343. *Organogermanium Polymers.*

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The main product of the reaction between germanium(II) iodide and phenyl-lithium is amorphous polymeric material containing Ph_3Ge, Ph_2Ge, PhGe, and Ge groups together with some tetraphenylgermane and, if an excess of phenyl-lithium is used, triphenylgermane. The polymer-forming reactions are considered to involve halogen–metal exchange of the type: $PhGeI + PhLi \longrightarrow PhGeLi + PhI$. Pyrolysis of diphenylgermane at 280—340° gives germanium, tetraphenylgermane, hydrogen, and benzene, in contrast to the tin analogue. The hydride, $(Ph_3Ge)_3GeH$, is formed in the reaction between germanium di-iodide and triphenylgermyl-lithium.

Experiments likely to produce organo-derivatives of germanium(II) have always resulted in associated or polymeric materials. Thus dichlorodiphenylgermane is reduced by sodium in boiling xylene to the colourless tetramer, $(Ph_2Ge)_4$, in 10—20% yield, together with much yellow resinous material having a mean molecular weight of about 900 and containing 30—32% of germanium (Ph_2Ge requires 32%).[1] Summers[2] also reported the formation of diphenylgermanium from germanium(II) iodide and phenyl-lithium though without analytical data. Attempts to prepare dialkylgermanium(II) compounds have been unsuccessful,[3] and Gilman and Gerow[4] have obtained evidence against the equilibrium: $Ph_3GeM \rightleftharpoons Ph_2Ge + PhM$. Phenylgermanium polymers have been more thoroughly studied: reduction of trichlorophenylgermane with potassium gave a polymer of composition approximating to $(PhGe)_6$, although bromination indicated the presence of germanium–oxygen bonds.[5] Metlesics and Zeiss[6] reinvestigated this reaction in detail, using potassium in toluene, and obtained a bright yellow amorphous solid ($M = 800$—1300), containing 1—5% of chlorine and 5—10% of oxygen.

Our original object was to study the preparation and reactions of diaryl derivatives of germanium(II) by methods analogous to those employed for tin, a number of compounds of the type $(Ar_2Sn)_n$ and $(R_2Sn)_n$ being known.[7] Diphenyltin has been obtained by decomposition of the hydride, Ph_2SnH_2, either at room temperature when it evidently gives the monomeric compound,[8] or in dimethylformamide when crystalline cyclic pentamer

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[1] Kraus and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 4031.
[2] Summers, *Iowa State Coll. J. Sci.*, 1952, **26**, 292.
[3] Jacobs, *Compt. rend.*, 1954, **238**, 1825.
[4] Gilman and Gerow, *J. Org. Chem.*, 1958, **23**, 1582.
[5] Schwarz and Schmeisser, *Ber.*, 1936, **69**, 579.
[6] Metlesics and Zeiss, *J. Amer. Chem. Soc.*, 1960, **82**, 3321.
[7] Ingham, Rosenberg, and Gilman, *Chem. Rev.*, 1960, **60**, 459.
[8] Chambers and Sherer, *J. Amer. Chem. Soc.*, 1926, **48**, 1054.

and hexamer are obtained.[9] Diphenylgermane, Ph_2GeH_2, is reported[10] to decompose slowly at room temperature but, in the absence of air, we find that it is unchanged after 8 hours at 250° even when irradiated with ultraviolet light. Between 280° and 340° decomposition occurs with the formation of a germanium mirror, hydrogen, tetraphenylgermane, and benzene. The first three products may be accounted for by the disproportionation: $2Ph_2GeH_2 \longrightarrow Ph_4Ge + GeH_4$, with subsequent decomposition of monogermane into germanium and hydrogen. However, since appreciable amounts of benzene are produced, hydrogen atoms must also attack the germanium–carbon bonds; tetraphenylgermane could then result from thermal decomposition of a diphenylgermanium intermediate: $Ph_2GeH_2 \longrightarrow H_2 + C_6H_6 + Ge + Ph_2Ge$; $2Ph_2Ge \longrightarrow Ph_4Ge + Ge$.

