CCXXXIV.—*Aromatic Derivatives of Germanium.*

By Gilbert T. Morgan and Harry Dugald Keith Drew.

When germanium tetrabromide is treated with a large excess of magnesium phenyl bromide (36 mols.) it yields *germanium tetraphenyl* or *tetraphenylgermane*, $Ge(C_6H_5)_4$, *triphenylgermanium bromide*, $Ge(C_6H_5)_3Br$, and the less phenylated germanium bromides, $Ge(C_6H_5)_2Br_2$ and $Ge(C_6H_5)Br_3$. The first two products are readily separated, but the latter pair, which do not solidify when mixed, have been identified by the isolation of their hydrolytic products.

Hexaphenyldigermane, $(C_6H_5)_3Ge{\cdot}Ge(C_6H_5)_3$, has not been detected among the products of the Grignard reaction, so that under these experimental conditions there is little or no tendency for junction of two atoms of the metal (compare with tin and lead), but the compound is readily prepared by the action of sodium on the triphenylgermanium bromide.

$$2GePh_3Br + 2Na = Ph_3Ge{\cdot}GePh_3 + 2NaBr.$$

The production of tetraphenylgermane and hexaphenyldigermane completes the following series :—

	CPh_4.	$SiPh_4$.	*$GePh_4$.*	$SnPh_4$.	$PbPh_4$.
M. p.	272°	233°	230—231°	225—226°	224—225°
	C_2Ph_6.	Si_2Ph_6.	*Ge_2Ph_6.*	Sn_2Ph_6.	Pb_2Ph_6.
M. p.	145—147°*	354°	340°	237°	155°*

* These abnormally low melting points are due to dissociation.

Hexaphenyldigermane when examined in dilute benzene solutions shows no recognisable tendency to dissociation.

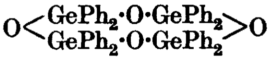
On hydrolysis the solid triphenylgermanium bromide yielded *triphenylgermanium oxide*, $(C_6H_5)_3Ge{\cdot}O{\cdot}Ge(C_6H_5)_3$, corresponding with the silicon compound, $Ph_3Si{\cdot}O{\cdot}SiPh_3$. The analogue, $Ph_3Ge{\cdot}OH$, of triphenylsilicon hydroxide was not isolated.

Hydrolytic Products from Diphenylgermanium Dibromide and Phenylgermanium Tribromide.—When only 5 molecular proportions of magnesium phenyl bromide are employed to one of germanium tetrabromide, there is no formation of tetraphenylgermane but the product contains a mixture of mono-, di-, and tri-phenylgermanium bromides.

Diphenylgermanium dibromide yielded on hydrolysis two well-defined complex substances derived by dehydration from the hypothetical dihydroxide or diol, $(C_6H_5)_2Ge(OH)_2$. These products, which have considerable capacity for crystallisation, are *trianhydrotetrakisdiphenylgermanediol*,

$$HO{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}OH$$

(I), m. p. 149°, and *tetra-anhydrotetrakisdiphenylgermanediol*,



$$O{<}\begin{matrix}GePh_2{\cdot}O{\cdot}GePh_2\\GePh_2{\cdot}O{\cdot}GePh_2\end{matrix}{>}O$$

(II), m. p. 218°.

The formation of these complicated anhydro-compounds recalls the results obtained by Kipping and his collaborators (J., 1912, **101**, 2108, 2125; 1914, **105**, 484) on hydrolysing diphenylsilicon dichloride, when the diol $Ph_2Si(OH)_2$ and four anhydrides were identified. The two silicon derivatives corresponding with formulæ I and II melt respectively at 128—129° and 200—201°. Diphenylgermanium dibromide also undergoes hydrolysis to an insoluble amorphous substance (p. 1765), from which it is regenerated by concentrated hydrobromic acid.

Owing to this tendency to form anhydrides it is obvious that hydrolysis of a mixture of diphenylgermanium dibromide and phenylgermanium tribromide might lead to an anhydro-diol derived from more than one of the reacting bromides. This anticipation was realised by the isolation of a substance (m. p. 275°) having a composition and molecular weight approximating to $Ge_5(C_6H_5)_8O_6$, which may be regarded as a combination of $3GePh_2O$ with $GePhO{\cdot}O{\cdot}GePhO$, these oxides being derived from the hydrolysis of diphenylgermanium dibromide and phenylgermanium tribromide, respectively. This product, which arises apparently from a chance condensation of the two different oxy-compounds, was only obtained in one experiment.

