by treatment of the organic layer in the usual way gave diethyldiphenylgermane, b.p 90-92°/10^{-2}mm., yield = 2.7 g., 64%.

14). Triphenylgermyl-lithium

Triphenylgermyl-lithium was prepared by the cleavage of either hexaphenyl-digermane, (6 g.,0.01 mole), with lithium shot, (1 g;, 0.144 g. atom), (31,70); or of tetraphenylgermane, (7.12 g., 0.0187 mole), with lithium, (2 g., 0.288 g. atom), (30). Both reactions were carried out in 1,2- di-methoxyethane. In both cases a yield of 60% of triphenylgermyl-lithium was assumed when the reagent was used for further reaction, and prepared as required.

15). Triphenylphosphinemonochlorocopper(I).

To a solution of triphenylphosphine, (18.5 g., 0.071 mole), in benzene, (300 cc), was added copper(I)chloride(137), (7 g., 0.071 mole). The resulting suspension was refluxed, with stirring, for 12 hrs. The heavy white precipitate was filtered off, after cooling, and recrystallised from benzene giving triphenylphosphinemonochlorocopper(I), 15 g., yield = 60%, as colourless crystals, m.p 194-203°.

Found: C,60.0; H,4.4,

$C_{18}H_{15}PCuCl$ requires: C,59.8; H,4.2%.

16). <u>Triphenylphosphinemonoiodosilver(1)</u>.

To a solution of triphenylphosphine, (7.85 g., 0.03 mole), in acetone, (150 cc), was added, with stirring, silver(I)iodide, (7.03 g., 0.03 mole), in saturated potassium iodide solution, (50 cc). An immediate white precipitate was obtained, which, after 1 hr at reflux was filtered off and washed with boiling acetone to give,as residue, triphenylphosphine-monoiodosilver(I), yield = 14 g., 94%, insoluble in all solvents, m.p 298-307°.

Found: C, 44.4; H,3.5; AgI,46.3.

$C_{18}H_{15}PAgI$ requires: C,43.5; H,3.0; AgI,47.2%.

Recrystallisation from acetone containing an excess of triphenylphosphine gave a crystalline material, <u>tris</u>(triphenylphosphine)mono-iodosilver(I), m.p 169-170°.

Found: C,64.2; H,4.9; AgI,23.5.

$C_{54}H_{45}P_3AgI$ requires: C,63.5; H,4.4; AgI, 23.0%.

17). <u>Triphenylphosphinemonochlorogold(I)</u> and <u>trimethylphosphinemonochloro-gold(I)</u>.

Both these compounds were available in the department and were recrystall-ised from ethanol, m.p 255°(dec) and 229°(dec) respectively.

18). <u>Triphenylaluminium etherate</u>(139).

To a solution of anhydrous aluminium chloride, (111 g., 0.83 mole), in ether, (400 cc), was added ethereal phenyl-lithium, (2.7 mole), at a rate

sufficient to maintain steady refluxing of the ether. The ether solution
was then decanted from the lithium halide and concentrated by distillation.
Crude triphenylaluminium etherate crystallised out on cooling and was
removed by filtration under nitrogen and recrystallised from boiling
toluene, to give pure triphenylaluminium etherate, which was dried under
vacuum at 110°. Yield = 175 g., 53%, m.p 131°.

19). <u>Diphenylphosphine</u>.

To lithium shot, (22.5 g., 3.21 g. atom), in tetrahydrofuran, (750 cc),
was added dropwise a solution of triphenylphosphine, (385 g., 1.47 mole),
in tetrahydrofuran, (1 litre). A vigorous reaction occurred with the
formation of a deep red solution. After complete reaction, deaerated
water was added until the colour was discharged. The solution was then
made just acid by the addition of concentrated hydrochloric acid. The
organic layer was separated (under N_2), washed, dried, and fractionated
under vacuum. Diphenylphosphine was collected, b.p $104°/10^{-2}$mm., yield =
215 g., 79%.

20). <u>Lithium diphenylphosphide</u>.

To lithium chips, (0.56 g., 0.08 g.atom), in tetrahydrofuran, (80 cc), was
added diphenylphosphine, (14.0 g., 0.075 mole, ρ = 1.0 g/cc). The deep
cherry-red colour of lithium diphenylphosphide rapidly developed and the
solution was stirred at room temperature for 3 hrs. The reagent was
filtered through a glass wool plug and estimated by titrating a hydrolysed
aliquot with standard acid. Yields of 85-90% were obtained.

PURIFICATION OF SOLVENTS.

1). <u>Benzene, toluene</u> (B.D.H. "analar grade"), and <u>diethyl ether</u> were dried by standing over sodium wire for 1 week.

2). <u>Tetrahydrofuran.</u>

Commercial tetrahydrofuran was stood over potassium hydroxide for 2-3 days and then distilled. Final drying and purification was carried out by refluxing with potassium and benzophenone in an atmosphere of nitrogen. The intense blue-black colour of potassium diphenyl-ketyl slowly developed and the tetrahydrofuran was then removed by distillation. Repetition of this process, or alternatively distillation from lithium aluminium hydride or from triphenylphosphine and lithium chips ($Ph_3P + Li \longrightarrow$ $Ph_2PLi + PhLi$) gave tetrahydrofuran in a form suitable for reaction, b.p 66°. The latter method was employed in the work described in Part D of this thesis.

3). <u>1,2-Dimethoxyethane</u> was purified in a way identical to that de-scribed for tetrahydrofuran, b.p 83°.

4). <u>Methylene chloride.</u>

Commercial methylene chloride was washed with 5% sodium carbonate solution and then with water. After drying with anhydrous calcium chloride the methylene chloride was fractionated, b.p 40°.

5). <u>Ethanol.</u>

A fraction of absolute alcohol was used to prepare magnesium ethoxide. The reaction was initiated with a crystal of iodine. After complete solut-ion of the magnesium the bulk of the alcohol was added and the total was

refluxed for 30 mins. Ethanol of 99% purity was distilled off under nitrogen, b.p 78.5°.

EXPERIMENTAL METHODS.

1). Infrared Spectra.

The region 2.5–20μ was recorded in mull (nujol) or solid form (KI or KBr disc), using a Grubb Parsons spectrometer, model GS2A; model DM2 was used for recording the region 20–50μ (nujol mull).

2). Vapour Phase Chromatography.

Vapour phase chromatograms were recorded on Griffin and George Mk.IIB apparatus. The stationary phase was silicone elastomer on kieselguhr, and this was maintained at temperatures ranging from 140 to 240°, depending on the volatility of the specimen. The carrrer gas employed was nitrogen; a flow rate of 1 litre/hr and an excess internal pressure of 15cm/Hg was maintained. The sample (3–5 drops) was injected by syringe through a rubber seal cap onto the column. Identification of the components of a mixture was carried out by the following method. A chromatogram of the mixture was obtained, and the number of components established. A sample of the mixture, to which had been added a small amount of an authentic compound whose presence was suspected in the mixture, was then chromatographed. The non appearance of an extra peak and the strengthening of one already present established its identity. In this way all components were identified. An example is shown in figure 4 page 123 for the identification of triethylphenylgermane.

3). Molecular Weight Measurements.

Molecular weights were determined by the familiar cryoscopic method. The solvent used was, in most cases, benzene, but nitrobenzene and 1,2–
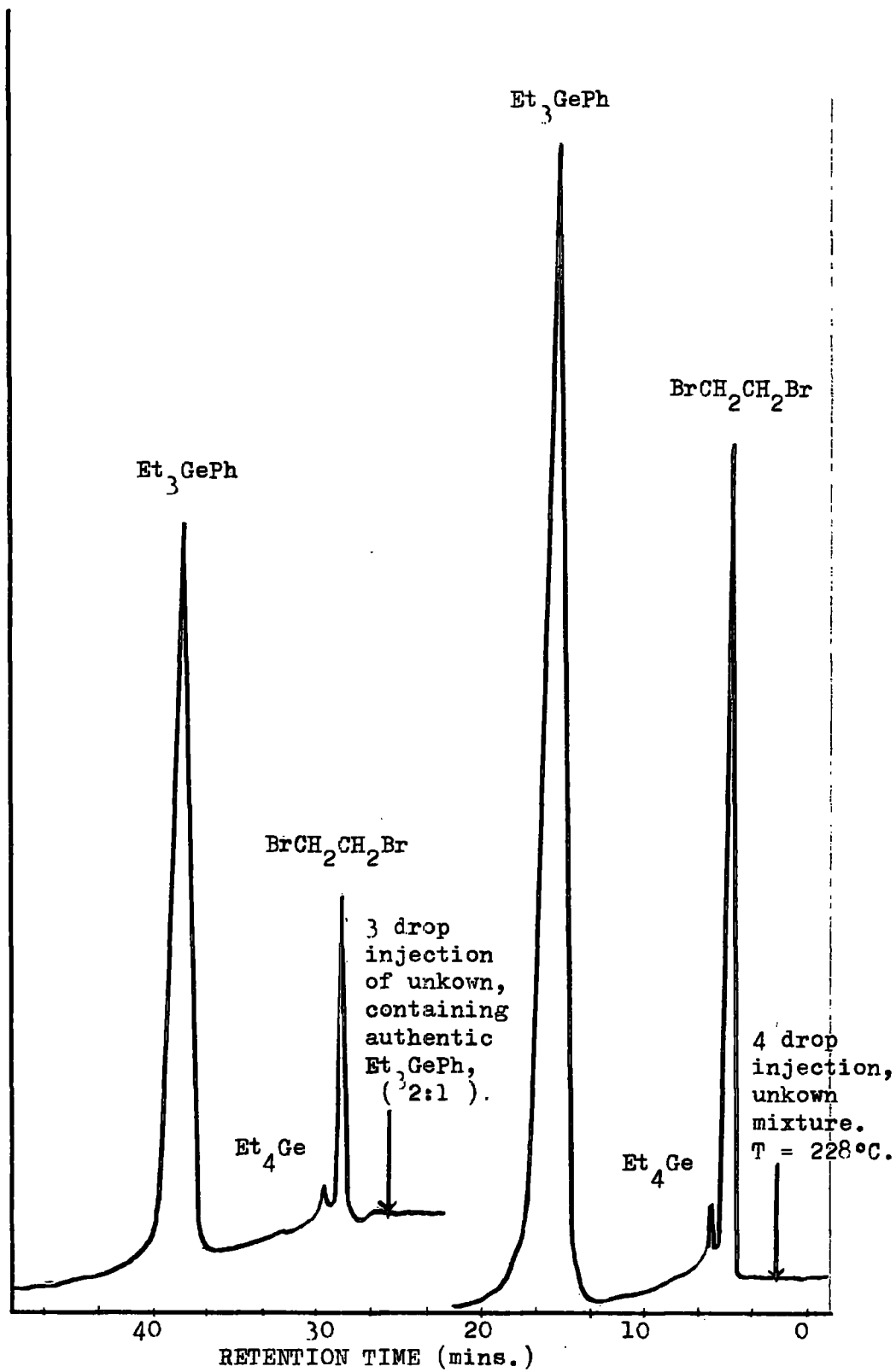
RETENTION TIME (mins.)

FIGURE 4.

dibromoethane were also used. It is of note to mention the following points, to which attention was paid to give results which were reliable, especially when the compound under investigation was sensitive to oxygen or water;

a) a slow strean of nitrogen was passed over the solution;

b) the addition of two pieces of molecular sieve (grade 5A) to the solution to remove traces of condensed water;

c) the benzene used was B.D.H "analar" grade which had been dried over sodium, other solvents were distilled prior to use. All solvents were standardised with biphenyl.

4). <u>Nitrogen Supply</u>.

All reactions and operations involving air sensitive compounds or reagents were carried out in an atmosphere of pure, dry, oxygen-free nitrogen. Purification of the nitrogen was effected by passing commercial "white spot" nitrogen through copper turnings at 300°, to remove traces of oxygen, and then through a column of molecular sieve to remove traces of water.

ANALYTICAL METHODS.

1). Carbon and hydrogen analysis were carried out on a semi-micro scale
by Miss V.Conway and Mr. T.Caygill of this department and also by Drs.
Weiler and Strauss of the micro-analytical laboratory, Oxford. Consider-
able difficulty was often experienced in obtaining satisfactory results,
especially for the compounds described in Parts C and D of this thesis.

2). Lead was determined in organic compounds by the method of Saunders
and Stacey(140). The sample, (0.2 g.), was decomposed with concentrated
nitric acid and the soluble lead precipitated as the chromate. The lead
chromate was then dissolved in dilute hydrochloric acid and titrated
with ferrous ammonium sulphate solution, using ferrous phenanthroline as
indicator. Standardization was carried out using pure lead nitrate.

3). Copper was estimated in organic compounds by strong acid decomposition,
(HNO_3 and HCl), and conversion to, and gravimetric determination as,
copper(1)thiocyanate. This method was employed for compounds containing
germanium and phosphorus.