The most commonly reported method for the preparation of diaryl(or alkyl) compounds of tin involves the reaction of tin(II) chloride with a Grignard or organolithium reagent. Diphenyltin is obtained in this way as a yellow amorphous solid which undergoes progressive polymerisation in solution, and is not homogeneous.[11] Moreover, there is evidence[9] that the mixture contains Ph_3Sn and PhSn groups in addition to Ph_2Sn. We have studied the analogous reaction using germanium(II) iodide and (*a*) phenyl-lithium in ether, (*b*) phenylmagnesium bromide in tetrahydrofuran, (*c*) triphenylaluminium in tetrahydrofuran and in toluene, and (*d*) mesitylmagnesium bromide in tetrahydrofuran; the products were similar in each case, and only the first was studied in detail.

Germanium(II) iodide and phenyl-lithium react at —25° to give a deep red, ether-insoluble oil from which an orange, air-sensitive, and non-crystalline material may be isolated having the approximate composition, Ph_2Ge_2I. In freezing benzene solution the degree of association varied with concentration within the range 2—3. Atmospheric oxidation of this phenylgermanium iodide was rapid in solution, and the yellow polymeric product ($M \approx 3350$) had the composition Ph_2Ge_2OI. We have no evidence that either the phenylgermanium iodide or its oxidation product is homogeneous and, on the basis of the work described below, we are inclined to consider the composition Ph_2Ge_2I fortuitous. It is likely that both these compounds involve a variety of partially phenylated germanium iodides such as PhGeI and $Ph_3Ge{\cdot}GeI$.

The phenylgermanium iodides dissolve to give deep blood-red solutions at room temperature when two or more equivalents of phenyl-lithium are used, and the products isolated after hydrolysis depend partly on whether an excess of phenyl-lithium is present. Using a 2 : 1 molar ratio of phenyl-lithium to germanium(II) iodide gave, after prolonged refluxing in ether, tetraphenylgermane, a red-brown amorphous polymer having a composition close to that of phenylgermanium, $(PhGe)_{10}$, and, as the main product a yellow amorphous polymer ($M = 800$—1700), intermediate in composition between phenyl- and diphenyl-germanium. It is unlikely that either of these polymeric materials is homogeneous; both are totally involatile, and purification was limited to fractional precipitation from benzene by addition of methanol or hexane. Both were free from halogen and oxygen (no Ge–O absorption at ~11·6 μ), and reacted vigorously with nitric acid (the phenylgermanium polymer inflames) in marked contrast to tetraphenylgermane or hexaphenyldigermane. Their *X*-ray powder photographs showed only two broad diffuse bands. Thermal decomposition to germanium metal occurred between 400° and 450°.

Similar experiments involving a large excess of phenyl-lithium gave, in addition to tetraphenylgermane, triphenylgermane which could only reasonably be formed by the hydrolysis of triphenylgermyl-lithium. Phenylgermanium polymers similar to those already described were again the main products. The reaction of phenylmagnesium bromide in tetrahydrofuran with germanium(II) iodide was quite strongly exothermic and again gave tetraphenylgermane and yellow polymeric material intermediate in composition between PhGe and Ph_2Ge. Polymers were also obtained by using triphenylaluminium as

[9] Neumann and König, *Angew. Chem.*, 1962, **1**, 212.
[10] Johnson and Harris, *Inorg. Syn.*, 1957, **4**, 74.
[11] Kuivila and Jakusik, *J. Org. Chem.*, 1961, **26**, 1426, 1430.

a milder phenylating agent, although complete reaction was never achieved; the polymers contained oxygen, presumably by hydrolysis of residual GeI groups, and in some cases iodine as well. The reaction of mesitylmagnesium bromide in tetrahydrofuran with germanium(II) iodide was also studied and followed essentially the same course as with the phenyl derivatives. With an excess of mesitylmagnesium bromide, the hydride, $(\text{mesityl})_3GeH$, was isolated together with yellow amorphous mesitylgermanium polymers intermediate in composition between mesitylgermanium and dimesitylgermanium. These were, in general, more soluble in organic solvents than the phenyl analogues.

