[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrogen Compounds of Silicon. I. The Preparation of Mono- and Disilane

BY WARREN C. JOHNSON AND SAMPSON ISENBERG

Although monosilane was prepared by Wöhler and Buff[1] as early as 1857, and by many other workers later, our knowledge of its physical and chemical properties is due almost entirely to Stock and co-workers, who began an extensive investigation in 1916.[2,3] The latter investigators allowed magnesium silicide, prepared by the reduction of silica with metallic magnesium at high temperatures, to drop into an aqueous hydrochloric acid solution, whereby there was evolved a mixture of gases consisting of approximately 40% SiH_4, 30% Si_2H_6, 15% Si_3H_8, 10% Si_4H_{10}, and 7% higher hydrogen compounds. The total yield of silicon-containing gases was such that 23% of the silicon from the magnesium silicide was converted into the various silanes.

Dennis, Corey and Moore[4] followed an analogous procedure for the preparation of germanes and obtained yields of the same order of magnitude, 20–25%. Recently, Kraus and Carney[5] have reported a very convenient and efficient method for the preparation of germanes in high yields, ranging from 60 to 70% and even higher. In this method ammonium bromide is dropped into a suspension of magnesium germanide in liquid ammonia; here the ammonium salt behaves as an acid in somewhat the same manner as does hydrogen chloride in an aqueous medium.

Requiring relatively large quantities of monosilane for the continuation of a program of work involving a study of the kinetics of the thermal decomposition of hydrogen compounds of weakly electropositive elements, the liquid ammonia method of preparation was chosen and found to give yields of the silanes ranging from 70 to 80%. In the course of the study, some important observations were made bearing upon the factors which influence the total yield of silanes as well as the yield of disilane in relation to that of monosilane. On the basis of these observations, some suggestions are made regarding the nature of the mechanism of the reactions which are responsible for the production of the higher silane homologs.

Experimental

Preparation of Magnesium Silicide.—Magnesium silicide is prepared at temperatures ranging from 475–1000° by allowing finely divided silicon to react with magnesium filings in an atmosphere of hydrogen. The magnesium was of the best grade obtainable in the form of rods from the American Magnesium Corporation, while the silicon was an analyzed sample from the Bureau of Standards. The latter did not contain any elements known to form volatile hydrogen compounds. In all of the preparations, an amount of magnesium, in 10% excess of that required for the compound Mg_2Si, is thoroughly mixed with the silicon powder, the mixture is placed in a Swedish iron (carbon free) boat, 1.3 × 30.4 cm. in dimensions, which is then inserted in a Vitreosil tube in an electric furnace and finally heated to 500° for at least twenty-four hours. In many instances the time of heating was increased and some of the preparations were extended to higher temperatures, but only after the initial heating at 500°. Although magnesium silicide has a melting point of about 1100°, a reaction takes place between these two metals at 500°.[6] After the heating process, the silicide is allowed to cool in the presence of hydrogen and is then removed from the furnace. It appears as a finely divided blue powder, unchanged in the presence of air and moisture.

Reaction of Magnesium Silicide with Ammonium Bromide in Liquid Ammonia.—The apparatus used for the preparation of the silanes is essentially the same as that described by Kraus and Carney; a few changes were found necessary due to the extreme reactivity of the silanes toward oxygen and dilute alkaline solutions, and due to the fact that our preparations were carried out on a much larger scale than has hitherto been attempted for this type of compound.

A reaction tube, previously described[7] was designed to contain about 500 cc. of liquid ammonia. To the ammonia is added ammonium bromide in an amount which is approximately 50% in excess of that required for complete conversion of the silicide into the silane gases. The magnesium silicide is placed in a side-tube which is free to rotate about its axis on a ground joint to allow for introduction into the ammonium bromide solution. At the top of the reaction tube is sealed a smaller tube, passing to the bottom of the ammonia solution, through which ammonia gas can pass to agitate the solution. When the silicide comes in contact with the ammonium bromide solution, a fairly rapid reaction takes place with the liberation of silanes and hydrogen. The gas stream, which also contains ammonia vapor, is directed through a water-collecting tube.[5] The water in this tube is previously heated to expel air and then made slightly acid with hydrogen chlo-

---

[1] Wöhler and Buff, *Ann.*, **103**, 218 (1857).

[2] Stock and Somieski, *Ber.*, **49**, 111 (1916).

[3] For a complete bibliography of this work see A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

[4] Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924).

[5] Kraus and Carney, *ibid.*, **56**, 765 (1934).

[6] Gire, *Compt. rend.*, **196**, 1404 (1933).

