790. *Diphenylphosphino-organogermanes*

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Lithium diphenylphosphide and the organohalogenogermanes, R_3GeX and R_2GeX_2, give thermally stable complexes, $R_3Ge{\cdot}PPh_2$ and $R_2Ge(PPh_2)_2$. Hydrolysis of the triethyl- and triphenyl-germyl complexes, $R_3Ge{\cdot}PPh_2$, gives $(R_3Ge)_2O$ and Ph_2PH, whilst oxidation cleaves the Ge–P bond forming $R_3Ge{\cdot}O{\cdot}P(O)Ph_2$. Other reagents which cleave the Ge–P bond are bromine, methyl iodide, and butyl- and phenyl-lithium. Silver iodide gives the co-ordination complex, $[(Et_3Ge{\cdot}PPh_2)AgI]_4$. $PhGeBr_3$ and $GeCl_4$ react differently with lithium diphenylphosphide (or $Ph_2PH + Et_3N$) giving tetraphenyldiphosphine and water-stable polymeric diphenylphosphinogermanes.

In a preliminary Communication [1] we reported the formation and some chemical reactions of diphenyl(triethylgermyl)phosphorus, $Et_3Ge{\cdot}PPh_2$, as the first example of an organogermane containing germanium bonded to phosphorus. This Paper is concerned with these and further studies on related compounds.

Organic derivatives of all the Group IV metals are now known to form covalent bonds to phosphorus: each element (M = Si,[2] Ge, Sn,[3] Pb [4]) forms complexes of the type $R_3M{\cdot}PR'_2$ and $R_2M(PR'_2)_2$, for which three general preparative methods are available: ($R_3MLi + R'_2PCl$), ($R_3MCl + R'_2PLi$), and ($R_3MCl + R'_2PH + Et_3N$). With the exception of lead, the complexes show considerable thermal stability. Each type is readily oxidised to $R_3M{\cdot}O{\cdot}P(O)R'_2$, and hydrolysed to $(R_3M)_2O + R'_2PH$. Both silicon and tin have yielded the tetrakis derivatives, $(Et_2P)_4Si$ and $(Ph_2P)_4Sn$. Extensive studies on tin–phosphorus compounds have revealed some surprising complexities, for example the reaction $R_3SnLi + Ph_2PCl$ gives, in addition to the expected product, a cyclic trimer $(R_2SnPPh)_3$, resulting

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[1] F. Glockling and K. A. Hooton, *Proc. Chem. Soc.*, 1963, **146**.

[2] G. Fritz and G. Poppenburg, *Angew. Chem.*, 1960, **72**, 208; *Angew. Chem. Internat. Edn.*, 1963, **2**, 262.

[3] H. Schumann, H. Kopf, and M. Schmidt, *J. Organometallic Chem.*, 1964, **2**, 159, and references contained therein.

[4] H. Schumann, P. Schwabe, and M. Schmidt, *J. Organometallic Chem.*, 1964, **1**, 366.

from the cleavage of one phenyl–phosphorus bond.[5] A related Ph–P cleavage reaction has been reported by Issleib and Fröhlich: [6]

$$3FeBr_2 + 6K(PPh_2) \longrightarrow 2Ph_3P + P[FePPh_2]_3$$

Lithium diphenylphosphide and triethyl- or triphenyl-bromogermanes react smoothly in tetrahydrofuran to give the thermally stable germylphosphines, $Ph_2P\cdot GeR_3$ ($R = Et$ or Ph), in high yield. Diphenyl(triphenylgermyl)phosphorus is a well-crystalline solid, m. p. 154—156°, whilst the triethyl compound, $Ph_2P\cdot GeEt_3$, is a colourless liquid. Hydrolysis of the Ge–P bond in $Ph_2P\cdot GeEt_3$ is not strikingly exothermic and, in homogeneous solution using a 10-fold excess of 10% aqueous 1,2-dimethoxyethane is complete within 5 minutes at 20°:

$$2Et_3Ge\cdot PPh_2 + H_2O \longrightarrow (Et_3Ge)_2O + 2Ph_2PH$$

In contrast the triphenylgermyl analogue required 6 hours for complete hydrolysis under similar conditions. Oxidation by dry oxygen at room temperature also results in cleavage of the Ge–P bond giving the monomeric phosphorus(V) esters, $R_3Ge\cdot O\cdot P(O)Ph_2$. The identity of this ester ($R = Et$) was confirmed by its preparation from diphenylphosphinic acid and bistriethyldigermoxane.

