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The Reaction of Hydrosilanes with Chlorosilanes in the Presence of Grignard Reagents. A New Method of Silicon-Silicon Bond Formation

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A new method has been developed for the formation of a silicon-silicon bond. Hydrosilanes having at least one phenyl or one trimethylsilyl group on a silicon atom were subjected to reaction with chlorosilanes to give unsymmetrically substituted disilanes in the presence of secondary or tertiary Grignard reagent which was inert to both chlorosilanes and hydrosilanes. The method was extended to the preparation of benzyl, allyl, and alkylsilanes.

Chemistry of organopolysilanes has recently become a subject of growing interest.[1] In investigations of organopolysilanes, it is frequently desirable to prepare unsymmetrically substituted organodisilane compounds. For this the Wurtz-type condensation between the two different kinds of halosilanes may be employed. However, it does not necessarily give the desired compound selectively unless one of the two halosilanes makes a stable silylalkali metal bond.[2]

It was reported that cyclohexylmagnesium bromide was also effective for the condensation of halosilanes.[3] A silyl Grignard reagent, "$Ph_3Si-MgX$", formed by the interaction between triphenylchlorosilane and cyclohexylmagnesium bromide was assumed as an intermediate. This was further coupled with another chlorosilane to form a new silicon-silicon bond. The presence of magnesium metal gave rise to more favorable results.[4] Some symmetrically substituted disilanes have been also obtained by the action of magnesium metal upon chlorosilanes[5] where an intermediacy of the "Si–MgX" compound formed directly from magnesium and the chlorosilane was presumed.

We have investigated the reaction of various hydrosilanes with sterically hindered Grignard reagents, such as isopropylmagnesium chloride in tetrahydrofuran (THF), primarily in the hope of preparing a stable silyl Grignard reagent. Although the convincing evidence of its formation was not available, some unsymmetrically substituted disilanes were obtained in good yield by adding chlorosilane to the reaction mixture.

Results and Discussion

An appropriate hydrosilane was added to a solution of Grignard reagent from *sec*- or *tert*-alkyl halides in THF and was heated to reflux. Trimethylchlorosilane was then added to the reaction mixture and the mixture was heated to reflux under nitrogen. After workup, an unsymmetrically substituted disilane was obtained as a result of the condensation between hydrosilane and chlorosilane. The products were identified by comparing their retention times on gas chromatography and IR and NMR spectra with those of authentic samples.

$$\equiv Si^1-H + \equiv Si^2-Cl \xrightarrow{RMgX} \equiv Si^1-Si^2\equiv + MgXCl + RH$$

It has been shown that the introduction of an alkyl group into silicon took place in the reaction of hydrosilanes with Grignard reagents derived from primary alkyl halides,[6] and thus the sterically hindered Grignard reagent formed from *sec*- or *tert*-alkyl halides was employed. It has been also established that *sec*- or *tert*-Grignard reagents give no substitution product in the reaction with trialkylchlorosilanes.[7]

The results are summarized in Table 1. It is interesting to note that the presence of an aromatic or an organosilyl group on silicon in a hydrosilane is apparently necessary for the condensation, just as in the formation of "silyl Grignard reagents,"[3,5] or silyl alkali metal compounds[2] from chlorosilanes. These groups may play a role in the stabilization of the negative charge, which would develop on the silicon atom of "silyl Grignard reagents." If hydrosilanes were converted into chlorosilanes under the present reaction conditions, the reaction may be trivial, since coupling of chlorosilanes by means of Grignard reagents is known. However, the fact that no such conversion of hydrides into chlorides really occurred was verified by several control experiments; for example, after a hydrosilane was heated at reflux with the starting alkyl halide or chlorosilane in the presence of magnesium metal, magnesium salts, or alkyl Grignard reagents, no traces of the corresponding chlorosilane could be detected.

