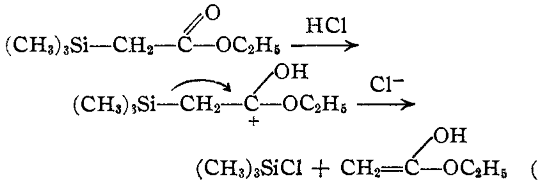
ion. The Si–C bond is broken and a new bond between silicon and hydroxyl is formed. The inertness of this ester to water is likely due to a concentration of either hydroxyl or hydrogen ions insufficient to permit the operation of mechanisms (2) or (3). Reaction with ethanol may be attributed in part to the homogeneity of the system.

The action of anhydrous hydrogen chloride upon ethyl trimethylsilylacetate may be pictured by mechanism (4).



$$(CH_3)_3Si{-}CH_2{-}C(=O){-}OC_2H_5 \xrightarrow{HCl} (CH_3)_3Si{-}CH_2{-}\overset{+}{C}(OH){-}OC_2H_5 \xrightarrow{Cl^-} (CH_3)_3SiCl + CH_2{=}C(OH){-}OC_2H_5 \quad (4)$$

Reaction with bromine may involve nucleophilic attack on silicon by the negative part of a bromine molecule, resulting in the rupture of the Si–C bond (Si/:C) and combination of Br^+ with the resulting negative fragment.

The above reaction mechanisms are made possible by the electropositive nature of silicon compared to carbon.[10]

Summary

1. Ethyl trimethylsilylacetate has been synthesized from ethyl chloroformate and the Grignard reagent of chloromethyltrimethylsilane.[5]

2. Reagents such as dilute, hot hydrochloric acid, dilute alkali, hydrogen chloride gas, bromine and hot absolute ethanol cleave the Si–C bond of this ester.

3. Possible mechanisms for these reactions are advanced.

STATE COLLEGE, PA. RECEIVED DECEMBER 22, 1947

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

t-Butylsilicon Compounds[1,2]

BY LESLIE J. TYLER,[3] LEO H. SOMMER AND FRANK C. WHITMORE

Although alkyl silicon compounds have been known for more than eighty years,[4] the synthesis of the first tertiary alkyl silicon compound was reported only recently.[5] In a subsequent paper the synthesis of 1,1,2-trimethylpropyltrichlorosilane by the addition of trichlorosilane to tetramethylethylene has been reported.[6]

Numerous unsuccessful attempts to prepare such compounds by the treatment of a *t*-alkyl Grignard reagent with silicon tetrachloride, ethyl orthosilicate, triethylchlorosilane, trimethylchlorosilane, trimethylbromosilane or trimethyliodosilane have been made in this Laboratory during the past six years under a wide range of conditions.

This paper reports the preparation of *t*-butyltrichlorosilane and some of its derivatives. *t*-Butyltrichlorosilane was prepared from *t*-butyllithium and silicon tetrachloride.[7] The purpose of this synthesis was to determine the effect of the presence of the *t*-butyl group on the reactivity of the silicon–chlorine bond.

It was found that *t*-butyltrichlorosilane behaves similarly to other alkyltrichlorosilanes with methylmagnesium bromide.[8] With this reagent *t*-butyltrimethylsilane was the product. It was also found that the silicon–chlorine bonds are quantitatively hydrolyzed by sodium hydroxide if a methanol solution of *t*-butyltrichlorosilane is used. In the absence of methanol, reaction is incomplete (58%).

The peroxide-catalyzed chlorination of *t*-butyltrichlorosilane with sulfuryl chloride[9] proceeded smoothly to give the one possible monochlorinated product, chloro-*t*-butyltrichlorosilane (α,α-dimethyl-β-chloroethyltrichlorosilane). This compound, when dissolved in methanol, titrates quantitatively with 0.1 *N* alkali for total chlorine with the evolution of isobutylene.

$$ClCH_2C(CH_3)_2SiCl_3 \xrightarrow{OH^-} CH_2{=}C(CH_3)_2 + Si(OH)_4 + 4Cl^-$$

Essentially, then, the β-elimination reaction with alkali of the chlorine β to silicon in this compound is not appreciably hindered by the presence of the two α-methyl groups. This is in agreement with the proposed mechanism of such β-elimination reactions which involve initial nucleophilic attack on silicon.[10]

As indicated above, our unsuccessful attempts to prepare *t*-alkyl silicon compounds by means of the *t*-butyl Grignard reagent revealed the relative inactivity of the latter in these preparations. Similarly we have found that *t*-butyllithium is much less reactive toward the silicon–chlorine

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[1] Paper XIX in a series on organosilicon compounds. For Paper XVIII see THIS JOURNAL, **70**, 2874 (1948).

[2] Taken from work submitted by Leslie J. Tyler to the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree.

