[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE GENERAL ELECTRIC COMPANY]

The Alkylation of Triethylsilane

BY ROBERT N. MEALS[1]

In the course of attempts to prepare triethylsilyllithium, it was discovered that triethylsilane reacted smoothly with butyllithium to give butyltriethylsilane. Further investigation showed that this was a general reaction for organolithium compounds. The solid by-product was isolated in one instance, and was found to behave like lithium hydride. The reaction therefore appears to be

$$(C_2H_5)_3SiH + RLi \longrightarrow (C_2H_5)_3SiR + LiH$$

Diethyl ether was a suitable reaction medium, but low-boiling petroleum ether either inhibited or failed to catalyze the reaction. This agrees with the general greater reactivity of organolithium compounds in ethers than in hydrocarbon solvents.

In this reaction the hydrogen attached to silicon splits off as hydride ion. Some previously reported reactions may be interpreted in this light, and a parallel may be drawn with the reactions of triethylsilane with water in the presence of alkalies,[2] with alcohol in the presence of lithium ethoxide, and with ammonia and amines in the presence of lithium amides.[3] It seems possible that hydrides are formed in all the above cases, but that they react with active hydrogen in the solvent, regenerating the base and liberating hydrogen gas. The proposed steps are

$$\begin{aligned} R_3SiH + MX &\longrightarrow R_3SiX + MH \\ MH + HX &\longrightarrow MX + H_2 \end{aligned}$$

where X can be OH, OC_2H_5, NH_2 or NHC_2H_5. Some attempts to use other anions were unsuccessful.

Pape[4] obtained tetrapropylsilane as well as tripropylsilane from trichlorosilane and dipropylzinc at 150°. Others reported no replacement of hydrogen by alkyl under milder conditions.[5] The relationship of Pape's reaction to the one described here is uncertain.

Experimental

Triethylsilane[3,6] was prepared by the addition of ethyldichlorosilane to an excess of ethylmagnesium chloride in ether. The yield was 50–55%, b. p. 109° at 755 mm., $d^{26.5}$ 0.744, $n^{25}{}_D$ 1.0492. The ethyldichlorosilane used in this synthesis was made by the action of ethyl chloride on copper silicon[7,8] at 300°. This reaction went readily. On the average about 10 or 20% of the liquid product was ethyldichlorosilane. The structure of this new compound was confirmed by independent synthesis from trichlorosilane and one mole of ethylmagnesium chloride. Both preparations boiled at 75.4° at 767 mm.; the absence of refraction lines on mixing indicated that they had the same refractive index.

Anal. Calcd. for $C_2H_6Cl_2Si$: Cl, 54.96. Found: Cl, 54.5. Dr. Robert O. Sauer hydrolyzed 0.333 g. of the liquid, using 15 ml. of water and 10 ml. of dioxane. The addition of concentrated sodium hydroxide and some dibutyl ether caused the evolution of 59.6 ml. of hydrogen at 749 mm. and 302°K. Calcd. for $C_2H_6Cl_2Si$: H attached to Si, 0.775. Found: H attached to Si, 0.72.

Reaction with Butyllithium.—Fifteen grams (0.13 mole) of triethylsilane and 0.13 mole of *n*-butyllithium in diethyl ether gave a very faint color test[9] after twenty-three hours of refluxing. Ethyl bromide was then added in order to characterize triethylsilyllithium if it formed.[3] After several hours the mixture was hydrolyzed, washed and dried. The principal fraction was 13 g. (58%) of liquid distilling at 190–192°, $d^{27.6}$ 0.777, $n^{27.6}{}_D$ 1.4308. Butyltriethylsilane[10,11] boils at 190.5–191.5° at 761.2 mm., $d^{27.6}{}_4$ 0.7743. $n^{20}{}_D$ 1.4348.

Reaction with Propyllithium.—A solution of 15 g. (0.13 mole) of triethylsilane and 0.2 mole of *n*-propyllithium in petroleum ether (b. p. 35–55°) was refluxed for forty-seven hours. Nine grams of triethylsilane was recovered after hydrolysis. There was no trace of propyltriethylsilane.

In diethyl ether, 11.2 g. of triethylsilane (0.097 mole) and 0.08 mole of *n*-propyllithium, after being refluxed for twenty-two hours, gave no apparent reaction with ethyl bromide. After hydrolysis there were obtained 9.4 g. (74.5%) of a liquid distilling in the range 167–173°, d^{25} 0.809, $n^{25}{}_D$ 1.4247. Propyltriethylsilane[10,11] boils at 172.4–172.8° at 760.4 mm., $d^{25}{}_4$ 0.7684, $n^{20}{}_D$ 1.4308.