The hydrolysis of phenylgermanium tribromide leads to *phenylgermanonic* or *germanibenzoic acid*, a colourless uncrystallised product soluble in aqueous caustic alkalis. Its properties in regard to degree of hydration vary with the experimental conditions of its preparation and isolation. In all probability its composition varies within the limits $C_6H_5{\cdot}GeO{\cdot}OH$ and $C_6H_5{\cdot}GeO{\cdot}O{\cdot}OGe{\cdot}C_6H_5$ (III) and the analytical numbers approximate to an intermediate complex formula still containing hydroxyl groups. Phenylgermanonic acid or germanibenzoic acid therefore comes into line with silicobenzoic acid and its analogues, which have been shown conclusively by Kipping and his collaborators (J., 1914, **105**, 679; 1915, **107**, 459) to consist of mixtures of condensation products varying in composition with the conditions of hydrolysis of the halogenated silicanes.

The foregoing results obtained with oxygenated phenylgermanium compounds indicate that the reactions of these substances are similar to those of the oxyarylsilicon derivatives but of a somewhat simpler type with less tendency to the formation of syrups, colloids and infusible mixtures. In this respect germanium forms a link between silicon and tin, and the germanium atom should exhibit a tetrahedral distribution of valencies.

EXPERIMENTAL.

I. *Interaction of Germanium Tetrabromide with a Large Excess of Magnesium Phenyl Bromide.*

1. The Grignard reagent from 5·7 g. of magnesium, 30·2 g. of bromobenzene, and 120 c.c. of ether (36 mols. PhMgBr) was added to 2·1 g. of germanium tetrabromide in 75 c.c. of ether, and the mixture heated for 2 hours. The dark orange-yellow liquid was poured on to ice and acidified with hydrobromic acid, when a creamy white powder remained consisting of *tetraphenylgermane* (0·8 g. or 40%). The ethereal filtrate and extracts, dried over sodium sulphate and concentrated, yielded 0·5 g. of *triphenylgermanium bromide*; the final mother-liquor containing the less phenylated products was worked up as described on p. 1765.

2. During the action of less Grignard reagent (8 mols. PhMgBr) on 4·4 g. of germanium tetrabromide in 25 c.c. of pure chloroform (Boots') heat was generated. The resulting liquid, after being warmed on the water-bath for 1½ hours, was treated as above and yielded 0·93 g. of tetraphenylgermane (22%) and 1·1 g. of triphenylgermanium bromide (26%), the separation of the latter being hastened by adding petroleum (b. p. 60—80°). The ether-petroleum mother-liquors, distilled in steam to remove diphenyl, left a semi-solid yellowish-brown mass which after trituration left 0·4 g. of colourless crystalline *triphenylgermanium oxide*. The oily bromides were worked up as on p. 1765, whereas the aqueous layer from the hydrolysis of the Grignard product by ice deposited gradually a small amount of *phenylgermanonic* or *germanibenzoic acid.*

Tetraphenylgermane (*Germanium tetraphenyl*), $GePh_4$, crystallised from petroleum (b. p. 60—80°) in lustrous, refractive, transparent, prismatic needles, colourless in small quantities, creamy white in bulk. Very stable on heating, it melted at 230—231° and could be volatilised without decomposition (Found: C, 75·4; H, 5·6; Ge, 18·5. $C_{24}H_{20}Ge$ requires C, 75·7; H, 5·3; Ge, 19·0%).

Tetraphenylgermane was insoluble in water, sparingly soluble in ether, light petroleum, or cold acetone, and dissolved more readily in benzene, separating therefrom in acicular prisms. Boiling aqueous caustic alkalis had no effect on this substance; it was insoluble in cold concentrated sulphuric acid, but on warming sulphonation occurred destructively with elimination of phenyl groups. Fuming nitric acid or a mixture of nitric and sulphuric acids caused nitration and oxidation with evolution of nitrous fumes.

Triphenylgermanium bromide, $GePh_3Br$, formed large, colourless, transparent, six-sided, refractive, prismatic needles or small, compact prisms. Insoluble in water but somewhat readily soluble in ordinary organic media, it was best crystallised from petroleum (b. p. 40—80°); it melted at 138° to a colourless liquid (Found: C, 56·6; H, 4·1; Br, 20·7. $C_{18}H_{15}BrGe$ requires C, 56·3; H, 3·9; Br, 20·8%).

