

The activity at comparatively low temperatures reported by Burwell¹ results from his having evacuated the catalysts at 400° between each run. This is shown in the present investigation to remove poison which otherwise steadily diminished the activity of the catalyst. The poison seems not to be contained in the alcohol but to result from a condensation reaction such as this catalyst is known to promote.⁹ The poison is not removed by evacuating at 238° but is by flushing with hydrogen at 400°. This behavior resembles that reported by Woodman and Taylor¹⁹ in the hydrogenation of ethylene by zinc oxide.

With a freshly flushed catalyst a rate starts high and steadily declines during a run apparently coming to a steady state at a rate equivalent to a 60° decrease in temperature. The addition of water to the alcohol reduces the rate by three-quarters but eliminates the decline. Poisoning may, thus, be partly due to water produced by condensation reactions.

Considerable racemization occurs upon passing *s*-butyl alcohol over freshly evacuated catalysts.¹ It is now shown that at a higher temperature a similar process occurs on previously used and unflushed catalyst. The values of racemization and fraction converted exclude the possibility that the racemization can be the result merely of rehydrogenation of ketone. Owing to the lack of con-

stancy in activity which appears inherent in the catalyst under these conditions it appeared fruitless to expend much optically active alcohol.

Isopropyl alcohol dehydrogenates at rates rather near those of *s*-butyl. This corresponds with previous reports^{5,6} of rates of dehydrogenation of some secondary alcohols on copper. Also, *n*-propyl alcohol dehydrogenates much more slowly than the secondary alcohol, a result analogous to that of Palmer and Constable³ on copper.

Summary

Rates of catalytic dehydrogenation and racemization of *l*-*s*-butyl alcohol have been measured simultaneously over copper and over zinc chromite catalysts.

Racemization is far more extensive than can be accounted for by the production of inactive alcohol by rehydrogenation of methyl ethyl ketone. On copper, dehydrogenation is inhibited by the reaction products relative to the racemization.

With zinc chromite, the reactions are poisoned probably by adsorption of products of concurrent condensation reactions. The activity of the catalyst is temporarily greatly increased by flushing with hydrogen at 400°. The rate of dehydrogenation of isopropyl alcohol is about equal to that of *s*-butyl while that of *n*-propyl is far less.

(19) Woodman and Taylor, *THIS JOURNAL*, **62**, 1393 (1940).

EVANSTON, ILLINOIS

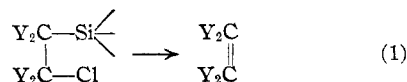
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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Further Studies of β -Eliminations Involving Silicon¹

BY LEO H. SOMMER, DONALD L. BAILEY AND FRANK C. WHITMORE

The remarkable reactivity of β -carbon-chlorine bonds in β -chloroalkyltrichlorosilanes ($\text{RCHCl-CH}_2\text{SiCl}_3$) with dilute alkali and Grignard reagents is associated with cleavage of the carbon-silicon bond.² These reactions, which are β -eliminations involving silicon and halogen, take place according to the general equation



The present paper reports further studies of these interesting reactions as given by

β -chloroethyldiethylchlorosilane, $(\text{ClCH}_2\text{CH}_2)(\text{C}_2\text{H}_5)_2\text{SiCl}$ (I)

β -chloroethyldiethylfluorosilane, $(\text{ClCH}_2\text{CH}_2)(\text{C}_2\text{H}_5)_2\text{SiF}$ (II)

and β -chloroethyltriethylsilane, $(\text{ClCH}_2\text{CH}_2)(\text{C}_2\text{H}_5)_3\text{Si}$ (III)

(1) Paper XVI in a series on organosilicon compounds. For Paper XV see *THIS JOURNAL*, **70**, 484 (1947). Paper XVI was presented in part before the Division of Organic Chemistry, American Chemical Society, New York City, September, 1947.

(2) Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, **68**, 1083 (1946).

Effective reagents are: alcoholic bases, aqueous alkali, water, potassium acetate in glacial acetic acid, methylmagnesium bromide, small amounts of aluminum chloride, silver nitrate in methanol, and heat alone with compound III.

It is evident from equation (1) that these reactions are formally similar to the dehydrohalogenation of ordinary organic halides. Further similarities, particularly with regard to mechanism and electronegativity relations, will be discussed below.

