396. Preparation of Germane. Part I. Reaction between Lithium Aluminium Hydride and Germanium Tetrachloride.

By E. D. MACKLEN.

A study of the effects of temperature and of the order of addition of reactants has been made for the reaction between lithium aluminium hydride and germanium tetrachloride in tetrahydrofuran. Higher reaction temperatures favour the production of germane, whereas temperatures below 0° favour side reactions which limit the yield of germane. The decomposition of trichlorogermane and the subsequent reaction of germanium dichloride with lithium aluminium hydride is suggested to explain the low yields of germane. Under the best conditions a 40% yield of monogermane was obtained.

ALTHOUGH monogermane was first produced in 1902 [1] its properties were little known until much later, as the yields and purity of samples were very low. The first successful preparation, by the action of dilute acids on magnesium germanide, was developed by Dennis, Corey, and Moore,[2] who obtained a 22·7% yield of mixed germanes containing 16·8% of monogermane. This method was later improved by Kraus and Carney [3] by replacing the dilute acid by ammonium bromide in liquid ammonia, and a yield of 70% of mixed germanes containing predominantly monogermane was obtained. No new method of preparation was reported until 1947 when Finholt, Bond, Wilzbach, and Schlesinger [4] prepared germane, silane, and stannane by the metathetical reaction between lithium aluminium hydride and the corresponding tetrachlorides in diethyl ether. For germane the reaction can be represented by the equation:

$$\mathrm{LiAlH_4 + GeCl_4 \longrightarrow GeH_4 + LiCl + AlCl_3} \quad . \; . \; . \; . \; . \; . \; . \; . \quad 1)$$

Although the preparation was quantitative for silane, the yields of germane (27·7%) and stannane [5] (20·4%) were rather low.

Since the production of litre quantities of germane was ultimately required it was felt that a more detailed study of the reaction between lithium aluminium hydride and germanium tetrachloride might result in a considerable improvement in yield. Details of investigations into the effect of temperature and order of addition of reactants are given here.

EXPERIMENTAL

Apparatus.—The reaction vessel consisted of a 500 ml. three-necked flask fitted with a water-cooled condenser and a cold-finger condenser, a thermometer pocket, a graduated tap funnel with adaptor for inert-gas entry, and a magnetic stirrer. The cold-finger condenser, kept at −80° with solid carbon dioxide–acetone, was connected *via* a preliminary cold trap at −80° to the collection system consisting of four traps in parallel enabling separate fractions to be collected by condensation with liquid nitrogen during reaction. Attached to a manifold common to the four traps were two storage vessels, V_1 and V_2, of volumes approximately 0·5 and 5·0 l., a three-column mercury manometer (one reference column and two measuring columns), and two limbs of volumes approximately 10 ml. and 100 ml. These limbs were used for vapour-pressure measurement and analysis by thermal decomposition respectively.

Materials.—Most of the work was carried out with tetrahydrofuran as solvent, and, except where stated, the following solutions were used.

Lithium aluminium hydride solution. Commercial tetrahydrofuran was dried by refluxing it for several hours with calcium hydride in dry nitrogen, then distilled directly on powdered

---

[1] Voegelen, *Z. anorg. Chem.*, 1902, **30**, 325.

[2] Dennis, Corey, and Moore, *J. Amer. Chem. Soc.*, 1924, **46**, 657.

[3] Kraus and Carney, *ibid.*, 1934, **56**, 765.

[4] Finholt, Bond, Wilzbach, and Schlesinger, *ibid.*, 1947, **69**, 2692.

[5] The yield of stannane from this reaction has recently been raised to 80—90% by inhibition of SnH_4 decomposition by traces of oxygen; Emeléus and Kettle, *J.*, 1958, 2444.

lithium aluminium hydride. The mixture was refluxed in nitrogen for one day to effect solution and drive off volatile impurity hydrides, then allowed to cool and settle. The solution was siphoned from the residual solid when required. The amount of active lithium aluminium hydride in the solution was determined by hydrolysis and by oxidation with iodine to be 8·0 g. per 100 ml. of solution (2·11M).

Germanium tetrachloride solution. A solution of approximately the same molarity as that of the hydride was prepared by diluting 26 ml. of germanium tetrachloride to 100 ml. with dry tetrahydrofuran (2·28M).

Reactants in dioxan. Dioxan was dried by refluxing it with calcium hydride for several hours. A slurry of 6 g. of powdered lithium aluminium hydride in 75 ml. of dioxan was prepared in the reaction flask. A solution of 13 ml. of germanium tetrachloride diluted to 50 ml. with dioxan was also prepared.