Reaction with Phenyllithium.—After twenty-five hours of refluxing, 17 g. of triethylsilane (0.146 mole) and 0.15 mole of a filtered solution of phenyllithium in diethyl ether yielded 22.8 g. (81%) of product boiling at 236.5° at 762 mm., $d^{26.3}$ 0.883, $n^{26.3}{}_D$ 1.4990. Phenyltriethylsilane[10,12] boils at 238.3–238.5° at 762.1 mm., $d^{26.3}{}_4$ 0.8864.

The white powder which formed during the reaction was filtered off before hydrolysis. It reacted vigorously with water to give hydrogen and an alkaline solution.

Reaction with Ethanol.—One gram (0.14 g. atom) of lithium was dissolved in 50 ml. of absolute ethanol. This solution was then heated with 25 g. (0.22 mole) of triethylsilane for three hours, during which hydrogen was steadily evolved. The product was hydrolyzed with water and acetic acid, and the water-insoluble portion was washed, dried and fractionated. No triethylsilane was recovered. The chief product was 25.5 g. (74%) of a liquid which distilled at 154–155°, $d^{25.5}$ 0.8310, $n^{25.5}{}_D$ 1.4914. This product was readily soluble in cold concentrated sulfuric acid, and hydrolysis of this solution gave a mixture with the camphor-like odor of triethylsilanol. Ethoxytriethylsilane[13] boils at 154°, d^0 0.84.

Miscellaneous.—Triethylsilane did not react with lithium acetate in glacial acetic acid; with lithium in *t*-

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[1] Present address: Buckman Laboratories, Memphis, Tenn.

[2] Kipping, *Proc. Roy. Soc.* (London), **A159**, 139 (1937).

[3] Kraus and Nelson, THIS JOURNAL, **56**, 195 (1934).

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

[5] Stock and Somieski, *ibid.*, **52**, 695 (1919).

[6] Ladenburg, *Ann.*, **164**, 300 (1872).

[7] Rochow, THIS JOURNAL, **67**, 963 (1945).

[8] Rochow, U. S. Patent 2,380,995; Rochow and Patnode, U. S. Patent 2,380,996; Sprung and Gilliam, U. S. Patent 2,380,998; Patnode and Schiessler, U. S. Patent 2,381,000.

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

[10] Bygdén, *Ber.*, **45**, 707 (1912); Inaug. Dissert. Upsala (1916) (*C. A.*, **14**, 1975 (1920)). The density given here was interpolated from the latter reference.

[11] Whitmore, Sommer, DiGiorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, THIS JOURNAL, **68**, 475 (1946).

[12] Ladenburg, *Ann.*, **173**, 158 (1872) gave b. p. 230°.

[13] Goddard, in Friend's "Text Book of Inorganic Chemistry," Vol. 11, Part 1, Griffin, London, 1928, p. 263.

butyl alcohol; or with *n*-butylsodium in petroleum ether (b. p. 35-55°).

Summary

1. Triethylsilane reacts with alkyl and aryllithium compounds in diethyl ether to give tetrasubstituted silanes.

2. No reaction occurs between triethylsilane and propyllithium or butylsodium in low-boiling petroleum ether.

3. Triethylsilane and ethanol in the presence of lithium ethoxide give ethoxytriethylsilane.

4. Ethyldichlorosilane has been prepared by direct action of ethyl chloride on copper silicon.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

New Alpha and Beta Chloroalkyl Silanes. Further Studies on the Alpha Silicon Effect[1]

BY L. H. SOMMER, D. L. BAILEY, W. A. STRONG AND F. C. WHITMORE

In continuation of work on the synthesis and properties of chloroalkyl silanes, we have prepared the monochlorinated triethylchlorosilanes and triethylfluorosilanes. The alpha C–Cl compounds have been used to prepare some new neosilicon chlorides (chlorides containing silicon attached to four carbon atoms). These have been used in a further study of the alpha silicon effect.[2]

Triethylchlorosilane was prepared from a concentrated sulfuric acid solution of hexaethyldisiloxane and ammonium chloride.[1] Triethylfluorosilane was prepared by a similar method, using ammonium fluoride. Chlorination of these compounds with sulfuryl chloride activated by benzoyl peroxide gave excellent yields of the following monochlorinated products.[3]