Experimental

β -Chloroethyldiethylchlorosilane and β -Chloroethyldiethylfluorosilane.—The synthesis and characterization of these two compounds by the chlorination of the corresponding triethylhalosilane with sulfuryl chloride and benzoyl peroxide catalyst has been described in a previous paper.⁸

β -Chloroethyltriethylsilane.—This compound was prepared by the chlorination of tetraethylsilane using phosphorus pentachloride catalyst and ultraviolet light according to the method of Ushakov and Itenberg.⁴ Chlorination of tetraethylsilane with sulfuryl chloride and benzoyl peroxide catalyst gave only the α -chloro compound.

(3) Sommer, Bailey, Strong and Whitmore, *THIS JOURNAL*, **68**, 1881 (1946).

(4) Ushakov and Itenberg, *J. Gen. Chem. U. S. S. R.*, **7**, 2495 (1937).

By using the former conditions we were able to obtain a 19% yield of fairly pure β -chloroethyltriethylsilane, b. p. $81-82^\circ$ (11 mm.), n_D^{20} 1.4564, d_4^{20} 0.9122.

Anal. Calcd. for $C_8H_{19}SiCl$: Cl, 19.83; neut. equiv., 178.7. Found: Cl, 19.94; neut. equiv., 177.6.

β -Chloroethyltriethylsilane is quite unstable to heat and slowly decomposes at its boiling point even under reduced pressure. Titration of β -chloroethyltriethylsilane in homogeneous alcohol solution using standard alkali directly was unsatisfactory since reaction was too slow. However, an alcohol solution of this compound reacted quantitatively with an excess of standard alkali during a period of twenty minutes.

Reactions with Methylmagnesium Bromide.—There was prepared, in the usual manner, 0.93 equivalent of methylmagnesium bromide from 24 g. (1.0 mole) of magnesium turnings, excess liquid methyl bromide and 400 cc. of anhydrous ether. To this there was added over a period of one hour 62 g. (0.33 mole) of β -chloroethyldiethylchlorosilane. The ethylene gas evolved during the addition was passed into bromine and identified by the formation of ethylene bromide in 25% yield. After refluxing for four hours the reaction mixture was hydrolyzed with ice and dilute hydrochloric acid. The ether layer was separated and the water layer extracted with 100 cc. of ether. Upon distillation of the ether the residue was washed with concentrated sulfuric acid in order to remove silicon-oxygen compounds, followed by washing with carbonate solution and drying over calcium chloride. Fractionation gave 22 g. (0.19 mole) of dimethyldiethylsilane,⁵ b. p. 93.5° , n_D^{20} 1.4013, in 57.5% yield.

β -Chloroethyldiethylfluorosilane, 45 g. (0.27 mole) was treated with 0.64 equivalent of methylmagnesium bromide by a procedure similar to that used for β -chloroethyldiethylchlorosilane. Fractionation of the product gave 18.3 g. (0.16 mole) of dimethyldiethylsilane, b. p. $94-94.5^\circ$, n_D^{20} 1.4011, in 59% yield. The yield of ethylene as ethylene bromide was 36%.

Reactions with Liquid Ammonia.—In a 200-cc., three-necked flask equipped with dropping funnel, mercury-sealed stirrer and reflux condenser, there was placed 90 cc. of anhydrous liquid ammonia. The flask was then immersed in a Dry Ice and acetone-bath and 58 g. (0.31 mole) of β -chloroethyldiethylchlorosilane was added from the dropping funnel during one-half hour. After stirring for two hours, the excess ammonia was evaporated and the contents of the flask were diluted with ether and filtered to remove ammonium chloride. The ether was then removed from the product which was fractionally distilled in a glass-helix packed column of about 20 theoretical plates. There was obtained 31 g. (0.19 mole) of β -chloroethyldiethylaminosilane, b. p. $65-65.5^\circ$ (7 mm.), n_D^{20} 1.4624, d_4^{20} 0.9769, in 60% yield.

β -Chloroethyldiethylaminosilane is quite unstable and slowly decomposes upon standing to give ammonium chloride, ethylene and other products.

Anal. Calcd. for $C_8H_{18}SiClN$: Cl, 21.40. Found: Cl, 21.82.

Reactions with Aluminum Chloride.—In a 200-cc., three-necked flask equipped with reflux condenser, mercury-sealed stirrer and dropping funnel there were placed 150 cc. of dry pentane and 50 g. of anhydrous aluminum chloride. Through the dropping funnel there was then added 33 g. (0.18 mole) of β -chloroethyldiethylchlorosilane. A vigorous evolution of ethylene gas was observed which was identified by the formation of ethylene bromide. After stirring the reaction mixture for one hour the pentane solution was decanted from the aluminum chloride and the pentane distilled. Fractionation of the residue gave 21 g. (0.135 mole) of diethyldichlorosilane, b. p. 127° , n_D^{20} 1.4309, d_4^{20} 1.0504, neut. equiv. 79.2 (calcd. 78.6), in 77% yield.

