[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Reactions of Triphenylsilane and Triphenyltin Hydride

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Previous reports[1a,b] have shown that triethylsilane reacts with organolithium compounds in ether to form tetrasubstituted silanes and lithium hydride. We are now reporting that the reaction of triphenylsilane with phenylithium, methyllithium and *n*-butyllithium resulted in the formation of tetraphenylsilane, methyltriphenylsilane and *n*-butyltriphenylsilane, respectively, in good yields. These reactions may be formulated as

$$(C_6H_5)_3SiH + RLi \longrightarrow (C_6H_5)_3SiR + LiH$$

It is interesting to note that some tetraphenylsilane was formed in the reaction with *n*-butyllithium, possibly as a consequence of disproportionation,[2] even under these mild conditions. However, lithium *p*-thiocresoxide was without effect on triphenylsilane when these reactants were heated in ether.

The extent of the reaction between triphenylsilane and phenylmagnesium bromide appeared to be insignificant, for 90% of the silane was recovered. Since it has been shown that the reactivity of Grignard reagents is increased when dioxane is added to their solutions,[3] triphenylsilane was treated with a phenylmagnesium bromide solution containing this compound. Apparently reaction was inappreciable because triphenylsilane was recovered to the extent of 90%.

In extending the examination of the reaction of organolithium compounds to other similar hydrides of Group IV elements, it was found that triphenyltin hydride reacts with phenyllithium to form tetraphenyltin (90%) and lithium hydride.

Pape[4] obtained tetrapropylsilane as well as the expected tripropylsilane when trichlorosilane and dipropylzinc were heated in a sealed tube at 150° for six hours. He wrote an equation to account for the transformations

$$\begin{aligned}&2SiHCl_3 + 4Zn(C_3H_7)_2 \longrightarrow \\ &\quad SiH(C_3H_7)_3 + Si(C_3H_7)_4 + 3ZnCl_2 + Zn + C_3H_8\end{aligned}$$

The formation of tetrapropylsilane along with free zinc and propane might be explained by a reducing action of the Si–H bond in tripropylsilane. It appears not unlikely, however, that the tetrapropylsilane may have been formed by a reaction similar to that described with RLi compounds. Organometallic compounds differ largely in rate of reaction rather than in kind of reaction,[5] and the forced conditions used by Pape may have been the determining factor in the results obtained by him. Inasmuch as Grignard reagents lie between organolithium and organozinc compounds in reactivity, it is probable that they also would react like organolithium compounds under appropriate conditions.

In order to determine whether triphenylsilane is a reducing agent, a solution of it in xylene was heated with acridine.[6] No products that might be formed by such a reduction were isolated.

It is highly probable that R_3GeH and R_3PbH[7] compounds would react like the corresponding silicon and tin compounds. However, triphenylmethane is known to react as follows with RLi compounds

$$(C_6H_5)_3CH + RLi \longrightarrow (C_6H_5)_3CLi + RH^{8}$$

Experimental

Triphenylsilane.—This compound was prepared in essential accordance with the directions of Reynolds, Bigelow and Kraus.[9] Our yield was 88% in a preparation starting with 0.62 mole of trichlorosilane. Hydrolysis was effected by pouring the reaction mixture on cracked ice containing sulfuric acid. Inasmuch as this compound melted at 44–45° instead of 36–37°[9] after two recrystallizations from 95% ethanol, it was analyzed.

Anal. Calcd. for $C_{18}H_{16}Si$: Si, 10.77. Found: Si, 10.67, 10.72.

Triphenyltin Chloride.—Triphenyltin chloride was prepared by a modification[10] of the procedure of Kocheshkow, Nadi and Aleksandrow[11] from 55 g. (0.1785 mole) of tetraphenyltin and 11.2 g. (0.0429 mole) of stannic chloride. The yield of triphenyltin chloride, melting at 103–104°, was 47.2 g. (72%). Repeated recrystallization from petroleum ether (b. p. 77–115°) did not raise the melting point.

Triphenyltin Hydride.—Triphenyltin chloride instead of the bromide was used in the preparation of this compound.[12] From 20 g. (0.0518 mole) of triphenyltin chloride was obtained 1.5 g. (8.3%) of triphenoltin hydride. In a second run, using 17.8 g. (0.046 mole) of triphenyltin chloride, the yield was 6.8 g. (42%) of triphenyltin hydride. The compound was purified by distillation *in vacuo* in an apparatus previously swept with nitrogen. No percentage yield was reported by the earlier workers.[12]

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(1) (a) Gilman and Massie, THIS JOURNAL, **68**, 1128 (1946); (b) Meals, *ibid.*, **68**, 1880 (1946); U. S. Patent 2,444,784, *C. A.*, **42**, 7317 (1948).

