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THE USE OF SODIUM HYDRIDE AS A REDUCING AGENT IN NITROGEN-CONTAINING SOLVENTS
I. THE REDUCTION OF CHLOROSILANES IN HEXAALKYLPHOSPHORIC TRIAMIDES AND TETRAALKYLUREAS*

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SUMMARY

A variety of chlorosilanes were reduced to the corresponding silicon hydrides with sodium hydride in hexamethylphosphoric triamide (HMPT), tetramethylurea (TMU) and related solvents. In HMPT and TMU, the reductions proceeded rapidly at room temperature under nitrogen in good yield.

No side reactions were noted for the simple alkyl- and arylchlorosilanes except for some inhibition periods if air was present and a little reduction of TMU to tetramethylmethylenediamine.

Allyldimethyl- and vinyldimethylchlorosilanes were reduced normally in TMU, but in HMPT olefin isomerization and vinyl polymerization occurred. These side reactions were shown to be due to the presence of sodium in the sodium hydride. The sodium may be leached out with HMPT, and the resulting sodium hydride gave improved yields for the reduction of tetramethyldichlorodisiloxane.

Other solvents either gave no chlorosilane reduction or were too reactive in side reactions. These included dioxane, tetramethylethylenediamine, dimethylformamide and dimethylacetamide. Pyridine, however, appeared to be a suitable solvent although the rate of chlorosilane reduction was slow compared to HMPT and TMU.

INTRODUCTION

Sodium hydride is potentially a more powerful reducing agent than lithium aluminum hydride. The latter reagent is far more widely used, however, presumably because of its greater solubility in ether solvents. The present investigation resulted from the hypothesis that sodium hydride should be more soluble in a polar medium such as hexamethylphosphoric triamide (HMPT) and therefore might find greater application in such solvents.

To test this suggestion, the reduction of chlorosilanes was chosen as a suitable reaction. Chlorosilanes are readily reduced to silicon hydrides by lithium aluminum hydride at room temperature in ether solvents. However, sodium hydride fails to

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reduce diethyldichlorosilane even on prolonged refluxing in dioxane[1]. Chlorosilanes have been reduced by sodium hydride, but only at high temperatures (200–300°) and in low yield[2,3].

Early results showed that chlorosilanes were readily reduced at room temperature by sodium hydride in HMPT. This system was therefore further investigated since sodium hydride is a cheaper material than lithium aluminum hydride so that its use may represent a more economical route to silicon hydrides. Other solvents were also examined for comparison purposes.

Lithium aluminum hydride has certain disadvantages[4]. These stem from the formation of aluminum chloride which can result in the disproportionation of silicon hydrides and the polymerization of allyl compounds. Lithium hydride has been used to obviate these difficulties, but this requires the use of high boiling ether solvents. Among the chlorosilanes investigated were, therefore, allyl- and vinylchlorosilanes. The latter are known to react readily with organometallics such as butyllithium. sometimes giving rise to a polymerization[5].

RESULTS

1. *Reduction of chlorosilanes and related compounds*

From Table 1, it can be seen that in hexamethylphosphoric triamide (HMPT) reduction of chlorosilanes is rapid at room temperature. These reactions were carried out on a small scale (2 ml chlorosilane) in order to survey the scope of the reaction. The silicon hydrides formed were isolated in most cases, but no attempt was made to optimize the work-up. Thus, although the alkylchlorosilanes were reduced nearly quantitatively to the corresponding silicon hydrides, the yield was generally only around 80% unless the silane was volatile enough to be separated by a simple vacuum distillation, when yields greater than 90% were obtained. In addition to the chlorosilanes listed in Table 1, phenyldimethylchlorosilane was reduced to phenyldimethylsilane using a stoichiometric amount of sodium hydride in HMPT (78% yield) and diphenyldichlorosilane was similarly reduced to diphenylsilane in 75% yield.

Alkoxysilanes are not reduced. Thus, triethylethoxysilane gave no triethylsilane after 24 h in HMPT using the conditions followed in Table 1. An attempt was therefore made to selectively reduce trimethoxychlorosilane, some reduction occurred, but infrared indicated that a mixture of silicon hydrides were formed in low yield.