Some structural information on the yellow phenylgermanium polymers was obtained by degradation with bromine under mild conditions, hexaphenyldigermane being used as a control. Bromotriphenylgermane, Ph_3GeBr, may be isolated directly and phenylgermanoic anhydride, $(PhGeO)_2O$, after hydrolysis of the crude brominated mixture. Thus, although the mean composition of the yellow polymer lies between PhGe and Ph_2Ge the material contains Ph_3Ge and PhGe groups. A more detailed study of the brominated degradation products was carried out by treating the crude mixture with an excess of ethylmagnesium bromide; the volatile products were characterised by vapour-phase chromatography, with the authentic compounds for comparison. In this way diethyldiphenylgermane, Et_2GePh_2, triethylphenylgermane, Et_3GePh, and a trace of tetraethylgermane were detected. The solid product, ethyltriphenylgermane, $EtGePh_3$, was also isolated together with a small amount of crystalline material which appeared to be a digermane, $Et_2Ge_2Ph_4$ (either $Ph_3Ge{\cdot}GePhEt_2$ or $Ph_2EtGe{\cdot}GeEtPh_2$). These products suggest that the yellow polymer contains Ph_3Ge, Ph_2Ge, PhGe, and Ge units. The bromination procedure did not result in the cleavage of germanium–carbon bonds since neither bromobenzene nor ethylbenzene was detected. In the control experiments on hexaphenyldigermane cleavage of two phenyl groups did occur to some extent (1—2%) but bromobenzene as well as Ph_3GeEt and Ph_2GeEt_2 were isolated. Bromination of the yellow polymer in 1,2-dibromoethane at room temperature proceeds rapidly at first and then very slowly, suggesting that unsaturated centres are present which take up bromine readily, the cleavage of germanium–germanium bonds proceeding more slowly. By interrupting the bromination at the end of the rapid stage and ethylating the crude mixture we were able to isolate only a non-crystalline yellow powder containing alkyl as well as aryl groups.

Any conclusions on the mechanism of formation and structure of these polymeric materials must be largely speculative. It seems reasonable to suppose, as did Metlesics and Zeiss,[6] that chains or rings of germanium atoms are involved. Actual isolation of Ph_4Ge and Ph_3GeH indicates the following stages:

$$GeI_2 + PhLi \longrightarrow PhGeI \tag{1}$$

$$PhGeI + PhLi \longrightarrow Ph_2Ge \tag{2}$$

$$Ph_2Ge + PhLi \longrightarrow Ph_3GeLi \xrightarrow{H_2O} Ph_3GeH \tag{3}$$

$$PhGeI + PhLi \longrightarrow PhGeLi + PhI \tag{4}$$

$$GeI_2 + PhLi \longrightarrow LiGeI + PhI \tag{5}$$

$$Ph_3GeLi + PhI \longrightarrow Ph_4Ge \tag{6}$$

Reactions (4) and (5), involving halogen–metal exchange, seem essential in order to produce iodobenzene for reaction (6), and to build up cyclic or linear polymers having all the degrees of phenylation indicated by the degradation studies. In connection with reactions involving sterically hindered R_3GeX compounds we have previously postulated a similar halogen–metal exchange,[12] as also have Gilman and Rosenberg for similar tin compounds.[13] Most polymeric structures having a mean composition intermediate between PhGe and

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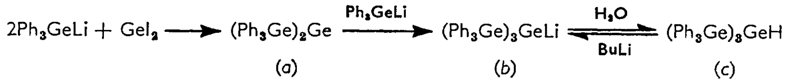
[12] Glockling and Hooton, *J.*, 1962, 3509.

[13] Gilman and Rosenberg, *J. Org. Chem.*, 1953, **18**, 680.

