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°, $n^{20}D$ 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. Distillation of the residue gave 12.9 g. of a clear oily polymer, boiling 290–340° (15 mm.), $n^{20}D$ 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 (carboethoxymethyltrimethylsilane[4]), a colorless, stable liquid possessing a pleasant, fruity odor, from ethyl chloroformate and the Grignard reagent of chloromethyltrimethylsilane.[5]

$$(CH_3)_3SiCH_2MgCl + ClCOOC_2H_5 \longrightarrow (CH_3)_3SiCH_2COOC_2H_5 + MgCl_3$$

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.

$$2(CH_3)_3SiCH_2COOC_2H_5 \xrightarrow[\text{or dil. acid}]{\text{dil. alkali}} (CH_3)_3SiOSi(CH_3)_3 + 2CH_3COOC_2H_5$$

$$(CH_3)_3SiCH_2COOC_2H_5 + HCl \longrightarrow (CH_3)_3SiCl + CH_3COOC_2H_5$$

$$(CH_3)_3SiCH_2COOC_2H_5 + Br_2 \longrightarrow (CH_3)_3SiBr + BrCH_2COOC_2H_5$$

$$(CH_3)_3SiCH_2COOC_2H_5 + C_2H_5OH \longrightarrow (CH_3)_3SiOC_2H_5 + CH_3COOC_2H_5$$

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 Hershberg[6] 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.), $n^{20}D$ 1.4149, d^{20} 0.8762, *MR*D 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., $n^{20}D$ 1.3773, 88%

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[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).

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

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

of theory. In order to establish the presence of acetic acid, derived from the second fission product, ethyl acetate, the aqueous layer was distilled and the distillate evaporated to dryness after rendering slightly alkaline with sodium hydroxide solution. Treatment of the resulting solid with *p*-phenylphenacyl bromide gave *p*-phenylphenacyl acetate, m. p. and mixed m. p. 110–111.5°.

A comparison experiment was run with 2.0 g. of ester and 30 cc. of 10% hydrochloric acid. Refluxing for only one-half hour altered the refractive index of the organic layer from n^{20}D 1.4149 to n^{20}D 1.4057, a drift of approximately 25% toward that of the ultimate fission product, hexamethyldisiloxane, n^{20}D 1.3772. It may be worthwhile to mention also that shaking of a sample of the ester with 10% hydrochloric acid at room temperature for fifteen minutes leaves the former virtually unchanged.

Reaction with Sodium Hydroxide Solution.—A mixture of 5.0 g., 0.031 mole, of ethyl trimethylsilylacetate and 100 cc. of 5% sodium hydroxide solution was refluxed for twenty-four hours. As in the reaction with hydrochloric acid, the odor of ethyl acetate was apparent when reflux commenced. Distillation of the organic layer gave 2.1 g., 0.013 mole, of hexamethyldisiloxane, b. p. 97.0–97.5° at 733 mm., n^{20}D 1.3772, 84% yield. The presence of acetic acid in the aqueous layer was proved, after acidification with sulfuric acid, by the same method used in the above experiment with 5% hydrochloric acid. The *p*-phenylphenacyl derivative was obtained, m. p. and mixed m. p. 110–111°.

It is interesting that the above-noted inertness of ethyl trimethylsilylacetate to cold hydrochloric acid contrasts sharply with its reactivity to cold alkali. When 5.0 g., 0.031 mole, of the ester was shaken for fifteen minutes at room temperature with 100 cc. of 5% sodium hydroxide solution, an exothermic reaction resulted which raised the temperature of the mixture to about 35°. The organic layer which was then separated proved to be hexamethyldisiloxane, 2.0 g., 0.012 mole, 80% yield, n^{20}D 1.3773, b. p. 98–100° at 740 mm.

Reaction with Gaseous Hydrogen Chloride.—A vertical glass tube, 1.8 cm. in diameter and 33 cm. in length, sealed at the bottom, was fitted with a small, glass gas bubbler and a reflux condenser leading to a Dry Ice–acetone trap. Ethyl trimethylsilylacetate, 25.0 g., 0.156 mole, was placed in the tube and dry hydrogen chloride was bubbled in slowly, heating occasionally with a small, open flame. After two hours, 5.5 g., 0.15 mole, of gas had been absorbed, 97%. No liquid had distilled into the Dry Ice–acetone trap. Fractionation of the product at 736 mm. in a column of about 25 theoretical plates gave: I, b. p. 58.0–58.9°, 12.0 g., 0.11 mole, of trimethylchlorosilane in 71% yield, % Cl 32.2, 32.3, % Cl (calcd.) 32.6, n^{20}D 1.3880; II, b. p. 58.9–76.5°, 3.3 g.; III, b. p. 76.5–77.5°, 9.0 g., 0.10 mole, of ethyl acetate in 66% yield, n^{20}D 1.3721; and 4.0 g. residue. The yields of I and III are each raised to approximately 80% if II is interpolated.

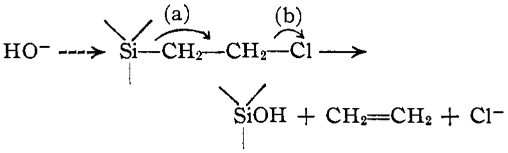
Reaction with Anhydrous Bromine.—In a 500-cc., three-necked flask, equipped with an air-driven glass stirrer sealed with rubber tubing, a reflux condenser, a Dry Ice–acetone trap, and a dropping funnel was placed 25.0 g., 0.156 mole, of ethyl trimethylsilylacetate. Having immersed the flask in an ice-bath, 25.0 g., 0.156 mole, of dry bromine was added from the dropping funnel over one hour, while stirring. The 50-g. reaction product, a fuming liquid slightly colored by a trace of free bromine, was fractionated at 740 mm. in a column of approximately 25 theoretical plates to give: I, b. p. 79.5–81.0°, 17.4 g., 0.114 mole, 73% yield of trimethylbromosilane; II, b. p. 81.0–155.0°, 3.4 g.; III, b. p. 155.0–155.8°, 18.9 g., 0.114 mole, 73% yield of ethyl bromoacetate, n^{20}D 1.4501; residue, 5.0 g. Interpolation of II raises the yields of I and III to about 80% each.