[7] Kraus and Brown, THIS JOURNAL, **52**, 4031 (1930).

TABLE I

DATA FOR THE PREPARATION OF MAGNESIUM SILICIDES AND SILANES

	Silicide preparation			Preparation of silanes							
Expt.	Silicide, g.	Temp., °C.	Time, hrs.	Temp., °C.	Vol. silanes, cc. (total)	Vol. H_2, cc.	Mol. wt. of mixed silanes	% Si_2H_6 calcd.	SiH_4, cc.	Si_2H_6, cc.	Yield, % Si converted
I	137.3	700–775	24	−33	22,000		33.7	5.5	20,800	1200	60
II	11.6	475–525	40	−33	2,520		33.0	2.8	2,450	71	80
III	13.6	500–525	60	−33	2,780	1550	32.6	1.5	2,740	42	73
		600–625	60								
IV	10.2	500–525	48	−33	1,720	1650	34.0	6.3	1,610	108	68
		600–650	24								
		750–800	36								
V	5.0	520–550	24	−33	700	1420	32.25	0.4	672	28	52
VI-a	7.9	480–500	24	−33	1,500	1360	32.9	2.7	1,460	40	72
		600–620	18								
VII-a	5.65	480–500	24	−33	1,020	1210	33.25	3.8	980	39	69
		720–750	18								
VIII	7.55	480–500	24	−33	1,380	1510	34.4	7.6	1,275	105	76
		730–750	18								
IX-a	6.95	480–500	24	−33	1,070	1480	34.2	6.9	996	74	65
		790–810	18								
X	6.5	480–500	24	−33	900	1720	35.3	10.6	805	95	58
		870–920	24								
XI	2.1	480–500	24	−33	8	200					
		1025–1050	24								
XII	2.1	480–500	24	−33	No reaction						
		1000–1020	24								
VI-b	4.2	480–500	24	−80	212	1050	32.3	0.7	210	1.5	18
		600–620	18								
XIII	50% Ferro-silicon (direct)			−33	No reaction						
XIV	6.1	480–500	24	−33	41	920	33.6	5.0	39	2	3.3
	50% Ferro-silicon + Mg										
XV	8.5	480–500	36	−33	140	2120	33.2	3.7	135	5.2	6
	50% Ferro-silicon + Mg										
XVI	9.0	480–500	24	−33	201	2020	35.9	12.5	175	26	13
		650–680	48								
		50% Ferro-silicon + Mg									
VII-b	2.4	480–500	24	−80	85	320	32.2	0.3	85		13
		720–750	18								
IX-b	1.8	480–500	24	+50	47						10
		790–810	18								
XVII	5.1	480–500	24	+50	67		48.4	54	31	36	4.5
XVIII	6.44	480–500	24	+50	44		50.3	60	18	26	2.6

ride to prevent decomposition of the silanes. The mixture of gases is allowed to pass slowly through a large tube filled with phosphorus pentoxide and then into a trap to be condensed at the temperature of liquid nitrogen.[8] The non-condensable gas, hydrogen, is removed slowly by the vacuum pumps with the main gas stream passing through several liquid nitrogen traps to catch any of the silanes which might be carried along.

The mixture of silanes is then condensed in a small tube attached to a large Pyrex bulb of known volume (1, 2, 3, or 5 liters), to which is sealed a mercury manometer; the gases are permitted to warm to room temperature, the pressure is measured and the total volume calculated. The molecular weight of the gas mixture is then determined by weighing a known volume at a given temperature and pressure.

When several liters of the silanes become available, the combined lots are subjected to fractional distillation and condensation procedures as a means of separation. For the separation of monosilane from the higher boiling homologs, the liquid mixture is evaporated very slowly so that the pressure of the gases in the system may be maintained at less than 2 cm., while they are allowed to pass through a trap at −150°, whereby di- and trisilane are condensed and the monosilane passes to a second trap to be condensed at liquid nitrogen temperatures. A carbon tetrafluoride vapor tension thermometer may be used to determine the temperature.[9] An inappreciable amount of trisilane is present with the disilane; it may be separated at −80° by a method similar to that described above.

The apparatus used in the experiments is constructed entirely of Pyrex glass, and is completely surrounded by a heavy wire screen to reduce the amount of flying glass in

---

(8) Liquid nitrogen was used in all of the experiments to condense the silanes in order to reduce the danger of serious explosions in case parts of the glass apparatus should break.

