

### 791. *Benzyl Derivatives of Germanium.*

By R. J. CROSS and F. GLOCKLING.

Tetrabenzylgermane is cleaved by lithium in ethylene glycol dimethyl ether to give  $(\text{PhCH}_2)_3\text{GeLi}$  and  $(\text{PhCH}_2)_2\text{GeLi}_2$ . At reflux temperature in the presence of an excess of lithium these benzyl-lithiogermenes react with the solvent, giving  $(\text{PhCH}_2)_3\text{GeMe}$ ,  $(\text{PhCH}_2)_2\text{GeMe}_2$ , and  $\text{PhCH}_2\text{GeMe}_3$ . The reaction between tribenzylgermane and lithium is not selective: both Ge-H and Ge-benzyl bonds are cleaved, and this lack of selectivity is also shown by hexabenzyl digermane. Tribenzylgermane and butyl-lithium react (i) by hydrogen-metal exchange, giving  $(\text{PhCH}_2)_3\text{GeLi}$ , and (ii) by nucleophilic attack by  $\text{Bu}^-$  with displacement of either  $\text{H}^-$  or  $\text{PhCH}_2^-$ .

THE cleavage of germanium-carbon and germanium-germanium bonds by alkali metals in liquid ammonia or ethylamine solution has been known for many years,<sup>1</sup> but the utility of this reaction is limited by ready ammonolysis reactions, *e.g.*,  $\text{Et}_3\text{GeLi} + \text{NH}_3 \longrightarrow \text{Et}_3\text{GeH} + \text{LiNH}_2$ . More recently triphenylgermyl-alkali metal compounds have been prepared by the cleavage of Ge-C,<sup>2</sup> Ge-Ge,<sup>3</sup> Ge-Br,<sup>4</sup> and Ge-H<sup>5</sup> bonds by the alkali metal in strongly-donating ether solvents, such as tetrahydrofuran and ethylene glycol dimethyl ether. An even more satisfactory method for triphenylgermyl-lithium involves hydrogen-metal exchange:  $\text{Ph}_3\text{GeH} + \text{RLi} \longrightarrow \text{Ph}_3\text{GeLi} + \text{RH}$ . In each of these five methods the triphenylgermyl anion is evidently resistant to further attack by the alkali metal or organo-lithium compound.

Triphenylgermyl-lithium has been used extensively in organogermanium chemistry. For example, carbonation gives the acid,  $\text{Ph}_3\text{GeCO}_2\text{H}$ ; reaction with benzophenone the carbinol,  $\text{Ph}_3\text{GeC}(\text{OH})\text{Ph}_2$ ; organic halides usually form the unsymmetrical germane,  $\text{Ph}_3\text{GeR}$ . Compounds of the type  $\text{Ph}_3\text{GeMR}_3$ , where  $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{or Pb}$ , have been obtained by the general reaction:  $\text{Ph}_3\text{GeLi} + \text{R}_3\text{MX} \longrightarrow \text{Ph}_3\text{GeMR}_3$ , although a frequent complication is halogen-metal exchange leading to the symmetrical products,  $\text{Ph}_6\text{Ge}_2$  and  $\text{R}_6\text{M}_2$ .

Attempts to cleave a germanium-carbon bond in organo-germanes other than the tetraphenyl in ethereal-type solvents with lithium or sodium-potassium alloy have been surprisingly unsuccessful.<sup>6</sup> In some cases, such as tetraethyl- and tetrabenzyl-germane coloured solutions have been obtained, and there is evidence that phenyl groups are more

<sup>1</sup> Johnson, *Chem. Rev.*, 1951, **48**, 259.

<sup>2</sup> Gilman and Gerow, *J. Amer. Chem. Soc.*, 1955, **77**, 4675.

<sup>3</sup> Gilman and Gerow, *J. Amer. Chem. Soc.*, 1955, **77**, 5740.

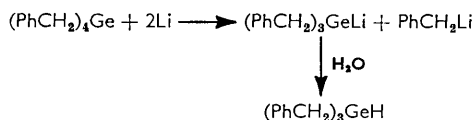
<sup>4</sup> George, Peterson, and Gilman, *J. Amer. Chem. Soc.*, 1960, **82**, 403.

<sup>5</sup> Gorisch, "Organometallic Chemistry," ed. Zeiss, Reinhold, New York, p. 331.

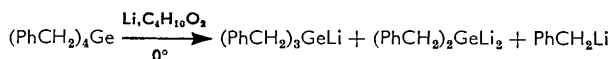
<sup>6</sup> Gilman, Hughes, and Gerow, *J. Org. Chem.*, 1959, **24**, 352.

susceptible to cleavage than alkyl groups. The present work is concerned mainly with the cleavage by lithium and butyl-lithium of tetrabenzylgermane, hexabenzylidigermene and tribenzylgermane. These reactions were considerably more complex than those reported for the phenyl analogues owing to the similar reactivity of Ge-H and Ge-CH<sub>2</sub>Ph towards nucleophilic attack, and the ease with which more than one benzyl group may be eliminated from tetrabenzylgermane.