Reaction with Absolute Ethanol.—Ethyl trimethylsilylacetate, 20.0 g., 0.125 mole, was refluxed for forty-eight hours with 40.0 g., 1.15 mole, of absolute ethanol (with which the ester is miscible). No loss in weight occurred during this time, but 5 g. was lost inadvertently while transferring to a flask. Fractionation at 736 mm. in a column of about 25 theoretical plates gave fractions of the following boiling ranges, weights (g.) and refractive indices (n^{20}D): I, 67.0–69.0°, 6.9, 1.3720; II, 69.0–73.0° (mainly 71–72°), 10.5, 1.3700; III, 73.0–79.0° (almost all at 79.0°), 30.9, 1.3610; residue, 6.0, 1.4138.

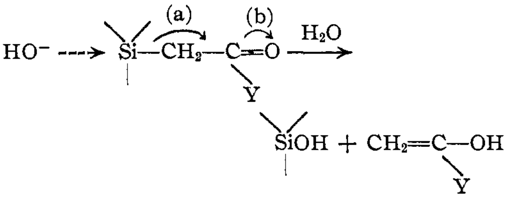
The narrow range over which all the products boil hindered efficient fractionation. Fraction I is presumably the azeotrope, slightly impure, of trimethylethoxysilane and ethanol[8]; II is the azeotrope of ethyl acetate and ethanol, containing 7.4 g., 0.084 mole, 73% yield of the acetate; III is recovered ethanol; and the residue is a 30% recovery (0.037 mole) of impure ethyl trimethylsilylacetate. The apparent low yield of I is attributable to loss due to poor fractionation, for fraction II was found to contain silicon. Furthermore, fractions I, II, and III were afterwards combined and shown by analysis to contain 94% of the calculated amount of silicon.

Discussion

Comparison of the β-eliminations of β-chloroalkylsilanes[9,10] with the hydrolytic cleavage of β-oxygenated[3] organosilicon compounds shows a striking similarity in possible mechanisms. In each case nucleophilic attack upon silicon by hydroxyl ion is accompanied by two coincident electron pair transfers; (a) from silicon to a β-carbon atom and (b) from a β-carbon atom to electron-attracting chlorine or oxygen atoms. The elimination of chloride ion in (1), however, finds no parallel in (2), where only one bond, that between silicon and carbon, is broken and a proton from the solvent is associated by the negative oxygen atom.



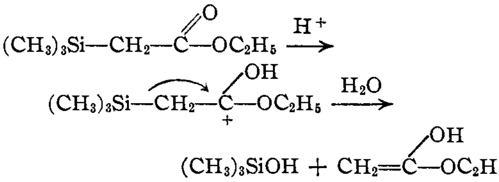
$$\mathrm{HO^- \dashrightarrow \overset{\diagdown\diagup}{\underset{|}{Si}}{-}CH_2{-}CH_2{-}Cl \longrightarrow \overset{\diagdown\diagup}{\underset{|}{Si}}OH + CH_2{=}CH_2 + Cl^-} \quad (1)$$



$$\mathrm{HO^- \dashrightarrow \overset{\diagdown\diagup}{\underset{|}{Si}}{-}CH_2{-}\underset{\diagdown Y}{C}{=}O \xrightarrow{H_2O} \overset{\diagdown\diagup}{\underset{|}{Si}}OH + CH_2{=}\underset{\diagdown Y}{C}{-}OH} \quad (2)$$

(Y is alkyl, alkoxyl, hydroxyl, etc.)

Previous work[10] has shown that β-carbonium ions (Si–C–C$^+$) derived from β-chloroalkylsilanes readily undergo Si–C cleavages. Accordingly, cleavage of ethyl trimethylsilylacetate by dilute acid in the present work probably occurs as the result of electrophilic attack by a proton on beta oxygen to give an actual or virtual β-carbonium



$$\mathrm{(CH_3)_3Si{-}CH_2{-}\overset{\diagup O}{C}{-}OC_2H_5 \xrightarrow{H^+} (CH_3)_3Si{-}CH_2{-}\underset{+}{\overset{\diagup OH}{C}}{-}OC_2H_5 \xrightarrow{H_2O} (CH_3)_3SiOH + CH_2{=}\overset{\diagup OH}{C}{-}OC_2H_5} \quad (3)$$

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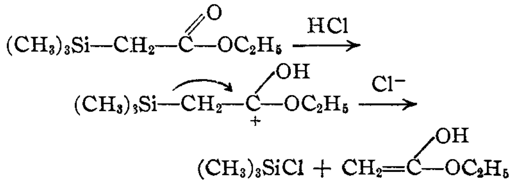
[8] Sauer, *ibid.*, **66**, 1707 (1944).

[9] (a) Sommer and Whitmore, *ibid.*, **68**, 485 (1946); (b) Sommer, Dorfman, Goldberg and Whitmore, *ibid.*, **68**, 488 (1946); (c) Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, **68**, 1083 (1946); (d) Sommer, Bailey, Strong and Whitmore, *ibid.*, **68**, 1881 (1946).

[10] Sommer, Bailey and Whitmore, *ibid.*, **70**, 2869 (1948).

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).



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

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.

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[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).