[3] American Chemical Society Pre-doctoral Fellow, 1946–1949.

[4] Friedel and Crafts, *Ann.*, **127**, 31 (1863).

[5] Tyler, Sommer and Whitmore, THIS JOURNAL, **69**, 981 (1947).

[6] Pietrusza, Sommer and Whitmore, *ibid.*, **70**, 484 (1948).

[7] The use of organolithium compounds in the preparation of organosilicon compounds has been reported recently. See (a) Fleming and Laurens, U. S. Patent 2,386,452 (1945); *C. A.*, **40**, 603 (1946); (b) Gilman and Clark, THIS JOURNAL, **68**, 1675 (1946); (c) Gilman and Clark, *ibid.*, **69**, 1499 (1947).

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

[9] Sommer and Whitmore, *ibid.*, **68**, 485 (1946).

[10] Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, **68**, 1083 (1946).

bond than are the primary and secondary lithium alkyls.[7] The latter react promptly with silicon tetrachloride to give excellent yields of tri- or tetra-substituted alkylsilicon compounds. In the present work attempts to prepare tri- or tetra-*t*-butyl silicon compounds were unsuccessful. However, at 70° *t*-butyllithium reacts with *t*-butyltrichlorosilane to give fair yields of di-*t*-butyldichlorosilane. But the reaction between this latter compound and *t*-butyllithium to give tri-*t*-butylchlorosilane does not proceed to any appreciable extent even when the reaction temperature is raised to 160°.

Experimental

***t*-Butyllithium.**—Because of the satisfactory yields obtained a detailed description of the preparation of *t*-butyllithium is included. Previous literature references[11] reported only poor or erratic yields in its preparation. It was found that particular attention to three factors was advantageous. These were the use of (1) lithium in the form of small pieces of thin foil, (2) "unsaturate-free" *n*-pentane as a solvent and (3) an especially pure *t*-butyl chloride.

The lithium was prepared for reaction by rolling it into thin sheets under a bath of mineral oil. A specially designed hand operated roller was used for this purpose. The shiny lithium foil was cut into small pieces of approximately one square centimeter. Pentane was rendered "unsaturate-free" by continuous agitation with concentrated sulfuric acid for three days and then fractionated. The fraction boiling 35–36° was used. Finally, only carefully fractionated *t*-butyl chloride, b. p. 50.0°, n^{20}_{D} 1.3850, was used.

Several individual preparations of *t*-butyllithium were carried out employing the following procedure. In a one-liter three-necked flask, equipped with a reflux condenser, dropping funnel, and mercury-seal stirrer, were placed 15.5 g., 2.2 moles, of shiny lithium foil, and 375 ml. of pentane. This mixture was heated to a gentle reflux and approximately 10% of a solution of 92.5 g., 1.0 mole, of *t*-butyl chloride in 300 ml. of pentane was added. External heat was used to maintain the reflux until the reaction was initiated. Thereafter, the heat evolved during the reaction kept the mixture at reflux temperature. The remainder of the *t*-butyl chloride was added during six hours. The addition was accompanied by *vigorous* stirring. Upon completion of the addition the reaction mixture was heated and stirred for an additional two hours. The average yield of sixteen successive runs was 66% with only one falling below 60% and with two above 75%.

***t*-Butyltrichlorosilane.**—Upon completion of the individual preparations of *t*-butyllithium an equi-molar quantity of freshly fractionated silicon tetrachloride was added to each reaction mixture during one hour. An immediate reaction occurred, exothermic enough to maintain gentle reflux. The reflux continued for an hour after completion of the addition of the silicon tetrachloride. The clear upper layer of the reaction mixture was then decanted from the excess lithium and lithium chloride and the products from several preparations were combined. To the total amount of *t*-butyllithium, 4.38 equivalents, was added 800 g., 4.70 moles, of silicon tetrachloride. Fractionation gave *t*-butyltrichlorosilane, 622 g., 3.24 moles, b. p. 132° (730 mm.), m. p. 98–99°, a 75% yield.

Anal. Calcd. for $C_4H_9SiCl_3$: Si, 14.6; Cl, 55.5. Found: Si, 14.7, 14.9; Cl, 55.5, 55.6. Cryoscopic molecular weight determinations in benzene gave: mol. wt., 189, 189 (calcd. 191.5).

t-Butyltrichlorosilane is unusual in several respects. Unlike other known alkyl trichlorosilanes, including even high molecular weight members such as myristyltrichlorosilane,[8] it is a white waxy solid. This becomes granular on standing and sublimes readily at room temperatures, giving well-defined fern-like crystals.[5] It is less easily hydrolyzed than other alkyltrichlorosilanes: it does not fume in moist air, and has only a faint acrid odor.

