

Methanolic Potassium Hydroxide.—A mixture of 22.5 g., 0.4 mole, of potassium hydroxide, 25 ml. of anhydrous methanol and 22.8 g., 0.2 mole, of allyltrimethylsilane was heated at reflux temperature for twenty-four hours. Propylene was slowly evolved. Conversion to propylene dibromide indicated a 70% yield. Upon fractionation of the original reaction mixture, 8.6 g. of an azeotrope of methanol (18% by weight) and trimethylmethoxysilane,¹² b. p. 50°, n_D^{20} 1.3634, was obtained, an approximate yield of 35%.

Aqueous Sodium Hydroxide.—A mixture of 20 ml. of 12 *N* sodium hydroxide and 3 g. of allyltrimethylsilane was refluxed for four days. A 5% yield of propylene, identified by conversion to propylene dibromide, was obtained.

Aluminum Chloride.—A 22.8-g., 0.2 mole, sample of allyltrimethylsilane reacted vigorously during ten minutes with 2.0 g. of anhydrous aluminum chloride to give a very viscous mixture. This was extracted with 75 ml. of pentane and washed with dilute hydrochloric acid. The pentane was evaporated under reduced pressure. Dis-

tillation of the residue gave 12.9 g. of a clear oily polymer, boiling 290–340° (15 mm.), n_D^{20} 1.4760.

Anal. Calcd. for $(C_6H_{14}Si)_n$: Si, 24.5. Found: Si, 20.0.

These analytical data indicate that something more than polymerization has occurred during the reaction.

Summary

1. Allyltrimethylsilane gave two types of reactions in the present work.
2. Type I involved addition to the double bond.
3. Type II gave cleavage of the allyl-silicon bond.
4. Mechanisms for these reactions are proposed.

STATE COLLEGE, PENNSYLVANIA

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(12) Sauer, *ibid.*, **66**, 1707 (1944).

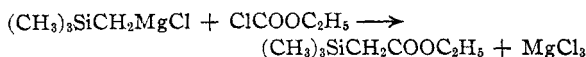
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Synthesis and Cleavage of Ethyl Trimethylsilylacetate^{1,2}

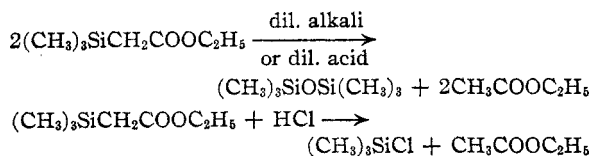
BY JACK R. GOLD, LEO H. SOMMER AND FRANK C. WHITMORE

Hydrolytic cleavage of the Si-C bond in β -oxygenated organosilicon compounds has, with the exception of β -hydroxy-*n*-propyltrimethylsilane, hitherto prevented their synthesis in this Laboratory.³

We have now synthesized ethyl trimethylsilylacetate (carboethoxymethyltrimethylsilane⁴), a colorless, stable liquid possessing a pleasant, fruity odor, from ethyl chloroformate and the Grignard reagent of chloromethyltrimethylsilane.⁵



This is the first ester derived from a silicon-containing aliphatic carboxylic acid. Although ethyl trimethylsilylacetate is practically inert to water when refluxed with the latter for as long as twelve hours, it does undergo unusual reactions with diverse reagents such as dilute hydrochloric acid, dilute alkali, anhydrous hydrogen chloride, anhydrous bromine and absolute ethanol.



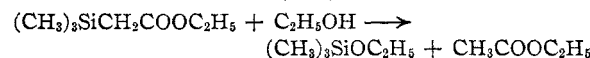
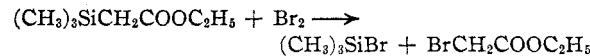
(1) Taken from work submitted by J. R. Gold to the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree.

(2) Paper XVIII in a series on organosilicon compounds. For Paper XVII, see *THIS JOURNAL*, **70**, 2872 (1948).

(3) Whitmore, Sommer, Gold and Van Strien, *ibid.*, **69**, 1551 (1947).

(4) The present uncertainty in the nomenclature of such compounds (*cf.* *Chem. Eng. News*, **24**, 1233 (1946)) leads us to propose "carboethoxymethyltrimethylsilane" as an alternate name.

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



Experimental

Ethyl Trimethylsilylacetate.—A solution of 325 g., 3 moles, of freshly-distilled ethyl chloroformate in 1000 cc. of anhydrous ether was placed in a 5-liter, three-necked flask fitted with a mercury-sealed, electrically-driven Hershberg⁶ stirrer, a reflux condenser leading to a sulfuric acid trap *via* a Dry Ice-acetone trap, and a dropping funnel containing the Grignard reagent prepared in 95% yield from 2 moles of chloromethyltrimethylsilane in 500 cc. of dry ether. While stirring, addition of the Grignard reagent at a rate sufficient to maintain reasonable reflux was followed by heating with a warm water-bath for five hours. Copious precipitation of magnesium chloride etherate necessitated addition of 1000 cc. of ether in order to maintain stirring; but after another twelve hours at room temperature, the reaction mixture had virtually solidified.

After hydrolysis with 1000 cc. of 3% hydrochloric acid, washing of the ether solution with water and dilute sodium carbonate, and drying over anhydrous sodium sulfate, the ether was distilled and the residue fractionated through a column of 15 theoretical plates to give 113.5 g., 1.05 moles, 35% recovery, of ethyl chloroformate, b. p. 43.5° at 120 mm.; 239.5 g., 1.50 moles, of ethyl trimethylsilylacetate, b. p. 75.5° at 42 mm. (157° at 730 mm.), n_D^{20} 1.4149, d_4^{20} 0.8762, *MRD* 45.76 (calcd.⁷ 45.95), 74.5% yield based on chloromethyltrimethylsilane; and 10 g. of residue.

Anal. Calcd. for $C_7H_{16}SiO_2$: Si, 17.5. Found: Si, 17.4, 17.5.

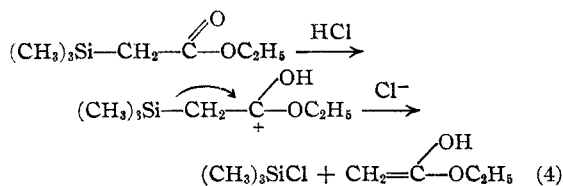
Reaction with Dilute Hydrochloric Acid.—Ethyl trimethylsilylacetate, 4.0 g., 0.025 mole, was refluxed with 50 cc. of 5% hydrochloric acid for twenty hours. The odor of ethyl acetate was noted at the top of the condenser during the first minutes of reflux, indicating cleavage of the Si-C bond. After cooling, distillation of the upper, organic layer proved it to be hexamethyldisiloxane, 1.7 g., 0.011 mole, b. p. 98–100° at 740 mm., n_D^{20} 1.3773, 88%

(6) Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

(7) Warrick, *THIS JOURNAL*, **68**, 2455 (1946).

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).



Reaction with bromine may involve nucleo-

philic 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.

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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

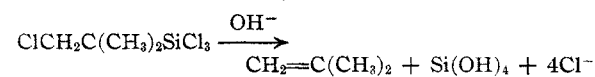
Numerous unsuccessful attempts to prepare such compounds by the treatment of a *t*-alkyl Grignard reagent with silicon tetrachloride, ethyl orthosilicate, triethylchlorosilane, trimethylchlorosilane, trimethylbromosilane or trimethyliodosilane have been made in this Laboratory during the past six years 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 chloride⁹ 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.



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

(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).