Procedure.—A known volume of one reactant was placed in the flask and hydrogen passed through for 30 min. before the second reactant was added slowly to the flask from the tap funnel. The flask temperature was kept constant. A steady temperature as recorded by the thermometer placed in mercury in the thermometer pocket was maintained before reaction commenced. The hydrogen and the germane evolved passed through the condensers and preliminary cold trap (used to remove entrained solvent) into the first of the four traps cooled with liquid nitrogen. The germane solidified and the hydrogen passed to exhaust. The addition of the second reactant was stopped after a fixed volume of solution had been added. After a further 15 min., during which any germane remaining in the flask was swept by the hydrogen into the collection system, the first liquid-nitrogen trap was closed, the second trap opened, and the addition of the second reactant continued. This was repeated until the four traps contained germane. The collection system was then evacuated of hydrogen and the contents of each trap were evaporated in turn by raising the trap temperature, the gas evolved expanded into one of the two vessels $V_{1,2}$, and the pressure read on the mercury manometer. The volume of gas at room temperature was then calculated and corrected to S.T.P. The germane was then recondensed in a storage trap and the four collection traps were then available for the collection of further fractions of germane. By this procedure the evolution of germane at each stage of the addition of the second reactant could be followed. Excess of the second reactant was added in every case to ensure complete removal of the first reactant. At the end of reactions at low temperatures the flask temperature was slowly raised to the boiling point of the solvent, and the gas evolved at each stage in the warming measured as before. In this way the complete removal of the germane from solution was ensured. The yield of germane at each stage in the reaction was calculated from the quantity of first reactant placed in the flask.

Results.—*Addition of lithium aluminium hydride to germanium tetrachloride.* The slow addition of lithium aluminium hydride solution to a solution of germanium tetrachloride in tetrahydrofuran at 35° resulted in a vigorous reaction but initially liberated no germane. After the mole ratio of added $LiAlH_4 : GeCl_4$ reached approximately 0·2, germane was steadily evolved until the equimolecular quantity of hydride had been added, when reaction ceased. The addition of excess of hydride gave no further germane. The flask temperature was then raised until the solvent was refluxing gently; some germane was evolved during this heating. In addition to the evolution of germane the initially colourless solution underwent several changes during the addition of the hydride. The solution first became pale yellow and a slight white precipitate appeared, then, as the addition continued, the yellow colour deepened and the precipitate became yellow. Finally an orange solution with a flocculent yellow-orange precipitate was obtained.

This reaction was repeated at 68° and similar results were obtained, except that the colour changes and precipitation occurred earlier than at 35°. A third reaction was carried out at −40° which resulted in a decreased yield of germane and a small quantity of yellow precipitate. On heating, the precipitate dissolved and the solution colour deepened until at 10° a clear red solution resulted which remained clear until 45°. At this temperature an orange precipitate appeared which slowly thickened as the flask was heated to 68°; germane was evolved throughout the heating. The reactions at 35° and −40° after refluxing resulted in approximately the same yields of germane as the reaction at 68°. The yields (based on $GeCl_4$) for these three reactions are plotted against the lithium aluminium hydride added in Fig. 1.

Addition of germanium tetrachloride to lithium aluminium hydride. In the addition of $LiAlH_4$

to $GeCl_4$ the active hydrogen of the hydride does not appear as germane until approximately one-fifth of the hydride has been added. This may be due to a stepwise replacement of chlorine by hydrogen with decreasing rates of reaction in each successive step: $GeCl_4 \longrightarrow GeHCl_3 \longrightarrow GeH_2Cl_2 \longrightarrow GeH_3Cl \longrightarrow GeH_4$. If this is so, then addition of $GeCl_4$ to $LiAlH_4$ may be expected to evolve germane from the beginning of the addition.

The addition of $GeCl_4$ solution to $LiAlH_4$ in tetrahydrofuran at 25° gave a vigorous reaction and as expected germane was evolved immediately the addition commenced. The solution became first yellow then, as addition proceeded, orange. A yellow precipitate appeared which also deepened to orange, and reaction finally subsided when equimolecular quantities of reactants were present; no further germane was evolved when $GeCl_4$ was added in excess. The reaction was repeated at 70° and an increase in yield obtained with the appearance of similar colorations and precipitates. A third reaction at —55° gave a poor yield of germane although only a slight quantity of yellow precipitate was present. When the solution was heated with excess of $GeCl_4$, germane was evolved at about 30°. The precipitate dissolved at 45° and remained in solution throughout refluxing. Germane was evolved steadily until 70° but the final yield was much reduced. A further reaction at —66° gave similar results with a further decrease in yield.