Triphenylgermanium bromide became hydrolysed superficially to its oxide by boiling water or by warm aqueous caustic alkalis. It arose as a by-product in the preceding preparations, but became the chief product when five molecular proportions of the Grignard reagent were employed to one of germanium tetrabromide. When 9·3 g. of the latter substance were used, the ethereal solution, after heating on the water-bath and subsequent treatment with ice and hydrobromic acid, yielded, on concentration of the ether layer, 2·5 g. (or 27%) of triphenylgermanium bromide. The residual oil was then treated with aquo-alcoholic silver nitrate, filtered from silver bromide, and the filtrate evaporated and distilled in steam, when diphenyl and *o*-nitrophenol were removed in the distillate. The non-volatile semisolid residue was fractionated from boiling petroleum (b. p. 60—80°) and from cold ether, when the following crystalline substances were separated: (i) a colourless compound (0·7 g.) melting at 275°, practically insoluble in cold ether or light petroleum and only sparingly soluble in the latter on warming (see pp. 1761, 1767); (ii) *tetra-anhydrotetrakisdiphenylgermanediol* (0·2 g.) melting at 218°, more soluble in ether or petroleum (see pp. 1761, 1766); (iii) an orange-yellow substance (0·1 g.) melting from 106° to 112°, very soluble in organic solvents or in water. This product (C, 51·3; H, 4·5%) contained no germanium and did not depress the melting point of ordinary *p*-nitrophenol (C, 51·8; H, 3·6%), but unlike the latter it was intensely yellow and more soluble in cold water. Being formed from phenylated germanium derivatives and silver nitrate in the absence of mineral acids, it may consist in part of an *aci*-form of *p*-nitrophenol. In addition to these solid products there was a considerable proportion of uncrystallisable germaniferous material which was worked up subsequently as described on p. 1766.

Triphenylgermanium Oxide, $Ph_3Ge\cdot O\cdot GePh_3$.—An alcoholic solution of triphenylgermanium bromide was boiled with silver nitrate, filtered from silver bromide, and diluted with water, when the oxide was obtained in quantitative yield. This product crystallised from hot petroleum (b. p. 60—80°) in transparent, colourless prisms melting to a colourless liquid at 182—183°; it separated from ethyl acetate in thin, six-sided plates (Found: C, 69·2; H, 4·9; Ge, 23·2. $C_{36}H_{30}OGe_2$ requires C, 69·35; H, 4·85; Ge, 23·2%).

In organic media triphenylgermanium oxide was more soluble than tetraphenylgermane but less so than triphenylgermanium bromide; it was unattacked by 50% aqueous caustic potash, but was reconverted quantitatively into triphenylgermanium bromide by hydrobromic acid (*d* 1·45).

Hexaphenyldigermane, $Ph_3Ge{\cdot}GePh_3$. — Triphenylgermanium bromide (3 g.) dissolved in 37 c.c. of dry xylene was heated for 3 hours with excess of " molecular " sodium. The filtered solution deposited on cooling 2·2 g. of hexaphenyldigermane, and a further amount was obtained on concentration. The final filtrate contained a small quantity of the more soluble triphenylgermanium oxide arising as a by-product.

Hexaphenyldigermane separated from hot benzene in large, colourless, transparent cubes crumbling into powder on exposure to air: loss of benzene at 100° = 24·3%, corresponding with 3 mols. of C_6H_6. It was sparingly soluble in cold but more soluble in hot chloroform, separating therefrom in colourless micro-crystals, m. p. 340° [Found: C, 70·8, 70·7; H, 5·1, 5·3; Ge, 23·5; *M*, ebullioscopic in benzene, 566 ($c = 0{\cdot}595$), 560 ($c = 1{\cdot}328$). $C_{36}H_{30}Ge_2$ requires C, 71·2; H, 5·0; Ge, 23·85%; *M*, 606·8].

Hexaphenyldigermane was insoluble in boiling aqueous caustic soda, but on boiling with alcoholic silver nitrate a slight blackening occurred owing to liberation of silver.

Phenylgermanonic Acid (*Germanibenzoic Acid*, p. 1761).—The aqueous mother-liquors from the hydrolysis of the Grignard mixture slowly deposited a white, colloidal precipitate, which was purified for analysis by redissolving in aqueous caustic soda, the filtered solution being then acidified, when the white, amorphous powder separated and was dried at 100° (Found: C, 39·9; H, 3·2. The simplest formula, $C_6H_6O_2Ge$, requires C, 39·5; H, 3·3%).