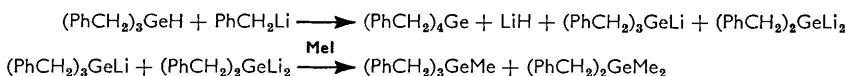
Provided water and peroxides are rigorously excluded, tetrabenzylgermane and lithium in ethylene glycol dimethyl ether solution undergo a rapid and exothermic reaction, even more readily than tetraphenylgermane. The resulting deep-brown solution contains largely tribenzylgermyl-lithium, as evidenced by the isolation of tribenzylgermane on hydrolysis.



In the early stages of this work we examined a number of simple reactions of tribenzylgermyl-lithium prepared in this way and often encountered considerable difficulty in isolating pure products in reasonable yield. Closer examination of the hydrolysis products showed the presence of dibenzylgermane, thus indicating that two benzyl groups can be cleaved from tetrabenzylgermane.

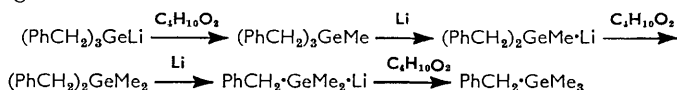


The dilithium compound could also result from the cleavage of a second benzyl group by benzyl-lithium, which is also present in the reaction mixture; in support of this, bibenzyl is among the reaction products obtained after hydrolysis. Moreover the dilithium derivative is certainly formed in the reaction between tribenzylgermane and benzyl-lithium, since dibenzylidimethylgermane is among the products isolated after treatment with methyl iodide.



Apart from indirect evidence based on the colour changes occurring when diphenylgermanium or tetraphenylgermane react with sodium in liquid ammonia,<sup>7,8</sup> this is the first clear evidence for the formation of a di-alkali-metal derivative of an organo-germane. This difference between tetrabenzyl- and tetraphenyl-germanes is presumably a reflection of the weaker Ge-C bond-strength in the case of the benzyl derivative, since the solvated anion, R<sub>2</sub>Ge<sup>2-</sup>, would be more stable with R = phenyl, when delocalisation of charge is possible.

The cleavage to tribenzylgermyl-lithium was strikingly dependent on the experimental conditions: the highest yields (75% after 1 hour at room temperature) were obtained using a large excess of lithium (800%). After 48 hours at 0° there was no unreacted tetrabenzylgermane, but appreciable conversion to the dilithium compound occurred. Most reaction conditions gave a mixture of (PhCH<sub>2</sub>)<sub>4</sub>Ge, (PhCH<sub>2</sub>)<sub>3</sub>GeLi, and (PhCH<sub>2</sub>)<sub>2</sub>GeLi<sub>2</sub>. Neither lithio derivative appears to react with the solvent during 24 hours at 0°. However, at reflux temperature and with an excess of lithium, a progressive series of reactions takes place, involving demethylation of the ether and further cleavage of benzyl groups, giving, finally, benzyltrimethylgermane.



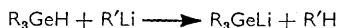
<sup>7</sup> Kraus and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 4031.

<sup>8</sup> Kraus and Foster, *J. Amer. Chem. Soc.*, 1927, **49**, 457.

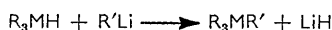


of germanium-benzyl bonds also occurs. With hexabenzyl digermane, reaction was slow and incomplete (50%) after 22 hours at 0°; the main product,  $(\text{PhCH}_2)_3\text{GeLi}$ , resulted from cleavage of the germanium-germanium bond but some cleavage of  $\text{Ge}-\text{CH}_2\text{Ph}$  bonds was again indicated since toluene was isolated after hydrolysis.

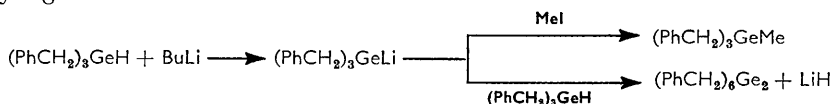
The formation of  $\text{R}_3\text{GeLi}$  compounds by hydrogen-metal exchange with organolithium reagents has been investigated in a number of cases with varying results:



Triphenylgermane,<sup>9</sup> tris(triphenylgermyl)germane,<sup>10</sup>  $(\text{Ph}_3\text{Ge})_3\text{GeH}$ , and  $\alpha$ -naphthylphenylmethylgermane,<sup>11</sup> are all cleaved smoothly and in high yield by butyllithium, whereas triethylgermane is only partly metallated<sup>12</sup> (10%). Some alkylation has also been observed in the reaction of triphenylgermane with methyl-lithium.<sup>9</sup> Under more drastic conditions triphenylgermane and phenyl-lithium give tetraphenylgermane or hexaphenyldigermane, depending on which reagent is present in excess.<sup>13</sup> In the analogous reactions of silicon and tin, alkylation takes place almost exclusively:<sup>14-16</sup>