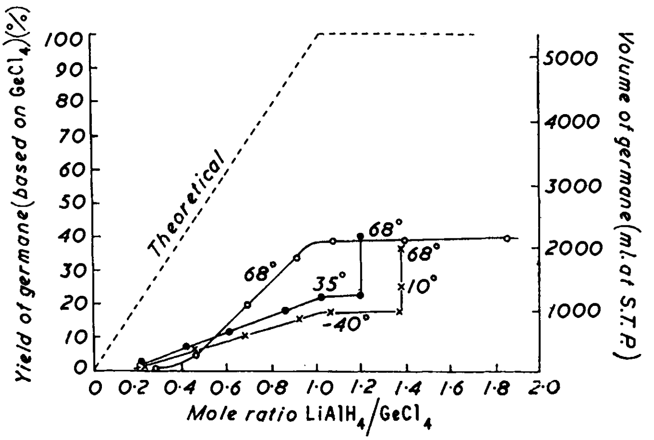


FIG. 1. *Addition of lithium aluminium hydride to germanium tetrachloride.*

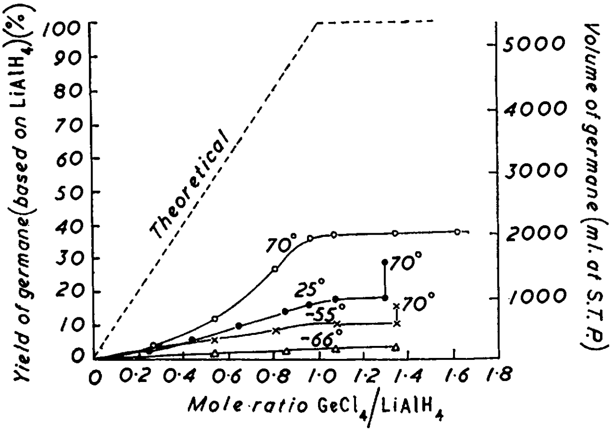


FIG. 2. *Addition of germanium tetrachloride to lithium aluminium hydride.*

The progressive evolution of germane from these four reactions is shown as a function of the addition of $GeCl_4$ in Fig. 2.

Reaction in dioxan. In tetrahydrofuran an increase in temperature favoured the yield of germane. The reaction temperature was limited by the boiling point of the solvent, so the higher-boiling solvent, dioxan, was employed. Since the solubility of $LiAlH_4$ in dioxan was much lower than in tetrahydrofuran a slurry of $LiAlH_4$ in dioxan was placed in the reaction flask, heated to 30°, and $GeCl_4$ in dioxan slowly added. The reaction was less vigorous than in tetrahydrofuran and germane was liberated from the beginning of the addition. A yellow solid developed early in the reaction. After a slight excess of $GeCl_4$ had been added the flask contents were heated to 96° and refluxed at that temperature for 1 hr. During this time the yellow precipitate became yellow-brown. The yield of germane was 26·4% of theoretical.

Effective solubility of germane in tetrahydrofuran. In order to determine whether the release of germane on heating the final solutions to the reflux temperature of the solvent was due to decreasing solubility of germane in the solvent or to reaction between products, the approximate solubility of germane in tetrahydrofuran was determined under conditions similar to those used in the preparations. A known volume of germane was condensed into a trap by use of liquid nitrogen. The trap temperature was slowly raised and the gaseous germane was bubbled through tetrahydrofuran in the reaction flask. A hydrogen atmosphere at a pressure of 1 atm. was maintained in the reaction flask. The undissolved germane passed into the collection system and was condensed in one of the liquid-nitrogen traps. After all the germane has passed through the solvent the trap and flask were swept out with hydrogen in a similar manner to that used during reactions. The volume of undissolved germane was measured and the volume of dissolved gas calculated from the difference in the original and the collected volumes. The temperature of the solvent was then raised and the germane evolved was collected and its volume measured. The solvent was finally boiled to expel all the germane. Results are as tabulated; a plot of log (volume dissolved) against $1/T$(°K) is linear.

Temp. (°C)	−73	−40	−30	−10	10	65
$10^3/T$ (°K)	5·00	4·29	4·12	3·80	3·53	3·38
Vol. (ml.) of GeH_4 dissolved in 150 ml. of tetrahydrofuran	2334	351	169	74	33	0

It can be seen that, at the end of the reaction at −40° with approximately 200 ml. of solvent present, the evolution of 419 ml. of germane on heating to 10° could be accounted for by decrease in solubility; but the further evolution of 568 ml. from 10° to 68° cannot be due to decrease in solubility alone. It seems probable, therefore, that some germane is evolved at higher temperatures by reaction between the low-temperature products.