From concentrated solutions of its sodium salt, phenylgermanonic acid separated at once (hydrogel form), but in dilute solutions it remained dissolved (hydrosol condition) and separated only after several weeks.

II. *Interaction of Germanium Tetrabromide and Magnesium Phenyl Bromide* (5 *mols*.).

A Grignard solution, prepared from 48·4 g. of bromobenzene (5 mols.), 9·1 g. of magnesium, and 200 c.c. of ether, was added slowly to an ice-cold solution of 24·5 g. (1 mol.) of germanium tetrabromide in 100 c.c. of ether, moisture and carbon dioxide being excluded. The heavy colourless oil which separated persisted after heating on the water-bath. The cooled mixture was decomposed by ice and 50 c.c. of hydrobromic acid (*d* 1·45), when the crackling sound produced by the hydrolysis of germanium tetrabromide showed that this substance was not completely attacked even by excess of Grignard reagent. The solution was extracted with ether and the mixed ethereal extracts were dried over sodium sulphate. The aqueous layer, which gave no precipitate of phenylgermanonic acid (germanibenzoic acid) either when left or when partially neutralised, contained no other organic derivatives of germanium.

The ethereal extract, concentrated to a small bulk, gave 9 g. (37·5%) of *triphenylgermanium bromide.*

The residual oil, which contained a complex mixture of triphenylgermanium bromide, the less phenylated germanium bromides, and chiefly diphenylgermanium dibromide together with diphenyl and traces of bromobenzene, was dissolved in 150 c.c. of alcohol and added to 20 g. of silver nitrate in 100 c.c. of alcohol and 40 c.c. of water, when a dark brown precipitate separated. The mixture was heated under reflux for an hour and the alcoholic filtrates (A) separated from a black precipitate (B). This precipitate B, which consisted mainly of silver bromide but contained some organic germanium compound, was boiled with ammonia (*d* 0·88),* when a black residue remained which was extracted successively with aqueous sodium thiosulphate and dilute nitric acid, leaving 1·5 g. of a white, amorphous organic germanium compound. This substance melted partly at 260° and was insoluble in organic solvents, aqueous alkalis or ammonia; it was converted by hydrobromic acid into an oily bromide, from which the original amorphous substance was recovered by the action of water. This uncrystallisable product was also obtained by the hydrolysis of the oily bromide from tetra-anhydrotetrakisdiphenylgermanediol, m. p. 218°.

The alcoholic filtrate A was evaporated and the oily residue distilled in steam, when diphenyl and *o*-nitrophenol passed over. The residue, a solid of pitchy consistence, was dissolved in ether and the yellow solution filtered and concentrated until an orange-yellow, semi-crystalline mass separated. This product, after extraction with cold petroleum (b. p. 80—100°) to remove diphenyl and other more soluble impurities, furnished 5 g. of an almost

---

* The ammoniacal filtrate deposited on cooling lustrous spangles of silver bromide having a highly refractive reflex. This product was an insensitive form of the bromide, for it retained its bright metallic lustre after months of exposure to light. The ammoniacal liquor, which contained traces of organic derivatives of germanium, had the property of converting more yellow silver bromide to this insensitive form, the spangles separating at the surface of the solution.

colourless mixture of organic germanium derivatives now free from bromine. Repeated solution of this mixture in ethyl acetate followed by fractional crystallisation and hand-picking of the resulting crystals led to a separation of the following substances :—

1. *Triphenylgermanium oxide*, m. p. 182—183° (see p. 1763), separating from ethyl acetate in thin, rhomboidal or pentagonal plates.

2. *Tetra-anhydrotetrakisdiphenylgermanediol* (Formula II), crystallising in colourless, cubical and prismatic forms, the latter with bevelled and facetted faces. This complex diol was purified by crystallisation from petroleum or ethyl acetate, in which it was readily soluble, and then melted indefinitely at 218° [Found : C, 59·4, 59·1 ; H, 4·25, 4·4. $(C_{12}H_{10}OGe)_x$ requires C, 59·4 ; H, 4·2%. Found : by the ebullioscopic method in benzene (c = 1·48), *M*, 905. $(C_{12}H_{10}OGe)_4$ requires *M*, 970].

FIG. 1.