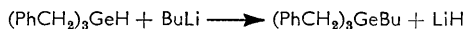


Tribenzylgermane and butyl-lithium showed the same lack of selectivity already encountered in the cleavage reactions involving lithium metal: alkylation, hydrogen-metal exchange, cleavage of  $\text{Ge}-\text{CH}_2\text{Ph}$  bonds and coupling to hexabenzyl digermane were all observed. The products isolated (after reaction with methyl iodide) depended partly on whether an excess of butyl-lithium was present and on the temperature. Direct hydrogen-metal exchange accounts for the isolation of tribenzylmethylgermane and hexabenzyl digermane:

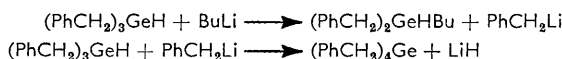


Formation of the complex mixture of products may be interpreted in terms of nucleophilic attack by  $\text{Bu}^-$  on the polar hydride  $(\text{PhCH}_2)_3\text{Ge}^{\delta+}-\text{H}^{\delta-}$  with displacement of either  $\text{H}^-$  or  $\text{PhCH}_2^-$ . In support of this view both tetrabenzylgermane and hexabenzyl digermane, which lack this polar character for nucleophilic attack, are virtually unreactive towards butyl-lithium under these experimental conditions.

Displacement of  $\text{H}^-$  gives tribenzylbutylgermane:



Displacement of  $\text{PhCH}_2^-$  leads to the formation of dibenzylbutylgermane and tetrabenzylgermane:



An independent experiment confirmed that tribenzylgermane and benzyl-lithium give, among other products, tetrabenzylgermane. Dibenzylbutylgermane retains the polar character of the original hydride and is therefore susceptible to further attack in the

<sup>9</sup> Gilman and Gerow, *J. Amer. Chem. Soc.*, 1956, **78**, 5435.

<sup>10</sup> Glockling and Hooton, *J.*, 1963, 1849.

<sup>11</sup> Brooks and Peddle, *J. Amer. Chem. Soc.*, 1963, **85**, 2338.

<sup>12</sup> Hughes, *Diss. Abs.*, **19**, 1921.

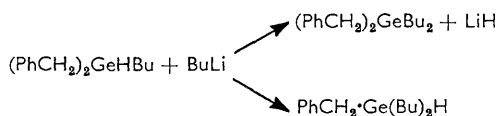
<sup>13</sup> Johnson and Harris, *J. Amer. Chem. Soc.*, 1950, **72**, 5566.

<sup>14</sup> Gilman and Melvin, *J. Amer. Chem. Soc.*, 1949, **71**, 4050.

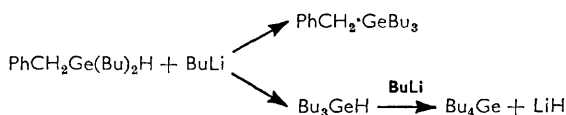
<sup>15</sup> Gilman and Massie, *J. Amer. Chem. Soc.*, 1946, **68**, 1128.

<sup>16</sup> Meals, *J. Amer. Chem. Soc.*, 1946, **68**, 1880.

presence of an excess of butyl-lithium, giving dibenzyltributylgermane and benzyltributylgermane:

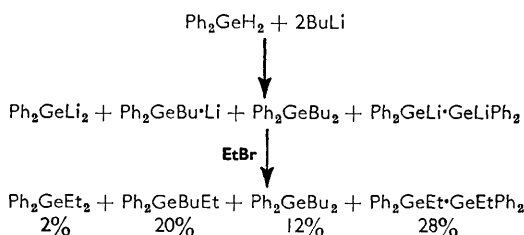


For the same reason benzyltributylgermane will react with butyl-lithium giving, finally, benzyltributylgermane and tetrabutylgermane.<sup>10</sup>



Separate experiments established that the benzylbutylgermanes,  $\text{PhCH}_2\cdot\text{GeBu}_3$  and  $(\text{PhCH}_2)_2\text{GeBu}_2$ , are insufficiently polar to react further with butyl-lithium under similar conditions, and these mixed compounds, like  $(\text{PhCH}_2)_4\text{Ge}$  and  $(\text{PhCH}_2)_6\text{Ge}_2$ , may also be subject to a large steric factor (as reported by Eaborn and his co-workers for nucleophilic attack by  $\text{OH}^-$  on benzyltrimethylgermane and related compounds).<sup>17</sup>

Experiments have been carried out on the reaction between diphenylgermane and butyl-lithium with a view to obtaining evidence for a dilithio derivative, and to examining the selectivity of the reaction. With two equivalents of butyl-lithium and subsequent reaction with ethyl bromide there was evidence for the formation of  $\text{Ph}_2\text{GeLi}_2$  (2%). Cleavage of phenyl groups was not observed but otherwise the behaviour was similar to that of benzylgermanes, metallation, alkylation, and coupling reactions taking place.



The digermane,  $\text{Ph}_2\text{GeEt}\cdot\text{GeEtPh}_2$ , m. p.  $126^\circ$ , is identical with that reported from degradative experiments on phenylgermanium polymers.<sup>10</sup>

Dibenzyl and diphenylgermane show, in addition to the Ge-H stretch at  $2034\text{ cm}^{-1}$ , a strong  $\text{GeH}_2$  deformation band<sup>18</sup> at  $866\text{ cm}^{-1}$  which appears at  $612\text{ cm}^{-1}$  in the corresponding deuteride,  $(\text{PhCH}_2)_2\text{GeD}_2$ .