The yields are independent of the presence of magnesium in the reaction mixture. However, the effect of solvent is very significant. Thus, although disilanes were not obtained in diethyl ether, the reaction took

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Table 1. Condensation of hydrosilane with halides in the presence of alkyl Grignard reagent (RMgX) in THF

Exp. No.	R-X	Hydrosilane	Chlorosilane or halide	Product	Yield (%)[a]
1[b]	*t*-BuCl	Ph_2SiH_2	Me_3SiCl	$Ph_2(H)Si–SiMe_3$	0
2	*t*-BuCl	Ph_2SiH_2	Me_3SiCl	$Ph_2(H)Si–SiMe_3$	22 (6)[c]
3	*t*-BuCl	Ph_2MeSiH	Me_3SiCl	$Ph_2MeSi–SiMe_3$	(trace)
4	*t*-BuCl	Ph_3SiH	Me_3SiCl	$Ph_3Si–SiMe_3$[b]	(trace)
5	*Cyclo*-$C_6H_{11}Cl$	Ph_2SiH_2	Me_3SiCl	$Ph_2(H)Si–SiMe_3$	(3)[d]
6[e]	*Cyclo*-$C_6H_{11}Cl$	Ph_2MeSiH	Me_3SiCl	$Ph_2MeSi–SiMe_3$	62 (25)
7	*i*-PrBr	Ph_3SiH	Me_3SiCl	$Ph_3Si–SiMe_3$	68 (6)
8	*i*-PrCl	Ph_3SiH	Me_3SiCl	$Ph_3Si–SiMe_3$	73 (29)
9	*i*-PrCl	Ph_2MeSiH	Me_3SiCl	$Ph_2MeSi–SiMe_3$	86 (50)
10	*i*-PrCl	Me_5Si_2H	Me_3SiCl	$Me_5Si_2–SiMe_3$	(14)[d]
11	*i*-PrCl	$PhCH_2Me_2SiH$	Me_3SiCl	$PhCH_2Me_2Si–SiMe_3$	0
12	*i*-PrCl	Ph_2MeSiH	$PhCH_2Cl$	$Ph_2MeSi–CH_2Ph$	76 (28)
13	*i*-PrCl	$PhMe_2SiH$	$PhCH_2Cl$	$PhMe_2Si–CH_2Ph$	57 (11)
14	*i*-PrCl	Ph_2MeSiH	$CH_2=CHCH_2Cl$	$Ph_2MeSi–CH_2CH=CH_2$	(trace)
15	*i*-PrCl	Ph_2MeSiH	MeI	$Ph_2MeSi–Me$	(19)[d]
16	*i*-PrCl	Ph_2MeSiH	*n*-BuI	$Ph_2MeSi–Bu$-*n*	(13)[d]

a) Excess amount of Grignard reagents and halides were used, yields being based on the amount of hydrosilanes.
b) in Et_2O. c) The conversion is shown in parentheses.
d) Yields were not determined, although the products were separated and identified.

Table 2. NMR data of some organosilicon compounds

	τ values				
a b c d	a	b	c	d	e
$(CH_3)_3Si–Si(C_6H_5)_3$	9.79(s)	2.47—2.77(m)			
$(CH_3)_3Si–Si(C_6H_5)_2(H)$	9.72(s)	2.39—2.90(m)	5.24(s)		
$(CH_3)_3Si–Si(C_6H_5)_2(CH_3)$	9.85(s)	2.37—2.93(m)	9.41(s)		
$(CH_3)_3Si–Si(C_6H_5)(CH_3)_2$	9.95(s)	2.49—2.86(m)	9.67(s)		
$[(CH_3)_3Si]_2–Si(CH_3)_2$	10.00(s)	10.02(s)			
$(CH_3)_3Si–Si(CH_3)_2(CH_2–C_6H_5)$	9.99(s)	9.96(s)	7.89(s)	2.83—3.33(m)	
a b c d e					
$(CH_3)(C_6H_5)_2Si(CH_2–CH=CH_2)$	9.75(s)	2.39—2.82(m)	8.37(d)	3.88—4.59(m)	4.97—5.39(m)
$(CH_3)_2(C_6H_5)Si(CH_2–C_6H_5)$	9.55(s)	2.47—3.27(m)	7.40(s)		
$(CH_3)_2(C_6H_5)_2Si$	9.48(s)	2.38—2.88(m)			
$(CH_3)(C_6H_5)_2Si(C_4H_9$-*n*$)$	9.48(s)	2.27—2.82(m)	8.27—9.27(m)		

place smoothly in more basic solvents such as hexamethylphosphoramide (HMPA) or especially in THF. However, the formation of δ-hydroxybutylsilane due to the cleavage of THF by magnesium salts[5a,8] causes the lowering of the yields, competing with the condensation between Si-H and Si-Cl.