(9) We are indebted to Dr. A. Burg for the use of several vapor tension thermometers designed for low temperature work.

case of an explosion. Pyrex stopcocks, lubricated with an ordinary rubber-base grease, may be used in all parts of the apparatus with very satisfactory results. Some of the containers have had the silanes in contact with these stopcocks for more than three years, with frequent use and without a change in the grease, and as far as may be determined, by appearance and by the constant pressure of the gas within the container, no reaction has taken place with the grease. It is accordingly not necessary to use mercury valves for the handling and study of these hydrogen compounds.

The results obtained in the preparations are collected in Table I, which is self-explanatory. A number of the earlier preparations are grouped together and the results are listed under experiment No. 1. Experiments which bear the same number, but different letters, refer to the same silicide preparation. A few experiments were carried out in an aqueous medium at 50° in order to compare the yields obtained with those of the ammonia method; thus in experiment IX-b, 2 *N* hydrochloric acid was used; in XVII, 0.5 *N* hydrochloric acid; and in XVIII, 2.7 *M* phosphoric acid. A large excess of magnesium was used in the preparation of the silicide from ferrosilicon in XV. In experiment VII-b, the gases generated in the reaction passed directly to the liquid nitrogen trap.

The 22 liters of mixed silanes, experiment I, were separated at −150° and 1175 cc. of disilane, molecular weight 62.0, was obtained. This value compares favorably with the calculated one, 1200 cc., based on the molecular weight of the mixed gases. The low boiling fraction was condensed at −196° and a determination of the molecular weight of the gas gave a value of 32.0, representative of very pure monosilane. A similar procedure was followed for the combined lots of gases from experiments V, VI-a, VII, VIII, IX-a and X, a total volume of 6570 cc. The lower boiling fraction showed a molecular weight of 32.2 and the higher boiling fraction, 62.6. The volume of the latter was 381 cc., which corresponds exactly with that calculated from the molecular weight of the mixed gases (Table I). Several samples of these two gases were analyzed for silicon and hydrogen by the thermal decomposition of a weighed quantity in a Pyrex tube at 500°. Table II shows the results.

TABLE II

ANALYSIS OF SILANES

	SiH_4	Si_2H_6
Molecular weight	32.2	62.6
Wt. of gas, g.	0.0284	0.0277
Wt. of Si, g. (found)	.0250	.0249
Wt. of Si, g. (calcd.)	.0249	.0250
H_2, cc. (found)	41.4	30.9
H_2, cc. (calcd.)	39.6	29.8

About 50 cc. of trisilane appeared when separated from the combined lots, 28.5 liters, of gases. This is only a little more than 0.01% of the total yield of silanes.

In order to substantiate the purity of the two silanes, the vapor pressure of each was determined at several temperatures. For monosilane, a vapor pressure of 604 mm. was found at −116.3°, 464 mm. at −120.4° and 98.4 mm. at −140.5°. The disilane gave values of 25.6 mm. at −78.5°, 69.6 mm. at −63.5° and 557 mm. at −22.9°. These values compare favorably with those calculated from an equation derived from the data of Stock and Somieski.[2,10]

Discussion of Results

An examination of the results given in Table I shows that the liquid ammonia method of preparation of silanes differs in many respects from the aqueous method. Although the aqueous method is usually carried out at 50° and the yields do not exceed 25%, the ammonia method gives yields of 70–80% at a comparatively low temperature, −33°. When the latter method is applied at a still lower temperature, −80°, the yield is reduced considerably, to less than 20% (experiments VI-b and VII-b). This effect is not one determined by the rate of the reaction, since in these two cases an unusually long period of time was allotted for its completion. In addition, it will be observed that the hydrogen liberated in these preparations is 4 to 5 times as great by volume as the silanes produced. In the companion experiments, VI-a and VII-a, the total yield of silanes is about 70% and the volume of hydrogen liberated is of the same order of magnitude as that of silanes.

On the basis of the substantial increase in the yield of silanes in ammonia with increasing temperature, it was thought advisable to study the reaction at still higher temperatures. For this experiment the aqueous method was chosen at 50° under conditions comparable to those previously employed by other workers. Experiments IX-b, XVII and XVIII correspond to these conditions. The results show a very low yield, not exceeding 10%, and in two instances less than 5%. The difference between the two methods of preparation is very striking here.

It is interesting to note that 50% ferrosilicon does not react with ammonium bromide in liquid ammonia. On the other hand, when the ferrosilicon is first heated with magnesium filings and then the product is subjected to an ammonia solution, silanes are liberated in appreciable amounts. It appears that the yield is dependent upon the time and temperature of heating. Ferrosilicon of this composition corresponds to the compound $FeSi_2$; undoubtedly, the reaction with magnesium involves the replacement of the iron of the silicide. It will be observed that the disilane content is unusually high (Expt. XVI).

