[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Reactions of Germanium Tetrachloride with Lithium Aluminohydrides. Lithium Tri-*t*-butoxyaluminohydride as an Efficient Reagent for the Preparation of Germane[1]

BY SEI SUJISHI AND JAMES N. KEITH

RECEIVED FEBRUARY 21, 1958

Two reactions for the preparation of germane were investigated. The reaction of germanium tetrachloride with lithium aluminum hydride was found to be unsatisfactory. Only 10–15% germane and 90–85% hydrogen were obtained. Evidence has been found for the formation of germanous chloride. It is suggested that the low yield of germane is due to the reduction of the germanium tetrachloride preferentially to germanous chloride. The reaction of germanium tetrachloride with lithium tri-*t*-butoxyaluminohydride was studied. Satisfactory yields of germane (70–80%) were obtained readily. The optimum conditions for this preparative method are given.

In the course of our study on the chemistry of the group IV hydrides it became necessary to prepare germane (GeH_4). At that time, the reaction of germanium tetrachloride with lithium aluminum hydride appeared to be the most promising one.[2,3] Although the conversions of germanium tetrachloride to germane reported are not good, 28%[2] and 25–35%,[3] it was considered that an improvement might be possible. Schlesinger and his coworkers report that only one experiment was performed in their work and suggest that the low yield obtained by them may have been due to the formation of elemental germanium.[2] Taylor and his co-workers do not give specific details on their preparation.[3]

Our attempts, however, to reproduce the earlier results and to improve the method gave consistently low yields of germane, 10–15%. The results indicate that hydrogen and germanous chloride were the chief products.

While these experiments with lithium aluminum hydride were in process, a communication concerning the preparation and the use of a new compound, lithium tri-*t*-butoxyaluminohydride, appeared in the literature.[4] Lithium tri-*t*-butoxyaluminohydride was reported to be a much milder reducing agent toward organic compounds than lithium aluminum hydride. It appeared possible that with this new compound germanium tetrachloride might be selectively converted to germane rather than to germanous chloride. Hence, the reaction of this new hydride with germanium tetrachloride was investigated. Germane yields of 70–80% were obtained readily.

After this phase of the work was completed, another method for the preparation of germane was reported.[5] In this method germanium dioxide, aqueous hydrobromic acid and sodium borohydride were used as the starting materials. The yields reported for germane are 60–75% and are comparable to those reported in the present work.

Results

Lithium Aluminum Hydride Reaction.—The experiments were performed under conditions similar to those reported by Schlesinger and his co-workers.[2] Germanium tetrachloride was condensed above a diethyl ether solution of lithium aluminum hydride at −196°, and the mixture was allowed to warm to room temperature. As the temperature rose and the germanium tetrachloride melted and dripped into the ether solution, a vigorous evolution of gas occurred. The gas was non-condensable at −196° and assumed to be hydrogen. A copious quantity of white precipitate formed at the same time. This precipitate became yellow on standing overnight at room temperature. The mixture was analyzed for germane and hydrogen. The results of several typical experiments are given in Table I.

TABLE I

REACTION OF $GeCl_4$ WITH $LiAlH_4$ AT 20–30°

Run	$LiAlH_4$, *M*	$GeCl_4$, cc.[a]	$\frac{LiAlH_4}{GeCl_4}$	H_2, cc.[a]	GeH_4, cc.[a]	GeH_4, %[b]	$\frac{H_2 + GeH_4}{GeCl_4}$
1	2	44.2	2:1	41.6	5.8	13[c]	1.07
2	1	47.4	2:1	43.7	2.3	5[c]	0.97
3	0.6	38.1	2:1	36.5	5.6	15[c]	1.10
4	2	46.0	1:1	35.6	6.8	15[c]	0.92
5[d]	2	73.7	2:3	39.4	6.8	15[e]	0.98[f]

[a] All quantities expressed in cc. are for the gas at S. T. P. [b] After *ca.* 24 hours. [c] Based on $GeCl_4$ used. [d] Precipitate became bright yellow when the solvent was removed. [e] Based on $LiAlH_4$. [f] $(H_2 + GeH_4)/LiAlH_4$.

As it may be seen in Table I, varying the concentration of lithium aluminum hydride or the relative concentrations of the lithium aluminum hydride to germanium tetrachloride had little effect on the yield of the products. The maximum yield of germane is 15%. It is to be noted also that the ratio $(H_2 + GeH_4)$:$GeCl_4$ is close to unity. This fact suggests that for each mole of hydrogen formed, a mole of germanium tetrachloride was prevented from being converted to germane.

