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Vinylsilanes, Chlorovinylsilanes and β-Styryltrimethylsilane. Further Studies on the α-Silicon Effect and β-Eliminations Involving Silicon[1]

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Syntheses of certain vinylsilanes and substituted vinylsilanes are described. The reactions of vinyltrimethylsilane with hydrogen bromide, hydrogen iodide, bromine, chlorine, ozone and butyraldehyde have been studied. While vinyltrimethylsilane gives non-Markownikoff addition with hydrogen iodide, isopropenyltrimethylsilane gives α-chloroisopropyltrimethylsilane with concd. hydrochloric acid. Preliminary data on the vinyl polymerization of α-chlorovinylsilanes are reported and the reactions of β-styryltrimethylsilane with concd. sulfuric acid and bromine have been found to give cleavage of the β-styryl group from silicon.

Introduction

Vinylsilanes are of considerable theoretical interest from the standpoint of the effect of silicon on the chemical behavior of an olefinic grouping directly linked to that atom. The π-electrons of a carbon-to-carbon double bond are highly polarizable and hence a study of these compounds should provide important information on the electrical effects of silicon in organosilicon compounds. In this communication we wish to report a fairly detailed study of the α-silicon effect[3] in vinyltrimethylsilane; the preparation and somewhat more limited study of other vinylsilanes, including compounds having substituents at the α- and β-carbon atoms of the vinyl grouping; and new data concerning β-eliminations involving silicon.

Preparation of Vinylsilanes.—For the preparation of vinylsilanes, three methods were employed. Method I involved dehydrochlorination of α- and β-chloroethylchlorosilanes with quinoline.[4] Application of this method to α-chloroethyldiethylchlorosilane gave vinyldiethylchlorosilane, and vinyltrichlorosilane resulted from dehydrochlorination of α- and β-chloroethyltrichlorosilanes.[4] Method II comprised dehydrochlorination of α-chloroethyltrialkylsilanes with potassium hydroxide in *n*-butyl alcohol. Thus, α-chloroethylmethyldiethylsilane was converted to the corresponding vinylsilane by this reagent in yields of about 45%. Method III involved treatment of vinylchlorosilanes with the appropriate Grignard reagents.

Of the above methods, method III now seems to offer the best approach. Method II suffers from yield limitations imposed by the α-fission reaction of α-chloroethyltrialkylsilanes with alcoholic bases. This type of reaction involves nucleophilic attack on silicon and results in cleavage of the α-chloroethyl group from silicon as ethyl chloride.[5] Method I for the preparation of vinylchlorosilanes to be used as starting materials in method III is now obsolete in view of the commercial availability of vinyltrichlorosilane.[6]

Table I lists the new vinylsilanes prepared in the present work and some of their properties.

TABLE I

VINYLSILANES

Silane	B.p. °C.	B.p. Mm.	n^{20}_D	d^{20}	*MR*D Found	*MR*D Calcd.	Method	Yield, %	Silicon, % Found	Silicon, % Calcd.
Vinyltrimethyl-[a]	55	739	1.3902	0.6903	34.43	34.44	III	71	27.7	28.0
Vinyldimethylethyl-[b]	88	737	1.4089	.7242	38.99	39.07	III	68	24.4	24.6
Vinyldiethylmethyl-[c]	118	734	1.4230	.7503	43.53	43.70	II	45	21.7	21.9
Vinyldiethylphenyl-[d]	123	29	1.5117	.9023	63.26	63.82	III	80	14.9	14.7
Vinyldiethylchloro-[e]	138	738	1.4392	.9061	43.16	43.33	I	31	18.8	18.9

[a] Vinyltrimethylsilane has been reported subsequent to our synthesis[7] by R. Nagel and H. W. Post, *J. Org. Chem.*, **17**, 1379 (1952). [b] Prepared from vinyltrichlorosilane by treatment with ethyl- and methylmagnesium bromides, in that order. [c] Prepared by treatment of α-chloroethylmethyldiethylsilane[19] with butanolic potassium hydroxide at the boiling point for 5 hours. [d] Prepared from vinyldiethylchlorosilane and phenylmagnesium bromide. [e] Prepared from the reaction of α-chloroethyldiethylchlorosilane[19] with quinoline; Cl, 23.6 (calcd. Cl, 23.8).

