other reagents used in one important respect. They are incapable of providing a nucleophilic anion for combination with silicon. Also, a driving force for dehydrohalogenation with quinoline, *i.e.*, formation of the hydrochloride salt, is absent for β-elimination involving silicon. Silicon halides do not form analogous salts with quinoline.

Summary

1. Further studies of β-eliminations involving silicon have been carried out with β-chloroethyldiethylchlorosilane, β-chloroethyldiethylfluorosilane and β-chloroethyltriethylsilane.

2. These probably give β-eliminations by mechanisms similar to those established for the dehydrohalogenation of ordinary organic halides with electrophilic and nucleophilic reagents.

3. Heating β-chloroethyltriethylsilane gives β-elimination in the absence of any added reagent.

4. The β-eliminations reported are attributed to the electropositive nature of silicon compared to carbon and hydrogen.

STATE COLLEGE, PA. RECEIVED DECEMBER 22, 1947

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

Reactions of Allyltrimethylsilane[1,2]

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

In continuation of previous work on the chemistry of organosilicon compounds containing functional groups attached to carbon, the present paper reports two types of reactions of allyltrimethylsilane.

Type I, involving addition to the double bond, was realized with hydrogen bromide, hydrogen iodide, chlorine, and catalytic hydrogenation. The hydrogen halides added according to Markownikoff's rule.

$$(CH_3)_3SiCH_2—CH{=}CH_2 + HX \longrightarrow (CH_3)_3SiCH_2—CHX—CH_3$$

The assigned structures of the products, β-bromo-*n*-propyltrimethylsilane and β-iodo-*n*-propyltrimethylsilane, are based on the following reactions which are typical of β-haloalkyl silicon compounds.[4] γ-Haloalkylsilanes are heat stable and

$$(CH_3)_3SiCH_2—CHX—CH_3 \xrightarrow[OH^-]{\text{dil.}} (CH_3)_3SiOH + CH_3—CH{=}CH_2 + X^-$$

$$(CH_3)_3SiCH_2—CHX—CH_3 \xrightarrow[\Delta]{} (CH_3)_3SiX + CH_3—CH{=}CH_2$$

do not give olefins on treatment with dilute alkali.[4b,5]

The compound obtained from the action of chlorine with allyltrimethylsilane, β,γ-dichloro-*n*-propyltrimethylsilane, readily undergoes thermal decomposition.

$$(CH_3)_3SiCH_2—CHCl—CH_2Cl \xrightarrow[\Delta]{} (CH_3)_3SiCl + CH_2{=}CH—CH_2Cl$$

Type II reactions of allyltrimethylsilane, involving cleavage of the allyl-silicon bond, were given by concentrated sulfuric acid, hydrogen chloride and bromine.

$$2(CH_3)_3SiCH_2—CH{=}CH_2 + H_2SO_4 \longrightarrow [(CH_3)_3Si]_2SO_4 + 2CH_3—CH{=}CH_2$$

$$(CH_3)_3SiCH_2—CH{=}CH_2 + HCl \longrightarrow (CH_3)_3SiCl + CH_3—CH{=}CH_2$$

$$(CH_3)_3SiCH_2—CH{=}CH_2 + Br_2 \longrightarrow (CH_3)_3SiBr + CH_2Br—CH{=}CH_2$$

Previous work has shown that β-carbonium ions ($Si–C–\overset{+}{C}$) can undergo cleavage of the silicon-carbon bond in certain reactions.[4d] Treatment of allyltrimethylsilane with electrophilic reagents may, on the basis of current theory concerning reactions of olefins, give rise to such an ion or its equivalent.

$$(CH_3)_3SiCH_2—CH{=}CH_2 \xrightarrow{A^+B^-} (CH_3)_3SiCH_2\overset{+}{C}H—CH_2A$$

Depending upon the nature of the attacking reagent and the reaction conditions, the formed carbonium ion may satisfy its electron deficiency in one of two ways: (1) It can unite with the negative part of the attacking reagent to give the addition product, as in Type I reactions. (2) It can undergo cleavage involving electron-release from silicon to the electronically deficient β-carbon. The resulting "siliconium ion" is then stabilized by simultaneous or subsequent union with the negative part of the attacking reagent. These processes, which lead to Type II reactions, are a direct consequence of the electropositive nature of silicon as compared to carbon.[4d]

$$(CH_3)_3Si—CH_2—\overset{+}{C}H—CH_2A + B^- \longrightarrow (CH_3)_3Si—CH_2—CHB—CH_2A \quad (1)$$

$$(CH_3)_3Si\overset{\curvearrowright}{—CH_2—}\overset{+}{C}H—CH_2A + B^- \longrightarrow (CH_3)_3SiB + CH_2{=}CH—CH_2A \quad (2)$$

Cleavage of the allyl-silicon bond was also realized with methanolic potassium hydroxide. In

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(1) Paper XVII in a series on organosilicon compounds. For Paper XVI see THIS JOURNAL, **70**, 2869 (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 M.S. degree.