From the table it is seen that the yield of disi-

---

(10) "I. C. T.," McGraw-Hill Book Co., New York, 1928, Vol. III, p. 214.

lane in the gas mixture increases quite regularly with increasing temperature employed in the preparation of the magnesium silicide. Thus, in experiments III and V, in which the silicide was prepared at 500–550°, the product consists almost entirely of monosilane; while in experiments VI-a, VII-a, VIII, IX-a and X, in which the silicide was prepared initially at 500° and subsequently heated to higher temperatures, specific for each preparation, there is a gradual increase in the disilane content ranging from 2.7 to 10.6%. On the other hand, a silicide prepared at temperatures higher than 1000° produces little, if any, silanes.

According to the thermal diagram for the system magnesium–silicon, which has been studied by Vogel,[11] only one compound, Mg_2Si, exists. Wöhler and Schliephake[12] have verified the existence of Mg_2Si and, in addition, have found MgSi. This silicide is described as being stable only at temperatures above 800°; at lower temperatures it decomposes to give Mg_2Si and silicon. Likewise, Mg_2Si decomposes to MgSi and magnesium above 800°. Above 1100° both silicides decompose into their constituent elements, according to these workers. Recently, Gire[6] has presented evidence for the existence of an intermediate silicide whose composition may be represented by Mg_3Si_2, the stability range of which lies between 550 and 650°.

It appears to us that one important factor which determines the formation of disilane in ammonia solution is the presence of higher magnesium silicides. Table I shows that when the silicide is prepared at a low temperature, about 500°, in the region of stability for magnesium silicide, very pure monosilane is formed. In contrast to these conditions, when a silicide is used which has been prepared at temperatures favorable for the formation of Mg_3Si_2 and MgSi, disilane is produced in appreciable amounts. A silicide prepared at very high temperatures is found to be inactive.

The yield of disilane is also related to the temperature of the reaction of ammonium bromide with the silicide. The silicides used in experiments VI-(a and b) and VII-(a and b) produced very little disilane at −80° but appreciable quantities at −33°. A third factor which influences the disilane content is the solvent. In experiments XVII and XVIII, which were carried out at 50° in an aqueous acid medium, the percentage of higher silanes is between 50 and 60. Silicides prepared in the same manner and permitted to react in ammonia show practically no higher silanes (Expt. V). One could explain this difference of behavior as being due primarily to a temperature change rather than one of solvent, but in view of the low total yield in water solutions such a conclusion does not appear valid to us.

Schwarz and co-workers[13] have proposed a mechanism for the formation of the higher silanes in aqueous hydrochloric acid solution. They isolated an intermediate product, $H_2Si(MgOH)_2$, when alcoholic hydrochloric acid was allowed to react with magnesium silicide. The assumption is then made that this product reacts with hydrochloric acid to give the transitory radical, SiH_2, the latter being polymerized and capable of further reaction as follows

$$(SiH_2)_2 + H_2O = SiH_2O + SiH_4 \qquad (1)$$
$$(SiH_2)_3 + H_2O = SiH_2O + Si_2H_6 \qquad (2)$$
$$(SiH_2)_4 + H_2O = SiH_2O + Si_3H_8, \text{ and so forth} \qquad (3)$$

The prosiloxane, SiH_2O, is polymerized immediately. Some support for this view has been advanced by Royen and Schwarz[14] from studies of the hydrolysis and also "cracking" of polygermene, $(GeH_2)_x$. Recently, Schwarz and Heinrich[15] have reported the preparation of polysilene, $(SiH_2)_x$; this substance is hydrolyzed with great difficulty in a bomb under pressure at 250° with the liberation of hydrogen only. On the other hand, when it is heated in a vacuum to 380°, disilane, trisilane and higher homologs are formed. It is possible, however, that an active or nascent SiH_2 group does exist in solutions containing aqueous hydrochloric acid and magnesium silicide. In such an event, reactions might occur in accordance with the equation mentioned above.

An examination of Table I reveals at once that the above mechanism cannot apply to the liquid ammonia method of preparation. If a reaction similar to that of equation (1) were to take place with the formation of some nitrogen analog of prosiloxane, it is obvious that the yield of monosilane could not exceed 50%; likewise, a reaction in accordance with equation (2) could produce disilane to the maximum extent of 67% yield. The yields recorded in Table I represent minimum

---

[11] Vogel, *Z. anorg. Chem.*, **61**, 46 (1909).