Chemical Properties of Vinyltrimethylsilane.—Since vinyltrimethylsilane is the simplest member of the vinyltrialkylsilane family and contains only one reactive function, this compound was selected for a detailed study concerning the chemical properties of a vinyl group directly linked to silicon.[7]

Hydrogen bromide does not add to vinyltrimethylsilane in the absence of a peroxide catalyst during a reasonable time. However, in the presence of benzoyl peroxide hydrogen bromide was almost quantitatively absorbed with the formation of β-bromoethyltrimethylsilane in 79% yield.

$$Me_3SiCH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} Me_3SiCH_2CH_2Br$$

Addition of hydrogen iodide to vinyltrimethylsilane gave β-iodoethyltrimethylsilane.

$$Me_3SiCH{=}CH_2 + HI \longrightarrow Me_3SiCH_2CH_2I$$

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(1) Paper 42 in a series on organosilicon chemistry; for paper 41 see THIS JOURNAL, **76**, 1609 (1954).

(2) Deceased.

(3) F. C. Whitmore and L. H. Sommer, THIS JOURNAL, **68**, 481 (1946).

(4) D. T. Hurd, *ibid.*, **67**, 1813 (1945).

(5) For a similar cleavage of the chloromethyl group in chloromethyltrimethylsilane see J. L. Speier, *ibid.*, **70**, 4142 (1948).

(6) Linde Air Products Co., Tonawanda, New York.

(7) The material in the present manuscript on the synthesis and chemical properties of vinyltrimethylsilane was presented before the Organic Division at the 111th Meeting of the American Chemical Society, Atlantic City, N. J., April 16, 1947.

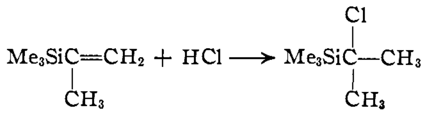
A similar result has been reported recently for the aluminum chloride catalyzed addition of hydrogen chloride to vinyltrichlorosilane which gave β-chloroethyltrichlorosilane.[8]

$$\mathrm{Cl_3SiCH{=}CH_2 + HCl \xrightarrow{AlCl_3} Cl_3SiCH_2CH_2Cl}$$

Taken together these data provide clear evidence for the non-Markownikoff addition of hydrogen chloride and iodide to certain vinylsilanes, a result which is contrary to the one expected on the basis of an established *inductive effect* of electron-release relative to alkyl for trimethylsilyl, $\mathrm{Me_3Si}$.[9] These experiments seem to indicate a non-inductive electrical effect of trimethylsilyl which operates when that group is *directly linked* to a vinyl grouping. Markownikoff addition takes place when allyltrimethylsilane is treated with hydrogen iodide.[10]

$$\mathrm{Me_3SiCH_2{-}CH{=}CH_2 + HI \longrightarrow Me_3SiCH_2CHICH_3}$$

Further, the above non-inductive effect of trimethylsilyl was shown to be easily overcome by the presence of a single α-methyl substituent at the vinyl grouping. While isopropenyltrimethylsilane[11] did not react in a reasonable time with hydrogen chloride gas, reaction with concd. hydrochloric acid gave α-chloroisopropyltrimethylsilane in the present work.



$$\mathrm{Me_3Si\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + HCl \longrightarrow Me_3Si\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_3}$$

Also, the intramolecular rearrangement of isopropenyltrimethylsilane with concd. sulfuric acid to give, after treatment with water, *t*-butyldimethylsilanol hemihydrate must involve addition of a proton to the terminal methylene group of the olefinic grouping in the step preliminary to rearrangement.[11]

Thus, the magnitude of the non-inductive effect of trimethylsilyl is indeed small, and while this effect might be ascribed to a very limited conjugative ability of the trimethylsilyl group,[12] we wish to postpone detailed discussion until more data have been accumulated.

