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PREPARATION OF ALKYLSILICON HYDRIDES

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INTRODUCTION

Several years ago we initiated an investigation of cleavage reactions of disilane and alkyldisilanes. At that time the only compound of the type $Si_2H_{6-x}R_x$ (where R is an alkyl group) reported was 1,2-dimethyldisilane which was obtained from a Wurtz reaction with methylsilyl iodide[1]. Since unsymmetrically substituted disilanes were required for meaningful product analyses in our cleavage studies, we proceeded to develop methods for the preparation of these compounds. The alkylation of silane with ethyllithium had been reported[2] and we extended this method to the preparation of ethyldisilane[3].

In this paper we report our results on other alkylation reactions and on the silent electric discharge preparation of alkyldisilanes.

In the past two years the compounds 1,1,2-trimethyldisilane, 1,1,2,2-tetramethyldisilane and pentamethyldisilane have been obtained from the lithium aluminum hydride reduction of the corresponding halides or ethoxides[4,5].

EXPERIMENTAL

All of the reactions were carried out in pyrex glass vessels of about 100 ml volume which were fitted with either a Teflon needle valve or a stopcock and a ground joint to allow for transfer of reactants and volatile products to and from a standard vacuum system. The reactions were carried out at room temperature. Separations were made by trap to trap distillations through standard low temperature baths.

All of the silanes used were prepared by the reduction of the corresponding chloro compounds with lithium aluminum hydride[6]. The propyl ether used as a solvent was dried over lithium aluminum hydride and then distilled into the reaction vessel. The alkyllithium compounds were obtained from the Lithium Corporation as slurries and used without purification. The transfer of these compounds was carried out in an inert atmosphere.

Infrared spectra were obtained in the gas phase in a 10 cm cell fitted with KBr windows on a Perkin–Elmer model 337 spectrophotometer. The NMR spectrum of 1,1-dimethyldisilane was obtained in chloroform on a Varian A-60 spectrometer.

1. *Alkalation of silane and disilane*

The silane and disilane used in these experiments was treated with 1,2-dimethoxyethane to remove the last traces of hydrogen chloride.

The infrared spectra of the silane[7] and disilane[8] and their vapor pressures[9] were in agreement with those reported in the literature. The vapor pressure of silane was 11 mm at −160° and that of disilane was 7 mm at −95°.

A. $LiCH_3+SiH_4$. Methyllithium (about 2 mmoles) in ethyl ether was transferred to a reaction vessel containing a magnetic stirrer. The reaction vessel was connected to the vacuum system and the ether was distilled off. Silane (1.99 mmoles) and propyl ether (about 2 ml) were condensed onto the methyllithium at −196°. After 21 h, the volatile fraction was distilled into the vacuum system for separation into its components. The fraction that passed the −112° trap and condensed in the −130° trap was dimethylsilane (0.56 mmoles). The infrared spectrum of this sample was identical to that reported for dimethylsilane[10]. It is significant that the most logical impurities, methylsilane and trimethylsilane, have very strong absorptions in windows of the dimethylsilane and these bands were not observed. The infrared spectrum of the condensate in the −160° trap (1.00 mmoles) was identical to that reported for methylsilane[10] with no shoulders observed from bands due to silane or dimethylsilane. The condensate in the −196° was silane (0.37 mmoles); identified from an infrared spectrum[7] which contained no bands from methylsilane[10].

This experiment was repeated with 8 mmoles of methyllithium and 2.06 mmoles of silane. After 3 days the volatile fraction contained silane (0.044 mmoles), dimethylsilane (0.054 mmoles), trimethylsilane (0.99 mmoles) and tetramethylsilane (about 1 mmole) of which only 0.36 mmoles was isolated pure. The silane and dimethylsilane were isolated and identified as described above. The trimethylsilane was found in the −112° trap and its infrared spectrum was identical to that reported[10] with no shoulders from dimethylsilane bands. The C–H and Si–H stretching absorptions were of about equal intensities as reported and thus at most, very small quantities of tetramethylsilane could have been present. The isolated tetramethylsilane was found in the −95° trap. The infrared spectrum of this sample was identical to that reported[10] and the 621 cm^{-1} absorption of trimethylsilane was absent. The condensate in the −78° trap was a mixture of the solvent and tetramethylsilane.