4). Silver, in the presence of germanium and phosphorus, in organic
compounds was estimated, after decomposition with concentrated nitric
acid, gravimetrically as the chloride in the usual way. For triphenyl-
phosphine complexes of silver(1)iodide, the residual silver(1)iodide was
determined by weighing, after removal of the triphenylphosphine in vacuum
at 150°.

5). Gold was estimated in organic compounds by one of the following
methods, the choice depending on the other elements present in the compound.

    a) Gold, carbon, hydrogen,and phosphorus.

The sample,(0.2 g.), was carefully ignited in a weighed covered crucible to gold metal and weighed directly.

b) Gold, carbon, hydrogen, phosphorus, germanium and lithium. Decomposition of the sample,(0.3 g.), was effected with aqua regia. After evaporation to low bulk the solution was diluted to 150 cc. with water and the soluble gold reduced to gold metal by the addition of hydrazine dihydrochloride. The gold metal was coagulated by boiling and collected in a weighed Gooch crucible. After drying at 120° the gold was weighed.

6). Germanium.

Most of the methods described in the literature(58,141,142,18,31) for the determination of germanium in an organic compound involve strong acid decomposition and conversion, either directly or indirectly, to the oxide GeO_2. The method employed in the present work depended on the other elements present in the compound.

a) Germanium, carbon and hydrogen.

The method employed was similar to that described by Rochow(58). The sample,(0.3 g.), was decomposed with fuming nitric acid at 0° and the solution allowed to warm up to room temperature when ammonium persulphate, (1 g.), and 6N. sulphuric acid,(2 cc.), were added. After standing overnight the solution was evaporated to dryness and the residue fumed with concentrated sulphuric acid followed by ignition of the oxide to constant weight. At the beginning of this work considerable difficulty was experienced in preventing mechanical loss during the evaporation proceedures. This was overcome by the use of a 50 cc. silica flask with a long neck,(10 cm.), in this, the sample was decomposed and the evaporation was carried out by

placing in an electrically heated mantle. Final ignition was effected by suspending the flask from a glass beam by platinium wire and heating with a naked flame.

b) In the presence of gold, co-ordinated phosphorus, lithium, carbon and hydrogen.

The sample (0.3 g.) was decomposed with concentrated sulphuric acid and warmed. After dilution and filtration through a Gooch crucible, to remove gold metal, the filtrate was made 6N. with sulphuric acid and saturated with hydrogen sulphide. After standing overnight the white precipitate of germanium(1V)sulphide was filtered off. Oxidation to the oxide was effected with 3% hydrogen peroxide in 10N. ammonia solution(141). Evaporation and ignition was carried out as for a).

c) In the presence of gold, nitrogen, carbon and hydrogen.

Decomposition was effected as for a), igniting to the mixed residue of gold and germanium(1V)oxide, the weight being determined. The gold was extracted with aqua regia and the solution treated as for 5b) for the estimation of gold. The gold was subtracted from the weight of the mixed residue to give the percentage of germanium in the sample.

d) In the presence of bonded phosphorus, carbon and hydrogen.

The treatment of compounds containing the germanium-phosphorus link by the method described in b) gave residual GeO_2 which contained phosphorus. The following method was employed for the estimation of germanium in these compounds.

The sample (0.3 g.) was decomposed with fuming nitric acid,(15 cc.), and concentrated sulphuric acid,(5 cc.). The nitric acid was fumed off

and, after cooling, the sulphuric acid residue was diluted with 200 cc. of water and made just alkaline with solid sodium hydroxide. The solution was filtered and to the filtrate was added concentrated sulphuric acid to neutrality, followed by a further 5 cc. After the addition of ammonium sulphate, (10 g.), the solution was boiled and the soluble germanium precipitated by the slow addition of a 10% solution of tannin, (20 cc.). The light buff precipitate was removed under suction and washed three times with a wash solution (5% ammonium nitrate solution containing 5 cc. 2N. nitric acid and 5 cc. tannin solution/ 100 cc.) and then with water. The paper and precipitate were then transferred to a silica flask and ignited, initially at 500° and finally at 900°, to germanium(1V) oxide.

This method proved unsuccessful for the determination of germanium in compounds in which the germanium atom was bonded to both phosphorus and carbon. The germanium could not, in these cases, be brought into solution.

DISCUSSION

PART A. <u>Triphenylgermyl Complexes of Copper, Silver and Gold.</u>

Organogermanium compounds in which the germanium atom is bonded also to a non-transition metal have been known for a number of years, and several of these are mentioned in the introduction to this thesis, (page 34).

The present work was undertaken in an attempt to prepare compounds in which the central germanium atom is bonded both to a transition metal and also to carbon. It has been reported that attempts to prepare compounds containing silicon-metal bonds by the reaction:

$$Ph_3SiLi \; + \; MX_n \longrightarrow (Ph_3Si)_nM,$$

$$X = halogen, \; M = Hg(II), \; Pb(II), \; Ag(I) \; etc.,$$

met with failure(89); decomposition of the desired product to hexaphenyl-disilane and the corresponding metal occurred:

$$2(Ph_3Si)_nM \longrightarrow nPh_6Si_2 \; + \; 2M.$$
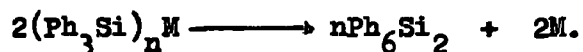
The stabilising effect of π-bonding ligands on compounds containing "transition metal-carbon" bonds is well recognised, and it was thought that co-ordination of the transition metal to a tertiary phosphine would lead to reasonably stable compounds containing metal-metal bonds. The investigation was confined to phosphine complexes of copper(I), silver(I) and gold(I), in each case complexes involving Ge-Cu, Ge-Ag, and Ge-Au bonds were isolated.

The compounds were prepared by the reaction between triphenylgermyl-lithium and the corresponding tertiary phosphine-metal halide complex in 1,2-dimethoxyethane:

$$Ph_6Ge_2(Ph_4Ge) \xrightarrow{\;2Li\;} 2Ph_3GeLi \xrightarrow{\;(R_3P)_nMX\;} Ph_3Ge-M(PR_3)_n \; + \; LiX.$$
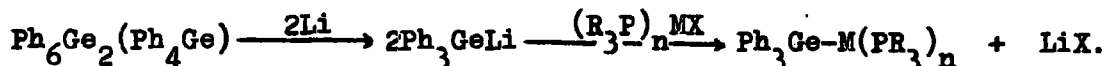
In the case of gold, both R = methyl and phenyl gave a stable compound, with n=1. For copper and silver, only triphenylphosphine gave isolable compounds and the stability depended much on the number of phosphine molecules co-ordinated; n = 3 gave complexes of much greater stability than n = 1.

The stability of these compounds was found to be greatest for gold and least for copper. Thus the gold compound, $Ph_3Ge.AuPPh_3$, is stable to air and water, and it separates from benzene as colourless plates with one molecule of solvent of crystallisation, which can be removed by heating at 120° under vacuum, to give a pale green compound, solvent free, identical to that obtained by recrystallisation from acetone.

Both the copper and silver analogues are susceptible to aerial oxidation at room temperature, especially when in solution.

There is a striking difference in stability depending on the structure of the phosphine ligand. The gold-trimethylphosphine complex, $Ph_3Ge.AuPMe_3$, is considerably less stable than the triphenylphosphine analogue, decomposing rapidly on exposure to the air. Tris(diethylphenylphosphine)bis(mono-iodosilver(I)), $(Et_2PhP)_3(AgI)_2$, gave a complex of such low stability that it deposited silver on attempted purification from benzene.

Triphenylphosphinemonoiodosilver(I), Ph_3PAgI, also gave a highly unstable compound on reaction with triphenylgermyl-lithium,

$$Ph_3GeLi \quad + \quad Ph_3PAgI \longrightarrow Ph_3Ge.AgPPh_3 \quad + \quad LiI,$$

which could not be purified because of its insolubility in common organic solvents. Addition of triphenylphosphine to this compound in 1,2-dimethoxy-

ethane resulted in the formation of triphenylgermyl-tris(triphenylphosphine)
silver(I), $Ph_3Ge.Ag(PPh_3)_3$,

$$Ph_3Ge.AgPPh_3 \quad + \quad 2PPh_3 \longrightarrow Ph_3Ge.Ag(PPh_3)_3$$
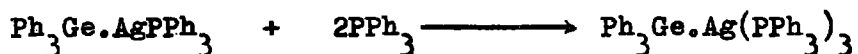
which separated from 1,2-dimethoxyethane as pale green plates, containing
two molecules of solvent of crystallisation, and which decomposed rapidly
on exposure to the atmosphere. This same compound was also prepared by
the interaction of preformed tris(triphenylphosphine)monoiodosilver(I)
with triphenylgermyl-lithium.

Similarly, triphenylphosphinemonochlorocopper(I), Ph_3PCuCl, gave
on treatment with triphenylgermyl-lithium, a highly insoluble and unstable
complex which fumed on exposure to the air,

$$Ph_3PCuCl \quad + \quad Ph_3GeLi \longrightarrow Ph_3PCu.GePh_3 \xrightarrow{PPh_3} Ph_3Ge.Cu(PPh_3)_3.$$
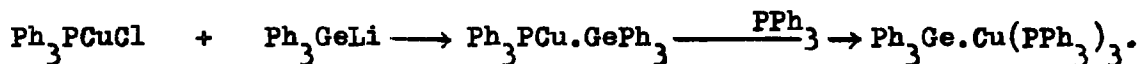
Treatment with triphenylphosphine again gave the more stable compound,
identical to that isolated from the reaction of tris(triphenylphosphine)-
monochlorocopper(I) with triphenylgermyl-lithium,

$$(PPh_3)_3CuCl \quad + \quad Ph_3GeLi \longrightarrow Ph_3Ge.Cu(PPh_3)_3.$$
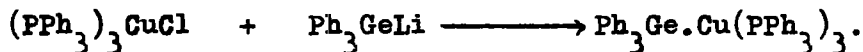
This material separated from 1,2-dimethoxyethane as pale grey crystals,
apparently solvent free, in low yield and with somedifficulty.

Of these compounds, only triphenylgermyl-trimethylphosphinegold(I)
was sufficiently soluble for cryoscopic molecular weight determinations
in benzene, and it was found to be monomeric. Molecular weight measurements
were thus attempted in 1,2-dibromoethane, but, for each of the complexes
described, a rapid, though not quantitative, reaction occurred at room
temperature in which the 1,2-dibromoethane behaved as a mild brominating

agent, cleaving the metal-metal bond with the simultaneous formation of
ethylene:

$$Ph_3Ge.M(PR_3)_n \; + \; C_2H_4Br \longrightarrow C_2H_4 \; + \; Ph_3GeBr \; + \; (R_3P)_nMBr,$$
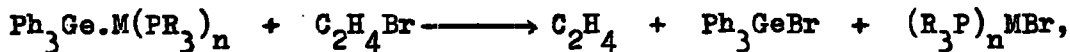
When M = Au; R = Me or Ph; n = 1,

and M = Cu,Ag; R = Ph; n = 3.

For the copper and silver compounds the tertiary phosphine-metal bromide
compound isolated was not the expected 3:1 complex, but the 3:2 complex in
the case of copper and the 2:1 complex in the case of the silver compound.
The yield of ethylene ranged from 75% for triphenylgermyl-triphenylphos-
phinegold(I) to 30% for triphenylgermyl-tris(triphenylphosphine)copper(I).
It is probable that this reaction proceeds through a four centred transit-
ion state (A) as shown, this requires a cis configuration for the 1,2-
dibromoethane at the moment of reaction:
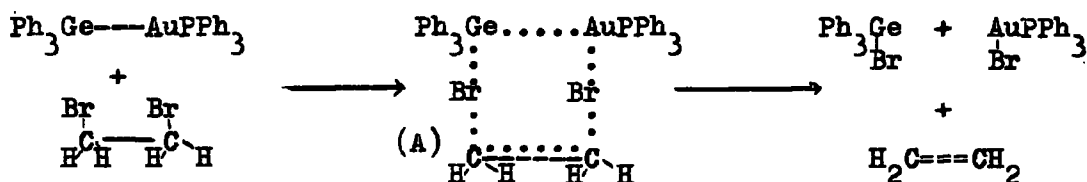
Under similar conditions ethyl bromide and 1,2- dichlorobenzene failed to
react.