Triphenylgermane is known to disproportionate on heating:<sup>13</sup>  $2\text{Ph}_3\text{GeH} \longrightarrow \text{Ph}_2\text{GeH}_2 + \text{Ph}_4\text{Ge}$ , and it seemed possible that this type of reaction could account for the isolation of dibenzylgermane from the reaction between tetrabenzylgermane and lithium. Tribenzylgermane is, however, stable in vacuum at  $240^\circ$  and only superficial decomposition occurs at  $310^\circ$ . At  $400^\circ$  decomposition is extensive, giving toluene, bibenzyl, *trans*-stilbene, hydrogen, and a brown polymer having the approximate composition,  $\text{Ge}_3(\text{CH}_2\text{Ph})_2$ . No dibenzylgermane was formed.

$^1\text{H}$  nuclear magnetic resonance spectra at 60 Mc./sec. of some organogermanes encountered in this work are given in Table 2. Chemical shifts relate to tetramethylsilane as an internal standard. Phenyl peaks were always complex.

<sup>17</sup> Bott, Eaborn, and Swaddle, *J.*, 1963, 2342.

<sup>18</sup> Srivastava, Griffiths, and Onyszczuk, *Canad. J. Chem.*, 1963, **41**, 2101.

TABLE 2.

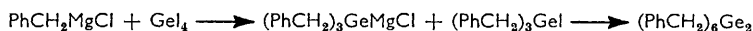
Compound	Solvent	Chemical shifts, $\tau$			
		Ge-H	Ph	CH <sub>2</sub>	Et
Ph <sub>3</sub> GeH .....	25% in CCl <sub>4</sub>	4.31	2.70	—	—
Ph <sub>2</sub> GeH <sub>2</sub> .....	—	4.91	2.77	—	—
(PhCH <sub>2</sub> ) <sub>2</sub> GeH <sub>2</sub> .....	—	5.98	3.06	7.87	—
(PhCH <sub>2</sub> ) <sub>3</sub> GeH .....	25% in CCl <sub>4</sub>	5.82	3.07	7.81	—
(PhCH <sub>2</sub> ) <sub>4</sub> Ge .....	—	—	3.11	7.93	—
(PhCH <sub>2</sub> ) <sub>3</sub> Ge·GeEt <sub>3</sub> .....	„	—	3.06	7.82	9.02

## EXPERIMENTAL

All air-sensitive intermediates were handled under an atmosphere of pure nitrogen. Ethylene glycol dimethyl ether and tetrahydrofuran were purified immediately before use by distillation from potassium-benzophenone or lithium aluminium hydride. Vapour-phase chromatography was carried out in a Griffin and George (Mk. II B) apparatus with a column of silicone elastomer on kieselguhr.

*Tribenzylbromogermane and Tribenzylgermane.*—Bromine (28.8 g.) in 1,2-dibromoethane (200 c.c.) was added to a solution of tetrabenzylgermane (70 g.) in the same solvent (500 c.c.); the reaction was complete after 6 hr. at room temperature. The solvent and benzyl bromide were separated by vacuum distillation and the residue, dissolved in a 1:1 ether-benzene mixture (700 c.c.) added slowly to lithium aluminium hydride (30 g.) in ether (400 c.c.). After 2 hr. at reflux the excess lithium aluminium hydride was destroyed by the cautious addition of 2N-sulphuric acid. The organic extract gave *tribenzylgermane* (47.4 g., 85%), m. p. 80–82° (methanol), Ge-H stretch at 2034 cm.<sup>-1</sup> (Found: C, 73.0; H, 6.2; Ge, 21.5; C<sub>21</sub>H<sub>22</sub>Ge requires C, 72.7; H, 6.4; Ge, 20.9%).

*Hexabenzylidigermane.*—The Wurtz reaction<sup>19</sup> between sodium and tribenzylbromogermane gave a very low yield (9% after 3 days at reflux temperature). The following method, based on the coupling of an intermediate germyl Grignard reagent, was more successful:<sup>20</sup>



Germanium(IV) iodide (169 g.) in toluene (500 c.c.) was added to ethereal (2.5 l.) benzyl magnesium chloride prepared from benzyl chloride (370 g.) and magnesium (80 g.) and the mixture, containing the excess magnesium, heated under reflux for 44 hr. Hydrolysis yielded a semi-solid organic product which was extracted with boiling ether, giving hexabenzylidigermane (11.5 g., 11.4%) as the insoluble fraction, m. p. 185° (chloroform).