Ph_2Ge imply a degree of π-double bonding between germanium atoms, and the yellow polymers do not show a banded structure in their visible or near-ultraviolet spectra.

The evidence for completely unphenylated germanium atoms in the polymer (isolation of Et_4Ge, after bromination) is surprising since one might have expected monophenylation to be complete (reaction 1). However, in a purely formal sense one can write a model structure (*a*) which includes unphenylated germanium.



$$2Ph_3GeLi + GeI_2 \longrightarrow \underset{(a)}{(Ph_3Ge)_2Ge} \xrightarrow{Ph_3GeLi} \underset{(b)}{(Ph_3Ge)_3GeLi} \underset{BuLi}{\overset{H_2O}{\rightleftharpoons}} \underset{(c)}{(Ph_3Ge)_3GeH}$$

Triphenylgermyl-lithium and germanium(II) iodide react exothermally forming a deep red solution from which, after hydrolysis, the well crystalline tristriphenylgermylgermane (*c*) may be isolated in 36% yield. Side reactions involving halogen–metal exchange were again evident since appreciable amounts of hexaphenyldigermane were isolated. The hydride (*c*) is clearly formed by hydrolysis of the lithium complex (*b*), but we were unable to isolate any bistriphenylgermylgermanium(II) (*a*) even when free germanium(II) iodide was present. This suggests that the reaction of material (*a*) with triphenylgermyl-lithium is rapid and irreversible (cf. ref. 4).

The Ge–H stretching frequency in tristriphenylgermylgermane is displaced from the normal value of 2037 to 1953 cm.$^{-1}$, and it is possible that the unphenylated germanium present in the polymers actually involves one or more germanium–hydrogen bonds, though examination of thick Nujol mulls of polymer failed to give convincing evidence for Ge–H bonds except when an excess of phenyl-lithium had been used. We also observed a strong infrared band in the spectrum of this hydride at 228 cm.$^{-1}$ which is absent from those of symmetrical digermanes and R_4Ge compounds and may be due to the Ge–Ge stretching vibration.[15] Tristriphenylgermylgermane reacted smoothly with butyl-lithium, forming the lithio-derivative (*b*) which, with methyl iodide gave methyltristriphenylgermylgermane, $(Ph_3Ge)_3GeMe$, and this compound also showed strong absorption at 228 cm.$^{-1}$.

EXPERIMENTAL

M. p.s are corrected. Operations on air-sensitive compounds were carried out in pure, dry nitrogen. Carbon–hydrogen analyses on the polymeric materials required a high temperature (oxy-gas torch) for complete combustion.

Pyrolysis of Diphenylgermane.—Diphenylgermane,[14] b. p. 63°/10^{-3} mm. (0·56 g.), was heated in an evacuated tube at 280—340° for 48 hr. Hydrogen (28N-c.c.), benzene (0·15 g.), tetraphenylgermane (0·07 g., from benzene), and germanium (0·11 g.) were isolated.

Germanium(II) *Iodide and Phenyl-lithium.*—(*a*) *Phenylgermanium iodides.* Ethereal phenyl-lithium (0·279 mole) was added at −30° to a stirred suspension of germanium(II) iodide (27 g., 0·083 mole) in ether (100 cc.) and, after 1 hr., the deep red solution was decanted from a viscous red oil which was washed repeatedly with ether. Extraction of the oil with benzene gave, after removal of solvent from the filtered solution, an orange-red glass (5 g.; decomp. 198°) containing iodine but not lithium [Found: C, 32·3; H, 2·1; Ge, 34·7. Calc. for $C_{12}H_{10}Ge_2I$ (*i.e.*, Ph_2Ge_2I): C, 33·8; H, 2·4; Ge, 34·1%]. In freezing benzene the following molecular-weight data were obtained (Wt. % solute, followed by *M*): 1·61, 638; 2·15, 702; 3·2, 793.

