

### 397. Preparation of Germane. Part II.\* Reaction between Sodium Borohydride and Germanium Tetrachloride.

By E. D. MACKLEN.

The preparation of monogermane from the reaction between germanium tetrachloride and sodium borohydride in aqueous solution has been studied at various temperatures. The effect of complete and partial neutralization of the hydrochloric acid liberated by hydrolysis of germanium tetrachloride, together with the rate and order of addition of reactants, has been investigated. Under the best conditions a yield of 79.1% of monogermane was obtained. Nascent hydrogen reduction of  $\text{Ge}^{\text{IV}}$  to metallic germanium is suggested to account for the smaller yield than theoretical.

In Part I\* the preparation of litre quantities of monogermane from the reaction between lithium aluminium hydride and germanium tetrachloride in tetrahydrofuran solution was described. However, the yield from this reaction under the best experimental conditions was limited to 40% by the occurrence of side reactions. Difficulties in the preparation of stannane by a similar procedure<sup>1,2</sup> were largely eliminated by replacing lithium aluminium hydride in ether by sodium borohydride in aqueous solution. Using this method, Schaeffer and Emilius<sup>3</sup> obtained an 84% yield of stannane from stannous chloride. This improvement in yield for stannane suggested that a similar improvement in the yield of germane might be expected from the action of aqueous sodium borohydride on germanium tetrachloride.

#### EXPERIMENTAL

*Apparatus and Procedure.*—The apparatus and technique were as in Part I.

*Materials.*—Most of the reactions were carried out in aqueous solution and the following solutions were prepared.

*Sodium borohydride solution.* 16 g. of commercial sodium borohydride were dissolved in 250 ml. of water, making a solution nominally 1.69M. As such a solution slowly hydrolyses, it was prepared immediately before use. No yields were based on  $\text{NaBH}_4$ , and the active hydride content of solutions was not determined.

*Germanium tetrachloride solution.* Attempts to prepare an aqueous solution of germanium tetrachloride result in almost complete hydrolysis, and a slurry of germanium dioxide in hydrochloric acid is produced. However, since the dioxide redissolves during reaction this slurry is acceptable. 2.5 ml. of  $\text{GeCl}_4$  were added to 60 ml. of water, and the equivalent of 0.37 mole of  $\text{GeCl}_4$ /l. of solution was obtained. In all cases where this slurry was used the hydrolysis was carried out in the reaction flask. A solution of 3 ml. of  $\text{GeCl}_4$  in 100 ml. of tetrahydrofuran was also prepared so that  $\text{GeCl}_4$  could be added to  $\text{NaBH}_4$  by means of a tap funnel.

*Results.*—Since the addition of germanium dioxide slurry in controllable quantities through a tap funnel was not possible, the initial reactions were carried out with the slurry in the flask. A reasonable yield of a gas condensable in liquid nitrogen was obtained from a preliminary reaction, and although vapour-pressure measurements on this gas indicated monogermane the absence of diborane could not be assumed, although the preparation of diborane from aqueous solution was highly unlikely. Pyrolysis of the gas gave a purity for the germane of 98.4% and chemical analysis of the residue from pyrolysis confirmed the absence of boron and the presence of germanium only.

In the following reactions all yields of germane were based on the original  $\text{GeCl}_4$  content, and even for the addition of  $\text{GeCl}_4$  in tetrahydrofuran to aqueous  $\text{NaBH}_4$  the final yield was calculated from the  $\text{GeCl}_4$  added rather than from the  $\text{NaBH}_4$ .

*Addition of sodium borohydride to germanium tetrachloride.* (a) *Effect of temperature.* The addition of  $\text{NaBH}_4$  to the dioxide slurry was carried out at 20°, 60°, and 80° and the volumes

\* Part I, preceding paper.

<sup>1</sup> Finholt, Bond, Wilzbach, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 2692.

<sup>2</sup> Wiberg and Bauer, *Z. Naturforsch.*, 1951, **6b**, 392.