*Benzylbutylgermanes* [PhCH<sub>2</sub>GeBu<sub>3</sub>, (PhCH<sub>2</sub>)<sub>2</sub>GeBu<sub>2</sub>, and (PhCH<sub>2</sub>)<sub>3</sub>GeBu].—Dropwise addition of a filtered solution of butyl magnesium bromide (0.26 mole), prepared from butyl bromide (35.6 g.) and magnesium (7 g.) in ether (250 c.c.), to germanium(IV) chloride (20 g.) in ether (50 c.c.) was followed immediately by the addition of ethereal benzyl magnesium chloride (0.4 mole). The resulting mixture was refluxed for 2 hr. and then hydrolysed by 2N-hydrochloric acid. Distillation of the organic extract gave: *benzyltributylgermane* (7.4 g., 27%), b. p. 100–110°/10<sup>-3</sup> mm. (Found: C, 67.8; H, 10.0. C<sub>19</sub>H<sub>34</sub>Ge requires C, 68.1; H, 10.2%); *dibenzylidibutylgermane* (16 g., 46%), b. p. 130–133°/10<sup>-3</sup> mm. (Found: C, 70.6; H, 9.3. C<sub>22</sub>H<sub>32</sub>Ge requires C, 71.6; H, 8.8%); and *tribenzylbutylgermane* (5.9 g., 16%), b. p. 150–163°/10<sup>-3</sup> mm. (Found: C, 74.7; H, 7.5. C<sub>25</sub>H<sub>30</sub>Ge requires C, 74.5; H, 7.5%).

*Cleavage of Tetrabenzylgermane.* (a) *Isolation of Tribenzylgermane.*—Tetrabenzylgermane (10 g.), lithium shot (2.5 g.), and ethylene glycol dimethyl ether (1 c.c.) were stirred to a paste, which turned yellow after a few minutes and then deepened to brown with spontaneous warming. Additional solvent (7 c.c.) was added and after 1 hr. the excess lithium was separated by filtration through glass wool. Hydrolysis of the filtrate (10% aqueous monoglyme) was exothermic and discharged the brown colour. Distillation of an ether extract gave tribenzylgermane (6 g., 76%), b. p. 164°/10<sup>-3</sup> mm., as colourless needles, m. p. 80–82° (methanol). The residue from the distillation gave tetrabenzylgermane from propanol, m. p. and mixed m. p. 110°.

<sup>19</sup> Bauer and Burschkies, *Ber.*, 1934, **67**, 1041.

<sup>20</sup> Glockling and Hooton, *J.*, 1962, 3509.



(b) *Isolation of Tri- and Di-benzylgermanes and the Corresponding Deutero-germanes.*—Tetrabenzylgermane (50 g.) and lithium shot (4 g.) were stirred at room temperature with ethylene glycol dimethyl ether (5 c.c.) until yellow specks appeared (5 min.). The mixture was then kept at 0° for 16 hr. after the addition of further solvent (40 c.c.). Hydrolysed by the slow addition of 10% aqueous monoglyme (100 c.c.), followed by extraction with benzene and water gave an organic layer (40.5 g.) which was distilled *in vacuo* giving a trace of bibenzyl, *dibenzylgermane* (2.3 g., 7.8%), b. p. 80–85°/10<sup>-3</sup> mm. (Found: Ge, 26.1. C<sub>14</sub>H<sub>18</sub>Ge requires Ge 28.3%), and tribenzylgermane (8.3 g., 21%), b. p. 176–187°/10<sup>-3</sup> mm. The residue consisted of pure tetrabenzylgermane.

Dibenzylgermane showed, in addition to the Ge–H stretch at 2034 cm.<sup>-1</sup>, a strong band at 866 cm.<sup>-1</sup> which is also present in the spectrum of diphenylgermane and is probably a GeH<sub>2</sub> deformation frequency.<sup>18</sup> (R<sub>4</sub>Ge, R<sub>3</sub>GeH, and R<sub>2</sub>GeR'<sub>2</sub> compounds, where R = benzyl and R' = methyl, do not absorb in this region). The nuclear magnetic resonance spectrum of dibenzylgermane at 60 Mc./sec. showed a large unresolved peak at low fields, a quintet at mid-fields and a triplet at high fields. The relative intensities, 10 : 2 : 4, are in agreement with the structure (PhCH<sub>2</sub>)<sub>2</sub>GeH<sub>2</sub>. A similar experiment with tetrabenzylgermane (10 g.) and lithium shot (0.8 g.), followed finally by the addition of deuterium oxide (5 c.c.), gave on vacuum distillation a few drops of liquid, probably dibenzyldeutero-germane (Ge–D stretch at 1464 cm.<sup>-1</sup>; GeD<sub>2</sub> deformation at 612 cm.<sup>-1</sup>). The main product, *tribenzyldeutero-germane* (5.4 g., 77%), had b. p. 170–176°/10<sup>-3</sup> mm., m. p. 81° (methanol), Ge–D stretch at 1464 cm.<sup>-1</sup> (Found: C, 72.4; H, 6.6; Ge 21.35. C<sub>21</sub>H<sub>21</sub>DGe requires C, 72.5; H, 6.7; Ge, 20.9%).