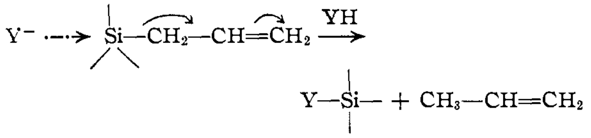
(3) American Chemical Society Pre-doctoral Fellow 1946-1949.

(4) (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 and Whitmore, *ibid.*, **70**, 2869 (1948).

(5) Unpublished results of R. E. Van Strien in this Laboratory.

$$(CH_3)_3Si{-}CH_2{-}CH{=}CH_2 + CH_3OH \xrightarrow{KOH} (CH_3)_3SiOCH_3 + CH_3{-}CH{=}CH_2$$

this case, nucleophilic attack on electropositive silicon is facilitated by the polarizability of the olefinic linkage.



Allyltrimethylsilane is polymerized by treatment with aluminum chloride.

Experimental

Allyltrimethylsilane was prepared by the reaction of allylmagnesium bromide with trimethylchlorosilane, using the method of Whitmore, *et al.*[6]

Trimethylchlorosilane, 542 g., 5.0 moles, was added to 5.8 equivalents of freshly prepared allylmagnesium bromide during four hours. Ether was distilled from the reaction mixture through a fractionating column until the reaction flask temperature reached 85°. The residue was heated at this temperature for twenty-four hours. It was then hydrolyzed with water and steam distilled. The combined organic distillates were dried and fractionally distilled through a column of approximately 15 theoretical plates. There was obtained 291 g., 2.55 moles, of allyltrimethylsilane, b. p. 84.9° (737 mm.), d^{20} 0.7193, $n^{20}\text{D}$ 1.4074, a 51% yield.

Anal. Calcd. for $C_6H_{14}Si$: Si, 24.57. Found: Si, 24.2.

Allyltrimethylsilane was first prepared in this Laboratory[7] from allyltrichlorosilane[8] and methylmagnesium bromide. However, the above method is more convenient.

Reactions of Allyltrimethylsilane

Hydrogen Bromide.—In a test-tube, equipped with a gas delivery tube, was placed 22.8 g., 0.2 mole, of allyltrimethylsilane. Into this was passed 0.2 mole of dry hydrogen bromide. It was necessary to initiate the reaction at room temperature, but once started it was continued in a Dry Ice–ether-bath. The hydrogen bromide added extremely readily at this temperature. The addition of the hydrogen bromide was stopped when the theoretical weight increase was obtained. Fractionation under reduced pressure gave 27.5 g., 0.14 mole, of β-bromo-*n*-propyltrimethylsilane, b. p. 31° (6 mm.), $n^{20}\text{D}$ 1.4580, d^{20} 1.113, a 70% yield.

Anal. Calcd. for $C_6H_{15}SiBr$: Br, 40.94. Found: Br, 40.8.

A 13.0 g., 0.066 mole, sample of this product was slowly heated for thirty minutes in a flask equipped with a reflux condenser. Decomposition occurred above 40°. Propylene was evolved. Its conversion to propylene dibromide indicated a 73% yield. Distillation of the residue gave 8.9 g., 0.059 mole, an 88% yield of trimethylbromosilane,[9] boiling 76–79°.

Anal. Calcd. for C_3H_9SiBr: Br, 52.2. Found: Br, 52.2.

An unsuccessful attempt was made to prepare γ-bromo-*n*-propyltrimethylsilane by making use of the "peroxide effect." Addition of hydrogen bromide to 22.8 g., 0.2 mole, of allyltrimethylsilane in the presence of 0.2 g. of benzoyl peroxide gave a 73% yield of β-bromo-*n*-propyltrimethylsilane.

Hydrogen Iodide.—In a 100-ml. two-necked flask, equipped with a reflux condenser and a gas delivery tube, was placed 22.8 g., 0.2 mole, of allyltrimethylsilane. The reaction flask was immersed in an ice-bath and dry hydrogen iodide was slowly bubbled into the allyltrimethylsilane. After 85% addition of the hydrogen iodide, as indicated by weight increase, the reaction was stopped. Fractionation under reduced pressure gave 22.7 g., 0.095 mole, of β-iodo-*n*-propyltrimethylsilane, b. p. 57° (6 mm.), $n^{20}\text{D}$ 1.496, a yield of 48%.

Anal. Calcd. for $C_6H_{15}SiI$: I, 52.41. Found: I, 52.3.