DISCUSSION

A comparison of the reactions between lithium aluminium hydride and other covalent chlorides ($SiCl_4$, BCl_3, $AsCl_3$, etc.), which give the corresponding hydrides in quantitative yield, with the reaction between lithium aluminium hydride and germanium tetrachloride indicates that the latter does not occur in the simple manner indicated by eqn. (1). However, a comparison of the yields of hydride obtained from the chlorides of Group IV elements (Si 99%,[4] Ge 40%, Sn 20% [4]) indicates that the position of germanium is not abnormal. An explanation for the low yield of stannane has been suggested which is based on the easy reducibility of Sn^{IV} to Sn^{II} causing reaction to proceed by two competitive routes (2) and (3).[6]

$$\begin{aligned}
&SnCl_4 + LiAlH_4 \longrightarrow Sn(AlH_4)_4 \\
&Sn(AlH_4)_4 - 4AlH_3 \longrightarrow SnH_4 \quad \ldots\ldots\ldots\ldots \quad (2) \\
&\left.\begin{aligned} &Sn(AlH_4)_4 - 2AlH_3 \longrightarrow Sn(AlH_4)_2 + H_2 \\ &Sn(AlH_4)_2 - 2AlH_3 \longrightarrow Sn + H_2 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (3)
\end{aligned}$$

Little stannane was obtained from these reactions since reaction (3) was faster than reaction (2). Silicon is not reduced to a lower valency under these conditions, and a quantitative yield of silane can be obtained from silicon tetrachloride. Germanium is intermediate between silicon and tin in that it does form stable bivalent compounds, but the reduction from Ge^{IV} to Ge^{II} does not occur so readily as for tin.

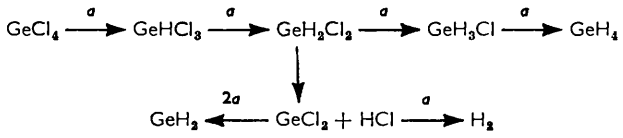
The low yield and the formation of a yellow germanium compound from the $GeCl_4$—$LiAlH_4$ reaction indicates that in addition to the main reaction producing germane at least one side reaction occurs. Metallic germanium was not produced, indicating that the

---

[6] Wiberg and Bauer, *Z. Naturforsch.*, 1951, **6b**, 392.

mechanism of the side reaction is not the same as that for the $SnCl_4$—$LiAlH_4$ reaction. A yellow precipitate similar to that obtained with $LiAlH_4$ has also been obtained in a LiH—$GeCl_4$ reaction in tetrahydrofuran, thereby eliminating $Ge(AlH_4)_4$ or $Ge(AlH_4)_2$ as a product of this reaction. This has been confirmed by analysis of the yellow precipitate, which showed little aluminium or lithium present.

The replacement of chlorine by hydrogen is thought to be a stepwise process, and an explanation of the reduced yield of germane has been sought from a consideration of the stability of the compounds intermediate between $GeCl_4$ and GeH_4. All these compounds decompose at room temperature or below. Chlorogermane slowly decomposes at room temperature:[7] $2GeClH_3 \longrightarrow GeH_4 + 2HCl + Ge$. Dichlorogermane decomposes more rapidly, yielding a mixture of products among which Ge, $GeCl_2$, $GeClH_3$, $GeCl_4$, HCl, and hydrogen have been identified.[7] Recently[8] it has been shown that trichlorogermane loses HCl readily at $-30°$, forming $GeCl_2$. This decomposition seems the most likely to occur under the conditions of the $GeCl_4 \longrightarrow LiAlH_4$ reaction, the side reaction being completed by the replacement of the chlorine atoms in $GeCl_2$ to form a bivalent hydride, the complete scheme being as follows, where a represents $\frac{1}{4}LiAlH_4$:



The existence of a yellow germanous hydride insoluble in solvents has been reported;[9] its properties suggest a long-chain polymer $(GeH_2)_x$. It is thought that the yellow colour in solutions at lower temperatures and the precipitation at higher temperatures may be due to the formation of a similar hydride in association with tetrahydrofuran. The precipitation may be due to the conversion of the monomer (stabilized by the solvent) into the polymer in a similar manner to that observed for aluminium hydride.[10]

The above reaction mechanism accounts for the cessation of reaction at the equimolecular ratio of reactants irrespective of the course taken by the reaction. The variations in yield with temperature may be accounted for by different changes in the reaction rate of the two competing reactions with temperature.

STANDARD TELECOMMUNICATION LABORATORIES LTD.,
ENFIELD, MIDDLESEX.

[*Received, January* 19*th*, 1959.]

---

[7] Dennis and Judy, *J. Amer. Chem. Soc.*, 1929, **51**, 2321.
[8] Moulton and Miller, *J. Amer. Chem. Soc.*, 1956, **78**, 2702.
[9] Royen and Schwarz, *Z. anorg. Chem.*, 1933, **211**, 412.
[10] Wiberg, Graf, and Uson, *ibid.*, 1953, **272**, 221.