Oxidation of this mixture of phenylgermanium iodides (1·0675 g.) by passing dry oxygen through a solution in benzene gave an immediate yellow precipitate of the oxide [1·1004 g.; m. p. 194° (decomp.)] showing strong Ge–O absorption at 11·6 μ [Found: C, 31·3; H, 2·3%; *M* (in 1,2-dibromoethane), 3350. Calc. for $C_{12}H_{10}Ge_2IO$: C, 32·6; H, 2·3; *M*, 442].

(*b*) *Isolation of phenylgermanium polymers by use of two equivalents of phenyl-lithium.* Germanium(II) iodide (29·3 g., 0·09 mole) and phenyl-lithium (0·18 mole) in ether (100 c.c.) were heated under reflux with stirring for 3 days, and then filtered in a nitrogen atmosphere. The residue was extracted with cold benzene (20 c.c.), the insoluble part being tetraphenylgermane (1 g.; m. p. 236°). The deep red benzene solution was added dropwise to methanol, giving a

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[14] Johnson and Harris, *J. Amer. Chem. Soc.*, 1950, **72**, 5564.

[15] Crawford, Rhee, and Wilson, *J. Chem. Phys.*, 1962, **37**, 2377.

red-brown solid (1·0 g.; m. p. >360°) which was free from halogen and oxygen. After re-precipitation from benzene it had a composition close to that of phenylgermanium (Found: C, 43·6; H, 3·2; Ge, 49·0%; *M*, 1508. Calc. for C_6H_5Ge: C, 48·1; H, 3·4; Ge, 48·5%). It was stable to water, but oxidised slowly in the air.

The ethereal filtrate was hydrolysed and the orange organic layer concentrated, giving more tetraphenylgermane (1·1 g.). The residue, in benzene (10 c.c.), was added slowly to methanol, giving an amorphous yellow solid (4·2 g.). Repetition of this procedure always gave yellow amorphous polymers which were free from halogen and oxygen; melting behaviour varied within the range 170—290° (with decomp.). Analyses were always intermediate for compositions between PhGe and Ph_2Ge [Found: C, 49·3—58·5; H, 3·9—5·0; Ge, 34·7—42·5%; *M* (freezing benzene), 850—1700. Calc. for C_6H_5Ge: C, 48·1; H, 3·4; Ge, 49·0. Calc. for $C_{12}H_{10}Ge$: C, 63·5; H, 4·4; Ge, 32·0%]. Reactions using phenylmagnesium bromide in tetrahydrofuran gave similar products.

(*c*) *By use of four equivalents of phenyl-lithium.* Germanium(II) iodide (29·3 g., 0·09 mole) and phenyl-lithium (0·36 mole) in ether (100 c.c.) were heated under reflux for 5 days. Tetraphenylgermane (2·5 g., from toluene) was separated by filtration, and titration of the lithium hydroxide formed by hydrolysis corresponded to 0·13 molar excess of phenyl-lithium. The organic layer was concentrated and added to methanol, giving a red oil from which red polymer (1·8 g.) approximating to PhGe was obtained by re-precipitation (Found: Ge, 45·7%; *M*, 1520—1920). Further precipitation by addition of methanol gave a cream polymer (2·7 g.) similar to the yellow polymer described under (*b*) (Found: Ge, 36·8%). Final distillation of the mother-liquors gave tetraphenylgermane (0·5 g.) and triphenylgermane (2·3 g.), b. p. 137—145°/10^{-2} mm., m. p. 24°, $\nu_{max.}$ 2037 cm.$^{-1}$ (Ge–H stretch).

Germanium(II) *Iodide and Triphenylaluminium.*—Triphenylaluminium–ether complex (47·3 g.) and germanium(II) iodide (21·1 g.) in tetrahydrofuran (400 c.c.) were heated under reflux for 2 days. The resulting bright yellow solution was filtered in nitrogen from unused germanium(II) iodide (1·4 g.). Acid hydrolysis gave, from the organic layer, a yellow viscous oil which was dissolved in benzene (10 c.c.) and added dropwise to methanol (50 c.c.), under nitrogen, giving a bright yellow solid (4·3 g.), m. p. 105—210° (decomp.). It contained iodine and oxygen (Found: C, 33·8; H, 2·6; Ge, 34·4%).