$$2Ph_2P(O)OH + (Et_3Ge)_2O \longrightarrow Et_3Ge\cdot O\cdot P(O)Ph_2 \xleftarrow{O_2} Et_3Ge\cdot PPh_2$$

Triethylgermyl diphenylphosphonate is a thermally stable liquid in which the Ge–O stretching frequency falls at 956 cm.$^{-1}$ in contrast to the more normal value of about 850 cm.$^{-1}$. It forms a volatile hydrate but, exposure to an excess of water over a long period at room temperature, results in hydrolysis to diphenylphosphinic acid and bistriethyldigermoxane.

In the oxidation reaction described above we obtained no evidence for an intermediate phosphine oxide with the Ge–P bond remaining intact, and this was also true of the reaction between methyl iodide and the triethyl- or triphenyl-germyl complexes, where only R_3GeI and dimethyldiphenylphosphonium iodide were isolated.

$$Et_3GePPh_2 \xrightarrow{MeI} Et_3GeI + [Ph_2PMe_2]^+I^-$$

This contrasts with the behaviour of similar silicon and tin compounds which have been converted into the phosphorus(V) complexes, $[Me_3Si\cdot PEt_3]I$ and $[Ph_3Sn\cdot P(Me)Ph_2]I$. Bromination of the Ge–P bond proceeds rapidly at —20° giving triethylbromogermane and diphenylbromophosphine; cleavage by n-butyl-lithium is also rapid at 0°.

$$Et_3Ge\cdot PPh_2 + BuLi \longrightarrow Et_3GeBu + Ph_2PLi \xrightarrow{EtBr} [Ph_2PEt_2]Br$$

Rather surprisingly phenyl-lithium in a similar reaction showed only 50% cleavage of the Ge–P bond after 2 hours in refluxing ether. The phosphorus atom in the triethylgermyl complex retains its donor character to an appreciable degree, since with silver iodide it readily forms a colourless crystalline 1 : 1 complex, $[Et_3Ge\cdot PPh_2\cdot AgI]_4$, which is rapidly decomposed on exposure to air or water. The triphenylgermyl analogue failed to yield a silver iodide complex, and neither complex reacted with hydrogen (1 atm.) in the presence of Adams catalyst.

Bis(diphenylphosphino)diphenylgermane, $Ph_2Ge(PPh_2)_2$, may be prepared from diphenyldibromogermane and lithium diphenylphosphide though in smaller yield than the monophosphino-complexes, and accompanied by the formation of tetraphenyldiphosphine (10%). With three halogen atoms attached to germanium, as in phenyltribromogermane, the reaction with lithium diphenylphosphide showed further complications, and none of the expected substitution product, $PhGe(PPh_2)_3$, was isolated but rather

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[5] H. Schumann, H. Kopf, and M. Schmidt, *Ber.*, 1964, **97**, 2395.

[6] K. Issleib and H. O. Frohlich, *Ber.*, 1964, **97**, 1659.

a pale yellow power having a mean composition approximating to $(PhGe{\cdot}PPh_2)_2$, together with tetraphenyldiphosphine.