It was anticipated that phenyl-lithium would cleave the germanium-
gold bond in triphenylgermyl-triphenylphosphinegold(I) forming triphenyl-
germyl-lithium and triphenylphosphinemonophenylgold(I), Ph_3PAuPh. However,
the addition of ethereal phenyl-lithium to a suspension of the complex in
ether at room temperature caused the gradual production of a pale pink
precipitate. This solid was highly unstable, depositing gold on standing,

even at $-20°$ in an atmosphere of nitrogen. The infrared spectrumof this compound showed the absence of triphenylphosphine. Analysis indicated an equi-molar ratio of gold to lithium, whilst hydrolysis afforded lithium hydroxide, hexaphenyldigermane and gold metal. It was therefore tentatively formulated as the anionic gold(I) complex(i):

$$\text{Li}^+\left[\text{Au(GePh}_3)_2\right]^- 4.\text{Et}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{LiOH} + \text{Ge}_2\text{Ph}_6 + \text{Au}.$$
$$\text{(i)}$$
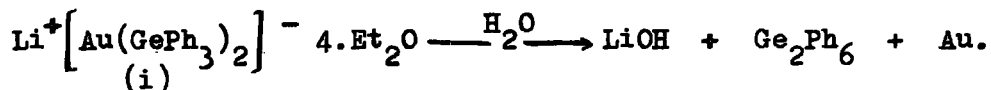
That this compound was indeed a salt was suggested by its high solubility in ethanol, without deposition of gold. Addition of tetraethylammonium iodide to such a solution gave an immediate precipitate of the unsolvated tetraethylammonium salt(ii) which separated from acetone as green plates:

$$\text{Li}^+\left[\text{Au(GePh}_3)_2\right]^- 4.\text{Et}_2\text{O} + \text{Et}_4\text{N}^+\text{I}^- \longrightarrow \text{Et}_4^+\text{N}\left[\text{Au(GePh}_3)_2\right]^- + \text{LiI}.$$
$$\text{(ii)}$$
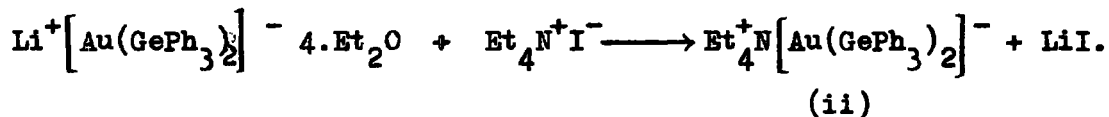
tetraethylammonium-bis(triphenyl-germyl)aurate(I).

Addition of benzyl chloride to the original mother liquors from the reaction involving phenyl-lithium, followed by the usual working-up process, led to the isolation of triphenylphosphinemonophenylgold(I) and no benzyl-triphenylgermane, thus the mother liquors contained no triphenylgermyl-lithium:

$$\text{Ph}_3\text{GeLi} + \text{PhCH}_2\text{Cl} \longrightarrow \text{Ph}_3\text{GeCH}_2\text{Ph} + \text{LiCl}.$$
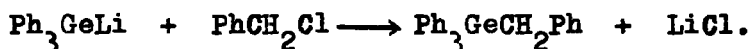
It thus appears that the reaction between phenyl-lithium and triphenyl-germyl-triphenylphosphinegold(I) involves initially the rupture of the metal-metal bond, as expected:

$$\text{Ph}_3\text{Ge.AuPPh}_3 + \text{PhLi} \longrightarrow \text{Ph}_3\text{GeLi} + \text{Ph}_3\text{PAuPh},$$
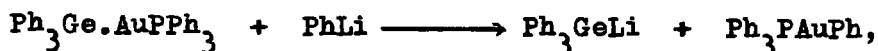
and this is followed by the rapid addition of triphenylgermyl-lithium to the original unreacted complex, with the simultaneous expulsion of tri-phenylphosphine:

$$Ph_3Ge.AuPPh_3 \ + \ Ph_3GeLi \xrightarrow{\ Et_2O\ } Li^+\left[(Ph_3Ge)_2Au\right]^-.4Et_2O \ + \ Ph_3P.$$
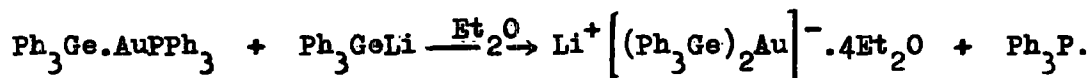
This view was supported by examining the reaction between preformed triphenylgermyl-lithium and triphenylgermyl-triphenylphosphinegold(I) in 1,2-dimethoxyethane, when a similar lithium salt was isolated, though in this case containing co-ordinated 1,2-dimethoxyethane, instead of diethyl ether, $Li^+\left[(Ph_3Ge)_2Au\right]^-.4C_4H_{10}O_2$. This lithium salt was slightly more stable than the corresponding etherate and gave an identical compound after reaction with tetraethylammonium iodide:

$$Ph_3GeLi \ + \ Ph_3Ge.AuPPh_3 \xrightarrow{\ 1,2-dimethoxy-\ ethane\ } Li^+\left[(Ph_3Ge)_2Au\right]^-.4C_4H_{10}O_2 + Ph_3P.$$

$$Et_4N^+I^-$$

$$Et_4N^+\left[(Ph_3Ge)_2Au\right]^-.$$
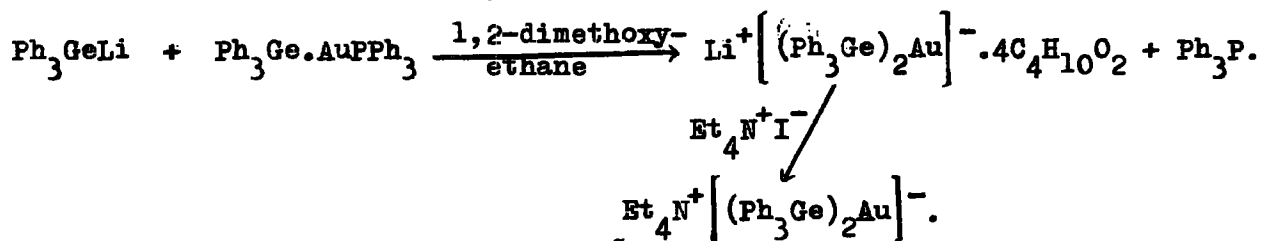
Satisfactory analytical data on $Li^+\left[(Ph_3Ge)_2Au\right]^-.4C_4H_{10}O_2$ were difficult to obtain due to contamination with lithium methoxide formed in the preparation of triphenylgermyl-lithium. An 82% recovery of triphenylphosphine was obtained from the mother liquors of this reaction.

PART B. <u>Hexa-aryldigermanes</u>.

Some of the work already described in this thesis required, as starting material, hexaphenyldigermane. The preparation of this compound by the interaction of germanium(1V)chloride and a large excess of phenylmagnesium bromide has been described(35,128). Also formed in this reaction is tetraphenylgermane, by normal substitution; and it is reported that good yields of the digermane can be obtained by a lower temperature of reflux than that employed for the preparation of tetraphenylgermane:

$$GeCl_4 \; + \; PhMgBr \longrightarrow Ph_4Ge \; + \; Ph_6Ge_2.$$
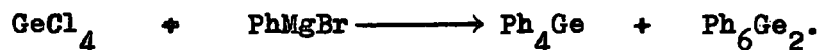
However closely the published procedure was followed, the yield of hexaphenyldigermane varied from 0 - 60%; such variations have also been reported by Gilman and Gerow(70). It thus appeared as though factors, other than mere temperature, were responsible for the preferential formation of hexaphenyldigermane rather than tetraphenylgermane, and it is difficult to see how hexaphenyldigermane, once formed, could decompose into tetraphenylgermane in the presence of an excess of phenylmagnesium bromide. An analogous case has been described recently by Seyferth(77) who carried out the reaction between germanium(1V)chloride and vinylmagnesium bromide, and obtained both hexavinyldigermane(25%) and tetravinylgermane(31%). The following reaction scheme was suggested:

$$GeCl_4 \; + \; 2RMgBr \longrightarrow R_2 \; + \; GeCl_2 \; + \; 2MgBrCl \ldots 1)$$

$$GeCl_2 \; + \; 3RMgBr \longrightarrow R_3GeMgBr \; + \; 2MgBrCl \ldots \ldots 2)$$

$$R_3GeMgBr \; + \; R_3GeCl \longrightarrow R_6Ge_2 \; + \; MgBrCl \ldots \ldots \ldots 3)$$

$$R = CH_2=CH-.$$
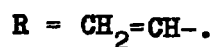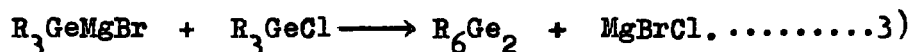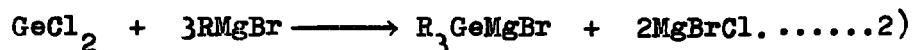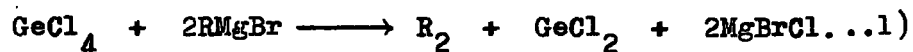
The first stage of this scheme is not very acceptable since germanium(1V) chloride often reacts with Grignard reagents to give high yields of the monogermane, R_4Ge, and negligible amounts of the digermane, R_6Ge_2. Furthermore, germanium(11)halides appear to react with organo-metallic reagents in a way more complicated than that suggested by reaction 2) of this scheme. part C of this thesis is concerned with this reaction. Reaction 2) involves the formation of a "germyl-Grignard" reagent, R_3GeMgX, which subsequently undergoes a coupling reaction with R_3GeCl, a product of the normal substitution of germanium(1V)chloride, to give the digermane, R_6Ge_2, (reaction 3). Considerable evidence for the existance of "germyl-Grignard" reagent has been obtained by Gilman and his co-workers(22,55), see page 29 of this thesis.

In considering alternative mechanisms to account for the formation of digermanes in the reaction between germanium(1V)chloride and Grignard reagents, it was thought that the reductive coupling process to give the digermane might be brought about by metallic magnesium, perhaps that present present as a reactive sludge from the Grignard preparation, which is not always removed by decantation or rough filtration through a glass wool plug. If this view is correct, then appreciable yields of the digermane are to be expected only if direct substitution of the halogen in R_3GeX is slow, due either to steric effects or to the relatively low reactivity of a particular Grignard reagent.

To test this view the reactions between germanium(1V)chloride and phenyl- and tolyl-magnesium bromides were carried out, both a), in the

presence of free magnesium, and b), in the absence of free magnesium; the latter condition was obtained by filtering the Grignard reagent prior to use through a Grade 4 sintered glass disc in an atmosphere of nitrogen. The results obtained from these reactions can be interpreted in terms of the following reaction scheme:

$$GeCl_4 + RMgX \longrightarrow R_3GeX \quad \ldots\ldots\ldots\ldots\ldots 1)$$
$$R_3GeX + RMgX \longrightarrow R_4Ge \quad \ldots\ldots\ldots\ldots\ldots 2)$$
$$R_3GeX + Mg \longrightarrow R_3GeMgX \quad \ldots\ldots\ldots\ldots 3)$$
$$R_3GeMgX + R_3GeX \longrightarrow R_6Ge_2 \quad \ldots\ldots\ldots\ldots 4)$$
$$R_3GeMgX + H_2O \longrightarrow R_3GeH \quad \ldots\ldots\ldots\ldots 5)$$
$$R_3GeX + RMgX \longrightarrow R_3GeMgX + RX \quad \ldots\ldots 6).$$
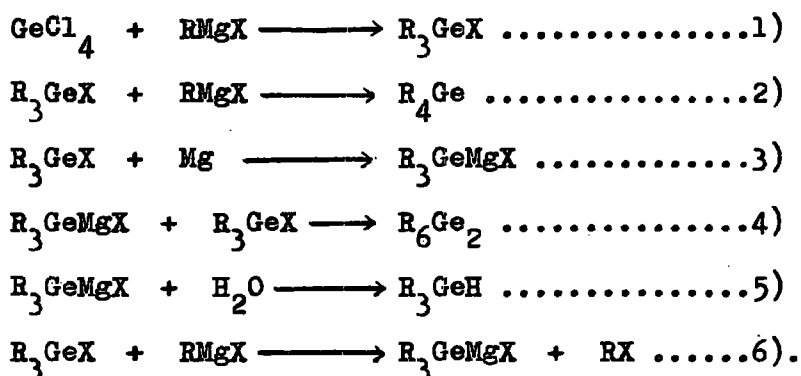
The highly reactive benzylmagnesium bromide gave high yields,(85-90%), of tetrabenzylgermane both in the presence, and in the absence of free magnesium metal. Thus only reactions 1) and 2) are involved.

Phenyl- and p-tolyl-magnesium bromides gave, in the presence of free magnesium metal, high yields of the digermanes, (reaction 1),3) and 4)), together with some monogermanes, (reaction 1) and 2)); but in the complete absence of free magnesium, only the monogermanes were isolated.