Germanium halides appear to be reduced normally to germanes (Table 1), but difficulty was experienced with chlorotin compounds. Thus, although trimethyltin chloride gave some trimethyltin hydride in a test tube experiment using HMPT as solvent, subsequent attempts on a larger scale appeared to react further to produce green solutions containing no tin hydride. It seems likely that tin hydrides are more reactive toward the solvent than the germanes and silanes.

The effect of solvent. A decrease in the amount of HMPT used decreases the rate of the reaction. Thus, in expt. 2, when the concentration of triethylchlorosilane was increased to 50% v/v, only 50% reduction was found after 30 minutes. A decrease in the amount of HMPT to catalytic proportions is shown by expt. 7. Although the reaction still proceeds, it is very slow.

Tetramethylurea (TMU) is nearly as effective as HMPT. In both solvents, reaction was accompanied by a noticeable exotherm effect after a few minutes stirring.

TABLE 1

REACTIONS OF CHLOROSILANES WITH SODIUM HYDRIDE AT ROOM TEMPERATURE[a]

Expt.	Chlorosilane	Solvent[b]	Time (h)	Extent of reaction (%)[c]
1	$(C_2H_5)_2SiCl_2$	HMPT	1.0	70
			16	87[e]
2	$(C_2H_5)_3SiCl$	HMPT	0.25	86
			0.50	~100[e]
3	$CH_2{=}CHCH_2Si(CH_3)_2Cl$	HMPT	0.3	>70
4	$[(CH_3)_2SiCl]_2O$	HMPT	3.5	80
			6.0	85
5	$C_4H_9SiCl_3$	HMPT	5	82[e]
6	$(C_2H_5)_3GeCl$	HMPT	1	60[e]
7	$(C_2H_5)_3SiCl$	Benzene/HMPT[d]	6	20
			12	30
8	$(C_2H_5)_3SiCl$	TMU	2.5	70[e]
9	$CH_2{=}CHCH_2Si(CH_3)_2Cl$	TMU	0.3	>70[e]
10	$[(CH_3)_2SiCl]^{O}_{2}$	TMU	1.3	53
			2.5	57
11	$(C_2H_5)_3SiCl$	Pyridine	20	34
			48	61
12	$(C_2H_5)_3SiCl$	DMA/TMED	7	21
			23	21
13	$C_2H_3Si(CH_3)_2Cl$	TMU	2.5	61[f]
14	$(C_2H_5)_3SiCl$	TEU	48	12
15	$(C_2H_5)_3SiCl$	HEPT	24	31
			48	~100

[a] 20% v/v solutions of the chlorosilane+excess sodium hydride. [b] HMPT=hexamethylphosphoric triamide; TMU=tetramethylurea; DMA=dimethylacetamide; TMED=tetramethylethylenediamine; TEU=tetraethylurea; HEPT=hexaethylphosphoric triamide. [c] Measured by infrared unless otherwise noted. [d] 78% benzene 2% HMPT v/v. [e] Yield on workup based on chlorosilane. [f] 80% yield based on non-recovered chlorosilane.

In both dimethylformamide (DMF) and dimethylacetamide (DMA), a vigorous reaction occurs leading to separation of the liquid into two phases. The upper layer consisted mainly of siloxane. No silicon hydride was found in the case of DMF. In DMA, the formation of siloxane was slower and accompanied by a little silicon hydride formation. The addition of tetramethylethylenediamine (TMEDA) (expt. 12) assisted silicon hydride formation, but the rate was still very slow. No silicon hydride formation was found in either TMEDA or dioxane as solvent in 20 h when these solvents were substituted for HMPT in expt. 2.

The use of HMPT as solvent results in some side reactions. One is the disproportionation of chlorosilicon hydrides[6], *e.g.*,

$$R_2SiHCl \rightleftarrows R_2SiH_2+R_2SiCl_2$$

Thus, although R_2SiHCl may be the first reduction product of R_2SiCl_2, a mixture of both silicon hydrides would soon result from disproportionation. In the reduction of diphenyldichlorosilane, the principal SiH absorption in the infrared was at 2155 cm^{-1} (diphenylsilane) with a shoulder to higher frequency (diphenylchlorosilane) throughout the reduction. No lability of the phenyl–silicon bond was found, however.