(2) Ladenberg, *Ann.*, **173**, 159 (1873); Calingaert, Soroos and Hnizda, THIS JOURNAL, **62**, 1107 (1940); Calingaert and Beatty, Chap. 24 in Gilman's "Organic Chemistry," 2nd. Edition, John Wiley and Sons, Inc., New York, N. Y., 1943.

(3) Bergman and Rosenthal, *J. prakt. Chem.*, [2] **135**, 267 (1932); Gilman and Gainer, THIS JOURNAL. **69**, 877 (1947).

(4) Pape, *Ber.*, **14**, 1873 (1881).

(5) For a discussion of relative reactivities of organometallic compounds, see Chap. 5 of Gilman, "Organic Chemistry," 2nd. Edition, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 518–524.

(6) J. L. Towle, in unpublished studies, has shown that thiols, under these conditions, will reduce acridine and related compounds. See, also, Gilman and Dickey, THIS JOURNAL, **52**, 4573 (1930).

(7) Compounds of the type R_3PbH have not been isolated. See Gilman and Bailie, *ibid.*, **61**, 731 (1939).

(8) Gilman and Young, *J. Org. Chem.*, **1**, 330 (1936).

(9) Reynolds, Bigelow and Kraus, THIS JOURNAL, **51**, 3070 (1929). See, also, Jenkins, Lavery, Guenther and Post, *J. Org. Chem.*, **13**, 862 (1948), for the most recent account of the preparation of R_3SiH types.

(10) The authors are grateful to C. E. Arntzen (Doctoral Dissertation, Iowa State College) for these directions.

(11) Kocheshkow, Nadi and Aleksandrow, *Ber.*, **67**, 1348 (1934).

(12) Chambers and Scherer, THIS JOURNAL, **48**, 1059 (1926).

Triphenylsilane and Phenyllithium.—To 26 g. (0.1 mole) of triphenylsilane dissolved in 50 ml. of ether was added 0.1 mole of phenyllithium in 107 ml. of ether with the immediate formation of a white precipitate. At the end of the addition Color Test I[13] was negative. A portion of the precipitate was removed and analyzed as described under "Identification of Lithium Hydride." Subsequent to hydrolysis and recrystallization from benzene, there was obtained 30.3 g. (90%) of tetraphenylsilane, m. p. 230–232°.

Anal. Calcd. for $C_{24}H_{20}Si$: Si, 8.33. Found: Si, 8.3, 8.3.

Triphenylsilane and Methyllithium.—Triphenylsilane (0.044 mole) and 0.044 mole of methyllithium were interacted as described above. After working up the reaction mixture in the customary manner and recrystallizing the product from ethanol, 11.6 g. (93%) of methyltriphenylsilane, m. p. 66–67°,[14] was obtained. This product was identified by the method of mixed melting points.

Triphenylsilane and *n*-Butyllithium.—To 0.05 mole of triphenylsilane dissolved in 25 ml. of ether was added 0.045 mole of *n*-butyllithium in 70 ml. of ether. Color Test I[13] was negative after one-half hour. After hydrolysis, the hydrolysate was extracted with hot benzene. The benzene layer was separated, dried and the solvent removed by distillation. The residue, a gummy material, was extracted with 95% ethanol and the solid remaining was shown to be tetraphenylsilane (10.7% of the product). From the ethanol was obtained 10 g. (63.5%) of *n*-butyltriphenylsilane melting at 86°. Disproportionation[2] has been reported to occur among silicon compounds, and this phenomenon might account for the formation of tetraphenylsilane.

Anal. Calcd. for $C_{22}H_{19}Si$: Si, 8.86. Found: Si, 8.67, 8.72.

Triphenylsilane and Phenylmagnesium Bromide.—Three experiments in which triphenylsilane was treated with phenylmagnesium bromide were carried out. In the first, 0.023 mole of phenylmagnesium bromide and 0.031 mole of triphenylsilane were refluxed in ether for twenty-four hours. In the second, 0.0154 mole of triphenylsilane in 15 ml. of ether was treated with 0.012 mole of phenylmagnesium bromide in 10 ml. of ether. Most of the ether was removed by distillation and replaced with 20 ml. of dry xylene in which the reactants were refluxed for twenty-four hours. In the third, a mixture of 0.022 mole of phenylmagnesium bromide containing 3 ml. of dioxane and 0.019 mole of triphenylsilane was stirred at room temperature for twenty-four hours. In each case, Color Test I[13] was positive at the end of the reaction time. The quantities of triphenylsilane recovered were 7.4 g. (92.5%), 3.5 g. (88%) and 4.5 g. (90%), respectively.