The results indicate that two competitive reactions occur when germanium tetrachloride is mixed with an ether solution of lithium aluminum hydride. One of these leads to the formation of the desired germane as indicated in reaction 1

$$GeCl_4 + LiAlH_4 = GeH_4 + LiCl + AlCl_3 \quad (1)$$

It has been suggested by previous workers[2] that the alternative fate of germanium tetrachloride is its conversion to elemental germanium. However, the color of the precipitate (white to yellow) and the quantity of hydrogen formed do not indicate the formation of elemental germanium in our ex-

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(1) Work supported by the Office of Ordnance Research, U. S. Army.

(2) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947). References to older methods for the preparation of germane are given in this paper.

(3) P. J. Fensham, K. Tamaru, M. Boudart and H. Taylor, *J. Phys. Chem.*, **59**, 806 (1955).

(4) H. C. Brown and R. F. McFarlin, THIS JOURNAL, **78**, 252 (1956).

(5) T. S. Piper and M. K. Wilson, *J. Inorg. Nucl. Chem.*, **4**, 22 (1957).

periments. It appears more likely that germanous chloride is formed by reactions 2a and 2b

$$GeCl_4 + 2LiAlH_4 = GeCl_2 + H_2 + 2LiCl + 2AlH_3 \quad (2a)$$

$$GeCl_4 + AlH_3 = GeCl_2 + H_2 + AlHCl_2 \quad (2b)$$

Germanous chloride has been reported to be white with occasional traces of yellow and to react with hydrogen chloride to yield trichlorogermane.[6] The trichlorogermane, however, decomposes at room temperature. The precipitate obtained in the present work behaved like germanous chloride in this respect. Thus, in run 5 all of the material volatile at room temperature was removed by distillation under high vacuum and a bright yellow solid was obtained as a residue. This solid reacted at room temperature with hydrogen chloride, changed color to white and yielded a volatile liquid. The liquid decomposed and deposited black and yellow solids when an attempt was made to purify it by fractional distillation.

Efforts to moderate the reaction of germanium tetrachloride with lithium aluminum hydride by running the reaction at −80° or by dropping an ethereal solution of germanium tetrachloride, at room temperature, into an ethereal solution of the hydride at −80° did not improve the yield of germane. Similarly, the use of lithium hydride suspension in ether, with a small amount of lithium aluminum hydride as a promoter,[7] gave unsatisfactory results. Changing the solvent to tetrahydrofuran or shortening the reaction time to 0.25 hr. did not help.

We conclude that with lithium aluminum hydride the rapid reduction of germanium tetrachloride to germanous chloride accounts for the poor yield of germane.

Lithium Tri-*t*-butoxyaluminohydride Reaction.—The reactions were carried out in the same manner as the ones with lithium aluminum hydride except that tetrahydrofuran was used as the solvent. The solution of germanium tetrachloride in the lithium tri-*t*-butoxyaluminohydride–tetrahydrofuran solution occurred very mildly and a precipitate formed. The color of the precipitate changed, during the first half hour, from yellow-green, through yellow to orange, and during several days to orange-brown or brown. Similar color changes have been reported for germanous chloride slightly deficient in chloride content.[6]

TABLE II

REACTION OF $GeCl_4$ WITH $Li(t\text{-}BuO)_3AlH$ AT 20–30°

Run	$GeCl_4$, cc.	H^-/ $GeCl_4$[a]	Time, hr.	H_2, cc.	GeH_4, cc.	GeH_4,[b] %
1	29.3	5.04	18	27.4	16.1	55
2	29.3	5.00	20	25.7	18.7	64
3	29.5	5.02	24	26.8	21.6	73
4	29.6	4.99	30	25.0	21.7	73
5	30.0	5.02	36	26.2	23.8	79
6	30.2	5.41	30	33.0	18.0	60
7	30.2	4.44	30	9.8	24.6	81
8	28.9	4.11	30	2.3	23.4	81

[a] This ratio is based on the observed equivalent weight, 243, for $Li(t\text{-}BuO)_3AlH$. [b] Based on the quantity of $GeCl_4$ used.

In order to find the optimum conditions for the preparation of germane, several variables were investigated. The results of a series of experiments performed with the same batch of lithium tri-*t*-butoxyaluminohydride are summarized in Table II and shown graphically in Figs. 1 and 2.

