

Reaction of triphenylsilyllithium with some symmetrical acetals

The use of tetrahydrofuran as solvent for the lithium cleavage of hexaphenyldisilane has provided a facile preparation of triphenylsilyllithium¹. However, at elevated temperatures, the solvent was cleaved with the formation of (4-hydroxybutyl)triphenylsilane². Subsequently, triphenylsilyllithium was found to open epoxide rings, giving β -silyl alcohols³, and to react with other cyclic ethers, such as trimethylene oxide, giving the corresponding silyl alcohols⁴. Refluxing a 1,2-dimethoxyethane solution of triphenylsilyllithium gave high yields of methyltriphenylsilane. Similarly, a number of aryl methyl ethers were cleaved by triphenylsilyllithium to give methyltriphenylsilane and the corresponding phenol⁵. These studies suggested an examination of the reaction of triphenylsilyllithium with a related system, the acetals.

The R group of a Grignard reagent has been reported to replace one of the -OR' groups of an acetal to give a secondary ether*. In contrast, some organolithium reactions have employed acetals as solvents exploiting their inertness in basic media^{8,9}.

The acetals reacted with triphenylsilyllithium in this study were methylal (dimethoxymethane), diethyl formal (diethoxymethane), dimethyl acetal (1,1-dimethoxyethane) and acetal (1,1-diethoxyethane). One ketal, 2,2-dimethoxypropane, was studied also. The reactions were carried out in tetrahydrofuran at mild reflux temperature. After 60 h, the reaction mixture containing triphenylsilyllithium and methylal gave a negative Color Test I¹⁰. The major products isolated were methyltriphenylsilane (10.6% crude), (hydroxymethyl)triphenylsilane (9.96% crude) and (4-hydroxybutyl)triphenylsilane (11.5%). When dimethyl acetal was reacted with triphenylsilyllithium under similar conditions, the products isolated were methyltriphenylsilane (6.94% crude), 1-(triphenylsilyl)ethanol (3.95%), and (4-hydroxybutyl)triphenylsilane (13.3%). Acetal and diethyl formal did not appear to react with triphenylsilyllithium, and the only product isolated from these reactions was (4-hydroxybutyl)triphenylsilane. 2,2-Dimethoxypropane gave a trace of 2-(triphenylsilyl)-2-propanol and a large yield of (4-hydroxybutyl)triphenylsilane (32.4%). The reaction conditions and all products isolated are summarized in Table 1.

In all of the reactions, (4-hydroxybutyl)triphenylsilane arose through triphenylsilyllithium cleavage of the tetrahydrofuran solvent at elevated temperatures². Tetraphenylsilane was present as an impurity. Methyltriphenylsilane, from methylal and from dimethyl acetal, was formed by a cleavage of the carbon-oxygen bond in the same manner as it was in its formation from 1,2-dimethoxyethane³. Once the methyl group was removed, the resulting anion probably collapsed to form the aldehyde. Triphenylsilyllithium then reacted rapidly with the aldehyde to give the corresponding hydroxy compound.

Triphenylsilyllithium does not readily alkylate with groups much bulkier than methyl, except with highly reactive systems such as the phosphate esters¹¹. Removal of the more bulky ethyl groups from the ethyl acetals, diethyl formal and acetal, did not occur, and thus the hydroxy compound also could not form. Very little reaction occurred with the methyl ketal, 2,2-dimethoxypropane, as indicated by isolation of only a trace of the hydroxy compound. This points up the extreme steric sensitivity

* For a recent report, see ref. 6; for a general review, see ref. 7.

TABLE I

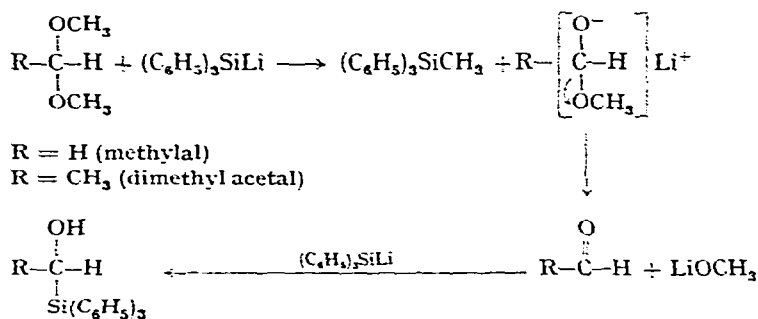
THE REACTION OF TRIPHENYLSILYL LITHIUM WITH SOME SYMMETRICAL ACETALS

Acetal	Temp. (°C)	Time (h)	Products (yield, %)
Methylal	50	36	CH ₃ SiPh ₃ (10.6 crude, 4.73 pure) Ph ₃ SiCH ₂ OH ¹³ (8.96 crude, 6.20 pure) Ph ₃ SiC ₄ H ₈ OH (11.5) Ph ₄ Si (0.94) Ph ₃ SiOH (2.90)
Dimethyl acetal	40	24	CH ₃ SiPh ₃ (6.94 crude)
	60	48	Ph ₃ SiCHOHCH ₃ ¹⁴ (3.95) Ph ₃ SiC ₄ H ₈ OH (13.3) Ph ₄ Si (1.19) Ph ₃ SiOH (2.18)
Diethyl formal	60	48	Ph ₃ SiC ₄ H ₈ OH (37.6)
	Reflux	48	Ph ₄ Si (1.40) Ph ₃ SiOH (1.45)
Acetal	60	48	Ph ₃ SiC ₄ H ₈ OH (40.1)
	Reflux	48	Ph ₄ Si (1.50)
2,2-Dimethoxypropane	50	24	Ph ₃ SiH (identified)
	60	24	Ph ₃ SiC(OH)(CH ₃) ₂ ¹⁵ (trace)
	Reflux	48	Ph ₄ Si (1.78) Ph ₃ SiOH (2.17) Ph ₃ SiC ₄ H ₈ OH (32.4)

* Reaction times were dictated by the length of time necessary to obtain a negative Color Test I¹⁰.

of reactions involving triphenylsilyllithium, an observation noted previously in the reaction of triphenylsilyllithium with some alkyl aryl ethers⁵.