A similar experiment carried out for 40 hr. in refluxing toluene gave a yellow solid, m. p. 140—150°, showing medium Ge–O absorption at 870—806 cm.$^{-1}$ (Found: C, 54·2; H, 4·5; Ge, 36·0%).

Germanium(II) *Iodide and Mesitylmagnesium Bromide.*—A solution of mesitylmagnesium bromide from bromomesitylene (40 g.) and magnesium (6·0 g.) in tetrahydrofuran (500 c.c.) was filtered, and germanium(II) iodide was added with stirring. The solution slowly became red, with precipitation of magnesium halides, and, after 8 hr. under reflux, it was hydrolysed and extracted with benzene. Removal of solvents left an orange-yellow semi-solid mass (11 g.) which was extracted with pentane. The pentane solution deposited a mesitylgermanium polymer (1·7 g.) at −20° as a deep yellow solid (Found: Ge, 31·4. Calc. for $C_9H_{11}Ge$: Ge, 37·9. Calc. for $C_{18}H_{22}Ge$: Ge, 23·3%). This polymer darkened progressively between 290° and 360° without melting. Fractional precipitation by adding a benzene solution to ethanol gave a deep yellow solid (Found: Ge, 33·3%) and a paler material (Found: Ge, 30·0%). Distillation of the pentane left a yellow oil which deposited trimesitylgermane from ethanol as colourless crystals, m. p. 194° (2·8 g.), $\nu_{max.}$ 2037 cm.$^{-1}$ (Ge–H stretch) (Found: Ge, 17·5. Calc. for $C_{27}H_{34}Ge$: Ge, 16·8%). Distillation of the ethanol left a yellow glass (7 g.) from which a further quantity of trimesitylgermane (2 g.) was obtained by evaporative distillation at 260—265°/10^{-3} mm., leaving an involatile orange oil.

The pentane-insoluble material dissolved readily in cyclohexane, giving a deep red solution from which a deep brown solid (0·6 g.), m. p. >360°, separated on addition of pentane (Found: Ge, 35·5%).

Degradation of Phenylgermanium Polymers by Bromine.—(*a*) Standard bromine solution in chloroform was added in small portions to the yellow polymer (C, 53·4; H, 4·0; Ge, 39·6%) (1·0 g.) in refluxing chloroform. After 1 week 2·58 g.-atoms of bromine had been absorbed per g.-atom of germanium. Distillation gave mixed bromophenylgermanes (1·4 g.), b. p. 65—158°/1 mm. Bromotriphenylgermane (0·2 g.), m. p. 136°, was obtained by extraction of the residue with hexane.

(*b*) The same polymer (1·5 g.) in 1,2-dibromoethane was brominated at room temperature for 1 week as described above; 2·9 g.-atoms of bromine reacted. Hydrolysis with 10% sodium hydroxide solution gave, after acidification of the aqueous solution, phenylgermanoic anhydride (0·3 g.).