Chlorosilanes containing double bonds also gave side reactions in HMPT. Dimethylvinylchlorosilane appeared to be reduced normally, but gave only low molecular weight polymer (MW ~500) on workup. Dimethylallylchlorosilane gave a volatile product, but the NMR spectrum indicated about 50% isomerization to the internal olefin. Poor yields were obtained unless the reaction mixture was worked up as soon as the reaction had gone to completion. In TMU, both unsaturated chlorosilanes were reduced normally in good yield (allyl 70%, vinyl 80%). Under the same conditions, higher homologues of HMPT and TMU were found to be less effective, *e.g.*, hexaethylphosphoric triamide (HEPT) and tetraethylurea (TEU) (Table 1). Hexacyclohexylphosphoric triamide was found to be unsuitable, being a solid with only a low solubility in suitable cosolvents such as benzene or dioxane. Phosphoric trimorpholide[7] is also a solid and did not appear to be very active when used with benzene as a cosolvent.

Octamethylpyrophosphoric tetramide (OMPPT) had a similar activity to HMPT. A 57% yield of triethylsilane was obtained after 4 h stirring of a mixture of 3 ml triethylchlorosilane, 3 ml OMPPT and 3 g of the 50% sodium hydride dispersion.

Pyridine gave rise to a slow reduction at room temperature, but it was accompanied by attack of solvent. At reflux temperatures, the pyridine was strongly attacked and appeared to polymerize.

The sodium hydride. An excess of sodium hydride was used in Table 1. When less sodium hydride was employed, the rate decreased somewhat. Thus, in expt. 2, the use of a stoichiometric amount of sodium hydride resulted in only 50% reaction after 30 minutes.

When using stoichiometric amounts of sodium hydride, variable inhibition periods were found to precede reaction. This phenomenon was found to be due to insufficient care in excluding air from the reaction. When expt. 2 was carried out in the presence of air, no reaction occurred during several hours. When the air was replaced by nitrogen, the reaction commenced and proceeded normally. Since the sodium hydride contains small amounts of sodium which reacts readily with air once it has dissolved in the HMPT, the reaction will tolerate small amounts of air which are presumably "gettered" by the sodium. Reaction can be readily initiated, in fact, by the addition of a trace of sodium. The sodium does not appear to be necessary in the absence of oxygen, however, since it can be leached out without affecting the reactivity of the sodium hydride as in expt. 4. In this particular case, the presence of the sodium impurity results in side reactions, and if not removed, will greatly lower the yield. For this reason the sodium hydride used in expt. 4 was extracted with HMPT and the blue solution of sodium decanted off. This extraction was repeated three times prior to use. No extraction was carried out when using TMU as a solvent, however (expt. 10). These reductions of tetramethyldichlorodisiloxane like those of allyldimethylchlorosilane required working up as soon as silicon hydride formation had reached an optimum value.

2. *Vinylsilane polymerization*

Both trimethylvinylsilane and phenyldimethylvinylsilane gave a 90% yield of low molecular weight polymer (~1000 by gel permeation chromatography). Their NMR spectra showed sharp bands at approximately τ 10 and a very broad absorption from 8–10 ppm.

DISCUSSION

The facile reduction of chlorosilanes in HMPT and TMU could result from either or both of two factors: (1) enhanced solubility of sodium hydride with increasing polarity of solvent; and (2) activation of the chlorosilane by solvent coordination.

One would expect lithium hydride to have a greater solubility, and calcium hydride to have a similar or lower solubility than sodium hydride. In agreement with this, lithium hydride was also found to reduce chlorosilanes readily in HMPT whereas calcium hydride would not. No significant solubility of either sodium or lithium hydride in HMPT at room temperature was found however. Thus, their saturated solutions gave no significant evolution of hydrogen on adding water.

Coordination of nitrogen-containing solvents to chlorosilanes is well documented. Silicon halides form complexes with amines[8,9], amides[10] and ureas[11]. Such coordination should increase the ionic character of the silicon to halogen bond and in one case has been reported to result in complete ionisation[12]. Similar complexes appear to be formed with HMPT and it seems likely that the disproportionation of chlorosilicon hydrides in HMPT[6] is a result of this phenomenon.

DMF and DMA, solvents likely to be effective by virtue of factors (1) and (2), were unsuitable because of side reactions. Siloxanes were formed rather than silicon hydrides, presumably due to reduction of the solvent. In TMU, a small amount of solvent reduction also occurred to form tetramethylmethylenediamine. The low yield obtained in the experiment with OMPPT was presumably also due to reaction of solvent.