<sup>3</sup> Schaeffer and Emilius, *J. Amer. Chem. Soc.*, 1954, **76**, 1203.

of germane liberated during the addition were measured. The values are shown in Fig. 1. It can be seen that although lower temperatures favour the yield of germane, little difference is apparent between the yields at 20° and 60° whereas a pronounced difference is observed at 80°. After the reaction at 20° the flask contents were heated to 60° but no further germane was evolved. The reactions at 60° and 80° produced a mirror of metallic germanium on the wall of the flask below the liquid level, the weight of which indicated that all germanium not evolved as germane had been thus deposited.

(b) *Effect of rate of addition of NaBH<sub>4</sub>.* The rate of addition of the hydride was kept at

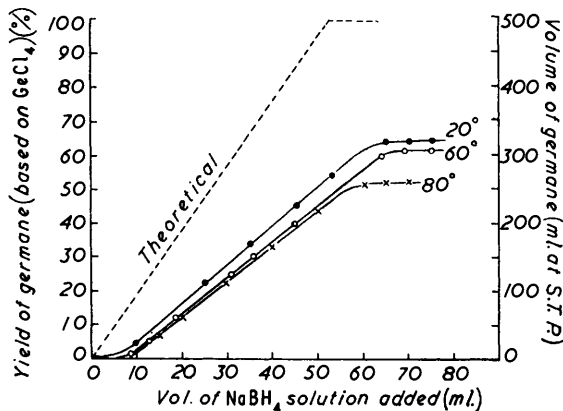
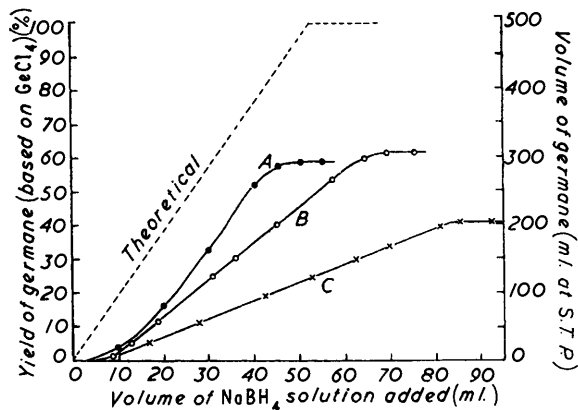


FIG. 1. Effect of temperature during addition of NaBH<sub>4</sub> to GeCl<sub>4</sub>.

FIG. 2. Effect of varying concentration of HCl in GeO<sub>2</sub> slurry at 60°.

A, HCl = 0.72N; B, HCl = 1.46N; C, HCl = 2.92N.



approximately 1 ml. of solution per minute in order to keep the temperature constant. The effect of adding the second reactant very rapidly was investigated by increasing this rate of addition to 20 ml./min. Reaction commenced at 25° but the temperature rapidly rose to 70° during the first few minutes of addition, and a final yield of 29% of germane was obtained. This was a large reduction in the yield compared with those obtained for slower addition, and all other reactions were carried out with addition of 1 ml./minute.

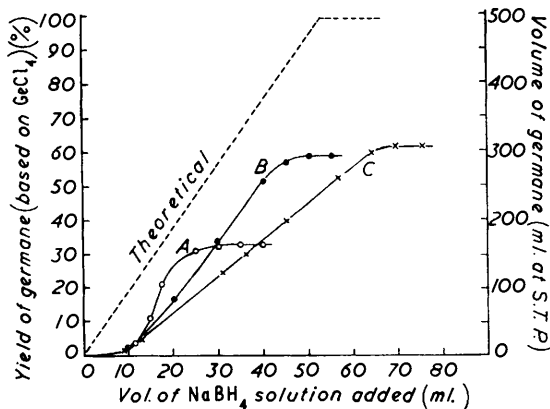
(c) *Effect of acid concentration.* The hydrolysis of germanium tetrachloride by water resulted in a slurry of germanium dioxide in 1.46N-hydrochloric acid. The effect of doubling the acid concentration by addition of hydrochloric acid was investigated. It was found that the quantity of NaBH<sub>4</sub> required to complete the reaction was increased; and also that the yield of germane was reduced to 41% at 60°. Neutralization of half of the hydrochloric acid with sodium hydroxide or ammonia had little influence on the yield of germane (60% at 60°), but decreased by a third the quantity of NaBH<sub>4</sub> required to complete the reaction. Complete neutralization of the acid almost entirely prevented the formation of germane (yield 6% at