[12] Wöhler and Schliephake, *ibid.*, **151**, 1 (1926).

[13] (a) Schwarz and Konrad, *Ber.*, **55**, 3242 (1922); (b) Schwarz and Hoefer, *Z. anorg. Chem.*, **143**, 321 (1925); (c) Schwarz and Royen, *ibid.*, **215**, 288 (1933).

[14] Royen and Schwarz, *ibid.*, **215**, 295 (1933).

[15] Schwarz and Heinrich, *ibid.*, **221**, 277 (1935).

values since there is always considerable loss due to the incomplete combination of silicon with magnesium in the preparation of the silicide, the inability to get all of the silicide in contact with the ammonium bromide solution due to sticking to the walls of the tube, and to the decomposition of the silanes, especially disilane, in the water tube.

On the basis of the studies carried out in ammonia solution, it is suggested that such factors as the temperature of the reaction, the nature of the solvent and the composition of the silicide are of significance in determining the total yield of silanes as well as the yield of disilane. It appears that any mechanism proposed for the formation of the silanes must take these factors into consideration.

We are indebted to Prof. T. R. Hogness for assistance rendered in the construction of the apparatus and for invaluable suggestions offered in the course of the study.

Summary

Mono- and disilanes are prepared in large quantities and in yields ranging from 70 to 80% by allowing magnesium silicide to drop into a solution of ammonium bromide in liquid ammonia at low temperatures.

A study is made of the conditions favorable for the production of these silanes. On the basis of these studies certain suggestions are offered relative to the course of the reaction.

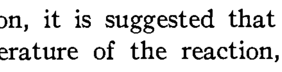
CHICAGO, ILLINOIS RECEIVED MAY 6, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF COLORADO]

The Action of Aromatic Aldehydes upon the Addition Products Obtained from Aromatic Amidines and Glyoxal

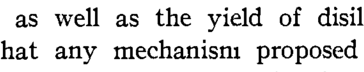
BY JOHN B. EKELEY AND ANTHONY R. RONZIO

Diels and Schleich[1] have shown that benzamidine forms with diacetyl an addition product whose structure seems to be



$$\begin{array}{l} HO-CCH_3-N \\ \quad\ | \qquad\qquad\quad \rangle CC_6H_5 \\ HO-CCH_3-NH \end{array}$$

since it reacts with benzaldehyde to form



$$C_6H_5CH\begin{array}{l} \langle OCCH_3-N \\ \qquad | \qquad\qquad \rangle CC_6H_5 \\ \langle OCCH_3-NH \end{array}$$

We found, however, that, when benzamidine reacts with glyoxal,[2] although an addition product is formed, this reacts in quite a different manner from the one obtained from diacetyl. It forms a base with an alkaline reaction. The benzamidineglyoxal addition product dissociates in water solution yielding the osazone of glyoxal with phenylhydrazine and glyoxal disemicarbazone with semicarbazide. Warming the product with alkalies yields a brilliant red compound, which, in turn, splits off water, forming a magenta-red compound probably related to glyoxaline-red.[3] It is our intention to study this reaction more in detail, and report upon it in a later paper.

With aromatic aldehydes in alkaline solution this and similar addition products of other aromatic amidines condense forming compounds highly colored, yellow to red, with high melting points, and usually soluble in various organic solvents, which may be regarded either as hydroxypyrimidines or as benzoylphenylglyoxalines. They are soluble in cold alkalies, and stable in boiling concentrated alkalies. Often these alkaline solutions show fluorescence if alcohol is added, the fluorescence being intensified by the addition of a little ether. Evaporation of the solutions hydrolyzes the alkali salts. That the solubility of the compounds in alkalies is due to an OH group is shown by the fact that the compound from benzaldehyde and meta-tolenyl amidine upon treatment with a PCl_5–$POCl_3$ mixture gave a monochlorinated product in which the OH had been replaced by chlorine. No oxime, phenylhydrazone, or semicarbazone of the compound could be prepared. The compound with benzaldehyde is soluble in concentrated hydrochloric acid, but soon separates out as a crystalline hydrochloride of varying composition, having formed initially an unstable dihydrochloride. Hot alcohol hydrolyzes the chloride. Boiling with concentrated hydrochloric acid very slowly hydrolyzes the

---

[1] Diels and Schleich, *Ber.*, **49**, 1711 (1916).

[2] We used Schuchardt's "polyglyoxal," a water soluble hydrated glyoxal containing some glyoxylic acid.

[3] Ruhemann and Stapleton, *Proc. Chem. Soc.*, **16**, 121 (1900).