(*c*) The above polymer (3·0 g.) was brominated as in (*b*), and most of the solvent removed under a vacuum. The residue, in benzene (20 c.c.), was refluxed with a filtered solution of ethylmagnesium bromide (0·1 mole) in ether (100 c.c.) for 3 hr. Solvents were separated by fractional distillation after hydrolysis, and the viscous residue was distilled. Each fraction was then examined by vapour-phase chromatography: (i) b. p. 57—63°/50 mm. (0·3 g.), characterised as $C_2H_4Br_2$; (ii) b. p. 154—156°/45 mm. (0·8 g.); $C_2H_4Br_2$, 25%; Et_4Ge, ~1%; Et_3GePh, 75%; (iii) b. p. 98—138°/0·03 mm. (0·4 g.); Et_2GePh_2, 75%; $EtGePh_3$, 25%; (iv) b. p. 138—176°/10^{-2} mm. (0·5 g.); $EtGePh_3$, m. p. 74—76° (from propan-2-ol); (v) the involatile residue gave, on extraction with propanol, colourless crystals (0·1 g.), m. p. 122—124°, of a diethyltetraphenyldigermane, $Ph_3Ge{\cdot}GeEt_2Ph$ or $Ph_2EtGe{\cdot}GeEtPh_2$ (Found: C, 64·9; H, 6·4%; *M*, 491. Calc. for $C_{28}H_{30}Ge_2$: C, 65·7; H, 5·9%; *M*, 511·7), whose infrared spectrum showed aliphatic and aromatic C–H bands. Neither bromo- nor ethyl-benzene was detected.

Bromination of Hexaphenyldigermane.—Hexaphenyldigermane (2·0 g.) was brominated as in (*b*), then ethylated as in (*c*). The three volatile fractions were examined by vapour-phase chromatography: (i) b. p. 18—40°/3·5 mm. (1·0 g.), characterised as ether, benzene, 1,2-dibromoethane, and bromobenzene (1%); (ii) b. p. 100—140°/0·03 mm. (0·05 g.), Et_2GePh_2; (iii) b. p. 140°/0·03 mm. (1·5 g.), $EtGePh_3$, m. p. 77° (from propan-2-ol).

Tristriphenylgermylgermane, $(Ph_3Ge)_3GeH$.—Triphenylgermyl-lithium, from hexaphenyldigermane (36·3 g.), and lithium (6·0 g.) in ethylene glycol dimethyl ether (60 c.c.), was added to a suspension of germanium(II) iodide (11·7 g.) in the same solvent (100 c.c.). The exothermic reaction produced a deep red solution which was stirred overnight at room temperature. Hydrolysis gave a red-brown solid from which *tristriphenylgermylgermane* (12·5 g.) was isolated by extraction with hot methylcyclohexane. After further purification from the same solvent it had m. p. 192—194° (Found: C, 64·8; H, 4·7; Ge, 29·6%; *M*, 919. $C_{72}H_{46}Ge_2$ requires C, 65·8; H, 4·7; Ge, 29·5%; *M*, 985·3), $\nu_{max.}$ 1953 cm.$^{-1}$ (Ge–H stretch). Its infrared spectrum showed a strong band at 228 cm.$^{-1}$, not present in the spectra of tetraphenylgermane or hexaphenyl digermane.

The material insoluble in methylcyclohexane was washed with benzene, forming a deep blood-red filtrate which was air-sensitive and did not yield a pure compound. Extraction of the benzene-insoluble part with chloroform gave hexaphenyldigermane (6·2 g.) and germanium(II) iodide (1·0 g.).

Methyltristriphenylgermylgermane, $(Ph_3Ge)_3GeCH_3$.—Tristriphenylgermylgermane (4·0 g., 4·05 mmole), in ether suspension, was treated with n-butyl-lithium (6·0 mmoles), giving a yellow solution which soon deposited the lithium complex, $(Ph_3Ge)_3GeLi$, as a yellow solid. After 5 min. methyl iodide (0·935 g.) was added, giving a clear colourless solution which was stirred at room temperature for 1 hr. and then hydrolysed. *Methyltristriphenylgermylgermane* was separated by filtration and, recrystallised from methylcyclohexane (2·2 g., 54%), had m. p. 194—196° (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%). The organic layer yielded *butylmethylbis(triphenylgermyl)germane*, $(Ph_3Ge)_2GeMe(C_4H_9)$ (0·2 g.), m. p. 187—190° (Found: C, 65·3; H, 5·2. $C_{41}H_{42}Ge_3$ requires C, 65·3; H, 5·6%). Two unidentified products were also isolated, in small yield, having m. p. 124—125° and m. p. 328—330°. Both showed aliphatic and aromatic C–H absorption in their infrared spectra.

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