60°), indicating that some hydrochloric acid is required for reaction. The evolution of germane with  $\text{NaBH}_4$  addition for slurries of different acid concentrations is shown in Fig. 2.

An alternative method of reducing the effect of the hydrochloric acid on  $\text{NaBH}_4$  was the use of solutions of  $\text{NaBH}_4$  made alkaline with sodium hydroxide. This had the additional advantage of stabilizing the borohydride solution so that the solution could be stored without appreciable hydrolysis. The effect of alkaline  $\text{NaBH}_4$  on the reaction was similar to that of partial neutralization of the acid before reaction. For 1.2N-sodium hydroxide a decrease in the quantity of  $\text{NaBH}_4$  required without appreciable alteration in the yield of germane was obtained, but 2.38N-alkali caused a more rapid evolution of germane and reduced the yield to 33% at 60°. These effects are shown in Fig. 3.

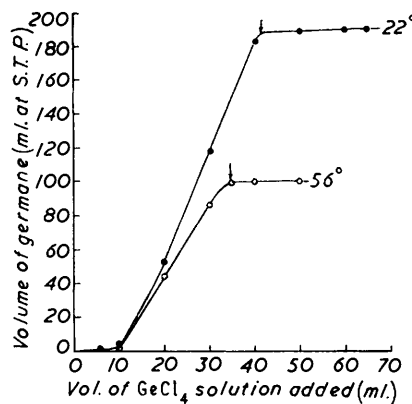
*Addition of germanium tetrachloride to sodium borohydride.* To obtain a more complete picture of the reaction, the addition of  $\text{GeCl}_4$  to sodium borohydride was required. This was accomplished by the use of a solution of germanium tetrachloride in tetrahydrofuran placed in the tap funnel which was added slowly to 4 g. of  $\text{NaBH}_4$  in 75 ml. of water in the reaction flask.

FIG. 3. Effect of varying concentration of NaOH in  $\text{NaBH}_4$  solution at 60°.



A, NaOH = 2.38N; B, NaOH = 1.21N; C, no NaOH.

FIG. 4. Effect of temperature during addition of  $\text{GeCl}_4$  to  $\text{NaBH}_4$ .



This reaction was carried out at 22° and 56° and the evolution of germane is plotted against the addition of  $\text{GeCl}_4$  in Fig. 4. Reaction in both cases had ceased at the point indicated by the arrow, and the yield of germane at this point was calculated from the quantity of  $\text{GeCl}_4$  added. Values of 79.1% at 22° and 49.7% at 56° were obtained.

For both of these reactions an orange precipitate was formed which remained between the water layer and the tetrahydrofuran layer in the flask. The properties of this precipitate indicated that it was similar to the bivalent reduction product of the reaction of germanium tetrachloride with lithium aluminium hydride in tetrahydrofuran.

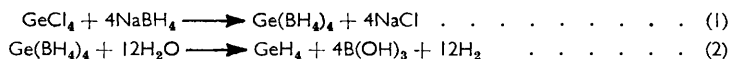
*Reaction in tetrahydrofuran.* A slurry of 3 g. of  $\text{NaBH}_4$  in 75 ml. of tetrahydrofuran was placed in the reaction flask and the temperature kept at 25°. A solution of 3 ml. of  $\text{GeCl}_4$  in 100 ml. of tetrahydrofuran was slowly added, but little germane was evolved. After 50 ml. of  $\text{GeCl}_4$  solution had been added the addition was stopped and the volume of germane collected was found to be 36.1 ml., corresponding to a yield of 12.4% based on  $\text{GeCl}_4$ . The addition of 7 ml. of water at this stage increased the yield to 40.3% after a vigorous reaction. The further addition of 43 ml. of water increased the yield to 43.7%. The orange germanium reduction product was again formed during the reaction.