Germanium tetrachloride showed similar complexities in its reaction with lithium diphenylphosphide. The orange-red colour of the lithium diphenylphosphide solution was immediately discharged up to the addition of 1·8—1·9 equivalents, and the solution then turned red whereafter the colour intensified progressively as the remaining 2·2—2·1 equivalents of the phosphide were added. Acid-base titrations showed that all four halogens in germanium tetrachloride react, but we have been unable to isolate the tetrakis-complex, $(Ph_2P)_4Ge$, although some might have been present in a crude pyrophoric mixture with lithium chloride. The products isolated were tetraphenyldiphosphine and a red polymeric powder of variable composition. Soxhlet extraction with methylcyclohexane gave material approximating in mean composition to $Ph_2P{\cdot}Ge$, whereas precipitation from benzene solution by light petroleum gave material having a lower carbon and hydrogen content, approximating to Ph_2PGe_2. Fritz and Poppenburg [2] who isolated the silicon analogue, $(Et_2P)_4Si$, also reported the formation of much tetraethyldiphosphine. The red polymer, which was very soluble in benzene, reacted rapidly with oxygen to give an insoluble yellow powder. The weight increase corresponded roughly to 2·3 g.-atoms of oxygen per $Ph_2P{\cdot}Ge$ unit. Infrared evidence suggested that this oxidised material contained $Ge{\cdot}O{\cdot}Ge$, $Ge{\cdot}O{\cdot}P$, and $P{:}O$ groups. In marked contrast to the singly-bonded Ge–P compounds already described the red polymer was unaffected by water. This behaviour is reminiscent of phenylgermanium polymers obtained from the reaction between germanium(II) iodide and phenyl-lithium [7] which were air but not water sensitive, and is possibly suggestive of some double bonding between germanium and phosphorus in the polymeric units.

Isolation of tetraphenyldiphosphine from reactions involving $PhGeBr_3$ and $GeCl_4$ was originally ascribed [1] to reduction of Ge(IV) to Ge(II): $GeCl_4 + 2Ph_2PLi \longrightarrow 2LiCl + GeCl_2 + Ph_4P_2$. However using this stoicheiometry gave only orange-red non-crystalline material which could not be purified, chlorine analyses indicated the composition, $(Ph_2P)_2GeCl_2$. We considered that this could be largely a co-ordination complex between tetraphenyldiphosphine and germanium(II) chloride, but the corresponding complex formed by germanium(II) iodide dissociated readily on heating *in vacuo*. We are now more inclined to the view that halogen-metal exchange reactions compete with normal substitution to give the red polymer; tetraphenyldiphosphine being formed partly by the reaction: $Ph_2PLi + Ph_2PCl \longrightarrow Ph_4P_2$, although processes of the type $(Ph_2P)_2GeCl_2 + Ph_2PLi \longrightarrow Ph_4P_2 + Ph_2PGe(Li)Cl_2$ may also contribute.

These complications led us to study the reaction between diphenylphosphine and germanium tetrachloride in the presence of an organic base, as a possible route to the tetrakis-derivative, $(Ph_2P)_4Ge$. Pyridine was ineffective, but in the presence of triethylamine the mixture, in benzene solution, turned deep red and yielded the amine hydrochloride, tetraphenyldiphosphine, and red polymeric material which was readily oxidised in air, but stable to water. Polymer formation implies exchange reactions, giving GeH intermediates, and condensation reactions involving the formation of Ge–Ge bonds, *e.g.*,

$$Ph_2P{\cdot}GeCl_3 + Ph_2PH \longrightarrow Ph_2P{\cdot}Ge(H)Cl_2 + Ph_2PCl$$

$$Ph_2P{\cdot}Ge(H)Cl_2 + Ph_2P{\cdot}GeCl_3 \longrightarrow Ph_2P(Cl)_2Ge{\cdot}Ge(Cl)_2PPh_2$$

It must be emphasised that no evidence is available that the polymer contains only $Ph_2P{\cdot}Ge$ units; quite possibly $(Ph_2P)_2Ge$ and even $(Ph_2P)_3Ge$ groups are involved. Oxidative cleavage however gave only diphenylphosphinic acid, so that cleavage of Ph–P bonds does not occur. An exchange reaction of this type in the absence of a base has been reported: [8] $Ph_3SnH + Ph_2PCl \rightleftharpoons Ph_2PH + Ph_3SnCl$; in hexane solution about 50% conversion occurs.

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[7] F. Glockling and K. A. Hooton, *J.*, **1963**, 1849.

[8] D. Seyferth, Y. Sato, and M. Takamizawa, *J. Organometallic Chem.*, **1964**, **2**, 367.

Infrared Spectra.—Comparison of the spectra of the triethylgermylphosphine compound and its silver iodide complex with the oxidation product, $Et_3Ge{\cdot}O{\cdot}P(O)Ph_2$, suggest that the Ge–P stretching frequency occurs at 474—476 cm.$^{-1}$. The phenylgermylphosphines had more complex spectra in this region, and an unambiguous assignment of ν(GeP) was not possible.