	$(CH_3CHCl)(C_2H_5)_2SiX$	$(ClCH_2CH_2)(C_2H_5)_2SiX$
X = Cl	I	II
X = F	III	IV

Experimental

Chlorinations.—In a 1-liter round-bottomed flask there were placed 411 g. (2.7 moles) of triethylchlorosilane, 297 g. (2.2 moles) of sulfuryl chloride and 2 g. of benzoyl peroxide. The flask was fitted with an efficient reflux condenser and the system was protected from moisture by a phosphorus pentoxide tube. The reactants were then heated on the steam-bath, resulting in a vigorous evolution of sulfur dioxide and hydrogen chloride. After four hours of refluxing, the reaction product was distilled in a column of 20 theoretical plates. In addition to unreacted triethylchlorosilane, 183.5 g. (1.2 moles), there were obtained: 99.5 g. (0.5 mole) of I, b. p. 114° (100 mm.); and 72.5 g. (0.4 mole), of II, b. p. 132° (100 mm.). This represents a 60% yield of monochlorinated products based on the unrecovered starting material. Compounds (I) and (II) were analyzed for chlorine content by fusion with sodium peroxide and sucrose in a Parr bomb followed by Volhard titration for chloride ion.

Anal. Calcd. for $C_6H_{14}SiCl_2$: Cl, 38.3. Found: for I, 38.2; for II, 38.6.

A similar procedure was used for the synthesis of III and IV. Chlorination of 463 g. (3.5 moles) of triethylfluorosilane gave: 195 g. (1.5 moles) of unreacted triethylfluorosilane; 113 g. (0.7 mole) of III, b. p. 93° (113 mm.); and 91 g. (0.6 mole) of IV, b. p. 101° (77 mm.). This is a 60% yield of monochlorinated products based on the unrecovered triethylfluorosilane.

Anal. Calcd. for $C_6H_{14}SiFCl$: Cl, 21.0. Found: for III, 20.9; for IV, 21.2.

Alkali Titrations of Compounds I–IV.—Compounds I–IV were titrated with 0.2 *N* alkali in the following manner: Weighed samples were added to 20 cc. of methanol and excess alkali, followed by back-titration with standard acid. Titration of I and III gave neutral equivalents 183 and 168, respectively. The calculated neutral equivalents corresponding only to halogen attached to silicon are 185 and 168, respectively. Titration of II and IV gave neutral equivalents 95 and 85, respectively. The calculated neutral equivalents corresponding to halogen attached to carbon and to silicon (total halogen) are 93 and 84, respectively.

The alpha C–Cl bonds were left intact. The beta C–Cl bonds were broken to the extent of 98%. The formation of ethylene in this reaction,[4] and in the reactions of these compounds with other reagents, is being further studied.

α-Chloroethyldiethylsilanol, $(CH_3CHCl)Et_2SiOH$. (V).—Compounds I and III gave this compound with dilute alkali. In a 1-liter separatory funnel there were placed 60 g. (0.32 mole) of I, 200 g. of cracked ice, and 20 g. (0.5 mole) of sodium hydroxide pellets. Shaking resulted in a considerable evolution of heat which melted the ice and made external cooling necessary. After thirty minutes, the reaction product was extracted with 150 cc. of ether in three portions and the ether extracts were washed with water and dried over anhydrous magnesium sulfate. Upon removal of the ether by distillation, the residual liquid (53 g.) was distilled in a column of 20 theoretical plates. There was obtained 44 g. (0.27 mole) of α-chloroethyldiethylsilanol, b. p. 101° (29 mm.), a yield of 84%. This compound was analyzed for chlorine content in the usual manner.

Anal. Calcd. for $C_6H_{14}ClSiOH$: Cl, 21.3. Found: Cl, 21.0.

A similar treatment of III gave an 82% yield of the same silanol.

α-Chloroethyldiethylsilanol is the first example of a chloroalkyl silanol. Its synthetic possibilities are being developed. No disiloxane was formed in the above reactions, indicating that this silanol is exceptionally stable toward intermolecular dehydration.[5]

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(1) Paper VII on organo-silicon compounds. For VI see Di Giorgio, Strong, Sommer and Whitmore, THIS JOURNAL, **68**, 1380 (1946).

(2) Whitmore and Sommer, *ibid.*, **68**, 481 (1946).

(3) Kharasch and Brown, *ibid.*, **61**, 2142 (1939); see (a) Sommer and Whitmore, *ibid.*, **68**, 485 (1946); (b) Sommer, Dorfman, Goldberg and Whitmore, *ibid.*, **68**, 488 (1946).

(4) For similar β-eliminations involving silicon see Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, **68**, 1083 (1946). (Paper V).

(5) (a) In the preparation of triethylsilanol from triethylchlorosilane, a special method of hydrolysis must be used to avoid formation of large amounts of hexaethyldisiloxane (unpublished work of Sommer, Pietrusza and Whitmore); (b) Krieble and Elliott [THIS JOURNAL, **67**, 1810 (1945)] have reported that hydrolysis of chloromethyldimethylchlorosilane gives the disiloxane exclusively.