*Tribenzylethylgermane.*—Tribenzylgermyl-lithium solution, prepared from tetrabenzylgermane (15 g.) and lithium shot (5 g.) in ethylene glycol dimethyl ether (20 c.c.), was filtered through glass wool after 48 hr. at 0° and the filtrate added to an excess of ethyl bromide in ether. The reaction was exothermic and the colour was discharged. The organic layer gave *tribenzylethylgermane*, b. p. 170–183°/10<sup>-3</sup> mm. (8.2 g., 64%) (Found: C, 73.0; H, 6.9; Ge, 19.1. C<sub>23</sub>H<sub>26</sub>Ge requires C, 73.6; H, 7.0; Ge, 19.4%). After repeated crystallisation from methanol it had m. p. 34–35° (in contrast to the literature value<sup>19</sup> of 56–57°).

*Tribenzylgermyltrimethylsilane.*—Tribenzylgermyl-lithium prepared from tetrabenzylgermane (6.8 g.) as described above (2.5 hr. at 5°) was added to chlortrimethylsilane (3.2 g., 2 mol.). The colour was discharged with evolution of heat and separation of a white solid. Hydrolysis, ether extraction and distillation of the ethereal extract gave a mixture containing toluene and hexamethyldisiloxane. Vacuum-distillation gave *tribenzylgermyltrimethylsilane*, b. p. 183°/10<sup>-3</sup> mm., m. p. 63.5–64.5° (needles, methanol) (Found: C, 68.6; H, 7.1%; *M* (freezing benzene), 415. C<sub>24</sub>H<sub>30</sub>GeSi requires C, 68.8; H, 7.2%; *M*, 419). The residue from the distillation consisted of tetrabenzylgermane.

*sym-Tribenzyltriethylgermane* (PhCH<sub>2</sub>)<sub>3</sub>Ge·GeEt<sub>3</sub>.—Bromotriethylgermane (5.5 g.) in ether (50 c.c.) was added to a solution of tribenzylgermyl-lithium prepared from tetrabenzylgermane (10 g.) as previously described (2 hr. at 20°). Normal work-up gave unreacted tetrabenzylgermane (4.3 g.) and *sym-tribenzyltriethylgermane*, (6.1 g.), b. p. 220–230°/10<sup>-3</sup> mm. (Found: C, 67.6; H, 7.3%; *M*, 541. C<sub>27</sub>H<sub>36</sub>Ge<sub>2</sub> requires C, 64.1; H, 7.2%; *M*, 506). The n.m.r. spectrum at 60 Mc./sec. showed three peaks of relative intensity 5 : 2 : 4.8, corresponding to phenyl, methylene (of PhCH<sub>2</sub>), and ethyl groups, respectively. Its infrared spectrum showed a weak band at 234 cm.<sup>-1</sup> which could be attributed to the Ge–Ge stretch.<sup>10</sup>

A similar reaction in which the tribenzylgermyl-lithium was added to pure bromotriethylgermane resulted in extensive halogen–metal exchange, giving hexabenzylidgermane and hexaethylidgermane.

*Tribenzylphenylacetoxylgermane and Tribenzylgermyltribenzylgermanecarboxylate* [(PhCH<sub>2</sub>)<sub>3</sub>GeOCOCH<sub>2</sub>Ph and (PhCH<sub>2</sub>)<sub>3</sub>GeOCOGe(CH<sub>2</sub>Ph)<sub>3</sub>].—Tribenzylgermyl-lithium, from tetrabenzylgermane (10 g.) and excess lithium as previously described (2 hr. at 20°), was treated with solid carbon dioxide and then water. Ether extraction of the alkaline solution gave unreacted tetrabenzylgermane (4.1 g.). Acidification of the aqueous solution and extraction with ether gave a mixture of non-acidic products (5.0 g.). Extraction with hexane gave first *tribenzylphenylacetoxylgermane* (1.5 g.) as colourless crystals, m. p. 146–148° (Found: C, 72.1; H, 5.5; Ge, 15.0. C<sub>29</sub>H<sub>28</sub>GeO<sub>2</sub> requires C, 72.4; H, 5.9; Ge, 15.1%). Concentration of the hexane solution yielded *tribenzylgermyltribenzylgermanecarboxylate*, m. p. 77–80° (methanol) (Found: C, 70.1; H, 5.7; Ge, 19.6. C<sub>43</sub>H<sub>42</sub>Ge<sub>2</sub>O<sub>2</sub> requires C, 70.2; H, 5.8; Ge, 19.7%).

*Tribenzylgermyl-lithium and Trichlorosilane.*—Tribenzylgermyl-lithium, prepared from

tetrabenzylgermane (26 g., 59.5 mmole) as previously described (18 hr. at 0°), was added to trichlorosilane (2.7 g., 20 m mole) in ether (60 c.c.) at -70°, and finally refluxed for 30 min. Hydrolysis and ether extraction gave polymeric material (18.1 g.) which was obtained as a white powder from isopropanol, m. p. 35–45° (Found: C, 69.6; H, 6.7%; *M* (freezing benzene, 2030–1320). This material showed a weak SiH stretch at 2101 cm.<sup>-1</sup>.