EXPERIMENTAL

Diphenyl(triethylgermyl)phosphorus, Et_3GePPh_2.—Lithium diphenylphosphide (0·13 mole) in tetrahydrofuran (260 c.c.) was added at room temperature to triethylbromogermane (31·2 g., 0·13 mole) in tetrahydrofuran (100 c.c.). The exothermic reaction resulted in immediate discharge of the cherry-red colour of the lithium diphenylphosphide solution. Distillation gave *diphenyl(triethylgermyl)phosphorus* (35·2 g., 79%) as a colourless liquid, b. p. 146°/10^{-3} mm. (Found: C, 62·1; H, 7·3%; *M*, 339. $C_{18}H_{25}GeP$ requires: C, 62·7; H, 7·3%; *M*, 345).

Reactions of Diphenyl(triethylgermyl)phosphorus.—(a) *Hydrolysis.* The complex (5·0 g.) was added to a solution of water (2·6 g.) in 1,2-dimethoxyethane (30 g.), and the mixture maintained at 20° for 18 hr., whereupon the excess of water was removed with anhydrous magnesium sulphate. Fractionation gave pure hexaethyldigermoxane, b. p. 60°/10^{-2} mm. (1·1 g., 45%), followed by a mixture of hexaethyldigermoxane and diphenylphosphine, b. p. 60—66°/10^{-2} mm. (2·0 g.), and finally pure diphenylphosphine, b. p. 100—110°/10^{-2} mm. (0·6 g., 22%).

A similar reaction mixture was rapidly introduced into an infrared spectral cell but no increase in absorption at 4·3735 μ (PH stretch) with time was observed; hence complete hydrolysis occurs within 5 min. under these conditions.

(b) *Oxidation.* Dry oxygen was bubbled through a solution of the complex (2·1 g.) in ether (50 c.c.) for 20 hr. Distillation gave *triethylgermyl diphenylphosphonate*, $Et_3Ge{\cdot}O{\cdot}P(O)Ph_2$, b. p. 160—162°/10^{-3} mm. (0·7 g.) (Found: C, 57·4; H, 6·8%; *M*, 381. $C_{18}H_{25}GeO_2P$ requires C, 57·3; H, 6·7%; *M*, 377). Its infrared spectrum was identical with that of specimen prepared by heating hexaethyldigermoxane and diphenylphosphinic acid (3 hr., 85°). In this process the Ge–O stretch of $(Et_3Ge)_2O$ at 855 cm.$^{-1}$ disappears with simultaneous formation of a Ge–OP stretch at 954 cm.$^{-1}$, and P=O stretch at 1220 cm.$^{-1}$. On prolonged contact with water at room temperature triethylgermyl diphenylphosphonate is hydrolysed to diphenylphosphinic acid, $Ph_2P(O)OH$, m. p. 190—191°, and hexaethyldigermoxane.

(c) *Cleavage by methyl iodide.* The complex (2·35 g., 6·8 mmole), methyl iodide (0·97 g., 6·8 mmoles), and benzene (40 c.c.) were kept at room temperature for 24 hr. Dimethyldiphenylphosphonium iodide which slowly separated was crystallised from methanol and then had m. p. 254—255° (0·6 g., 26%) (Found: I, 36·8. Calc. for $C_{14}H_{16}IP$: I, 37·1%).

A similar experiment with an excess of methyl iodide (4·56 g.) gave, after 3 days, dimethyldiphenylphosphonium iodide (2·0 g., 86%). The filtrate was refluxed for 10 hr. with a filtered solution of phenylmagnesium bromide (0·04 mole). Acid hydrolysis gave, from the organic extract, triethylphenylgermane, b. p. 100°/3 mm. (0·5 g., 31%), characterised by vapour-phase chromatography and its infrared spectrum.