It would be of interest to assume the intermediacy of the "silyl Grignard reagent" in this reaction. However, hydrolysis with deuterium oxide after heating hydrosilanes and Grignard reagent in THF gave no deuterium-containing product.

The reaction was extended to the preparation of benzyl, allyl, and alkylsilanes.

$$Ph_nMe_{3-n}SiH + RX + i\text{-}PrMgCl \longrightarrow Ph_nMe_{3-n}SiR + MgXCl + C_3H_8$$

$$RX = PhCH_2Cl,\ CH_2=CHCH_2Cl,\ MeI,\ n\text{-}BuI$$

Results are shown in Table 1. All the products were separated by preparative GLC and identified by NMR. NMR data are given in Table 2.

Experimental

Alkyl chlorides were prepared from the corresponding alcohols by known methods. Triphenylsilane, diphenylsilane, and pentamethyldisilane were prepared by reduction with lithium aluminum hydride of the corresponding chlorosilanes. Diphenylmethylsilane was prepared by partial phenylation of methyldichlorosilane with phenylmagnesium chloride. All physical constants and GLC analyses confirmed the purity of the materials.

Typical Runs of Condensation. a) The Reaction of Diphenylmethylsilane with Trimethylchlorosilane: From a dropping funnel diphenylmethylsilane (2.5 g, 0.0125 mol) was added to the Grignard reagent prepared from isopropyl chloride (15.7 g, 0.20 mol) and magnesium (4.8 g, 0.20 mol) in THF in a three-necked flask. After refluxing for one hour, trimethylchlorosilane (22 g, 0.20 mol) was added to this solution, and additional refluxing was continued for 10 hr. By GLC analysis of the reaction mixture 1,1-diphenyltetramethyldisilane (1.32 g, 0.0049 mol) and diphenylmethylsilane (1.04 g, 0.0052 mol) were detected. After hydrolysis, however, an additional product identified to be δ-hydroxybutyldiphenylmethylsilane (0.44 g, 0.0016 mol), was obtained. It had n_D^{20}

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1.5685 (lit,[8] 1.5693, 1.5688). These products were separated by preparative glc and characterized by IR and NMR spectra and by the known physical constants.

b) The Reaction of Diphenylmethylsilane with Benzylchloride: By means of essentially the same procedure, diphenylmethylbenzylsilane (1.00 g, 0.00344 mol), mp 64°C was obtained from diphenylmethylsilane (2.5 g, 0.0125 mol) and benzyl chloride (2.50 g, 0.020 mol). The product was separated by glc.

An Attempt of Detection of a Silyl Grignard Reagent. In a three-necked flask were refluxed isopropylmagnesium chloride and diphenylmethylsilane for 20 hr in THF. After quenching with deuterium oxide, the product was separated by preparative glc. The silicon-deuterium bond in the compound could not be characterized by IR, NMR or mass spectra.

An Attempted Redistribution between Diphenylmethylsilane and Trimethylchlorosilane Catalyzed by Magnesium Bromide. Diphenylmethylsilane (2.5 g, 0.0125 mol) was heated with stirring in THF for 6 hr in the presence of magnesium bromide prepared *in situ* from magnesium (3.6 g, 0.15 mol) and 1,2-dibromoethane (9.4 g, 0.0125 mol). Diphenylmethylbromosilane was not detected by careful examination by glc. Trimethylchlorosilane (10.8 g, 0.1 mol) was then added to the mixture, which was heated for 4 hr. glc examination revealed that neither diphenylmethylchlorosilane nor 1,1-diphenyltetramethyldisilane was formed.

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