By a procedure similar to that used for β -chloroethyldiethylchlorosilane, diethyldichlorosilane, 19.4 g. (0.124 mole), b. p. $126-127.5^\circ$, n_D^{20} 1.4313, d_4^{20} 1.0516, neut.

equiv. 79.8 (calcd. 78.6) was obtained in 71% yield from the reaction of 29 g. (0.17 mole) of β -chloroethyldiethylfluorosilane and anhydrous aluminum chloride in pentane solution. The expected product, diethylchlorofluorosilane, was not obtained.

Reaction of 15 g. (0.084 mole) of β -chloroethyltriethylsilane with 2 g. of aluminum chloride in 25 cc. of dry pentane by a procedure similar to that used for β -chloroethyldiethylchlorosilane gave a rapid evolution of ethylene and 10 g. (0.066 mole) of triethylchlorosilane, b. p. $144-146^\circ$, n_D^{20} 1.4304, d_4^{20} 0.8985, in 79% yield.

Pyrolysis of β -Chloroethyltriethylsilane.—In a 50-cc., round-bottom flask equipped with a reflux condenser which was connected to a bromine trap, there was placed 12 g. (0.067 mole) of β -chloroethyltriethylsilane. The contents of the flask was heated to reflux for three hours during which time the ethylene gas evolved was absorbed in the bromine trap and identified by the formation of ethylene bromide in 50% yield. Distillation of the liquid reaction product gave 6.5 g. (0.043 mole) of triethylchlorosilane, b. p. $144-147^\circ$, d_4^{20} 0.8987, neut. equiv. 153 (calcd. 151), in 64% yield.

Reactions with Miscellaneous Reagents.—The reaction of β -chloroethyldiethylchlorosilane with aqueous alkali will be described as typical.

In a 200-cc., three-necked flask equipped with reflux condenser, mercury-sealed stirrer and dropping funnel, there was placed 180 ml. of 1.25 *N* sodium hydroxide solution. The flask was connected through the condenser to a gas buret of one-liter capacity which contained saturated salt solution as the displacing liquid. Through the dropping funnel there was added 5.3 g. (0.029 mole) of β -chloroethyldiethylchlorosilane. A rapid rate of gas evolution occurred during the addition and after stirring the reaction mixture for five minutes, 710 cc. was evolved at 732 mm. and 24° . This gas was analyzed in an Orsat apparatus by absorbing the unsaturates in a salt solution saturated with bromine. The gas contained 89% unsaturates which represented an 87% yield of ethylene from the reaction. The liquid product from the reaction was probably diethylpolysiloxane since cleavage of ethyl-silicon linkages under the conditions used is unlikely. Distillation of the liquid product gave material having a boiling range of $250-400^\circ$.

The above reaction was repeated using larger quantities of reactants and the ethylene identified by absorption of the evolved gases in bromine. After removing the excess bromine with sodium bisulfite distillation of the crude product gave ethylene bromide, b. p. $128-130^\circ$, n_D^{20} 1.5391, d_4^{20} 2.179, in 69% yield.

The reaction of β -chloroethyldiethylchlorosilane with alkali to yield chloride ion was shown to be quantitative by titration of this compound in methanol with standard sodium hydroxide solution.⁶

Results with other reagents, obtained by a similar procedure, are found in Table I.

Discussion

Common Aspects of β -Elimination Involving Silicon and Dehydrohalogenation.—Dehydrohalogenation and β -elimination involving silicon and halogen are similar in three general ways: (1) Both types give olefins by a 1:2 elimination reaction. (2) Both types involve removal of an element more electropositive than carbon (silicon or hydrogen)⁶ together with an element more electronegative than carbon (chlorine). (3) Both types, regardless of the detailed mechanism, involve electron-release to carbon from an element more electropositive than carbon.

Mechanism.— β -Eliminations involving silicon, given by the reaction of β -chloroalkyltri-

(6) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 60.

(5) A. Bygden, Dissertation, Uppsala, 1916.