Triphenyltin Hydride and Phenyllithium.—In the first of two runs of this reaction, 0.0043 mole of triphenyltin hydride was treated with 0.0044 mole of phenyllithium, a precipitate being formed at once. Then 0.0044 mole of benzyl chloride was added to react with any triphenyltinlithium that might have formed. On hydrolysis an ether-insoluble solid separated. This was collected on a filter, washed with five 5-ml. portions of ether and dried over sulfuric acid in a vacuum desiccator. The yield of tetraphenyltin melting at 228–230° (mixed m. p., 228–230°) was 1.7 g. (91%). In the second run, using 0.0117 mole of triphenyltin hydride, 0.0119 mole of phenyllithium and 0.0119 mole of benzyl chloride, a portion of the solid formed was analyzed as described under "Identification of Lithium Hydride." Subsequent to working up the mixture, the yield of tetraphenyltin was 4.5 g. (90%).

Identification of Lithium Hydride.—When triphenylsilane and triphenyltin hydride, respectively, were treated with phenyllithium, a white precipitate immediately formed. In each case the solid was allowed to settle and the ether decanted in a nitrogen atmosphere. The residue was then centrifuged for one and one-half hours and the supernatant ether was decanted. The solid was twice washed with anhydrous ether, centrifuged, and the ether decanted. The residual solvent was removed by heating the solid on a steam-bath *in vacuo*. The combined ether washings completely distilled at 36–38°, indicating the absence of benzene.

A sample of the dried precipitate was hydrolyzed, the solution was titrated for total alkalinity, and the solid residue was recovered. From 1.4300 g. of the solid formed in the reaction between triphenylsilane and phenyllithium was obtained 1.3968 g. of residue, identified as tetraphenylsilane. The total alkali, 0.00415 mole, was in agreement with the loss in weight of the sample (0.0332 g.) when this was calculated as lithium hydride (0.00418 mole). On hydrolysis of 0.2895 g. of the precipitate formed in the reaction between triphenyltin hydride and phenyllithium, 0.2842 g. of solid residue, identified as tetraphenyltin, was recovered. The total alkali (0.00067 mole) again checked with the loss in weight of the sample (0.0053 g.) when this was calculated as lithium hydride (0.00067 mole).

Triphenylsilane with Acridine, and with Lithium *p*-Thiocresoxide.—Twenty-six grams (0.11 mole) of triphenylsilane and 4.8 g. (0.027 mole) of acridine were dissolved in 80 ml. of dry xylene under nitrogen connected to a trap,[15] and the solution refluxed for thirty hours. On cooling, a solid was formed. This was dissolved in acetone and treated with ethanolic hydrogen chloride to precipitate acridine hydrochloride which, in turn, was treated with 10% sodium hydroxide to liberate the base. The base was recrystallized from ethanol, and 4.7 g. (98%) of acridine, melting at 106°, was recovered. No depression occurred when a mixed melting point determination with an authentic specimen was made. From the acetone solution 24.7 g. (95%) of triphenylsilane was obtained.

Lithium *p*-thiocresoxide was prepared from 5 g. (0.04 mole) of *p*-thiocresol in 20 ml. of ether and 0.036 mole of phenyllithium in ether. Color Test I[13] was negative at the end of the addition, and a solid separated. Then was added 7.8 g. (0.03 mole) of triphenylsilane dissolved in 25 ml. of ether. The mixture was refluxed, by external heating, for twenty-four hours with stirring. After working up the mixture, 7.5 g. (95%) of triphenylsilane was recovered. From the aqueous layer, 4.4 g. (88%) of *p*-thiocresol (mixed m. p.) was obtained.

Summary

The reaction between triphenylsilane and some organolithium compounds has been investigated, and it has been shown that the reaction which takes place is

$$(C_6H_5)_3SiH + RLi \longrightarrow (C_6H_5)_3SiR + LiH$$

A similar reaction occurs with triphenyltin hydride. Under corresponding conditions, phenylmagnesium bromide seems to be without effect in this type of reaction with triphenylsilane.

Disproportionation appears to occur in the reaction between triphenylsilane and *n*-butyllithium, inasmuch as some tetraphenylsilane was obtained in addition to the expected *n*-butyltriphenylsilane.

Triphenylsilane did not reduce acridine, nor did it react with lithium *p*-thiocresoxide.

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[13] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[14] Marsden and Kipping, *J. Chem. Soc.*, **93**, 198 (1908).

[15] Gilman and Hewlett, *Rec. trav. chim.*, **48**, 1124 (1929).