In order to conclusively identify β-bromoethyltrimethylsilane and β-iodoethyltrimethylsilane obtained from the addition of hydrogen bromide and hydrogen iodide to vinyltrimethylsilane, the corresponding α-isomers were prepared from α-chloroethyltrimethylsilane.[13]

$$\mathrm{CH_3CHClSiMe_3 \xrightarrow{Mg} CH_3CH(MgCl)SiMe_3}$$

$$\mathrm{CH_3CH(MgCl)SiMe_3 \xrightarrow{Br_2} CH_3CHBrSiMe_3}$$

$$\mathrm{CH_3CHClSiMe_3 \xrightarrow[acetone]{NaI} CH_3CHISiMe_3}$$

In striking contrast to the β-isomers obtained from reaction of vinyltrimethylsilane, α-bromoethyltrimethylsilane and α-iodoethyltrimethylsilane are relatively unreactive with dilute alkali, whereas β-bromoethyltrimethylsilane and β-iodoethyltrimethylsilane give complete reaction on titration with 0.1 *N* sodium hydroxide. These latter reactions are extremely rapid β-eliminations involving silicon typical of β-haloalkylsilanes and are not given by α-haloalkylsilanes.[14]

$$\mathrm{Me_3SiCH_2CH_2X \xrightarrow{OH^-} Me_3SiOH + CH_2{=}CH_2 + X^{\ominus}}$$

α-Chloro-isopropyltrimethylsilane as obtained from reaction of isopropenyltrimethylsilane with concd. hydrochloric acid is a typical α-chloroalkylsilane and gives no reaction on titration with dilute alkali.

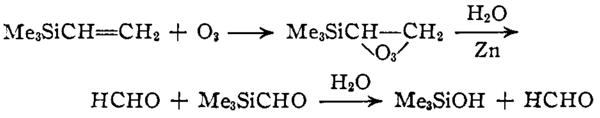
Vinyltrimethylsilane reacts with both bromine and chlorine to form the corresponding α,β-dihaloethyltrimethylsilanes.

$$\mathrm{Me_3SiCH{=}CH_2 \xrightarrow{X_2} Me_3SiCHXCH_2X}$$

These compounds, which have both α- and β-halogen atoms undergo β-elimination with dilute alkali and form vinyl halides.

$$\mathrm{Me_3SiCHXCH_2X \xrightarrow{OH^-} Me_3SiOH + CH_2{=}CHX + X^{\ominus}}$$

The addition of ozone to vinyltrimethylsilane results in the formation of a thick, sirupy ozonide which appears to be stable at room temperature. However, upon hydrolysis with hot water and zinc dust trimethylsilylformaldehyde was not obtained. Instead, the products were trimethylsilanol and formaldehyde.



$$\mathrm{Me_3SiCH{=}CH_2 + O_3 \longrightarrow Me_3Si\underset{\diagdown O_3 \diagup}{CH{-}CH_2} \xrightarrow[Zn]{H_2O}}$$

$$\mathrm{HCHO + Me_3SiCHO \xrightarrow{H_2O} Me_3SiOH + HCHO}$$

Thus, the present work indicates hydrolytic instability for an organosilicon structure having a carbonyl group directly bound to silicon. Organosilicon compounds containing a carbonyl group linked to α-carbon, *e.g.*, $\mathrm{Me_3SiCH_2COCH_3}$, also undergo cleavage of the organo-functional group from silicon.[15]

Fission of the aldehyde group from silicon is undoubtedly made possible by the electronegative character of that group and the high polarizability of the carbonyl function.[16]

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[8] G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953).

[9] (a) L. H. Sommer, J. R. Gold, G. M. Goldberg and N. S. Marans, THIS JOURNAL, **71**, 1509 (1949); (b) L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

[10] L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

[11] L. H. Sommer and F. J. Evans, *ibid.*, **76**, 1030 (1954).

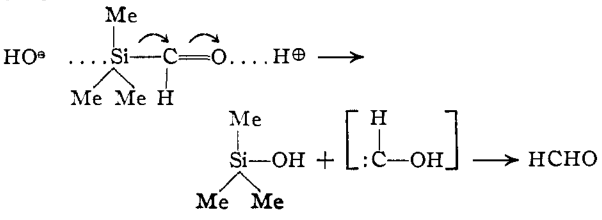
[12] R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953); J. L. Speier, *ibid.*, **75**, 2930 (1953).

[13] L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485 (1946).

[14] (a) L. H. Sommer, G. M. Goldberg, E. Dorfman and F. C. Whitmore, *ibid.*, **68**, 1083 (1946); (b) L. H. Sommer, D. L. Bailey and F. C. Whitmore, *ibid.*, **70**, 2869 (1948).