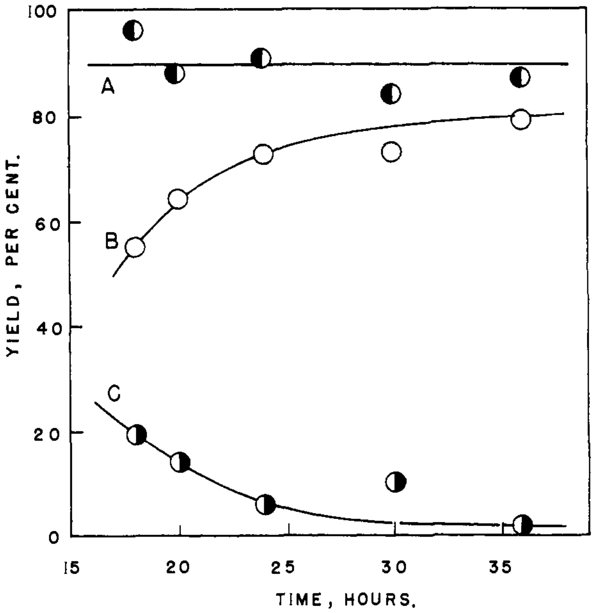

Fig. 1.—Curve A, H_2 yield *vs.* time; curve B, GeH_4 yield *vs.* time; curve C, $[H^-]/[H^-]_0$ *vs.* time.

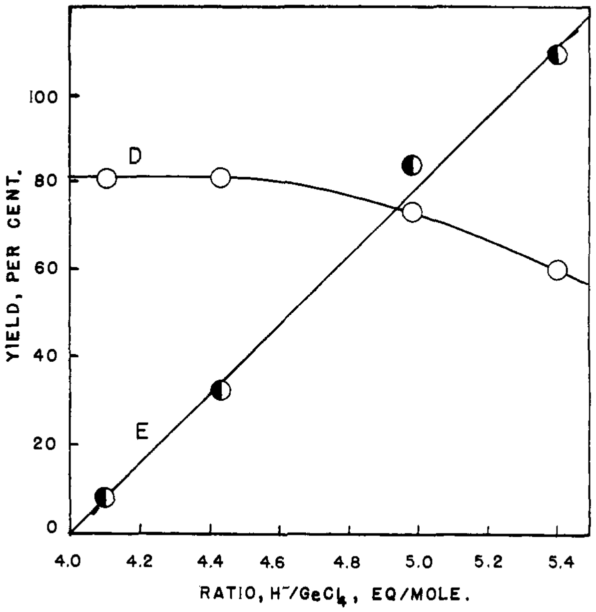

Fig. 2.—Curve D, GeH_4 yield *vs.* $[H^-]$; curve E, H_2 yield *vs.* $[H^-]$.

The curves in Fig. 1 represent those experiments in which the lithium tri-*t*-butoxyaluminohydride: germanium tetrachloride ratio was kept constant at five (runs 1–5), and the time of the reaction was varied. Curve B is the plot of the germane yield. It shows that the rate of formation of germane was

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[6] C. W. Moulton and J. G. Miller, THIS JOURNAL, **78**, 2702 (1956).

[7] J. E. Johnson, R. H. Blizzard and H. W. Carhart, *ibid.*, **70**, 3664 (1948).

slow and that about 28 hr. were required for complete reaction. The maximum yield of germane was 73–79%.

Curve A is a plot of the hydrogen yield based on the quantity of germanium tetrachloride used. It shows that the hydrogen yield was constant at about 0.9 after 18 hr. and that the maximum amount of hydrogen was formed much earlier than that of the germane.

Curve C is a plot of the fraction of the initial lithium tri-*t*-butoxyaluminohydride which was present in the solution. This fraction was calculated by assuming that for each hydrogen atom in the germane and hydrogen gas produced, a molecule of lithium tri-*t*-butoxyaluminohydride was consumed. The fraction includes the hydrogen which may have been present in partially hydrogenated compounds such as chlorogermane. The curve demonstrates that practically all of the hydride was consumed in 28 hr.

The curves in Fig. 2 represent those experiments in which the time of the reaction was kept constant at 30 hr. and the relative concentration of lithium tri-*t*-butoxyaluminohydride to germanium tetrachloride was varied (runs 4 and 6–8). Curve D is a plot of the germane yield. The best yields, 81%, were obtained when the relative concentration was between 4 and 4.5. Curve E is a plot of the hydrogen yield. The quantity of the hydrogen formed increased linearly with the excess quantity of the lithium tri-*t*-butoxyaluminohydride.

We are unable to offer a simple explanation for the formation of hydrogen in this system. The reaction (or reactions) is more complex than the one which is suggested for the lithium aluminum hydride reaction.