(d) *Cleavage by n-butyl and phenyl-lithium.* The complex (5·45 g., 15·8 mmoles) in ether (100 c.c.) was added to ethereal n-butyl-lithium (15·8 mmoles). An immediate reaction occurred with the formation of a yellow colour and, after 5 hr. at 0°, ethyl bromide (1·8 g.) was added with discharge of the colour. Fractionation gave n-butyltriethylgermane, b. p. 43°/0·03 mm., 180—185°/760 mm. (1·4 g., 41%), and ethyldiphenylphosphine, b. p. 90—92°/0·02 mm., characterised by reaction with methyl iodide giving *ethylmethyldiphenylphosphonium iodide*, m. p. 184—185° (from methanol) (Found: I, 35·7. $C_{15}H_{18}IP$ requires I, 35·6%). A higher boiling fraction (0·4 g.), b. p. 120°/0·02 mm., consisted mainly of starting material.

Phenyl-lithium behaved similarly: after 1 hr. under reflux, 50% of the diphenyl(triethylgermyl)phosphorus was recoverable; triethylphenylgermane, b. p. 53°/0·1 mm., and ethyldiphenylphosphine were isolated as described above.

(e) *Bromination.* A standard solution of bromine (2·13 g., 13·3 mmoles) in carbon tetrachloride was added slowly to the complex (4·6 g., 13·33 mmoles) in the same solvent (60 c.c.) at −20°. The bromine was rapidly decolourised and after the addition of 0·4 mol. a yellow solid (possibly Ph_2PBr_3) separated which slowly redissolved after 0·6 mol. of bromine had been added. Fractionation of the final solution gave trimethylbromogermane, b. p. 32—40°/10^{-2} mm., 190°/760 mm. (2·2 g., 69%), and diphenylbromophosphine, b. p. 105°/10^{-2} mm. (2·3 g., 65%).

The latter on heating for 2 hr. with an excess of phenylmagnesium bromide gave, on normal work-up, triphenylphosphine oxide (1·7 g.), m. p. and mixed m. p. 153°.

Diphenyl(triethylgermyl)phosphorus Silver Iodide.—Diphenyl(triethylgermyl)phosphine (2·2 g., 6·4 mmoles) was added to a suspension of silver (I) iodide (1·48 g., 6·3 mmoles) in methylcyclohexane, and the pale yellow filtered solution slowly evaporated at 0° whereupon colourless prisms of tetrameric *diphenyl(triethylgermyl)phosphine silver*(I) *iodide* separated, m. p. 183° (decomp.) (2·2 g., 60%) (Found: AgI, 40·0%; *M*, 2238. $C_{18}H_{25}AgGeIP$ requires AgI, 40·5%; *M*, 580). The same complex, $[(Et_3Ge{\cdot}PPh_2)AgI]_4$, was isolated when a four-fold excess of the germylphosphine was used.

Diphenyl(triphenylgermyl)phosphine, $Ph_3Ge{\cdot}PPh_2$.—Lithium diphenylphosphide (0·05 mole) was added to bromotriphenylgermane (19·2 g., 0·05 mole) in tetrahydrofuran (100 c.c.) with immediate discharge of the orange colour. The solvent and traces of unchanged diphenylphosphine were removed *in vacuo* (120°/10^{-3} mm.), and the colourless residue extracted with methylcyclohexane giving colourless needles of *diphenyl(triphenylgermyl)phosphine*, m. p. 154—156° (16·3 g., 67%) (Found: C, 71·6; H, 5·0%; *M*, 463. $C_{30}H_{25}GeP$ requires C, 73·7; H, 5·1%; *M*, 489).

Cleavage of this germylphosphine by ethyl bromide (2 days at 40°) gave *diethyldiphenylphosphonium bromide*, m. p. 195—196° (21%) (Found: C, 58·9; H, 6·1. $C_{16}H_{20}BrP$ requires C, 59·5; H, 6·2%), and triphenylbromogermane, m. p. 135—136° (25%). Similarly the complex (0·4 g.) in benzene (15 c.c.) and methyl iodide (0·114 g.) deposited dimethyldiphenylphosphonium iodide after 24 hr. at 20°, m. p. 255—256° (Found: C, 48·5; H, 4·6. Calc. for $C_{14}H_{16}IP$: C, 49·1; H, 4·7%). The benzene solution gave, by sublimation triphenyliodogermane (0·3 g., 87%), m. p. 154°, ν (GeI) 282 cm.$^{-1}$.