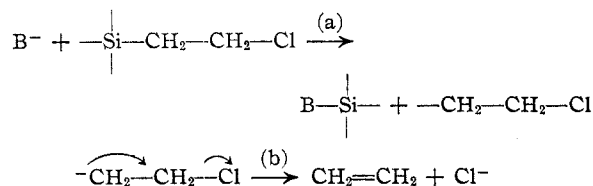
TABLE I

Compound	Reagent	Temperature	Reaction time, minutes	% β -El. ^c
I	H ₂ O	Room	5	30-40
II, III	H ₂ O	Room	5	<1
II	H ₂ O	Reflux	5	35-45
I, II	1.25 N NaOH in H ₂ O	Room	5	85-90
III	1.25 N NaOH in H ₂ O	Room	5	<5
III	50% CH ₃ OH-H ₂ O	Reflux	5	<5
III	1.25 N NaOH in 50% CH ₃ OH-H ₂ O	Reflux	5	40-50
I, II, III	CH ₃ OH	Reflux	5	<5
I	1.25 N KOH in CH ₃ OH	Room	5	70-75 ^b
II	1.25 N KOH in CH ₃ OH	Room	5	60-70 ^b
I	1.25 N NaOCH ₃ in CH ₃ OH	Room	5	60-70 ^b
II	1.25 N NaOCH ₃ in CH ₃ OH	Room	5	50-60 ^b
III	1.25 N NaOCH ₃ in CH ₃ OH	Room	5	<10 ^b
I, II	Anhydrous HOAc	Reflux	5	<5
I	1.25 N KOAc in HOAc	Reflux	5	30-40
II	1.25 N KOAc in HOAc	Reflux	5	40-50
I, II	Dry pyridine	Reflux	5	<5
I	0.2 N AgNO ₃ in CH ₃ OH	Room	10	97 ^c
II	0.2 N AgNO ₃ in CH ₃ OH	Room	30	45 ^c
III	0.2 N AgNO ₃ in CH ₃ OH	Room	10	95 ^c

^a Unless otherwise indicated, % β -elimination represents the yield of ethylene from the reaction which was determined by Orsat analysis. ^b Due to the solubility of ethylene in methanol at room temperature the values obtained are somewhat too small. ^c Values represent the yield of chloride ion from the reaction.

chlorosilanes with alkali, have been assumed to proceed by a mechanism involving initial nucleophilic attack of hydroxyl ion on silicon.² This hypothesis receives additional support in the present work which shows that bases greatly facilitate these reactions in methanol and acetic acid, as well as in water, and that nucleophilic anions other than hydroxyl, *i.e.*, methoxide and acetate, also exert a favorable effect. In contrast to compounds I and II, compound III reacts slowly with bases. Apparently, substitution of the halogen by alkyl inhibits nucleophilic attack on silicon.

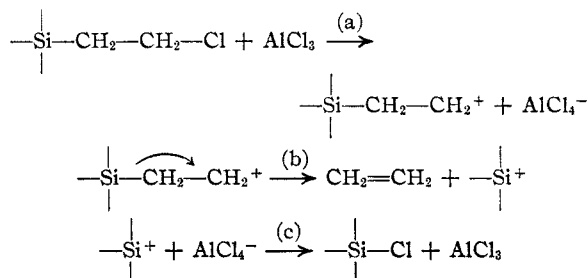
If the mechanism previously proposed (essentially a one-stage mechanism) is visualized in terms of two steps for convenience it at once becomes apparent that all of the facts reported are in accord with such a mechanism. Step (a), which



is rate-controlling, is naturally aided by an increased concentration of nucleophilic anions (B^-). Step (b) is very fast. Thus (a) and (b) are effectively simultaneous. This mechanism is similar to that established for the E_2 eliminations of ordinary organic halides which involve initial nucleophilic attack on β -hydrogen as in (a).^{7,8}

Dehydrohalogenation is also caused by electrophilic reagents such as aluminum chloride and

heavy metal salts. In these reactions the assumed mechanism, which is in harmony with the usual role of these reagents, involves electrophilic attack on halogen followed by electron-release from β -hydrogen to the formed carbonium ion or its equivalent.⁸ A similar mechanism for the β -eliminations here reported as catalyzed by aluminum chloride and silver nitrate in methanol is probable. In step (a) aluminum chloride, which



is known to aid the ionization of a C—Cl bond, gives a beta carbonium ion. Step (b) involves electron-release from electropositive silicon to electronically-deficient carbon. Step (c) which may be simultaneous or subsequent with (b) gives a chlorosilane by combination of chloride ion with a "siliconium ion," thus regenerating the catalyst.