Evidence for the existance of the triarylgermyl-Grignard reagents in the reaction involving free magnesium (reaction 3)) was obtained for the o-, m-, and p-tolyl- derivatives, since, on hydrolysis, the corresponding hydrides were isolated by distillation in appreciable yields,(reaction 5)). Furthermore, in the reaction involving p-tolylmagnesium bromide and free magnesium was isolated, after brief reflux of the reaction mixture

followed by carbonation and hydrolysis, the acid $(\underline{p}\text{-tolyl})_3GeCOOH$:

$$(\underline{p}\text{-CH}_3C_6H_4\text{-})_3GeMgBr \quad + \quad CO_2 \longrightarrow (\underline{p}\text{-CH}_3C_6H_4\text{-})_3GeCOOMgBr \xrightarrow{\quad H_2O \quad}$$

$$(\underline{p}\text{-CH}_3C_6H_4\text{-})_3GeCOOH.$$
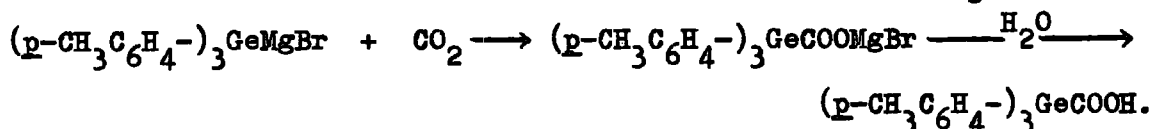
It thus follows that for the hydrides and the acid to be isolated from these reactions, the formation of the "germyl-Grignard" reagent,(reaction 3)), is more rapid than the coupling reaction,(reaction 4)). It was confirmed that the hydrides do not arise from metal/acid reduction of the halides:

$$R_3GeX \quad + \quad H_2 \longrightarrow R_3GeH \quad + \quad HX.$$
$$(Mg/acetic\ acid)$$
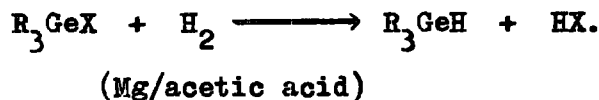
$\underline{m}$-Tolylmagnesium bromide gave a mixture of tetra-$\underline{m}$-tolylgermane and hexa-$\underline{m}$-tolyldigermane in the presence of free magnesium. In the complete absence of free magnesium metal, although the main product was tetra-$\underline{m}$-tolylgermane as expected, some 6% of hexa-$\underline{m}$-tolyldigermane was obtained.

With $\underline{o}$-tolylmagnesium bromide only the digermane, $(\underline{o}\text{-tolyl})_6Ge_2$, was isolated, either in the presence, or in the absence of free magnesium metal, though it is significant that in the presence of free magnesium the hydride, $(\underline{o}\text{-tolyl})_3GeH$, was obtained, whilst in the absence of free magnesium bromotri-$\underline{o}$-tolylgermane was the only other product isolated. Steric hindrance, together with the low reactivity of the Grignard reagent are probably the reasons for no $(\underline{o}\text{-tolyl})_4Ge$ being isolated. Tetra-$\underline{o}$-tolyl-germane has been prepared under conditions more vigorous than those employed in this work(16).

The formation of the digermane in the complete absence of free

magnesium in these two cases cannot be explained in terms of reactions 1)-5), and reaction 6) is postulated to occur in those cases where the halide R_3GeX is sterically hindered to the introduction of the fourth R group and hence may be converted slowly into the digermane by reaction 4). This slow reaction rate is reflected in the recovery of R_3GeBr from the reaction involving o-tolylmagnesium bromide when no free magnesium was present. Reaction 6) could be considered to involve an equilibrium:

$$R_3GeX \quad + \quad RMgX \quad \rightleftharpoons \quad R_3GeMgX \quad + \quad RX,$$

though it is probable that the species RX will undergo, to a certain extent, a Wurtz-type coupling reaction with the excess Grignard reagent present:

$$RX \quad + \quad RMgX \longrightarrow R_2 \quad + \quad MgX_2.$$

As has been described in the introduction to this thesis (page 32), hexaphenyldisilane has been produced by the coupling of chlorotriphenyl-silane, using either magnesium metal(71,83) or a Grignard reagent of the usual type(80). To determine the relative effectiveness of these two reactions, the reaction carried out by Selin and West(80), i.e. chloro-triphenylsilane and cyclohexylmagnesium bromide, was repeated using, in the first place, a filtered solution of the Grignard reagent and, in the second, an excess of free magnesium. Striking results were obtained which were completely compatible with the germanium analogues as described above. It was found that in the presence of free magnesium a high yield(75%) of the disilane was obtained, whereas, in the complete absence of free magnesium, under identical reaction conditions only a 8% yield of the

disilane was obtained, and the main of the chlorotriphenylsilane remained unreacted. Thus the reaction:

$$Ph_3SiCl \quad + \quad Mg \longrightarrow Ph_3SiMgCl,$$
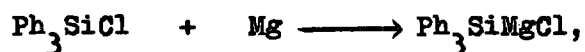
proceeds rapidly, whereas the exchange reaction:

$$Ph_3SiCl \quad + \quad C_6H_{11}MgBr \longrightarrow Ph_3SiMgBr \quad + \quad C_6H_{11}Cl,$$
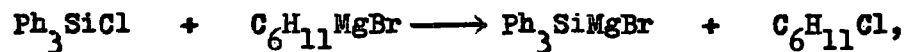
is slow. The usual coupling reaction then leads to the formation of hexaphenyldisilane,

$$Ph_3SiMgCl \quad + \quad Ph_3SiCl \longrightarrow Ph_6Si_2 \quad + \quad MgCl_2.$$

PART C. Phenylgermanium Polymers.

As has already been described in the introduction to this thesis (page 37), all attempts to prepare authentic organogermanium(11) compounds have probably met with failure.

Summers(79) reported that the reaction between phenyl-lithium and germanium(11)iodide in ether proceeded slowly and, after 3 days at reflux, red-brown reaction mixtures were obtained. Treatment of these with benzyl chloride followed by hydrolysis led to the isolation of diphenylgermanium (11), together with traces of tetraphenylgermane. However no experimental data were given, and in his review Rijkens reported that all attempts to prepare diphenylgermanium(11) had failed.

The present work was carried out in an attempt to prepare diphenyl-germanium(11). Though this aim was not realised, considerable information regarding the reaction of phenyl-lithium with germanium(11)iodide was obtained.

Germanium(11)iodide and phenyl-lithium react at $-25°$ to give a deep red, ether-insoluble oil from which was obtained an orange, air sensitive, and non-crystalline material, which had the composition approximating to $(Ph_2Ge_2I)_n$. In freezing benzene the degree of association varied with concentration within the range $n = 2-3$. Oxidation with oxygen was rapid in solution and the yellow polymeric product (M ca. 3350) had the composition Ph_2Ge_2OI.

It is unlikely that these compounds are homogeneous, and, on the basis of the work described below, the composition Ph_2Ge_2I is thought to

be somewhat fortuitous. It is probable that these compounds involve a variety of partially phenylated germanium iodides, such as PhGeI and $Ph_3Ge.GeI$.

The phenylgermanium iodides dissolved to give a deep blood-red solution at room temperature when two or more equivalents of phenyl-lithium were used, and the products isolated after hydrolysis depended partly on whether an excess of phenyl-lithium was present.

A 2:1 molar ratio of phenyl-lithium to germanium(11)iodide gave, after prolonged refluxing in ether, tetraphenylgermane, a red-brown amorphous polymer having a composition close to that of phenylgermanium, $(PhGe)_n$, n = 10 in freezing benzene, and, as main product, a yellow amorphous polymer (M = 800-1700) intermediate in composition between phenyl- and diphenyl-germanium. Treatment of the reaction mixture result-ing from the interaction of phenyl-lithium and germanium(11)iodide, 2:1 mole ratio, at −25° with benzyl chloride, followed by brief refluxing gave a similar yellow polymer and no benzyltriphenylgermane was obtained, suggesting the absence of triphenylgermyl-lithium at this stage of the reaction.

It is unlikely that either the red-brown or yellow polymeric material is homogeneous; both were totally involatile under vacuum and purification was limited to fractional precipitation from benzene solution by the addition of methanol. Both were free from halogen and oxygen (no Ge-O absorption was observed at 11.6μ in the infrared spectra). Oxidation of the material $(PhGe)_n$ by oxygen was rapid, both as the solid and in solution

but the yellow polymeric materials were essentially stable to aerial oxidation, though long exposure to the atmosphere caused some oxidation, as shown by the appearance of Ge-O absorption in the infrared spectrum. Oxidation of both these materials with fuming nitric acid was vigorous, the red polymer $(PhGe)_n$ actually took fire; this is in sharp contrast to the behaviour of hexaphenyldigermane and tetraphenylgermane, which react but slowly. Decomposition to germanium metal occurred at 400-450°.

Similar experiments involving a large excess of phenyl-lithium gave, in addition to tetraphenylgermane and yellow to red phenylgermanium polymers similar to those described above, triphenylgermane, which could only reasonably be formed by the hydrolysis of triphenylgermyl-lithium.

Triphenylaluminium also reacted with germanium(11)iodide in refluxing tetrahydrofuran to give bright yellow amorphous materials which, however, contained iodine and the infrared spectrum showed some Ge-O absorption, the latter presumably being formed by the hydrolysis of some residual Ge-I groups:

$$Ge-I \ + \ H_2O \longrightarrow Ge-OH \longrightarrow Ge-O-Ge \ + \ H_2O,$$
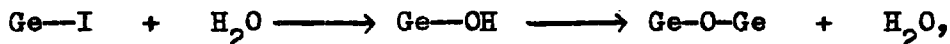
since the entire working-up process was carried out in an atmosphere of nitrogen.

The yellow phenyl-germanium polymers obtained from the experiments involving phenyl-lithium were subjected to bromine degradation under mild conditions, with a view to obtain -ing structural information about the polymer.

Bromination in either chloroform or 1,2-dibromoethane solution proceeded rapidly at first and then less quickly, until, after 1 week, from

2.5-3.0 g.equivalents of bromine/g.atom of germanium had been absorbed. The resulting mixture of bromophenylgermanes was difficult to purify, and only bromotriphenylgermane, Ph_3GeBr, could be isolated directly from the crude mixture:

$$Ph_3Ge- \ + \ Br_2 \longrightarrow Ph_3GeBr.$$
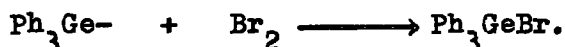
Hydrolysis of the mixture led to the isolation of phenylgermanoic anhydride,

$$PhGe^{\equiv} \ + \ 3Br_2 \longrightarrow PhGeBr_3 \xrightarrow{H_2O} (PhGeO)_2O.$$

Thus, although the composition of the polymeric material lies between that of PhGe and Ph_2Ge, it evidently contains Ph_3Ge- and $PhGe^{\equiv}$ groups.

A more detailed study of the brominated degradation products was carried out by treating the crude brominated mixture with an excess of a filtered solution of ethylmagnesium bromide; the volatile products were then characterised by vapour phase chromatography using the authentic compounds for comparison. In this way diethyldiphenylgermane, triethylphenylgermane and a trace of tetraethylgermane were isolated

$$Ph_2Ge{<} \ + \ 2Br_2 \longrightarrow Ph_2GeBr_2 \xrightarrow{EtMgBr} Ph_2GeEt_2,$$

$$PhGe{\leq} \ + \ 3Br_2 \longrightarrow PhGeBr_3 \xrightarrow{EtMgBr} PhGeEt_3,$$

$$/Ge{\sim} \ + \ 4Br_2 \longrightarrow GeBr_4 \xrightarrow{EtMgBr} Et_4Ge.$$
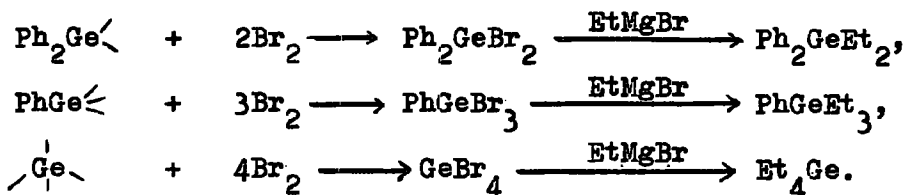
Thus the presence of $Ph_2Ge{<}$, $PhGe{<}$, and $/Ge{\sim}$ groups in the polymer is suggested.

The solid products isolated were ethyltriphenylgermane:

$$Ph_3Ge- \ + \ Br_2 \longrightarrow Ph_3GeBr \xrightarrow{EtMgBr} Ph_3GeEt,$$
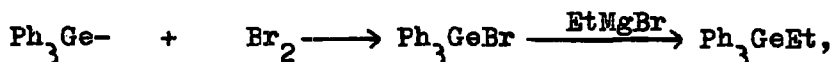
and a small amount of a crystalline compound which appeared to be a digermane of composition $Et_2Ge_2Ph_4$ which may be either $Ph_3Ge.GePhEt_2$ or

$Ph_2EtGe.GeEtPh_2$.