*Cleavage of Ethylene Glycol Dimethyl Ether by Tetrabenzylgermane and Lithium.* (a) *Reaction Time 4 Hr.*—Tetrabenzylgermane (10 g.) and lithium shot (2.5 g.) in monoglyme (5 c.c.) were stirred until the yellow colour developed, when further solvent (25 c.c.) was added and the mixture heated under reflux for 4 hr. Filtration from lithium followed by hydrolysis gave, from the organic extract, *tribenzylmethylgermane*, (2.2 g.; 27%) as colourless needles from methanol, m. p. 82–85° (Found: C, 73.6; H, 6.3; Ge, 20.4%; *M*, 356. C<sub>22</sub>H<sub>24</sub>Ge requires C, 73.2; H, 6.7; Ge, 20.1%, *M*, 361).

(b) *Reaction Time 19 Hr.*—In a similar reaction in which refluxing was continued for 19 hr., the final organic extract contained toluene and ethylbenzene (ratio 9:1). Vacuum-distillation gave a liquid (0.5 g.), b. p. 26–82°/10<sup>-3</sup> mm., consisting of benzyltrimethylgermane and dibenzylmethylgermane (v.p.c. characterisation) and *dibenzylmethylgermane* (2.3 g.), b. p. 82–100°/10<sup>-3</sup> mm., m. p. 53–55° (methanol) (Found: C, 67.3; H, 7.2%; *M*, 273. C<sub>16</sub>H<sub>20</sub>Ge requires C, 67.4; H, 7.1%; *M*, 285).

(c) *Reaction Time 6 Days.*—Tetrabenzylgermane (20 g.) and lithium shot (8 g.) in ethylene glycol dimethyl ether were heated under reflux for 6 days in a nitrogen atmosphere, the emergent gases being passed through a trap at -78°. Fractional condensation of the contents of the trap gave methyl vinyl ether (1185 c.c. at S.T.P.; 3.07 g.) (Found: *M*, 56.2. Calc. for C<sub>3</sub>H<sub>6</sub>O, 58) but no tetramethylgermane. The final organic extract (7.3 g.) gave benzyltrimethylgermane (3.6 g.), b. p. 204–206°/760 mm. (Found: C, 57.7; H, 7.8. Calc. for C<sub>10</sub>H<sub>16</sub>Ge: C, 57.5; H, 7.7%), and an unidentified higher boiling fraction.

*Cleavage of Hexabenzylidigermane by Lithium.*—Hexabenzylidigermane (4.75 g., 4.68 m mole) and lithium shot (1.2 g.) were mixed to a paste with ethylene glycol dimethyl ether (4 c.c.). Golden-brown specks appeared after 10 min. and spread throughout the mixture in 2½ hr., when more solvent (8 c.c.) was added and stirring continued for 22 hr. at 0°. Hydrolysis and distillation of the organic extract gave tribenzylgermane (1.2 g., 25%). The residue from the distillation gave unreacted hexabenzylidigermane (2.4 g.), m. p. 182–185° *ex* toluene. Examination of the solvent mixture by vapour-phase chromatography showed a trace of toluene, indicating that some cleavage of benzyl groups had occurred.

*Cleavage of Tribenzylgermane by Lithium.*—Tribenzylgermane (2.2 g., 6.35 m mole), lithium shot (0.5 g.) and ethylene glycol dimethyl ether (2 c.c.) were mixed to a paste. Black specks formed on the lithium surface and the solution turned pale brown. Solvent (14 c.c.) was then added and the mixture stirred at 0°. The solution was dark green after 7 hr. and black after 24 hr. when excess lithium was separated, and methyl iodide (7 g.) in ether (20 c.c.) added. Normal work-up gave a liquid, b. p. 120–140°/10<sup>-3</sup> mm. (0.1 g.), consisting of dibenzylmethylgermane (v.p.c. characterisation), and a more volatile component. Since the mixture showed strong Ge–H absorption at 2034 cm.<sup>-1</sup>, the unidentified component was probably dibenzylmethylgermane. Toluene was detected in the solvent mixture and tribenzylmethylgermane (0.8 g.), m. p. 82–84° *ex* methanol, was also isolated by vacuum-distillation.

*Cleavage of Tribenzylgermane by n-Butyl-lithium.*—Tribenzylgermane (10 g., 28.8 m mole) in ether (200 c.c.) was added over 3½ hr. to butyl-lithium (28.8 m mole) in ether (40 c.c.) at -10°. The yellow solution containing suspended solid was stirred at -12° for 20 hr. when methyl iodide (6 g.) was added with discharge of the colour. Hydrolysis with water gave hydrogen. Hexabenzylidigermane (1.25 g., 12.5%) was separated by filtration. Vacuum-distillation of the organic extract gave a liquid mixture (6.5 g.) b. p. 130–200°/10<sup>-3</sup> mm. Tetrabenzylgermane (2 g., 16%) m. p. and mixed m. p. 106–110°, was isolated from the residue of the distillation. Redistillation gave tribenzylbutylgermane (3 g., 26%), b. p. 150–163°/10<sup>-3</sup> mm., tribenzylmethylgermane (1.25 g., 12%), b. p. 140–160°/10<sup>-3</sup> mm., m. p. 78–81° (methanol), and a liquid mixture (0.6 g.), b. p. 50–140°/10<sup>-3</sup> mm. Infrared and n.m.r. spectra on the mixture indicated that this was probably benzylidibutylgermane, PhCH<sub>2</sub>Ge(Bu)<sub>2</sub>H, and dibenzylbutylgermane, (PhCH<sub>2</sub>)<sub>2</sub>Ge(Bu)H. The n.m.r. spectrum at 60 Mc./sec. of a higher-boiling cut from this mixture showed three peaks of relative intensity, 10:4:12; and ν(Ge–H stretch), 2020 cm.<sup>-1</sup>.