***t*-Butyltrimethylsilane.**—Reaction of *t*-butyltrichlorosilane, 19.1 g., 0.1 mole, with 0.5 equivalent of methylmagnesium bromide, followed by hydrolysis, steam distillation and fractionation gave *t*-butyltrimethylsilane, 8.1 g., 0.061 mole, b. p. 103° (740 mm.), m. p. 73.5° (75–77 micro), a yield of 61%.

Anal. Calcd. for $C_7H_{18}Si$: Si, 21.54. Found: Si, 21.6, 21.7. Cryoscopic mol. wt. determination. Calcd.: 130.3. Found: 131, 132.

t-Butyltrimethylsilane is a white waxy solid with a faint camphor-like odor. It sublimes readily at room temperatures depositing leaf-like crystals.

Chloro-*t*-butyltrichlorosilane.—In a 200-ml. round bottom flask, equipped with a reflux condenser, were placed 48.0 g., 0.25 mole, of *t*-butyltrichlorosilane, 36 g., 0.25 mole, of sulfuryl chloride and 0.5 g. of benzoyl peroxide. Heating on the steam-bath initiated an immediate reaction as evidenced by a vigorous evolution of sulfur dioxide and hydrogen chloride. The mixture was heated for twelve hours. Fractionation then gave 22.6 g., 0.1 mole, of chloro-*t*-butyltrichlorosilane, b. p. 180° (739 mm.), m. p. 46–47°, a 40% yield.

Anal. Calcd. for $C_4H_8SiCl_4$: Si, 12.4; Cl, 62.5. Found: Si, 12.4; Cl, 63.1, 63.1.

This compound is a wax-like solid at room temperature and shows little tendency to sublime. Upon standing it assumes a granular nature. It does not fume in moist air but possesses a sharp acrid odor and mild lachrymatory properties.

Hydrolysis of chloro-*t*-butyltrichlorosilane, 9.0 g., 0.04 mole, was effected by its slow addition to 12.0 g. of potassium hydroxide in 30 ml. of ethanol. There was evolved 0.0376 mole, a 94% yield, of gas. Reaction of the evolved gas with bromine gave 3.3 g., of isobutylene dibromide, b. p. 151°, n^{20}_{D} 1.5121, a 39% yield. When the hydrolysis was performed by the addition of 10 ml. of water to 9.0 g., 0.04 mole, of chloro-*t*-butyltrichlorosilane, less than 0.01 mole of gas was evolved. However, there was also obtained 1.9 g., 0.02 mole, of *t*-butyl chloride, b. p. 50–52°, n^{20}_{D} 1.3848.

Hydrolysis of *t*-Butyltrichlorosilane.—It was found that *t*-butyltrichlorosilane was quantitatively hydrolyzed at room temperature with 0.1 *N* alkali if first dissolved in methanol. However, intermittent shaking with water for one-half hour gave only 28% hydrolysis. Similar treatment with 20% aqueous sodium hydroxide gave 58% reaction. Under similar conditions other alkyltrichlorosilanes react quantitatively.

Di-*t*-butyldichlorosilane.—In a 1000-ml. three-necked flask, equipped with a fractionation column, mercury-seal stirrer and dropping funnel was placed 0.72 equivalent of *t*-butyllithium in 750 ml. of pentane under an atmosphere of dry nitrogen. To this was added 135 g., 0.70 mole, of *t*-butyltrichlorosilane. No reaction occurred at room temperature. The mixture was then heated to reflux with continuous stirring for four days. During this time the reaction temperature was slowly raised to 70° by the intermittent removal of pentane through the fractionation column. At the end of this period a large quantity of finely divided lithium chloride had precipitated. The mixture was then diluted with 500 ml. of pentane and 52 g., 0.33 mole, of silicon tetrachloride was added to react with any unused *t*-butyllithium. The mixture was stirred for an hour and then the clear upper layer was decanted. Fractionation gave 90.3 g., 0.42 mole, of di-*t*-butyldichlorosilane, b. p. 190° (729 mm.), m. p. −15°, n^{20}_{D} 1.4561, d^{20} 1.009, a 59% yield.

Anal. Calcd. for $C_8H_{18}SiCl_2$: Si, 13.16; Cl, 33.26. Found: Si, 13.1; Cl, 33.1, 33.2. Cryoscopic mol. wt. in

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[11] Gilman, Moore and Baine, *ibid.*, **63**, 2480 (1941); Bartlett, *ibid.*, **63**, 3229 (1941).

benzene: Calcd. 213.2. Found: 214, 216. MR_D: Calcd. 57.30. Found: 57.44.

This compound is a water-white liquid with a pleasant odor. Unlike other dialkyldichlorosilanes it does not fume in moist air and it does not titrate quantitatively with an excess of dilute alkali.