B. $LiCH_3+Si_2H_6$. A similar reaction between methyllithium (1.0 mmoles and disilane (0.94 mmoles) was carried out. After 15 min, the volatile fraction was distilled from the reaction vessel to the vacuum system and passed through various cold traps. The condensate in the −196° trap was silane (0.15 mmoles); identified by an infrared spectrum. The fraction which condensed in the −160° trap (0.23 mmoles) was identified from an infrared spectrum as consisting of disilane with some methylsilane. The condensate in the −111° trap was methyldisilane (0.19 mmoles); identified from an infrared spectrum[11]. The strongest bands in the methylsilanes and the 830 cm^{-1} absorption in disilane were not present. Further, the relative intensities reported[12] for the band centered at 849 cm^{-1} to that at 725 cm^{-1} in methyldisilane is 3.40 while for our sample this ratio was 3.47. Since disilane has no absorption in the 725 cm^{-1} region, our sample could contain only a trace of disilane.

C. $LiCH_3+CH_3Si_2H_5$. The reaction between methyldisilane and methyllithium was carried out as described above. In a typical experiment, 2 mmoles of methyllithium and 1.52 mmoles of methyldisilane were used as reactants. After 20 minutes, the volatile fraction was separated into its components. Silane (0.34 mmoles), methylsilane (0.22 mmoles) and dimethylsilane (0.078 mmoles) were isolated and identified as described above. The condensate in the −95° trap was a mixture of the two dimethyldisilanes (0.45 mmoles). This identification was based on an infrared spectrum of the mixture and the following experiment. The dimethyldisilane mixture, along with 2 ml of 1,2-dimethoxyethane, were condensed onto excess potassium hydride. After 20 min, the volatile fraction was separated into methylsilane (0.40 mmoles) and dimethylsilane (0.08 mmoles) as described above*.

D. $LiC_2H_3+C_2H_3SiH_3$. Vinyllithium (1 mmole) in tetrahydrofuran was transferred to a reaction vessel containing a magnetic stirrer. The vessel was connected to a vacuum system and the ether was distilled off. Vinylsilane (1.17 mmoles) and propyl ether (1 ml) were condensed onto the vinyllithium at −196°. After 6 min, the volatile fraction was distilled into a vacuum system for separation of the components. The condensate in the −196° trap was vinylsilane (0.31 mmoles) with a trace of divinylsilane; identified by an infrared spectrum[10]. The condensate in the −95° trap was divinylsilane (0.24 mmoles); identified from an infrared spectrum[14] from which the strongest band of vinylsilane[10] was absent. The condensate in the −63° trap was a mixture of propyl ether, divinylsilane and a trace of trivinylsilane.

E. $LiC_2H_3+Si_2H_6$. The reaction between vinyllithium (2 mmoles) and disilane (2.06 mmoles) was carried out as described above. Three minutes after the liquid nitrogen dewar was removed, the volatile fraction was distilled into the vacuum system and separated into three fractions. The condensate in the −196° trap was silane (0.40 mmoles) while that in the −160° trap was a mixture of disilane and a small amount of vinylsilane (1.04 mmoles, total). The third fraction (0.22 mmoles) passed a trap cooled to −63° and condensed in the −95° trap. The infrared spectrum of this sample showed that divinylsilane was present along with a compound "A" which had strong absorbances at 888 and 793 cm^{-1}. This experiment was repeated and similar mixtures of divinylsilane and compound A were obtained. A typical reaction between such a mixture (0.341 mmoles) and lithium deuteride in 1,2-dimethoxyethane for 14 h produced vinylsilane (0.11 mmoles) and silane (0.14 mmoles). After the reaction, compound A was no longer present while the divinylsilane had not reacted. Separate experiments demonstrated that neither vinylsilane nor divinylsilane react with lithium deuteride in 1,2-dimethoxyethane. The silane and vinylsilane were isolated and identified as described above.