A similar experiment carried out at room temperature using tribenzylgermane (12 g.) and



butyl-lithium (2 mols.) gave hexabenzyl digermane (0.9 g., 7.5%), tetrabenzylgermane (3 g., 20%) and tribenzylbutylgermane (7 g., 50%). A lower-boiling fraction (1.3 g.), b. p. 90—140°/10<sup>-3</sup> mm., was shown by vapour-phase chromatography (using the authentic compounds for comparison) to contain dibenzyl dibutylgermane, benzyltributylgermane, and tetrabutylgermane. No tribenzylmethylgermane was isolated from this experiment and no volatile products containing Ge-H bonds. Tribenzylgermane (0.6 g.) and butyl-lithium (2 mols.) in ether (30 c.c.) under the same conditions gave, on hydrolysis, hydrogen (19.6 c.c. at S.T.P.).

*Cleavage of Tribenzylgermane by Benzyl-lithium.*—Tribenzylgermane (3.8 g., 11 m mole) in ether (100 c.c.) was treated at room temperature with a tetrahydrofuran-ether solution of benzyl-lithium<sup>21</sup> (11 m mole) and, after 18 hr. excess methyl iodide was added. Normal work-up gave by distillation a trace of dibenzyl dimethylgermane, b. p. 80—100°/10<sup>-3</sup> mm. (v.p.c.-characterised), tribenzylmethylgermane, b. p. 165°/10<sup>-3</sup> mm. (0.5 g., 12%) and tetrabenzylgermane, b. p. 200—210°/10<sup>-3</sup> mm. (2.9 g., 60%).

*Cleavage of Tetrabenzylgermane by n-Butyl-lithium.*—Tetrabenzylgermane (10 g., 22.9 m mole) and butyl-lithium (25 m mole) in ether (50 c.c.) were stirred at 20° for 10 hr. Hydrolysis and normal work-up gave an almost quantitative recovery of starting material; toluene was detected by vapour-phase chromatography.

*Diphenylgermane and n-Butyl-lithium.*—Diphenylgermane (5 g., 22 m mole) in ether (100 c.c.) was treated with n-butyl-lithium (44 mmoles) at -10°. After 4 hr. ethyl bromide (4.8 g.) was added to the cloudy yellow solution with discharge of the colour. Hydrogen was evolved on hydrolysis and the organic extract (4 g.) gave a liquid distillate (2.4 g.), b. p. 20—140°/10<sup>-3</sup> mm., consisting of (i) diphenyldiethylgermane (0.1 g., 2%) (v.p.c.-characterisation); (ii) *n*-butylethyldiphenylgermane (1.4 g., 20.5%), b. p. 100—110°/10<sup>-3</sup> mm. (Found: C, 69.0; H, 7.7%; *M*, 327. C<sub>18</sub>H<sub>24</sub>Ge requires C, 69.1; H, 7.7%; *M*, 313.0); (iii) *Dibutyldiphenylgermane* (0.9 g., 12%), b. p. 130—140°/10<sup>-3</sup> mm. (Found: C, 70.5; H, 8.3; *M*, 350. C<sub>20</sub>H<sub>28</sub>Ge requires C, 70.4; H, 8.3%; *M*, 341.1). The residue from the distillation gave 1,2-diethyl,1,1,2,2-tetraphenyldigermane from propanol (1.5 g., 28%), m. p. 125—126.5° (Found: C, 64.7; H, 5.8. C<sub>28</sub>H<sub>30</sub>Ge<sub>2</sub> requires C, 65.7; H, 5.9%). Its infrared spectrum and mixed m. p. were identical with the compound isolated in earlier work.<sup>10</sup>

*Pyrolysis of Tribenzylgermane.*—Tribenzylgermane (1 g.) in an evacuated, sealed tube was heated for 24 hr. Slight decomposition occurred at 370° and at 390° complete decomposition took place, giving toluene (0.55 g.), bibenzyl (0.1 g.), a trace of *trans*-stilbene, and a dark brown polymer (0.3 g.) which was shown by *X*-ray powder photograph to contain no germanium metal (Found: C, 40.4; H, 3.0%).

The authors are indebted to Drs. J. W. Emsley and L. Phillips for n.m.r. spectra and to the Germanium Research Council for a gift of chemicals. One of us (R. J. C.) thanks the D.S.I.R. for a maintenance grant.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,  
SOUTH ROAD, DURHAM.

[Received, December 4th, 1963.]

<sup>21</sup> Gilman and Schwebke, *J. Org. Chem.*, 1962, **27**, 4265.