Isolation of the substituted digermane indicates the definite existence of a metal—metal bonded structure, for example:

$$Ph_3Ge.\overset{/}{\underset{Ph}{Ge}}\text{-} \;+\; 2Br_2 \longrightarrow Ph_3Ge.GePhBr_2 \xrightarrow{\;EtMgBr\;} Ph_3Ge.GePhEt_2.$$

It is possible to account for the isolation of diethyldiphenylgermane by a scheme which does not involve $Ph_2Ge\langle$ groups in the polymer, such a scheme would involve cleavage of a germanium—carbon bond:

$$Ph_3Ge\text{-} \;+\; 2Br_2 \longrightarrow Ph_2GeBr_2 \;+\; PhBr$$
$$\Big\downarrow EtMgBr$$
$$Ph_2GeEt_2 \;+\; EtPh,$$
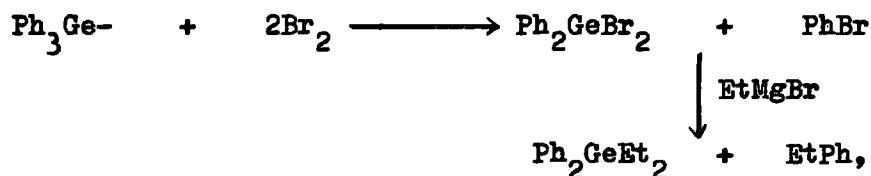
in which case either bromobenzene or ethylbenzene would be isolated. However, as no such species were isolated it was thought that cleavage of metal—carbon bonds did. not occur to any significant extent under the mild conditions employed, and certainly not to such an extent as to account for the relative high yield of diethyldiphenylgermane. This was shown to be so by the bromination of hexaphenyldigermane under identical experimental conditions, which afforded only traces of diethyldiphenylgermane and bromobenzene,

$$Ph_3Ge.GePh_3 \;+\; Br_2 \xrightarrow{\;EtMgBr\;} Ph_3GeEt \;+\; (\;Et_2GePh_2 \;+\; PhBr).$$
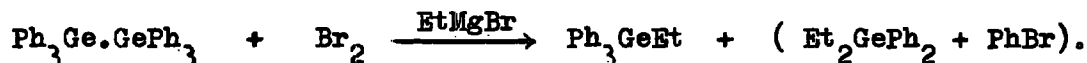
The fact that the bromination reaction proceeds rapidly at first and then more slowly suggests that there are present in the polymer, unsaturated centres which take up bromine readily, the actual cleavage of metal—metal bonds proceeding more slowly. By interrupting the bromination at the end of the rapid stage and ethylating the crude mixture, a yellow involatile

amorphous product was obtained which contained both ethyl- and phenyl-groups. These centres of unsaturation may involve what is approaching a germanium-germanium double bond, for example:

$$\underset{\substack{Ph \quad Ph}}{-Ge{=}{=}Ge-} \xrightarrow{Br_2} \underset{\substack{Ph \quad Ph}}{\overset{Br \quad Br}{-Ge{-}Ge-}} \xrightarrow{EtMgBr} \underset{\substack{Ph \quad Ph}}{\overset{Et \quad Et}{-Ge{-}Ge-}} .$$
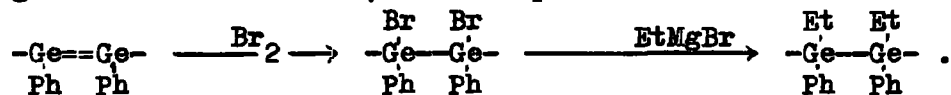
Any conclusions on the mechanism of formation and structure of these polymeric materials must be largely speculative. It seems reasonable to suppose, as did Zeiss(69), that chains or rings of germanium atoms are involved. The actual isolation of pure samples of tetraphenylgermane and triphenylgermane from these reactions indicate the following stages:

$$GeI_2 \ + \ PhLi \longrightarrow PhGeI \ + \ LiI\ldots\ldots\ldots\ldots1).$$

$$PhGeI \ + \ PhLi \longrightarrow Ph_2Ge \ + \ LiI\ldots\ldots\ldots\ldots2).$$

$$Ph_2Ge \ + \ PhLi \longrightarrow Ph_3GeLi \xrightarrow{H_2O} Ph_3GeH\ldots\ldots.3).$$
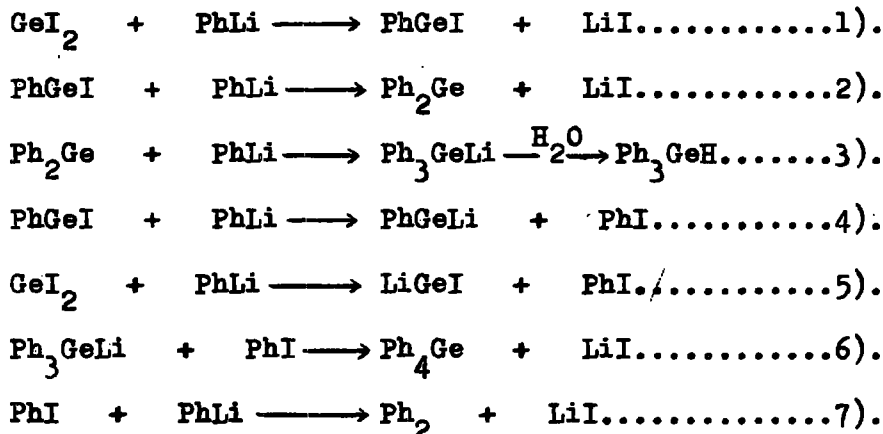
$$PhGeI \ + \ PhLi \longrightarrow PhGeLi \ + \ PhI\ldots\ldots\ldots4).$$

$$GeI_2 \ + \ PhLi \longrightarrow LiGeI \ + \ PhI.\ldots\ldots\ldots5).$$

$$Ph_3GeLi \ + \ PhI \longrightarrow Ph_4Ge \ + \ LiI\ldots\ldots\ldots\ldots6).$$

$$PhI \ + \ PhLi \longrightarrow Ph_2 \ + \ LiI\ldots\ldots\ldots\ldots7).$$

Reaction 1),2) and 3) involve normal substitution and the addition of phenyl-lithium to diphenylgermanium(11) to give triphenylgermyl-lithium. Reaction 4) and 5) involve metal-halogen exchange processes which seem essential in order to produce iodobenzene for reaction 6), to account for the formation of tetraphenylgermane, and to build up polymers having all the degrees of phenylation as indicated by the bromine degradation studies. Similar metal-halogen exchange reactions of sterically hindered halides

of the type R$_3$GeX is discussed in Part B of this thesis,(page139).

The isolation of triphenylgermane from reactions involving an excess of phenyl-lithium is not really surprising since the triphenylgermyl-lith-ium from which the hydride is obtained, and which is probably less reactive than phenyl-lithium, is competing for Ge-I groups with a vast excess of phenyl-lithium.

The isolation of biphenyl from these reactions could indicate that reaction 7) occurs, however Wûrtz coupling in the actual preparation of the phenyl-lithium should not be overlooked.

The evidence for completely unphenylated germanium atoms in the polymer (isolation of tetraethylgermane) is surprising since one might have expected mono-phenylation to be complete (reaction 1). However in a purely formal sense one can write partial structures such as a) or b) which involve unphenylated germanium:

$$2Ph_3GeLi \quad + \quad GeI_2 \longrightarrow (Ph_3Ge)_2Ge\ldots\ldots a).$$

$$LiGeI \quad + \quad GeI_2 \longrightarrow IGe.GeI \xrightarrow{Ph_3GeLi} IGe.Ge.GePh_3\ldots\ldots b).$$
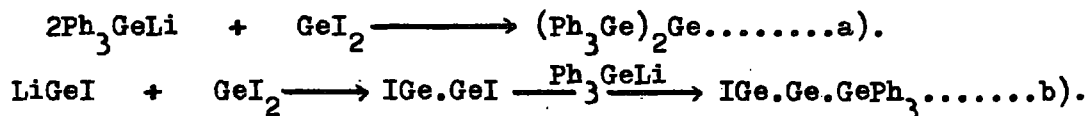
The possibility of obtaining bis(triphenylgermyl)germanium(11), a), was examined by adding preformed triphenylgermyl-lithium to germanium(11) iodide in 1,2-dimethoxyethane. An immediate exothermic reaction occurred in which a deep red-brown solution was formed, very similar to those resulting from the interaction of phenyl-lithium and germanium(11)iodide. After hydrolysis, which did not cause decolourisation, the well crystalline compound, tris(triphenylgermyl)germane (d), was obtained in 36% yield.

$$\underset{(a)}{(Ph_3Ge)_2Ge} \xrightarrow{Ph_3GeLi} \underset{(c)}{(Ph_3Ge)_3GeLi} \xrightarrow{H_2O} \underset{(d)}{(Ph_3Ge)_3GeH}.$$
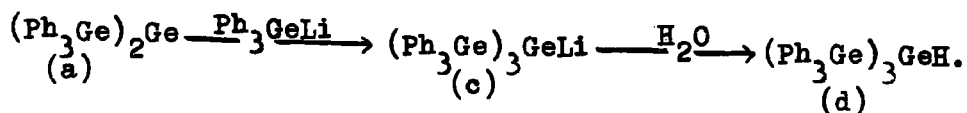
Such a compound could only be formed by hydrolysis of the lithio-salt(c).
Side reactions involving metal-halogen exchange were again evident, and
probably account for the intense colour of the solution. However, the
only product isolated which could arise from such reactions was hexaphenyl-
digermane,

$$Ph_3GeLi \quad + \quad GeI_2 \longrightarrow Ph_3GeI \quad + \quad GeILi.$$

$$Ph_3GeI \quad + \quad Ph_3GeLi \longrightarrow Ph_6Ge_2 \quad + \quad LiI.$$

No bis(triphenylgermyl)germanium(ll), a), was isolated, even in the pres-
ence of excess germanium(ll)iodide. It thus appears as though the reaction

$$Ph_3GeLi \quad + \quad (Ph_3Ge)_2Ge \rightleftharpoons (Ph_3Ge)_3GeLi$$

is rapid, and, essentially irreversible.

The Ge-H stretching frequency in tris(triphenylgermyl)germane is
displaced from the normal value of 2037 cm^{-1} in triphenylgermane to
1953 cm^{-1}, and it is possible that the unphenylated germanium atoms which
are present in the phenylgermanium polymers actually involve one or more
Ge-H bonds. Bromination of such systems would still result in the format-
ion of germanium(lV)bromide. Examination of thick nujol mulls of various
polymers in the region 4 - 6μ failed to show any Ge-H absorption except
in those formed in the reaction involving excess phenyl-lithium, when a
weak absorption was observed at 1970 cm^{-1} (not sharp). It should be noted
that the polymer used in the bromination studies showed no such absorption.

Tris(triphenylgermyl)germane also showed strong absorption at 228 cm^{-1},
which is absent from the spectra of tetraphenylgermane and hexaphenyldi-
germane, and it may be due to a Ge-Ge stretching frequency. Absorption

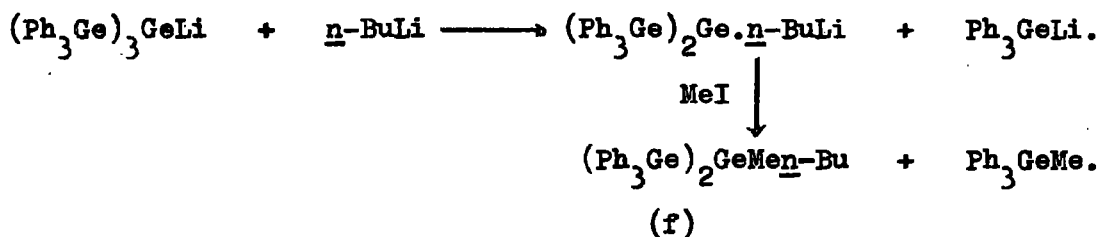maximum at 229 cm^{-1} in the Ramen spectrum of digermane, Ge_2H_6, has been assigned to Ge—Ge stretch(132). More recent measurements indicate a value of 269.8 cm^{-1} for Ge_2H_6 and 261.5 cm^{-1} for Ge_2D_6 (133).

Tris(triphenylgermyl)germane underwent an immediate reaction with n-butyl-lithium in diethyl ether to give the yellow, moderately soluble, lithium salt(c).Reaction of this compound with methyl iodide gave methyl-tris(triphenylgermyl)germane(e), which also showed strong absorption at 228 cm^{-1}.

$$(Ph_3Ge)_3GeLi \quad + \quad MeI \longrightarrow (Ph_3Ge)_3GeMe \quad + \quad LiI.$$
$$(c) \hspace{8cm} (e)$$
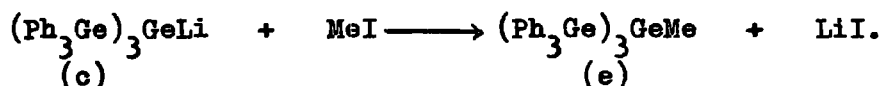
Evidence was obtained that cleavage of germanium-germanium bonds occurred with the excess n-butyl-lithium employed, to give what appeared to be n-butylmethyl-bis(triphenylgermyl)germane(f).

$$(Ph_3Ge)_3GeLi \quad + \quad n-BuLi \longrightarrow (Ph_3Ge)_2Ge.n-BuLi \quad + \quad Ph_3GeLi.$$
$$MeI \downarrow$$
$$(Ph_3Ge)_2GeMen-Bu \quad + \quad Ph_3GeMe.$$
$$(f)$$

Two unidentified compounds were also isolated.