[15] For the mechanisms of these latter cleavages (*e.g.*, of $\mathrm{Me_3SiCH_2COMe}$) with electrophilic and nucleophilic reagents, and for pertinent references see L. H. Sommer and R. P. Pioch, *ibid.*, **76**, 1606 (1954).

[16] With water alone, bearing in mind the considerable contribution of the dipolar form, $\oplus\overset{|}{\underset{|}{C}}{-}O^{\ominus}$, to the ground state of the carbonyl group, a concerted mechanism of the following type seems likely



$$\mathrm{HO^{\ominus}\;\ldots\overset{\displaystyle Me}{\overset{|}{\underset{\displaystyle Me\ \ Me}{Si}}}{-}\underset{\displaystyle H}{\underset{|}{C}}{=}O\ldots H^{\oplus} \longrightarrow}$$

$$\mathrm{\overset{\displaystyle Me}{\overset{|}{\underset{\displaystyle Me\ \ Me}{Si}}}{-}OH + \left[:\overset{\displaystyle H}{\overset{|}{C}}{-}OH\right] \longrightarrow HCHO}$$

Kharasch[17] has reported the addition of butyraldehyde to olefins in the presence of a catalytic amount of diacetyl peroxide. We have found that vinyltrimethylsilane behaves like an ordinary olefin in this reaction.

$$\mathrm{Me_3SiCH{=}CH_2 + C_3H_7CHO \xrightarrow{\text{peroxide}} Me_3SiCH_2CH_2COC_3H_7}$$

7,7-Dimethyl-7-silaoctane-4-one, the butyraldehyde adduct, readily forms a semicarbazone and a 2,4-dinitrophenylhydrazone. It does not readily give cleavage of the ketoalkyl group from silicon, thus showing that the above structure is the correct one, since the alternate mode of addition would give $Me_3SiCH(CH_3)COC_3H_7$. The addition of the C_3H_7CO radical to the terminal carbon of vinyltrimethylsilane is characteristic of ordinary olefins.[17]

Chloroethylchlorosilanes and Chlorovinylsilanes.—Following the discovery of the use of sulfuryl chloride in the presence of benzoyl peroxide as a chlorinating agent for aliphatic compounds,[18] we applied this excellent method to ethyltrichlorosilane and obtained a 90% yield of monochlorinated product which consisted of the α- and β-chloroethylsilanes in a molar ratio of 1 to 2.5, respectively.[13] Subsequently it was found that triethylchlorosilane gives the α- and β-monochloro derivatives in a ratio of 1.2 to 1, while chlorination with sulfuryl chloride of tetraethylsilane gives only α-chlorotriethylsilane and none of the β-isomer.[14b,19] To amplify these data concerning the effect of structural variations on the directive effects of silicon in free radical chlorinations, we now report a study of the sulfuryl chloride chlorination of diethyldichlorosilane, α-chloroethyltrichlorosilane and β-chloroethyltrichlorosilane.

Chlorination of diethyldichlorosilane gave a 40% yield of monochlorinated product,[20] 15% of α- and 25% of β-chloroethylethyldichlorosilane. Thus sulfuryl chloride chlorinations of ethylsilanes show a progressive change in the directive effects of silicon, with $SiCl_3$ directing strongly to the β-carbon and $SiEt_3$ being strongly α-directing.