Oxidation of this complex in benzene solution with dry oxygen gave *triphenylgermyl diphenylphosphonate*, $Ph_3Ge{\cdot}O{\cdot}P(O)Ph_2$, as a pale yellow viscous oil (Found: C, 69·7; H, 5·3. $C_{30}H_{25}GeO_2P$ requires C, 69·3; H, 4·8%). Its infrared spectrum showed ν(Ge–OP) at 947 and ν(P=O) at 1122 cm.$^{-1}$.

Hydrolysis of this complex at 20° was followed by observing the increase in ν(P–H) with time. The complex (0·4 g.) in 1,2-dimethoxyethane (11·5 g.) was mixed with 1,2-dimethoxyethane (4 c.c.) containing water (78·5 mg.), and the resulting solution introduced into an infrared spectrometer, with the appropriate amount of solvent mixture in the reference beam. The optical density at 4·374 μ [ν(P–H)] increased over 6 hr. at 20°.

Bis(diphenylphosphino)diphenylgermane, $(Ph_2P)_2GePh_2$.—Lithium diphenylphosphide (0·04 mole) was added to diphenyldibromogermane (7·6 g., 0·02 mole) in tetrahydrofuran (100 c.c.) with immediate discharge of the orange colour. Removal of the solvent *in vacuo* left a sticky residue from which diphenylphosphine and tetraphenyldiphosphine (0·7 g.; m. p. 118—121°) were separated by heating at 120°/10^{-3} mm. for 8 hr. Extraction of the residue with methylcyclohexane gave colourless needles of *bis(diphenylphosphino)diphenylgermane* (3·7 g.). After three crystallisations from the same solvent it had m. p. 182—185° (Found: C, 71·4; H, 5·2%; *M*, 554. $C_{36}H_{30}GeP_2$ requires C, 72·4; H, 5·1%; *M*, 597). The methylcyclohexane mother-liquors failed to yield any pure compound.

Phenylgermane and Phenyltribromogermane.—Phenylmagnesium bromide, from bromobenzene (0·18 mole) in ether (110 c.c.), was added to germanium tetrachloride (32·2 g., 0·15 mole) in ether (150 c.c.) with stirring at 0° for 4 hr. Lithium aluminium hydride (11·5 g., 0·3 mole) in ether (100 c.c.) was then added and, after 3 hr. under reflux, the mixture was hydrolysed (2NH_2SO_4). Fractionation of the organic extract gave phenylgermane, b. p. 48°/23 mm. (6·3 g., 28%), diphenylgermane, b. p. 79°/10^{-2} mm. (4·5 g., 13%), and triphenylgermane, b. p. 128—136°/10^{-2} mm. (3·3 g., 7%).

Phenylgermane (5·6 g.) in chloroform (250 c.c.) was treated with bromine (6 g. at 0° + 11·7 g. at 20°). Solvents and unchanged bromine were removed after 1 hr. under reflux giving phenyltribromogermane, b. p. 82—83°/10^{-2} mm. (9·7 g., 68%).

Phenyltribromogermane and Lithium Diphenylphosphide.—Dropwise addition of lithium diphenylphosphide (73·5 mmoles) in tetrahydrofuran (80 c.c.) to phenylbromogermane (9·5 g., 24·4 mmoles) in the same solvent (75 c.c.) resulted initially in discharge of the colour of the phosphide solution. The solution then turned light green (12 mmoles) and finally deep red (56 mmoles). The red colour intensified as the remainder of the lithium diphenylphosphide solution was added. Removal of the solvent, after being kept overnight, left a sticky residue from which diphenylphosphine was separated by heating at 120° *in vacuo*. Extraction with hot methylcyclohexane gave a pale yellow amorphous powder (4·1 g.) which, after one further extraction, had m. p. 108—112°. Its composition approximated to a diphenylphosphinophenylgermane $(Ph_2P{\cdot}GePh)_2$ (Found: C, 57·0; H, 4·6%; *M*, 684. $C_{18}H_{15}GeP$ requires C, 64·6; H, 4·5%; *M*, 335). Tetraphenyldiphosphine (3·7 g.) was isolated by cooling the methylcyclohexane-mother-liquors to $-20°$.