Bromination of tris(triphenylgermyl)germane followed by treatment with ethylmagnesium bromide led to the isolation of ethyltriphenylgermane as the only product, the small scale of the reaction was probably the reason for no tetraethylgermane being isolated,

$$(Ph_3Ge)_3GeH \quad + \quad 4Br_2 \xrightarrow{EtMgBr} 3Ph_3GeEt \quad + \quad (GeEt_4).$$

PART D. Organo-Germylphosphines.

Despite the fact that there are several organogermanes described which contain the germanium – nitrogen link (see pages 23 and 53 of this thesis), analogous compounds containing the germanium – phosphorus bond are unknown, in fact for the entirity of Group IV only Me_3SiPPh_2 (158), Et_3SnPPh_2 (158) and $(Et_2P)_4Si$ (166) are known.

The present work was undertaken in an attempt to prepare organo-germylphosphines, to examine the reactivity of the germanium – phosphorus bond inthese compounds, and to compare these properties with those reported for the analogous germylamines.

Triethylgermyldiphenylphosphine (I) was prepared by the reaction of bromotriethylgermane with lithium diphenylphosphide in tetrahydrofuran. The reaction was rapid and exothermic:

$$Et_3GeBr \quad + \quad LiPPh_2 \quad \longrightarrow \quad Et_3GePPh_2.$$
$$(I)$$
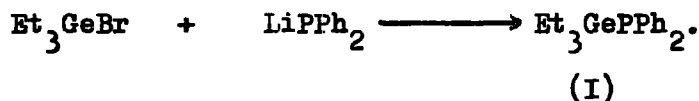
Isolation was easily effected by distillation under high vacuum (b.p $146°/10^{-3}$mm.).

As for the analogous nitrogen compound, hydrolysis of the germanium – phosphorus bond was rapid, being complete after 5 minutes in a 10% solution of water in 1,2-dimethoxyethane containing a 10 fold excess of water, and gave hexaethyldigermoxane and diphenylphosphine:

$$Et_3GePPh_2 \quad + \quad H_2O \quad \longrightarrow \quad Ph_2PH \quad + \quad Et_3GeOH \longrightarrow (Et_3Ge)_2O \quad + \quad H_2O.$$

Oxidation of triethylgermyldiphenylphosphine with dry oxygen in ether solution was rapid and resulted in the oxidation of P(III) to P(V) and the insertion of oxygen into the germanium – phosphorus bond

to give the triethylgermyl ester of diphenylphosphinic acid (II):

$$Et_3Ge-PPh_2 \quad + \quad O_2 \longrightarrow Et_3Ge-O-P(O)Ph_2.$$

triethylgermyldiphenylphosphonate

(II)
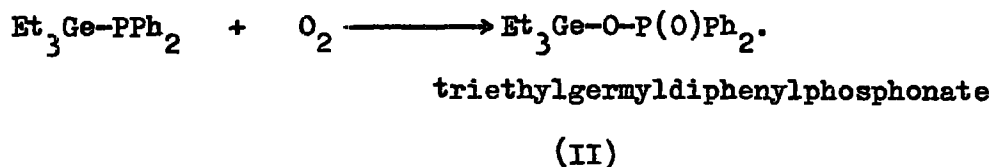
The infrared spectrum of (II) is shown in relationship to hexaethyl-
digermoxane and the parent compound (I), figure 2 page 90. The most
interesting feature of this is the shift in frequency of the Ge-O
vibration from 855 cm^{-1} in hexaethyldigermoxane to 954 cm^{-1} in the
ester (II). The P=O stretching frequency at 1220 cm^{-1} in (II) lies
close to the range quoted for alkyl and aryl esters of diphenylphosphinic
acid, (1350 - 1250 cm^{-1}) (170). That the oxidation product (II) was
in fact triethylgermyldiphenylphosphonate was checked by preparing this
compound unambiguously from hexaethyldigermoxane and diphenylphosphinic
acid:

$$(Et_3Ge)_2O \quad + \quad 2Ph_2POOH \longrightarrow 2Et_3GeO-P(O)Ph_2 \quad + \quad H_2O.$$

Complete disappearance of the Ge-O absorption at 855 cm^{-1} in $(Et_3Ge)_2O$
and the appearance of Ge-O absorption at 954 cm^{-1} in the product ester
was observed. The entire infrared spectrum of the ester was identical to
that of the oxidation product of the parent compound (I).
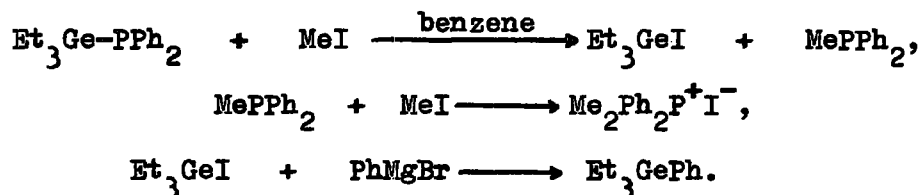
Triethylgermyldiphenylphosphonate was a thermally stable liquid
which could be distilled under vacuum (b.p 160-62°/10^{-3}mm.). In the
presence of a dilute solution of water in 1,2-dimethoxyethane it
appeared to give a low hydrate which could be distilled. However,
exposure to an excess of water over a long period (6 weeks) caused

hydrolysis of the Ge—O—P bond:

$$Et_3Ge-O-P(O)Ph_2 \quad + \quad H_2O \longrightarrow Ph_2POOH \quad + \quad (Et_3Ge)_2O,$$

the diphenylphosphinic acid crystallised out at the water – ester interface.

Experiments were carried out to determine whether triethylgermyl-diphenylphosphine formed quaternary salts with alkyl halides, the compound $Me_3Si\overset{+}{N}Me_3I^-$ having been reported (157). The reaction of (I) with methyl iodide resulted, however, in the rapid, and almost quantitative cleavage of the germanium – phosphorus bond. The methyldiphenyl-phosphine formed quaternised in the normal way:

$$Et_3Ge-PPh_2 \quad + \quad MeI \xrightarrow{\text{benzene}} Et_3GeI \quad + \quad MePPh_2,$$

$$MePPh_2 \quad + \quad MeI \longrightarrow Me_2Ph_2P^+I^-,$$

$$Et_3GeI \quad + \quad PhMgBr \longrightarrow Et_3GePh.$$

The triethyliodogermane was characterised as triethylphenylgermane by the addition of phenylmagnesium bromide to the solution after removal of the dimethyldiphenylphosphonium iodide.

Organo-lithium reagents also cleaved the germanium – phosphorus bond in (I); n-butyl-lithium , which proceeded to 85% after 5 hrs at 0°, was far more reactive than phenyl-lithium. The products,using n-butyl-lithium, triethyl-n-butylgermane and lithium diphenylphosphide, were those expected on the basis of the assumed polarity of the germanium – phosphorus bond:

$$Et_3Ge-PPh_2 \quad + \quad n-BuLi \longrightarrow Et_3Ge-n-Bu \quad + \quad Ph_2PLi.$$

The lithium diphenylphosphide was characterised as ethyldiphenylphosphine
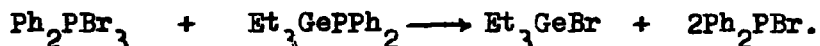
after the addition of one mole equivalent of ethyl bromide.

Low temperature bromination of (I) also proceeded rapidly to give, as final products, bromodiphenylphosphine and bromotriethylgermane:

$$Et_3GePPh_2 \ + \ Br_2 \xrightarrow[-20°]{CCl_4} Et_3GeBr \ + \ Ph_2PBr.$$
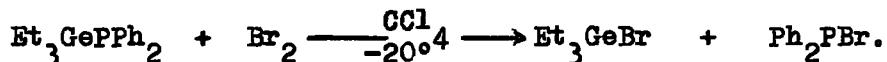
An intermediate insoluble yellow solid was formed in this reaction after the addition of 0.4 mole equivalents of bromine but this gradually redissolved after the addition of a further 0.2 mole equivalents. This solid was probably tribromodiphenylphosphorus(V):

$$Ph_2PBr \ + \ Br_2 \longrightarrow Ph_2PBr_3$$
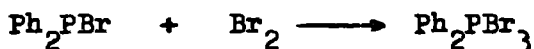
which then acts as a brominating agent:

$$Ph_2PBr_3 \ + \ Et_3GePPh_2 \longrightarrow Et_3GeBr \ + \ 2Ph_2PBr.$$

The final solution was clear and colourless.

Triethylgermyldiphenylphosphine caused the rapid solution of silver(I)iodide in methylcyclohexane to give the 1 : 1 complex $Et_3GePh_2P \rightarrow AgI$, which was approximately tetrameric in freezing benzene. This complex was, however, very unstable and deposited silver(I)iodide on exposure to the atmosphere or to water. This behaviour should be compared to that of the highly air sensitive tertiary alkyl- or mixed alkyl-aryl- phosphines which, on complexing with metal halides, give air stable complexes, the centre of reactivity (the phosphorus atom) being removed. In triethylgermyldiphenylphosphinesilver(I)iodide, however, the germanium-phosphorus bond is an added centre of reactivity, which is not directly involved in complex formation and is thus susceptible to attack.

The phosphine (I) showed no tendency to form a higher complex with silver(I)iodide than the 1 : 1 complex described above.

An alternative method of preparation of the compound (I) was attempted by the interaction of diphenylphosphine and bromotriethyl-germane in the presence of pyridine:

$$Ph_2PH + BrGeEt_3 \xrightarrow[\text{T.H.F.}]{\text{pyridine}} Ph_2P\text{-}GeEt_3 + PyHBr.$$

None of the desired product was isolated however, starting materials being recovered.

The reactions of the members of the series of arylhalogermanes, Ph_nGeX_{4-n}, $n = 0,1,2,3$; X = halogen, with lithium diphenylphosphide in tetrahydrofuran were carried out with the aim of preparing the corresponding phosphinogermanes:

$$Ph_nGeX_{4-n} + (4-n)Ph_2PLi \longrightarrow Ph_nGe(PPh_2)_{4-n} + (4-n)LiCl.$$
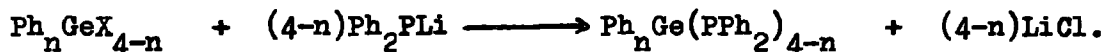
However, only in the cases of bromotriphenylgermane and dibromodiphenyl-germane were the desired products obtained, polymeric materials with a lower ratio of Ph_2P : Ge than expected were obtained in the other two cases.

The reaction of lithium diphenylphosphide with bromotriphenylgermane in tetrahydrofuran was rapid and gave triphenylgermyldiphenylphosphine (III) in high yield. The final reaction mixture was colourless.
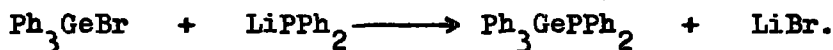
$$Ph_3GeBr + LiPPh_2 \longrightarrow Ph_3GePPh_2 + LiBr.$$
$$(III)$$

Triphenylgermyldiphenylphosphine was a high melting, well crystalline, white opaque compound (needles), very soluble in benzene and could be

recrystallised readily from methylcyclohexane.

Bis(diphenylphosphino)diphenylgermane (IV) was similarly prepared from dibromodiphenylgermane and lithium diphenylphosphide. Again the final reaction mixture was colourless except for traces of unreacted lithium diphenylphosphide:

$$Ph_2GeBr_2 \quad + \quad 2LiPPh_2 \longrightarrow Ph_2Ge(PPh_2)_2 \quad + \quad 2LiBr.$$
$$(IV)$$
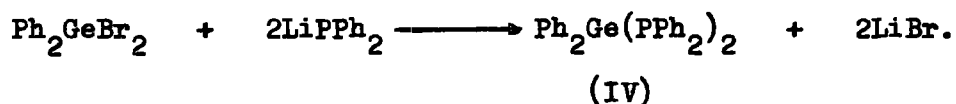
Purification of this compound (IV) proved to be somewhat difficult due to contamination with some tetraphenyldiphosphine (10%) and some unidentified organogermane formed along with the tetraphenyldiphosphine. The behaviour of dibromodiphenylgermane is in this respect intermediate between that of bromotriphenylgermane, which gives no tetraphenyldiphosphine and high yields of the required germylphosphine, and tribromophenylgermane which gives high yields of tetraphenyldiphosphine and no tris(diphenylphosphino)phenylgermane. The mode of formation of tetraphenyldiphosphine in these reactions is discussed below. Note should be made that Fritz and Poppenburg(166) obtained some tetraethyldiphosphine from the reaction of silicon(IV)chloride and lithium diethylphosphide, however, they also isolated some tetrakis(diethylphosphino)germane.