Two of the solvents examined, pyridine and TMED, should only be effective by virtue of factor (2). TMED was found to be inactive, but pyridine had a low order of activity. The combination of TMED and a high dielectric solvent (DMA) was still relatively inactive.

A significant difference between HMPT and TMU was the occurrence of olefin isomerization and vinyl polymerization in only the former solvent. This is probably caused by the presence of sodium in the sodium hydride, since only the former solvent gives relatively stable solutions of the metal[6,14].

Although solutions of sodium in HMPT react rapidly with chlorosilanes, they are stable to silicon hydrides so that once the reaction is complete, sodium from the excess sodium hydride could be effective in olefin isomerization or vinyl polymerization. In separate experiments, a solution of sodium in HMPT was found to cause the isomerization of allyldimethylsilane and to polymerize vinyltrimethylsilane.

The disproportionation of chlorosilicon hydrides catalyzed by HMPT was not noted to occur in TMU. Thus, methyldichlorosilane did not noticeably disproportionate in two hours at room temperature in TMU. For this reason, an attempt was made to partially reduce trichlorosilanes in TMU. Methyldichlorosilane was identified among the products of reduction of methyltrichlorosilane in low yield. Butyltrichlorosilane gave only butylsilane.

The very large decrease in catalytic activity in going from $R = CH_3$ to $R = C_2H_5$ in the hexaalkylphosphoric triamides and tetraalkylureas could be ascribed to either a decrease in polarity of the solvent (factor 1) or steric hindrance to the formation of a bond to silicon (factor 2).

The initial hypothesis that sodium hydride should find greater application when used in more polar solvents appears to be amply justified. An enhanced solubility of the sodium hydride may be responsible, but a more important reason in the case of chlorosilane reduction may be the activation of the silicon–chloride bond by coordination of solvent to silicon.

The application of HMPT and TMU as solvents for the reduction of other substrates by sodium hydride will be the subject of future investigations.

EXPERIMENTAL

Hexamethylphosphoric triamide (HMPT) and other solvents were dried over molecular sieves and then over calcium hydride.

Silanes were obtained from Peninsular and General Electric Silicone Products Department and used without purification.

Sodium hydride was a 50% dispersion in mineral oil obtained from Metal Hydrides Incorporated. It contained an unknown amount of metallic sodium.

Reaction of chlorosilanes and related compounds with sodium hydride

The reactions were carried out under nitrogen stirring magnetically at room temperature (Table 1) and the formation of silicon hydride followed by measuring the growth of the infrared band at 4.7 microns due to the Si–H stretch. The concentration of the chlorosilane (10–20%) was chosen such that a quantitative yield of silicon hydride corresponded to a standard solution made up for comparison purposes. The extent of the reaction could thus be calculated directly from infrared measurements. Separation of the silicon hydride was effected by a distillation on a vacuum line for the more volatile silanes. Alternatively, the solvent was removed by extracting with water after first separating excess sodium hydride and other solids by centrifuging. Products were then examined by GLC, and the silane identified, after further purification where necessary, by means of infrared, NMR and refractive index measurements.

Polymerization of vinylsilanes

A 40% w/w dispersion of sodium in mineral oil was shaken with pentane, centrifuged and the excess solvent decanted off. This procedure was repeated twice more. 0.03 g of the resulting sodium was dissolved in 6 ml of HMPT and 2 ml of this solution added to 5 ml of the vinylsilane in 10 ml HMPT. The mixture was then stirred under nitrogen for 3 h after which the reaction was terminated with a little methanol. Pentane (100 ml) and water (300 ml) were then added and the mixture shaken. The pentane solution was separated, washed with further water, dilute hydrochloric acid and further water. The pentane solution was then evaporated to dryness to give 3 g of a viscous liquid.

Isomerization of allyldimethylsilane

Allyldimethylsilane (0.5 ml) from expt. 9 was dissolved in 5 ml HMPT and one drop of sodium dispersion in mineral oil added while stirring magnetically. After 5 min, the mixture was distilled on a vacuum line to give 0.3 ml of a mixture of 1-propenyldimethylsilane and allyldimethylsilane in the approximate ratio 2/1 respectively.

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