Germanium(IV) *Chloride and Lithium Diphenylphosphide;* 1 : 4 *Ratio.*—Dropwise addition of lithium diphenylphosphide (0·184 mole) to germanium(IV) chloride (9·4 g., 0·044 mole) in tetrahydrofuran (100 c.c.) resulted in immediate discharge of the colour of the lithium reagent in an exothermic reaction up to 0·079 mole (1·8 equivalents). The mixture then became deep red and the colour intensified as the remainder of the lithium diphenylphosphide was added. The final solution was heated under reflux for 18 hr. and then hydrolysed with air-free water. The dried organic extract was distilled at $100°/10^{-3}$ mm. giving diphenylphosphine (11·7 g.) and a sticky residue from which was obtained a red-brown powder (3·4 g.), m. p. 135—185°, by Soxhlet extraction with methylcyclohexane. This solid, from which traces of tetraphenyldiphosphine were removed by heating at $125°/10^{-3}$ mm., approximated in composition to a diphenylphosphinogermanium, $(Ph_2P{\cdot}Ge)_3$ (Found: C, 50·0; H, 4·1; Ge, 28·5%; *M*, 817. $C_{12}H_{10}GeP$ requires C, 55·9; H, 3·9; Ge, 28·2%; *M*, 257·8). Concentration and cooling of the methylcyclohexane mother-liquors gave crude tetraphenyldiphosphine (17 g.), m. p. 117—120°. The residue from the Soxhlet extraction was not examined.

The red-brown polymer formed an intense blood-red solution in benzene which, on oxidation with dry oxygen, gave a bright yellow precipitate, m. p. 120—130°, showing Ge·O·Ge absorption at 833 $cm.^{-1}$, Ge·O·P absorption at 980 $cm.^{-1}$ and, less well defined, P:O absorption at 1179 $cm.^{-1}$.

In a similar experiment in which germanium tetrachloride (1 mol.) and lithium diphenylphosphide solution (8 mol.) were used, hydrolysis of an aliquot portion and titration of the free base gave a reaction ratio of 4·2 mol. of Ph_2PLi per mol. of $GeCl_4$. Distillation of the tetrahydrofuran left a red sticky residue which was extracted with hot benzene. The insoluble part, mainly lithium chloride but possibly containing some $(Ph_2P)_4Ge$, fumed and took fire in air. Hydrolysis of the red benzene solution with air-free water gave an organic extract from which diphenylphosphine and tetraphenyldiphosphine were separated by heating at $140°/10^{-4}$ mm. The red sticky residue was dissolved in benzene and the red polymer precipitated by the addition of light petroleum (Found: C, 41·9; H, 3·5%). Oxidative hydrolysis of this material by alkaline hydrogen peroxide gave, on acidification, diphenylphosphinic acid, m. p. 195°. Neither H_3PO_4 or $PhPO(OH)_2$ were detectable in the mother-liquors.

Polymeric Diphenylphosphinogermanium.—Diphenylphosphine (3·72 g.) in benzene (100 c.c.) was added slowly to a mixture of germanium tetrachloride (1·07 g.), triethylamine (2·02 g.), and benzene (60 c.c.). Triethylammonium chloride was separated by filtration when solvent, excess of diphenylphosphine and tetraphenyldiphosphine were distilled from the orange solution ($140°/10^{-3}$ mm.) leaving a dark brown residue which on oxidation with 3% alkaline hydrogen peroxide gave only diphenylphosphinic acid, m. p. 196°.

Germanium Analyses.—No satisfactory method was found for complexes containing C–Ge–P groupings; oxidative breakdown with HNO_3–H_2SO_4–$Am_2S_2O_8$ followed by precipitation of the sulphide and conversion into GeO_2 invariably gave phosphorus-containing material. Germanium-phosphorus polymers were degraded with HNO_3–H_2SO_4, the excess of nitric acid fumed off, and the tannin complex precipitated from acid solution. Ignition, initially at 500° and finally at 900°, gave GeO_2.

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