Electron-release from silicon to electronically-deficient beta carbon as in (b) apparently represents a general mechanism whereby cleavage of the carbon-silicon bond can occur in a variety of organosilicon structures capable of giving a beta carbonium ion. This point will be demonstrated again and again in forthcoming papers from this Laboratory.

Dehydrohalogenation of reactive organic halides by Grignard reagents is not uncommon, and hence it is not surprising that methylmagnesium bromide gives β -elimination involving silicon with compounds I and II. A cyclic mechanism for these changes in which a carbanion R^- from a Grignard reagent attacks silicon in the 1:6 relation to it has been proposed.²

Thermal β -elimination of compound III probably involves "ionic" bond cleavage, but free-radical cleavage is not impossible in reactions of this type.

In the reactions discussed thus far, it is found that β -elimination involving silicon takes place far more readily than the dehydrohalogenation of analogous primary alkyl chlorides. An apparent exception to this has been reported by Hurd⁹ in which quinoline gives a good yield of the dehydrohalogenation product from α - and β -chloroalkyltrichlorosilanes. We have repeated this work with pure β -chloroethyltrichlorosilane and find that vinyltrichlorosilane is obtained in good yield (dehydrohalogenation) although a small amount of silicon tetrachloride (β -elimination involving silicon) is also formed. An explanation for this may be sought in the fact that tertiary organic bases, such as quinoline or pyridine, differ from the

(7) Skell and Hauser, *THIS JOURNAL*, **67**, 1661 (1945).

(8) Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(9) Hurd, *THIS JOURNAL*, **67**, 1813 (1945).

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 -chloroethyl-

diethylchlorosilane, 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.

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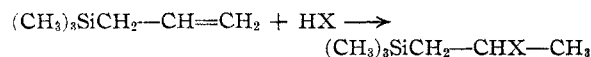
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Reactions of Allyltrimethylsilane^{1,2}

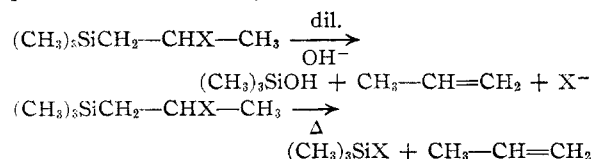
BY LEO H. SOMMER, LESLIE J. TYLER³ AND FRANK C. WHITMORE

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.

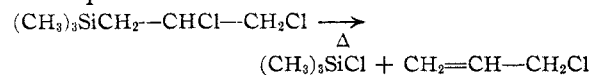


The assigned structures of the products, β -bromo-*n*-propyltrimethylsilane and β -iodo-*n*-propyltrimethylsilane, are based on the following reactions which are typical of β -haloalkyl silicon compounds.⁴ γ -Haloalkylsilanes are heat stable and



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.



(1) Paper XVII in a series on organosilicon compounds. For Paper XVI see *THIS JOURNAL*, **70**, 2869 (1948).

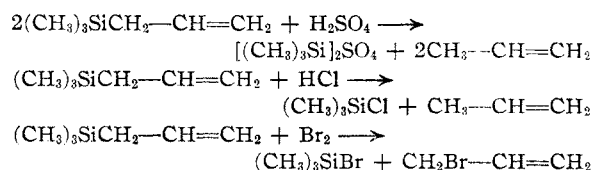
(2) Taken from work submitted by Leslie J. Tyler to the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the M.S. degree.

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

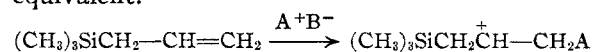
(4) (a) Sommer and Whitmore, *ibid.*, **68**, 485 (1946); (b) Sommer, Dorfman, Goldberg and Whitmore, *ibid.*, **68**, 488 (1946); (c) Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, **68**, 1083 (1946); (d) Sommer, Bailey and Whitmore, *ibid.*, **70**, 2869 (1948).

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

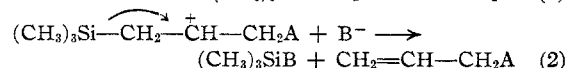
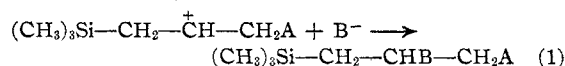
Type II reactions of allyltrimethylsilane, involving cleavage of the allyl-silicon bond, were given by concentrated sulfuric acid, hydrogen chloride and bromine.



Previous work has shown that β -carbonium ions (Si---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.



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}



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