2. *Silent electric discharge reactions*

The silent electric discharge system used was similar to one described by Spanier and MacDiarmid[15]. The ozonizer outer diameter was 18 mm while the inner diameter was 12 mm. The volume of the ozonizer system varied from 1500 ml to 1800 ml due to the operation of the Toepler pump.

1,1-*Dimethyldisilane.* The silent electric discharge reaction between silane and dimethylsilane was run at a potential of 6800 volts. The trap used to stop the 1,1-dimethyldisilane was cooled to −78° which maintained the dimethylsilane at a pressure of 38 mm. The initial silane pressure was about 76 mm and after 2 h the apparatus was recharged with silane to a pressure of about 80 mm and the experiment was continued for another 1½ h.

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* It has been demonstrated[13] that 1 mole of 1,1-dimethyldisilane reacts with potassium hydride to yield 1 mole of dimethylsilane, while 1 mole of 1,2-dimethyldisilane reacts with potassium hydride to produce 1 mole of methylsilane.

Since the vapor pressures of trisilane and 1,1-dimethyldisilane are very similar, a chemical separation was devised. The trisilane and 1,1-dimethyldisilane fraction was condensed into a 1,2-dimethoxyethane slurry of lithium hydride. The trisilane was cleaved producing silane and disilane which are easily separated from 1,1-dimethyldisilane.

Hydrogen chloride was then condensed into the 1,1-dimethyldisilane and 1,2-dimethoxyethane mixture. This procedure facilitated the separation of these components by trap-to-trap distillation, as a complex between the solvent and hydrogen chloride was formed.

In a typical experiment, 4.75 mmoles of silane and 1.35 mmoles of dimethylsilane were consumed and 0.82 mmoles of 1,1-dimethyldisilane was obtained.

The identification of 1,1-dimethyldisilane was based on the following results:
1. The products of the reaction between potassium hydride and 1,1-dimethyldisilane in 1,2-dimethoxyethane were potassium silyl and dimethylsilane[13]. This result demonstrates that two methyl groups are bonded to one silicon atom which is bonded to a silyl group.

TABLE 1

INFRARED SPECTRUM OF 1,1-DIMETHYLDISILANE[a]

Wavelength (cm^{-1})	*Assignment*	*Wavelength* (cm^{-1})	*Assignment*
2969 m	C–H stretch	930 m	SiH_3SiH deform.
2141 vs	Si–H stretch	844 vs	SiH_3SiH deform.
1645 w		702 m	Si–C stretch
1260 m	CH_3 deform.	485 m	
1135 w	CH_3 deform.		

[a] Obtained on a Perkin–Elmer Model 621 Spectrophotometer.

2. A molecular weight (by vapor density) of 91.0 ± 1.0 (theoretical 90.3) was obtained.
3. The infrared spectrum (Table 1) was compatible with that expected for 1,1-dimethyldisilane and different from the reported spectrum of the 1,2-derivative[1].
4. The proton NMR spectrum (Table 2) was consistent with that expected for 1,1-dimethyldisilane and reasonably analogous to that reported for methyldisilane[16] and ethyldisilane[3].

TABLE 2

PROTON NMR SPECTRUM OF 1,1-DIMETHYLDISILANE

Absorption	*Relative integrated intensity*	*Assignment*
Doublet at −0.285 ppm[a]	6.00	2 CH_3
Doublet at −3.08 ppm	3.05	SiH_3
Complex system at −3.46 ppm	1.00	SiH

[a] Chemical shifts with a minus sign are downfield from tetramethylsilane at 0.0 as an external standard.

The vapor pressure of 1,1-dimethyldisilane was found to obey the following equation from −63° to 25°.

$$\log P_{\mathrm{mm}} = -\frac{1364}{T} + 6.991$$

By this method, 1,2-dimethyldisilane was obtained from methylsilane while methyldisilane was obtained from a mixture of methylsilane and silane.