This compound fumed in air, and was readily decomposed on heating above 75° or on treatment with dilute alkali or anhydrous aluminum chloride. Heating of 81.0 g., 0.33 mole, at 80° for thirty minutes gave a 55% yield of propylene. Fractionation of the residue gave 31.6 g., 0.16 mole, of trimethyliodosilane,[10] b. p. 106°; a 46% yield.

Anal. Calcd. for C_3H_9SiI: I, 63.5. Found: I, 62.3.

Chlorine.—Into 11.4 g., 0.1 mole, of allyltrimethylsilane kept at −70° was passed 7.0 g., 0.1 mole, of chlorine at the rate of 0.003 mole per minute. Fractionation under reduced pressure gave 10.3 g., 0.056 mole, a 56% yield of β,γ-dichloropropyltrimethylsilane, b. p. 36° (4 mm.), $n^{20}\text{D}$ 1.4581, d^{20} 1.030.

Anal. Calcd. for $C_6H_{14}SiCl_2$: Cl, 38.4; Cl attached to β-carbon, 19.2. Found: Cl, 38.4, Cl attached to β-carbon, 19.3.

The analysis for chlorine attached to β-carbon was made by titration with dilute alkali.

β,γ-Dichloropropyltrimethylsilane, 7.2 g., was decomposed by heating above 90° for thirty minutes. Fractionation of the reaction mixture gave 2.6 g. of allyl chloride, b. p. 44.5°, $n^{20}\text{D}$ 1.4148, an 87% yield, and trimethylchlorosilane, 3.4 g., b. p. 57°, $n^{20}\text{D}$ 1.3880, an 81% yield.

Anal. Calcd. for C_3H_9SiCl: Cl, 32.7. Found: Cl, 32.3.

Hydrogen.—From the hydrogenation of 22.8 g., 0.2 mole, of allyltrimethylsilane over Raney nickel catalyst at 45 lb. per sq. in. hydrogen pressure during twelve hours was obtained 14.6 g., 0.125 mole, of *n*-propyltrimethylsilane,[6] b. p. 89°, $n^{20}\text{D}$ 1.3929, a 63% yield.

Concentrated Sulfuric Acid.—Upon treatment of 5.7 g. of allyltrimethylsilane with 2.5 g. of concentrated sulfuric acid at −20° there was obtained 5.2 g. of somewhat impure trimethylsilyl sulfate, melting at 49–52°.[11]

Anal. Calcd. for $C_6H_{18}Si_2SO_4$: SO_4, 40.4. Found: SO_4, 40.4. Propylene (48% yield) was also formed in this reaction.

Hydrogen Chloride.—The reaction of 22.8 g., 0.2 mole, of allyltrimethylsilane with dry hydrogen chloride gas at reflux temperature, during twenty-four hours resulted in the formation of 4.4 g., 0.04 mole of trimethylchlorosilane, b. p. 57°, $n^{20}\text{D}$ 1.3878, a 20% yield. Propylene (15% yield) was evolved. There was recovered 10.9 g., 0.095 mole, of unreacted allyltrimethylsilane.

Bromine.—In a 100-ml. two-necked flask, equipped with a stirrer, were placed 22.8 g., 0.2 mole, of allyltrimethylsilane and 50 ml. of anhydrous ethyl ether. The reaction flask was immersed in a Dry Ice–ether-bath and the mixture vigorously stirred. To this was slowly added 32 g., 0.2 mole, of bromine. Fractionation indicated formation of allyl bromide, b. p. 71°, and trimethylbromosilane, b. p. 80°. In order to effect a better separation the reaction product was treated with water in order to convert trimethylbromosilane to the disiloxane. Fractionation then gave allyl bromide, 3.8 g. 0.019 mole, b. p. 71°, $n^{20}\text{D}$ 1.4660, a 10% yield, hexamethyldisiloxane, b. p. 99°, $n^{20}\text{D}$ 1.3778, 9.4 g., 0.058 mole, a 58% yield, and 1,2,3-tribromopropane, b. p. 218°, m. p. 13°, $n^{20}\text{D}$ 1.582, 5.2 g., a 7% yield. No β,γ-dibromopropyltrimethylsilane could be isolated.

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

(7) W. A. Strong, Pennsylvania State College Ph.D. Thesis, 1944.

(8) Hurd, *ibid.*, **67**, 1813 (1945).

(9) Gilliam, Meals and Sauer, THIS JOURNAL, **68**, 475 (1946).

(10) Pray, Sommer, Goldberg, Kerr, DiGiorgio and Whitmore, *ibid.*, **70**, 433 (1948).

(11) Sommer, Pietrusza, Kerr and Whitmore, *ibid.*, **68**, 156 (1947).

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).