The addition of a solution of lithium diphenylphosphide to tribromophenylgermane in tetrahydrofuran caused the immediate discharge of the cherry-red colour until 0.5 mole equivalents had been added. At this point the reaction mixture took on a pale green colour which was displaced by a red colour after 2 mole equivalents had been added. This

red colour intensified during the rest of the addition. From this
reaction mixture was isolated tetraphenyldiphosphine (28%) and a cream
powder (from methylcyclohexane) which was intermediate in composition
between $PhGe(PPh_2)$ and $PhGe$. The molecular weight of this material,
determined cryoscopically in benzene, was 684, corresponding to an
average chain length of from 2 to 3 germanium atoms:

$$PhGeBr_3 \quad + \quad 3LiPPh_2 \longrightarrow Ph_4P_2 \quad + \quad Polymer.$$
No tris(diphenylphosphino)phenylgermane was isolated.

The reaction of germanium(IV)chloride with lithium diphenylphosphide
resulted in a most interesting colour change. Initially the deep cherry -
red colour of the lithium diphenylphosphide solution was discharged on
adding it to the germanium(1V)chloride in tetrahydrofuran, until 1.8
mole equivalents of this reagent had been added, when the reaction
mixture rapidly turned deep red. This red colour intensified during the
addition of the remainder of the lithium diphenylphosphide. In contrast
to the behaviour of triethylgermyldiphenylphosphine, these red solutions
were stable to deaerated water, and afforded, together with tetraphenyl-
diphosphine (52%), a deep red - brown polymeric material. The composition
of this polymer was approximately Ph_2PGe and the molecular weight,
determined cryoscopically in benzene, was 817, corresponding to an
average chain length of approximately 3 germanium atoms.

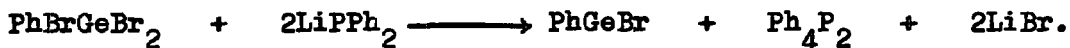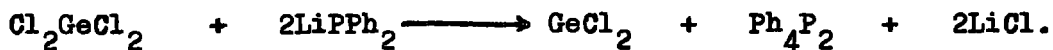$$GeCl_4 \quad + \quad 4LiPPh_2 \longrightarrow Ph_4P_2 \quad + \quad Polymer.$$
No tetrakis(diphenylphosphino)germane was obtained.

This red polymer was very soluble in benzene but only sparingly

soluble in methylcyclohexane. Oxidation with dry oxygen in solution was rapid and involved the absorption of 2.3 gm.atoms of oxygen / Ph_2P unit. The product of oxidation was a benzene insoluble yellow powder, the infrared spectrum of which, though somewhat confused showed Ge-O-Ge absorption at 837 cm^{-1}. This behaviour is in contrast to the mode of oxidation of triethylgermyldiphenylphosphine and indicates that the germanium atoms, though probably not all, are in a low valency state or that they are involved in chemically unsaturated systems in the polymer, such systems would give rise to Ge-O-Ge groupings on oxidation. There is probably little doubt that they are completely analogous to the phenyl-germanium polymers described in Part C of this thesis. On the basis of this it is suggested that this polymer, and the one derived from tribromophenylgermane, are not homogeneous and probably contain germanium atoms, in all possible states of "phosphination" linked together and having germanium - germanium unsaturated systems.

Any mechanism for the production of tetraphenyldiphosphine and the formation of the phosphinogermanium polymers in these reactions must be somewhat speculative. The following possibilities present themselves and it is possible that the reactions follow ones of the paths described, though in fact some "hybrid" involving all schemes could be nearer to the truth.

1) The initial reduction of germanium(1V)chloride to germanium(11) chloride and tribromophenylgermane to phenylgermanium(11)bromide by lithium diphenylphosphide:

$$Cl_2GeCl_2 \quad + \quad 2LiPPh_2 \longrightarrow GeCl_2 \quad + \quad Ph_4P_2 \quad + \quad 2LiCl.$$

$$PhBrGeBr_2 \quad + \quad 2LiPPh_2 \longrightarrow PhGeBr \quad + \quad Ph_4P_2 \quad + \quad 2LiBr.$$

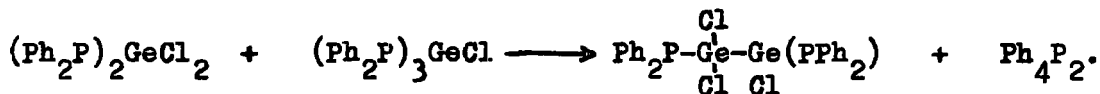The germanium(11)halide would then react with lithium diphenylphosphide
in a way similar to the mode of reaction of germanium(11)iodide with
phenyl-lithium (Part C of this thesis) to give polymeric products. If
this were so then high yields of tetraphenyldiphosphine would be isolated
from the reaction involving a 2 : 1 molar ratio of lithium diphenylphosphide
and germanium(1V)chloride. Such a reaction was carried out but <u>no</u>
tetraphenyldiphosphine was isolated. The crude product from this reaction
was an oil which rapidly darkened on heating under vacuum and appeared to
be a mixture of various diphenylphosphine substituted germanium halides.
The possibility that the tetraphenyldiphosphine was complexing with the
germanium(11)halide should not be overlooked, in fact tetraphenyldiphosphine
was shown to give a complex with germanium(11)iodide. This complex lost
tetraphenyldiphosphine rapidly upon heating under vacuum.

2) Inter- or intra- elimination reactions, involving partially
substituted chlorogermanes could occur:

$$(Ph_2P)_3GeCl \longrightarrow Ph_4P_2 \quad + \quad Ph_2PGeCl,$$

or,

$$(Ph_2P)_2GeCl_2 \quad + \quad (Ph_2P)_3GeCl \longrightarrow Ph_2P\overset{Cl}{\underset{Cl}{-}}\overset{|}{Ge}-Ge(PPh_2) \quad + \quad Ph_4P_2.$$
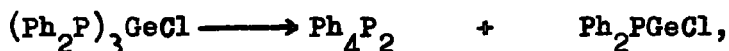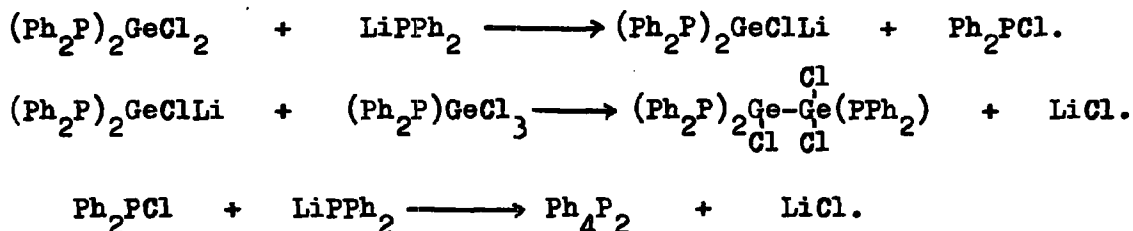
Similarly chlorodiphenylphosphine could be eliminated which would give
tetraphenyldiphosphine on reaction with lithium diphenylphosphide.

3) Normal substitution could occur to give, for example,
$(Ph_2P)_2GeCl_2$ which could then undergo a metal - halogen exchange reaction

followed by coupling of the usual type:

$$(Ph_2P)_2GeCl_2 \quad + \quad LiPPh_2 \longrightarrow (Ph_2P)_2GeClLi \quad + \quad Ph_2PCl.$$

$$(Ph_2P)_2GeClLi \quad + \quad (Ph_2P)GeCl_3 \longrightarrow (Ph_2P)_2\overset{Cl}{\underset{Cl\ Cl}{Ge-Ge}}(PPh_2) \quad + \quad LiCl.$$

$$Ph_2PCl \quad + \quad LiPPh_2 \longrightarrow Ph_4P_2 \quad + \quad LiCl.$$

The product digermane could then undergo a similar sequence to build up

polymeric materials. Unsaturated Ge-Ge systems would arise, in this

mechanism, from the elimination of lithium chloride from, for example,

$(Ph_2P)\underset{Li\ Cl}{Ge-Ge}Cl_2$.
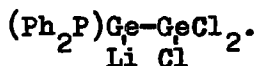
This latter mechanism is probably the most attractive one as one

would expect a rapid colour change to be associated with the formation
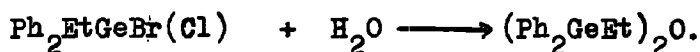
of the germyl-lithium reagents.

An attempt to detect the presence of Ge-Li groups in the reaction

mixtures resulting from the interaction of germanium(1V)chloride and

both 1.8 and 3.0 mole equivalents of lithium diphenylphosphide by

carrying out the following reaction sequence proved inconclusive.

The reaction mixtures were in both cases, treated with an excess

of ethylbromide at reflux point to effect cleavage of all Ge-P bonds with

the formation of Ge-Br groups and to convert any Ge-Li groups into Ge-Et

groups. No diethyldiphenylphosphonium bromide was isolated from the

reaction involving 1.8 mole equivalents of lithium diphenylphosphide and

only trace amounts were formed in the reaction involving 3.0 mole

equivalents. In a control experiment ethyl bromide cleaved triphenylgermyl-

diphenylphosphine under the same conditions to give bromotriphenylgermane

and diethyldiphenylphosphonium bromide. It would thus appear that the reaction intermediates, if they were cleaved by ethylbromide, underwent reverse addition of ethyl bromide,to give diphenylbromophosphine and ethyl-germanium groups. If this were so then any Ge—Et groups formed from Ge—Li entities would be masked. The reaction mixtures were then treated with phenylmagnesium bromide in order to substitute all halogen by phenyl groups. However, the reaction was further complicated by the incompleteness of this Grignard reaction. What appeared to be a mixture of bromoethyl-diphenylgermane and chloroethyldiphenylgermane was isolated from the react-ion involving 1.8 mole equivalents of the lithium reagent.

Both reactions gave some triphenylphosphine oxide. This could have been formed from the interaction of bromodiphenylphosphine and phenyl-magnesium bromide followed by oxidation. In addition, the reaction involving 3 mole equivalents of lithium diphenylphosphide gave some diphenylphosphinic acid. This could have arisen from the exposure of the tetraphenyldiphosphine formed in this reaction to the atmosphere, all diphenylphosphine being removed by distillation.

Both reactions gave what appeared to be a mixture of <u>sym</u> tetraphenyl-diethyldigermoxane, $Ph_2EtGeOGeEtPh_2$, and the ester diphenylethylgermyl-diphenylphosphonate, $Ph_2EtGeOP(O)Ph_2$ (only small amounts of this mixture were isolated in the reaction involving 1.8 mole equivalents of lithium diphenylphosphide). These compounds could be formed by the following schemes:

$$Ph_2EtGeBr(Cl) \quad + \quad H_2O \longrightarrow (Ph_2GeEt)_2O.$$

$$Ph_2EtGePPh_2 \quad + \quad H_2O \longrightarrow (Ph_2EtGe)_2O,$$

$$Ph_2PGeEtPh_2 \quad + \quad O_2 \longrightarrow Ph_2EtGe-O-P(O)Ph_2,$$

$$(Ph_2EtGe)_2O \quad + \quad 2Ph_2POOH \longrightarrow 2Ph_2EtGe-O-P(O)Ph_2 \quad + \quad H_2O.$$
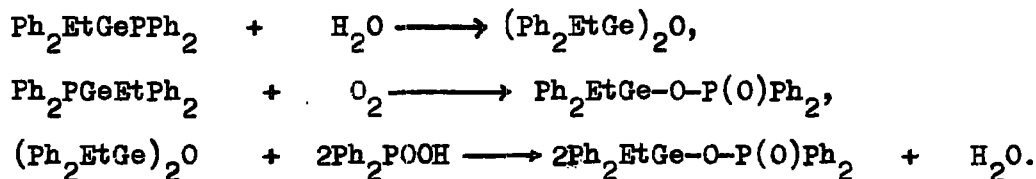
The infrared spectrum of this mixture was identical to that of the ester triethylgermyldiphenylphosphonate except for bands expected for Ge-Ph groups (at 1092 cm^{-1} and 455 cm^{-1}) and Ge-O-Ge stretch at 842 cm^{-1}.

What is perhaps the most surprising result of these reactions is the fact that no tetraphenylgermane was isolated. This would seem to infer that mono-substitution of germanium(1V)chloride, even by 1.8 mole equivalents of lithium diphenylphosphide is complete and rapid.

The principal bands in the infrared spectra of the various organo-germylphosphines are reported in Tables 1 and 2 (pages 163 and 164) for the region 5 - 50μ. The actual spectrum of triethylgermyldiphenylphosphine is shown in figure 2 page 90 and the principal bands in the far infrared spectrum are given in Table 3(page 164).