The low yield of germane from the reaction in tetrahydrofuran may be partially due to the inability of the  $\text{NaBH}_4$  to ionize to any extent, but the presence of water may also be necessary to complete the formation of  $\text{GeH}_4$  from the primary reaction product of  $\text{GeCl}_4$  and  $\text{NaBH}_4$ .

#### DISCUSSION

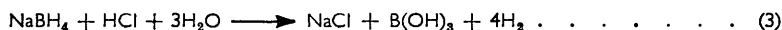
The reaction of sodium borohydride with germanium tetrachloride in an aqueous medium provides one of the most efficient methods of preparing monogermane in litre quantities

with reasonable yields. However, the emergence of metallic germanium as a reaction product indicates that the yield of germane is reduced by at least one side reaction. By analogy with other reactions involving  $\text{NaBH}_4$  it seems likely that the primary reaction producing germane is a two-stage reaction in which germanium borohydride is first formed by the action of sodium borohydride on germanium tetrachloride, then decomposed by the water, evolving monogermane:



In this way the water performs two functions, initially promoting the formation of  $\text{BH}_4^-$  ions for reaction (1), and finally decomposing the  $\text{Ge}(\text{BH}_4)_4$ . The low yield of germane from the reaction in tetrahydrofuran together with the immediate evolution of germane after the addition of water to this system illustrate the necessity for the presence of water if reasonable yields of germane are to be obtained.

The second reaction sequence which occurs in this system involves the reduction of quadrivalent germanium to the free metal. This mode of behaviour has been observed in other systems; silver, bismuth, arsenic, and antimony salts have been reduced to free metals by interaction with sodium borohydride,<sup>4</sup> and  $\text{Ce}^{\text{IV}}$ ,  $\text{Cr}^{\text{VI}}$ ,  $\text{Tl}^{\text{III}}$ ,  $\text{Hg}^{\text{II}}$ , and  $\text{Fe}^{\text{III}}$  reduced to the next lower stable valency.<sup>5</sup> It seems likely that the reduction of  $\text{Ge}^{\text{IV}}$  to  $\text{Ge}^{\text{II}}$  and finally to metallic germanium in aqueous solutions occurs not by direct reaction with  $\text{NaBH}_4$  but by means of nascent hydrogen evolved either in reaction (2) or by the reaction of hydrochloric acid (obtained by hydrolysis of  $\text{GeCl}_4$ ) with  $\text{NaBH}_4$ :



In solutions of tetrahydrofuran the occurrence of the orange bivalent germanium reduction product indicates that the reduction of germanium ceases at  $\text{Ge}^{\text{II}}$ , no metallic germanium having been found in such systems.

Since the evolution of hydrogen from aqueous sodium borohydride solutions increases rapidly with increase in temperature,<sup>6</sup> the reduction in yield of germane with increase in temperature may be explained in terms of the increased availability of nascent hydrogen thus favouring the reduction of  $\text{Ge}^{\text{IV}}$  to metallic Ge. The reduction of germane yield from germanium dioxide slurries containing additional hydrochloric acid may be similarly explained by the increased availability of nascent hydrogen.

The author thanks Dr. S. G. Foord for advice and criticism.

STANDARD TELECOMMUNICATIONS LABORATORIES LTD.,  
ENFIELD, MIDDLESEX.

[Received, January 19th, 1959.]

<sup>4</sup> Schlesinger and Brown, U.S.P. 2,461,661 (Feb. 15th, 1949).

<sup>5</sup> Schaeffer and Frank, unpublished work.

<sup>6</sup> Schlesinger, Brown, Finholt, Gilbreath, Hoekstra, and Hyde, *J. Amer. Chem. Soc.*, 1953, **75**, 218.