Attempted Preparation of Tri-*t*-butylchlorosilane.—In a 200-ml. three-necked flask, equipped with a reflux condenser, dropping funnel and thermometer, were placed 0.10 equivalent of *t*-butyllithium in 125 ml. of pentane and 21.3 g., 0.1 mole, of di-*t*-butyldichlorosilane. No reaction occurred at room temperature. Pentane was slowly distilled from the reaction mixture until the reaction temperature reached 75°. During twenty-four hours no formation of lithium chloride or other evidence of reaction was noted at this temperature.

Then, during forty-eight hours, pentane was slowly removed from the reaction mixture until the temperature reached 160°. The slow increase in the temperature was accompanied by the formation of a white deposit on the wall of the reaction flask. At the end of this time 125 ml. of pentane was added and a titration indicated that less than 5% of the *t*-butyllithium remained. The clear upper layer was decanted and, after removal of the solvent, fractionation gave 15.4 g. of unreacted di-*t*-butyldichlorosilane, a 72% recovery. Only 3.9 g. of a tarry high boiling residue remained.

Summary

1. The first tertiary alkylsilicon compound, *t*-butyltrichlorosilane (I) has been synthesized in good yield from *t*-butyllithium and silicon tetrachloride.

2. (I) has been found to react with an excess of methylmagnesium bromide to give *t*-butyltrimethylsilane.

3. The peroxide catalyzed chlorination of (I) with sulfuryl chloride proceeds smoothly to give chloro-*t*-butyltrichlorosilane. This latter compound undergoes a β-elimination reaction, evolving isobutylene, when treated with alkali.

4. At room temperature (I) does not react with *t*-butyllithium. At slightly higher temperatures a fair yield of di-*t*-butyldichlorosilane (II) was obtained. However, in an attempted reaction between (II) and *t*-butyllithium a third *t*-butyl group could not be introduced even under strenuous conditions.

STATE COLLEGE, PENNSYLVANIA

RECEIVED DECEMBER 22, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Dissociation of the Addition Compound of Trimethylboron with Quinuclidine; Further Evidence for the Steric Configuration of Triethylamine[1]

BY HERBERT C. BROWN[2] AND SEI SUJISHI[2,3]

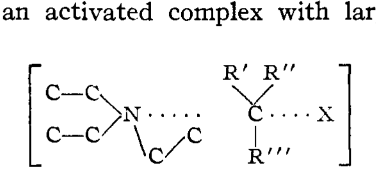
Despite the general similarity in structure, trimethylamine and triethylamine exhibit marked differences in their behavior. For example, in aqueous solution triethylamine is a considerably stronger base than trimethylamine.[4] Yet, in spite of its greater strength, triethylamine reacts at a considerably lower rate with alkyl halides[5] and forms a much less stable addition compound with trimethylboron.[6]

These differences in the behavior of the two amines have been attributed to the peculiar steric configuration of the triethylamine molecule.[7] The present investigation was undertaken to test the proposed explanation and to examine some of its consequences.

Discussion

It was originally proposed[7] that in triethylamine only two of the three ethyl groups can be removed to the "rear" of the nitrogen atom, away from the group adding or reacting at the vacant position of the nitrogen atom. For steric reasons the third ethyl group cannot be similarly accommodated, but is required to take up a position such that the group projects into the region usually assigned to the unshared electron pair (Fig. 1). With this arrangement, triethylamine resembles a typical hindered amine, such as 2-picoline (Fig. 2), much more closely than it does a relatively unhindered tertiary amine, such as trimethylamine (Fig. 3).

According to the interpretation advanced, formation of an addition compound by reaction of the amine with a bulky component, such as trimethylboron, introduces F-strain of high magnitude and leads to marked instability of the product (Fig. 4). Similarly, reaction of triethylamine with alkyl halides, particularly in cases where the steric requirements of the alkyl groups are large, should lead to an activated complex with large steric strains.



The rate of the reaction is thereby decreased relative to the corresponding reactions of less hindered amines. On the other hand, the ability of such hindered amines to react with aqueous acids is not noticeably affected because of the low steric requirements of the proton.

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[1] Acid–Base Studies in Gaseous Systems. V. Paper no. XIII in the series, Studies in Stereochemistry.

[2] Present address: Department of Chemistry, Purdue University.

[3] Ethyl Corporation Fellow at Wayne University, 1945–1947.

[4] Hall and Sprinkle, THIS JOURNAL, **54**, 3479 (1932), report values for the ionization constants of trimethyl- and triethylamine at 25° of 6.30×10^{-5} and 54.9×10^{-5}, respectively.

[5] For example, the reaction at 80° of trimethylamine with isopropyl iodide is 61 times faster than the corresponding reaction involving triethylamine; Perrin and Williams, *Proc. Roy. Soc.* (*London*), **A159**, 162 (1937).

[6] Brown, THIS JOURNAL, **67**, 1452 (1945).

[7] Brown and Taylor, *ibid.*, **69**, 1332 (1947).