One can, with some certainty assign the absorption at 473 cm^{-1} in triethylgermyldiphenylphosphine to the Ge - P symmetric stretching vibration (ν_S). This absorption disappears on oxidation to the ester $Et_3Ge-O-P(O)Ph_2$, (figure 2, page 90), as would be expected.

Triethylgermyldiphenylphosphine shows ν_s Ge-C(Et) at 532 cm^{-1} and ν_{as} Ge-C(Et) at 569 cm^{-1}; see reference 168 for the assignment of various Ge-C(alkyl) stretching vibrations.

For the phenylgermylphosphines the situation is somewhat more complicated as the region of interest is also that in which absorption

due to Ge-Ph groups occurs (455 cm^{-1}). It is possible, however, that Ge-P ν_s in triphenylgermyldiphenylphosphine occurs at 481 cm^{-1} and in <u>bis</u>(diphenylphosphino)diphenylgermane at 473 cm^{-1}. The latter compound would be expected to show Ge$\underset{P}{\overset{P}{\diagdown}}$ asymmetric stretching vibration, ν_{as}. It is probable that this absorption accounts for the broadening of the band at 494 cm^{-1} (due to Ph$_2$P- grouping). The red and yellow polymeric materials gave poor spectra at the lower frequencies, though weak absorption at 472 cm^{-1} is apparent in both compounds. These polymers were, except for a weak band at 321 cm^{-1} in the yellow polymer, transparent in the region $22 - 50\mu$.

All the phenylgermylphosphines showed a strong band in the range 1085 cm^{-1} (in Ph$_3$GePPh$_2$) to 1075 cm^{-1} (in the yellow polymer), characteristic of phenyl - germanium groups.

TABLE 1

INFRARED SPECTRA OF THE PHENYLGERMYLPHOSPHINES.(5 – 22μ).[§]

Ph_3GePPh_2 .	$Ph_2Ge(PPh_2)_2$.	Yellow Polymer. $PhGePPh_2$.	Red Polymer Ph_2PGe.
1961 (w)	1961 (w)	1961 (w)	
1887 (w)	1887 (w)	1887 (w)	
1818 (w)	1818 (w)	1818 (w)	
1582 (m)	1582 (s)	1582 (m)	1580 (m)
1477 (s)	1477 (s)	1477 (s)	1475 (s)
1473 (m,sh)	1473 (m,sh)		
1431 (s,sh)	1431 (s,sh)	1429 (s)	1429 (s)
1427 (s)	1427 (s)		
1372 (w)	1372 (w)	1372 (w)	
1302 (w)	1302 (m)	1302 (m)	
1263 (w)	1264 (w)	1264 (w)	
1185 (m)	1182 (m)	1181 (m)	1183 (w)
1152 (w)	1155 (w)	1156 (w)	
1093 (w,sh)	1087 (m,sh)		1088 (w)
1085 (s)	1077 (s)	1075 (m)	
1064 (w)	1064 (m)	1064 (m)	1068 (w)
1021 (s)	1021 (s)	1021 (m)	1026 (m)
995 (m)	995 (s)	998 (m)	1000 (m)
854 (w)	851 (w)		
750 (m)	749 (m,sh)		
738 (s)	738 (s,sh)		
730 (s)	734 (s)	729 (s)	735 (s)
694 (s)	690 (s)	690 (s)	690 (s)
673 (m)	669 (m,sh)	669 (m,sh)	
497 (m)	494 (m) (b)	495 (w)	499 (m)
481 (m)	473 (m)	472 (m)	472 (m)
462 (s,sh)	461 (m)		
458 (s)	452 (s)	452 (s)	

§ All spectra were recorded in potassium iodide (disc).

TABLE 2

INFRARED SPECTRA OF THE PHENYLGERMYLPHOSPHINES. (22 – 50 μ).§

Ph$_3$GePPh$_2$.	Ph$_2$Ge(PPh$_2$)$_2$.	Yellow Polymer. PhGePPh$_2$.	Red Polymer. Ph$_2$PGe.
430 (s)	431 (s)		
	392 (m)		
373 (s)	372 (s)		
328 (s)		321 (w)	
	310 (s)		
273 (s)	287 (s)		
254 (s)	257 (s)		
	246 (s)		
239 (w)	235 (w)		
221 (w)			

§ All spectra were recorded as nujol mulls between CsI discs.

TABLE 3

INFRARED SPECTRA OF TRIETHYLGERMYLDIPHENYLPHOSPHINE ETC. (22 – 50 μ).§

| (Et$_3$Ge)$_2$O	Ph$_2$P(O)OGeEt$_3$	Et$_3$GePPh$_2$
444 (m)	452 (w)	
	435 (w)	435 (m)
395 (w)		
	366 (w)	369 (m)
	339 (w)	
324 (s,br)		
		313 (m,br)
294 (s,sh)		294 (m,sh)

§ All spectra were recorded as liquid contact films (CsI discs).

PART E. <u>Dimesityl-lead(II)</u>.

Evidence has previously been obtained which suggests that the reaction between phenyl-lithium or phenylmagnesium bromide and a lead(II)halide involves a final equilibrium stage (III), (119,85):

$$PbX_2 + PhLi(MgX) \longrightarrow PbXPh + Li(MgX)X \ldots\ldots(I)$$

$$PbXPh + PhLi(MgX) \longrightarrow PbPh_2 + Li(MgX)X \ldots\ldots(II)$$

$$PbPh_2 + PhLi(MgX) \rightleftharpoons Ph_3PbLi(MgX) \ldots\ldots\ldots\ldots(III).$$
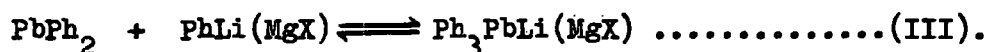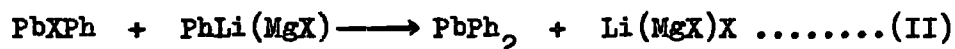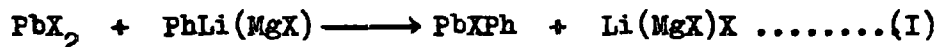
The equilibrium (III) can be displaced in favour of diphenyl-lead(11) by the addition of water to the blood red or green solutions. This however causes hydrolysis of the lead-phenyl bonds:

$$Ph_3PbLi(MgX) \rightleftharpoons Ph_2Pb + PhLi(MgX) \xrightarrow{H_2O} Pb(OH)_2 + PhH + Li(MgX)OH.$$
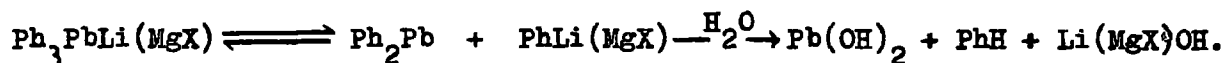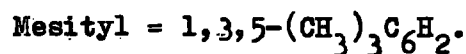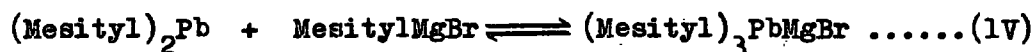
The initial aim of the present investigation was to obtain, in a pure form, an organo-lead(11) compound. Although this was not successful, evidence was obtained for the presence of this species in solution. Some further properties of the equilibrium reaction(III) were also obtained.

The preparation of dimesityl-lead(11) was attempted, from mesityl-magnesium bromide and lead(11)bromide in tetrahydrofuran at -30°, in preference to diphenyl-lead(11), because of the greater thermal stability of mesityl-lead bonds compared to phenyl-lead bonds. This stability is shown by the fact that lead(11)bromide may be refluxed for a limited period in tetrahydrofuran with a large excess of mesitylmagnesium bromide without the separation of lead (85), in contrast to the reaction involving phenylmagnesium bromide in which decomposition to lead is rapid.

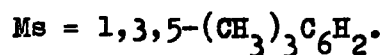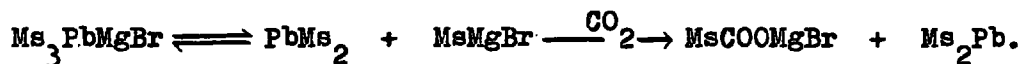The reaction between a 3:1 molar ratio of mesitylmagnesium bromide

and lead(11)bromide resulted in an identical change of colour to that
reported for the reaction involving phenylmagnesium bromide, the final
reaction mixture being deep red-brown in colour.

It was thought that, for the isolation of dimesityl-lead(11), the
equilibrium:

$$(Mesityl)_2Pb \; + \; MesitylMgBr \rightleftharpoons (Mesityl)_3PbMgBr \;\ldots\ldots(1V)$$
$$Mesityl = 1,3,5-(CH_3)_3C_6H_2.$$

must be displaced in favour of dimesityl-lead(11). Reagents were thus
required which would effect this without the simultaneous decomposition
of the dimesityl-lead(11).

The dropwise addition of dry ethanol to solutions resulting from
the interaction of three equivalents of mesitylmagnesium bromide with
lead(11)bromide caused the immediate discharge of the red colour and the
production of a heavy white precipitate, indicating decomposition of the
dimesityl-lead(11). When these solutions were poured on to solid carbon
dioxide, however, the red colour intensified and no decomposition occurred:

$$Ms_3PbMgBr \rightleftharpoons PbMs_2 \; + \; MsMgBr \xrightarrow{CO_2} MsCOOMgBr \; + \; Ms_2Pb.$$
$$Ms = 1,3,5-(CH_3)_3C_6H_2.$$

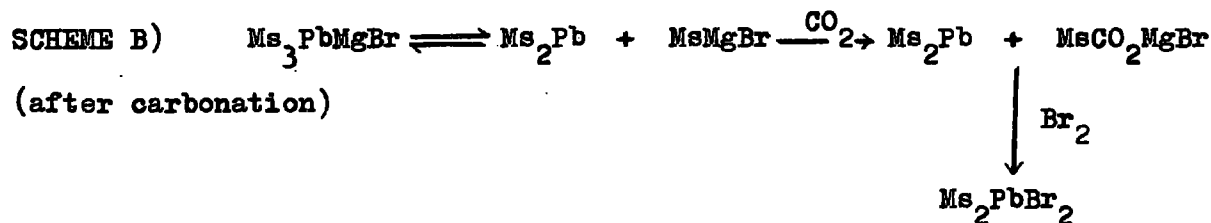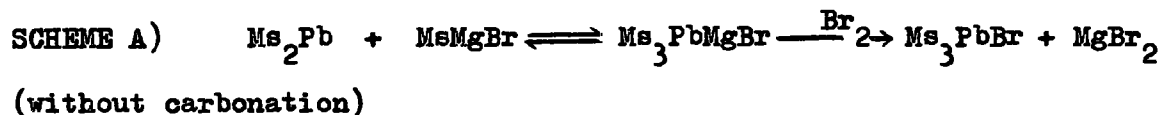However, all attempts to isolate a pure organo-lead(11) compound from these
carbonated solutions met with failure, owing to the similar solubility
properties of the organo-lead compounds present and magnesium bromide, the
latter presumably present as a tetrahydrofuran complex. The method of
attempted purification involved removal of the tetrahydrofuran at -20°
under vacuum, followed by dissolution of the resulting red glass in

methylene chloride and partial precipitation with hexane.

In contrast to the uncarbonated reaction mixtures, these solutions which resulted from the carbonation reactions were thermally unstable, decomposing rapidly at 0°. Aerial decomposition at room temperature of the carbonated solutions gave tetramesityl-lead and a basic lead bromide.

That carbon dioxide did in fact displace the equilibrium (1V) was inferred by comparative bromination studies. The reaction mixtures result-ing from the interaction of a 3:1 molar ratio of mesitylmagnesium bromide and lead(11) bromide were brominated at -60°, both prior to, and after carbonation. The results obtained suggested the two schemes A) and B):

SCHEME A) $\quad Ms_2Pb + MsMgBr \rightleftharpoons Ms_3PbMgBr \xrightarrow{Br_2} Ms_3PbBr + MgBr_2$
(without carbonation)

SCHEME B) $\quad Ms_3PbMgBr \rightleftharpoons Ms_2Pb + MsMgBr \xrightarrow{CO_2} Ms_2Pb + MsCO_2MgBr$
(after carbonation)

$$\downarrow Br_2$$

$$Ms_2PbBr_2$$

Trimesityl-lead bromide was isolated in A), and dimesityl-lead dibromide in B).

A reaction was carried out between mesityl-lithium and lead(11)chlor-ide in tetrahydrofuran, in the hope that the solubility of the lithium halide-tetrahydrofuran complex would differ sufficiently from that of dimesityl-lead(11) for a separation to be effected. A colour change of green to red was observed for the addition of from 1 to 3 equivalents of mesityl-lithium, but attempted isolation of Ms_2Pb from this reaction

mixture after carbonation met with failure.

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