An attempt was made to prepare triphenylsilyllithium using acetal as the solvent; however, hexaphenyldisilane was not cleaved by lithium at room tempera-



ture or at elevated temperatures. Reaction of chlorotriphenylsilane with lithium did not occur at room temperature, but at elevated temperatures a small amount (28.8%) of crude hexaphenyldisilane was isolated. It appears that the acetals will not be suitable solvents for the preparation of silylmetallic reagents. This is in contrast to the recent report of the preparation of (methoxymethyl)lithium in methylal solvent¹².

Experimental

All melting points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride. The acetals were Eastman White Label Grade Chemicals. Infrared spectra of these acetals showed no evidence of carbonyl groupings.

Triphenylsilyllithium with methylal. The following reaction and work-up conditions are typical of the techniques used for the reactions summarized in Table I. A tetrahydrofuran solution of 0.05 mole of triphenylsilyllithium was added slowly to a solution of 3.80 g (0.05 mole) of methylal and 50 ml of tetrahydrofuran. The reaction mixture was warmed at 50° with stirring. After 24 h, Color Test I¹⁰ was slightly positive, but became negative after 36 h. Hydrolysis was carried out with concentrated ammonium chloride solution. The layers were separated and the organic layer dried over anhydrous sodium sulfate. Evaporation of the solvent left a yellow tarry residue which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60–70°) gave 1.45 g (10.6%) of crude methyltriphenylsilane melting over the range 53–64°. Several recrystallizations from ethanol gave 0.65 g (4.73%) of pure material, m.p. 65–67°, which showed no depression when admixed with an authentic sample. Further elution of the column with the same solvent gave, subsequent to recrystallization from ethyl acetate, 0.13 g (0.94%) of tetraphenylsilane, m.p. 230–233° (mixture melting point, infrared spectra comparison). Still further elution with the same solvent gave 1.30 g (8.96%) of crude (hydroxymethyl)triphenylsilane¹³, 108–115° melting range. Recrystallization from petroleum ether (b.p. 80–110°) gave 0.90 g (6.20%) of pure product, m.p. 116–117.5° (mixture melting point, infrared spectra comparison).

Elution of the column with benzene gave 1.90 g (11.5%) of (4-hydroxybutyl)triphenylsilane, m.p. 107–109° after recrystallization from petroleum ether (b.p. 80–110°) (mixture melting point, infrared spectra comparison). Further elution with benzene gave, subsequent to recrystallization from petroleum ether (b.p. 80–110°), 0.40 g (2.90%) of triphenylsilanol, m.p. 150.5–152° (mixture melting point).

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PRELIMINARY NOTE

The cleavage of tetraphenylsilane by Raney nickel

Raney nickel catalysts have been used frequently to hydrogenate organic groups bonded to silicon¹. A relevant example² is the preparation of tetracyclohexylsilane by the hydrogenation of tetraphenylsilane in the presence of W-7 Raney nickel at 100° and 60-100 atm.

We have found that tetraphenylsilane reacts with excess Raney nickel at atmospheric pressure and at temperatures between *ca.* 20° and 101° to give benzene and cyclohexane. Thus, a solution of tetraphenylsilane (0.018 mole) in boiling dioxane (200 ml; containing *ca.* 10% methanol) was treated for four hours with W-7 Raney nickel³ (prepared from 125 g of 1:1 nickel-aluminium alloy; washed first with methanol and then with dioxane) to give 17% benzene and 49% cyclohexane*. The same quantity of catalyst reacted with 0.015 mole of tetraphenylsilane at room temperature during 48 hours to give 35% benzene and 2% cyclohexane*; 60% of the silane was recovered. Catalysts containing less hydrogen (*e.g.*, W-1 Raney nickel⁴) gave more benzene and less cyclohexane without lowering the total yield of these hydrocarbons, indicating that the primary product of the hydrogenolysis of tetraphenylsilane was benzene. By-products isolated in yields below 1% include biphenyl, triphenylsilanol, and tetracyclohexylsilane. The fate of the silicon atom in this reaction has not been determined, but *ca.* 50% of the silicon introduced as silane was found in the residue left after digestion of the spent catalyst with hydrochloric acid**. Silicon hydrides were not detected*, but in view of the alkaline nature of the catalyst (*cf.* ref. 3) this was not to be expected⁵.

We have also measured the poisoning coefficient⁶ of tetraphenylsilane⁷ (0.11) and conclude that chemisorption of this compound occurs mainly via the silicon atom, as for electronic⁸ and steric reasons adsorption involving one of the phenyl groups should be less favoured than, for example in triphenylamine (poisoning co-

* Determined by gas chromatography using a 12-foot column packed with B.D.S. (10%) on gaschrom P.

** This determination was carried out by Dr. K. NORRISH with a vacuum fluorescent X-ray spectrograph on a sample fused in lithium borate glass.