RESULTS AND DISCUSSION

Our results indicate that the reaction between an alkyllithium compound and a monosilane to produce alkylsilanes is a rather general reaction. However, the extension to disilane is not always simple. With methyllithium or ethyllithium the alkyldisilane can be produced and easily isolated.

When vinyllithium was used as the alkylating agent with disilane, the results were less satisfactory. The yield of vinyldisilane was low due to the formation of silane and its vinyl derivatives. This is attributed in part to the vinyllithium-catalyzed disproportionations of disilane and vinyldisilane which appear similar to the alkali metal salt-catalyzed disproportionation reactions of disilane[17]. Even in short runs (1 min), considerable divinylsilane was obtained. The problem here is that the separation of the desired vinyldisilane from divinylsilane is difficult. We did not isolate the vinyldisilane and our identification of compound A as vinyldisilane is based on the following results:

1. We were unable to separate divinylsilane from compound A by trap-to-trap distillation. Thus, the compounds must have similar molecular weights. The difference in the molecular weight between divinylsilane and vinyldisilane is 4.05.
2. The two strongest infrared absorptions in compound A are centered at 885 cm^{-1} and 795 cm^{-1}. The "Si_2H_5" deformations in ethyldisilane are centered at 888 cm^{-1} and 793 cm^{-1} (ref. 3).
3. When a mixture of compound A and divinylsilane was treated with lithium deuteride in 1,2-dimethoxyethane, the volatile products were silane and vinylsilane while the divinylsilane remained. When ethyldisilane was treated with lithium deuteride, the products obtained were silane and ethylsilane[13]. As a control reaction, we demonstrated that lithium deuteride does not react with vinyl or divinylsilane.

The different results obtained from the disilane–methyllithium or –ethyllithium reaction and the disilane–vinyllithium reaction can be explained by considering the following reactions where R = methyl or ethyl, Vi = vinyl and LB refers to a Lewis Base.

$$\mathrm{RSi_2H_5} \overset{\mathrm{LB}}{\underset{k_1}{\rightarrow}} \mathrm{RSiH_3 + SiH_4 + polymer} \quad \text{(ref. 13)} \tag{1}$$

$$\mathrm{ViSi_2H_5} \overset{\mathrm{LB}}{\underset{k_2}{\rightarrow}} \mathrm{ViSiH_3 + SiH_4 + polymer} \tag{2}$$

$$\mathrm{RSiH_3 + LiR} \underset{k_3}{\rightarrow} \mathrm{R_2SiH_2 + LiH} \tag{3}$$

$$\mathrm{ViSiH_3 + LiVi} \underset{k_4}{\rightarrow} \mathrm{Vi_2SiH_2 + LiH} \tag{4}$$

Thus our results can be explained if $k_2 > k_1$ and $k_4 > k_3$. This order of rate constants would be expected if one considers the rate of the base catalyzed reactions (eqns. 1

and 2) and the alkylation reactions (eqns. 3 and 4) to be directly related to the partial charge (Lewis acidity) on the silicon atoms undergoing nucleophilic attack. It has been demonstrated that trivinylborane is a stronger Lewis acid than trimethylborane[18] and one would expect the same trend to hold for silicon compounds. This same point is important when one considers our results concerning the reaction between methyllithium and methyldisilane. The second methyl group was added to the unsubstituted silicon to a much greater extent than to the substituted silicon atom. While this result does not prove that methyl attack occurs mainly at the more acidic unsubstituted silicon we feel that this is strongly suggested. Since hexaphenyldisilane reacts with phenyllithium[19], steric factors do not appear too important. Therefore, the position of nucleophilic attack is probably directed by electronic effects which would predict that methylation should be favored at the unsubstituted silicon atom in methyldisilane.

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SUMMARY

All four methylsilanes, vinylsilane and divinylsilane were isolated as products from the reaction between silane and the appropriate alkyllithium compound. Methyldisilane was obtained from reaction with disilane. Further methylation of methyldisilane produced 1,2-dimethyldisilane and 1,1-dimethyldisilane in a five to one ratio. The reaction between disilane and vinyllithium was also investigated. Methyldisilane and both dimethyldisilanes were obtained from silent electric discharge reactions.

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