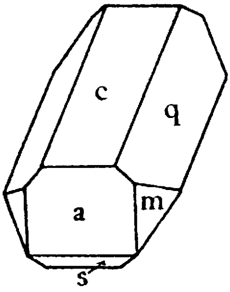
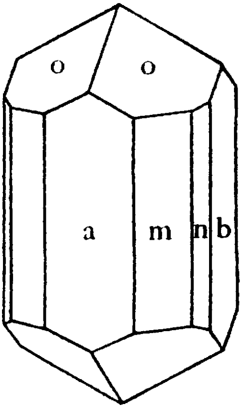


FIG. 2.



3. *Trianhydrotetrakisdiphenylgermanediol* (Formula I), m. p. 149°, obtained in colourless, hexagonal prisms or flattened, rhomboidal crystals with bevelled edges (Found : C, 58·8 ; H, 4·6. $C_{48}H_{42}O_5Ge_4$ requires C, 58·3 ; H, 4·25%).

Crystallographic Examination.

Two of the foregoing substances (Nos. 2 and 3) were kindly examined by Dr. T. V. Barker, who reports as follows :—

Tetra-anhydrotetrakisdiphenylgermanediol (Fig. 1).—The crystals of this substance are monoclinic with the forms *m*(110), *a*(100), *q*(011), *c*(001) and *s*(201) developed in the proportions given in Fig. 1. The axial ratios, *a* : *b* : *c* = 1·491 : 1 : 1·018, β = 111° 42′, were computed from the following results given by four crystals.

	m.	*a*.	*q*.	*c*.	*s*.
φ..............	0° 0′	0° 0′	68° 21′	*68° 18′	*137° 0′
ρ..............	35 45	90 0	*46 35	90 0	90 0

Optically, the crystals are positive; the axial plane is *b*(010), and one optic axis is nearly normal to *a*(100).

Trianhydrotetrakisdiphenylgermanediol (Fig. 2).—The crystals are orthorhombic with the forms *a*(100), *m*(110), *n*(120), *b*(010), and *o*(111) developed in the proportions given in Fig. 2. The axial ratios, $a : b : c = 0{\cdot}9539 : 1 : 0{\cdot}5399$, were computed from the following measurements derived from four crystals.

	b.	*n*.	*m*.	*a*.	*o*.
ϕ	0° 0′	27° 50′	*46° 21′	90° 0′	46° 21′
ρ	90 0	90 0	90 0	90 0	*38 2

Optically, the positive acute bisectrix is parallel to the *c*-axis, and the axial plane is *a*.

The Complex Diol melting at 275°.—When recrystallised from ethyl acetate, it separated in large, transparent, colourless prisms melting at 231° and containing solvent of crystallisation. At 140° the loss of weight was 4·45%, corresponding approximately with 2 mols. of diol combined with one of ethyl acetate (theory 3·9%). Crystallised from carbon tetrachloride, the compound melted to a transparent, colourless liquid at 277—278° but rather indefinitely [Found: C, 53·8; H, 3·9; Ge, 33·6; *M*, ebullioscopic in benzene ($c = 1{\cdot}000$), 1003. $C_{48}H_{40}O_6Ge_5$ requires C, 53·6; H, 3·7; Ge, 33·7%; *M*, 1074].

This complex diol was insoluble in water, dilute alcohol, ether, or petroleum and only sparingly soluble in other organic media.

Note on the Analysis of Aromatic Germanium Compounds.

In estimating carbon and hydrogen the combustion was effected entirely with oxygen in a tube containing copper oxide and lead chromate. The oxygenated germanium compounds required very prolonged heating at high temperatures in order to oxidise the last traces of carbon, which otherwise remained in the boat or on the side of the tube as a refractory black material.

For the estimation of germanium the weighed substance was digested during 8 or 10 hours with 18 c.c. of concentrated sulphuric acid (A.R. quality) in a flask with a ground-in air-condenser. The cooled liquid and undissolved germania were washed into a conical flask with 150 c.c. of water, any adherent germania being removed by boiling aqueous sodium carbonate (A.R.). The clear solution was thoroughly saturated with washed hydrogen sulphide and left in the closed flask for a day. The pinkish-white sulphide containing free sulphur and some organic matter was collected on a Gooch crucible with ashless paper filter, and washed successively with 4*N*-sulphuric acid saturated with hydrogen sulphide and aqueous hydrogen sulphide. After drying at 100° the precipitate and the portion remaining on the filter-paper were converted into germania in separate porcelain crucibles by treatment with dilute and then with concentrated nitric acid. On igniting the crucibles strongly, germania was obtained in a perfectly white condition.

The authors desire to express their thanks to Messrs. Brunner Mond and Company, Limited, for a grant which has partly defrayed the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, June 24th,* 1925.]