However, it is evident that the reaction of germanium tetrachloride with lithium tri-*t*-butoxyaluminohydride is a convenient one for the preparation of germane. With the relative concentrations of lithium tri-*t*-butoxyaluminohydride to germanium tetrachloride of about 4.2 and in 30 hr. at room temperature, germane may be obtained in 80% yield.[8]

$$GeCl_4 + 4Li(t\text{-}BuO)_3AlH = GeH_4 + 4LiCl + 4(t\text{-}BuO)_3Al \quad (3)$$

Experimental Part

Germanium tetrachloride (Fairmount Chem. Co.) was purified by fractional distillation through a small column attached to a vacuum line. The sample used was tensimetrically homogeneous with a vapor pressure of 24.5 mm. at 0° (lit. val.[9] 24.5 mm.). Lithium aluminum hydride (Metal Hydrides, Inc.) was ground, dissolved in absolute ether at room temperature and the solution filtered through a fritted disc in a dry nitrogen atmosphere. An aliquot of the solution was hydrolyzed and the quantity of the hydrogen evolved was measured. The concentration of the hydride was 2.1 molar. Lithium tri-*t*-butoxyaluminohydride was prepared by the method described by Brown and McFarlin.[4] An ether solution of lithium aluminum hydride was treated with *t*-butyl alcohol (redistilled) in one to three mole proportion. The lithium tri-*t*-butoxyaluminohydride was isolated either by filtration or by distilling the solvent away and dried under reduced pressure (10^{-3} mm.) at 80–90°. A weighed sample of the product was dissolved in tetrahydrofuran, hydrolyzed and the quantity of the hydrogen measured. The equivalent weight of lithium tri-*t*-butoxyaluminohydride obtained in this way for four different preparations varied from 244 to 278 (calcd. for $Li(C_4H_9O)_3AlH$, 254). However, no significant difference in the reactions of these different samples with germanium tetrachloride was noted. The tetrahydrofuran was dried over calcium hydride and distilled through an efficient fractionating column.

Lithium Aluminum Hydride–Germanium Tetrachloride Reaction.—A measured volume of the ether solution of lithium aluminum hydride was pipetted in a dry nitrogen atmosphere into a vessel, which was then connected to the vacuum line by means of a ground glass joint, and the solution was degassed. The germanium tetrachloride was measured as a gas and then condensed at −196° as a ring above the solution. The reactants were allowed to warm to room temperature and stirred with a glass enclosed magnetic bar. After the desired time interval, the mixture was chilled to −196°. The hydrogen was pumped off with a Toepler pump through a U-tube kept at −196° and its volume measured. The germane was separated by distilling the residue at room temperature through traps kept at −112° and −160°. The vapor pressure of germane was 179–182 mm. at −111.8° (lit. val.[10] 183 mm.).

Lithium Tri-*t*-butoxyaluminohydride–Germanium Tetrachloride Reaction.—The procedure was similar to that used for the lithium aluminum anhydride reactions, except in one respect. It was found that the lithium tri-*t*-butoxyaluminohydride–tetrahydrofuran solution slowly evolved hydrogen. For this reason standardized solutions were not used and the lithium tri-*t*-butoxyaluminohydride was weighed out and dissolved in 5 ml. of tetrahydrofuran in each experiment. The concentration of hydride in the solution was based on the experimentally determined equivalent weights and was approximately one molar. The germane was isolated by distillation through traps kept at −80° and −127°. The vapor pressure of the product was 180–182 mm. at −111.8°.

In making measurements to determine the time necessary for complete reaction, it was found that chilling the reaction mixture to −196° markedly inhibited further reaction. Therefore, separate reaction mixtures were prepared and analyzed at different time intervals (runs 1–5).

Incidental to the main objective of this work the possibility of forming Li_2GeCl_6 was investigated briefly. Since both lithium chloride and germanium tetrachloride are appreciably soluble in tetrahydrofuran, it appeared possible that the compound might form in this solvent. Consequently, 0.0937 g. of lithium chloride (2.21 mmoles) and 25.3 cc. of germanium tetrachloride (1.13m moles) were dissolved in 2.3 g. of tetrahydrofuran. After one hr. at room temperature, during which time no visible change occurred, the material volatile at room temperature was distilled away under high vacuum. The weight of the residual white solid was 0.0946 g. Hence, Li_2GeCl_6 cannot be obtained under these conditions.

CHICAGO 16, ILLINOIS

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(8) With one preparation of lithium tri-*t*-butoxyaluminohydride, yields of 85–95% were obtained, but this could not be duplicated with other preparations.

(9) A. W. Laubengayer and D. L. Tabern, *J. Phys. Chem.*, **30**, 1047 (1926).

(10) H. J. Emeleus and E. R. Gardner, *J. Chem. Soc.*, 1900 (1938).