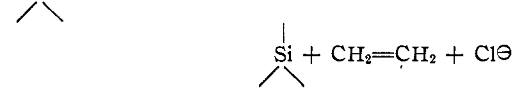
Chlorination of β-chloroethyltrichlorosilane gave a 72% yield of β,β-dichloroethyltrichlorosilane. α-Chloroethyltrichlorosilane yielded 31% of α,α-dichloroethyltrichlorosilane and 32% of α,β-dichloroethyltrichlorosilane. Even in the unlikely event that a 28% yield of α,β-dichloroethyltrichlorosilane was obtained initially from β-chloroethyltrichlorosilane and was then converted to a trichloroethyltrichlorosilane, the ratio of β- to α-chlorination would still be 2.6 to 1. By the same argument, the maximum initial yield of α,β-dichloroethyltrichlorosilane from chlorination of α-chloroethyltrichlorosilane might have been 70%, about half of which was converted to trichloroethyltrichlorosilane. However, even if this unlikely situation were the correct one, the ratio of β- to α-chlorination would be only 2.3 to 1. On balance, therefore, it seems clear that in β-chloroethyltrichlorosilane the strong β-directing effect of $SiCl_3$ completely overbalances the normal repelling tendency of the first chlorine for the second, and that in α-chloroethyltrichlorosilane the α-chlorine atom exerts an effect of considerable magnitude which opposes the β-directing effect of $SiCl_3$ and directs the second chlorine to the α-carbon. A situation somewhat parallel to that for α-chloroethyltrichlorosilane obtains in the chlorination of methyltrichlorosilane, where introduction of the first α-chlorine so activates the α-carbon as to make isolation of the monochloro compound quite difficult. In fact, the only product readily available from the reaction of chlorine and methyltrichlorosilane in the *liquid phase* is trichloromethyltrichlorosilane.[21] While the origin and nature of the directive effects of silicon in radical chlorinations are of considerable interest, the data at hand are not yet sufficient to warrant detailed discussion. For example, data on the sulfuryl chloride chlorination of compounds such as Cl_3CEt appear to be unavailable.

Dehydrochlorination of β,β-dichloroethyltrichlorosilane with quinoline gave β-chlorovinyltrichlorosilane in 50% yield.

$$\mathrm{Cl_2CHCH_2SiCl_3 \xrightarrow{C_9H_7N} ClCH{=}CHSiCl_3}$$

Subsequent to the above synthesis,[22] the preparation of β-chlorovinyltrichlorosilane from reaction of *cis*- and *trans-sym*-dichloroethylene with trichlorosilane at 610° was reported.[23] Our synthesis of β-chlorovinyltrichlorosilane by an unequivocal method confirms the assigned structure of the product obtained in the above high temperature process.

The reactivity with dilute alkali of the β-carbon–chlorine bond in β-chlorovinyltrichlorosilane as compared to β-chloroethylsilanes was of interest in connection with our mechanism for these β-eliminations involving silicon, *viz.*



In our first paper on this subject,[14a] we stated that in these reactions "two bonds are broken, but each fission assists the other, the two together constituting a single synchronized process." Subsequently it was shown that electronegative substituents at the silicon which facilitate nucleophilic attack at that atom and thus aid fission (1) give an increased rate of β-elimination.[24] In the present work, β-chlorovinyltrichlorosilane provides an excellent means for studying the effect of hindering fission (2) in view of the fact that vinyl halides are well known to be less reactive than their satu-

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[17] M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

[18] M. S. Kharasch and H. C. Brown, This Journal, **61**, 2142 (1939).

[19] L. H. Sommer, D. L. Bailey, W. A. Strong and F. C. Whitmore, *ibid.*, **68**, 1881 (1946).

[20] The lower yield of monochlorinated product in comparison to the ethyltrichlorosilane chlorination is reasonably attributed to the presence of two ethyl groups and the consequent formation of bis-chloroethyldichlorosilanes in significant amounts.

[21] P. A. DiGiorgio, L. H. Sommer and F. C. Whitmore, This Journal **70**, 3512 (1948). *Cf.* J. Y. Speier, *ibid.*, **73**, 824 (1951).

[22] G. M. Goldberg, Ph.D. thesis, The Pennsylvania State College, 1949.

[23] C. L. Agre and W. Hilling, This Journal, **74**, 3895 (1952).

[24] Compare the reactivity of β-chloroethyldiethylchlorosilane with that of β-chloroethyltriethylsilane toward alcoholic and aqueous bases, ref. 14b.

rated analogs in displacement reactions involving the carbon–halogen bond. In agreement with the above mechanism, β-chlorovinyltrichlorosilane gave no β-elimination on titration with dilute alkali, in contrast to β,β-dichloroethyltrichlorosilane, α,β-dichloroethyltrichlorosilane and other known β-haloalkylsilanes which give quantitative β-elimination under these conditions.

Dehydrochlorination of α,α-dichloroethyltrichlorosilane gave α-chlorovinyltrichlorosilane in 58% yield.

$$CH_3CCl_2SiCl_3 \xrightarrow{C_9H_7N} CH_2{=}CClSiCl_3$$

The preparation of α-chlorovinyltrichlorosilane by this unequivocal method confirms the structure of the dehydrochlorination product from α,β-dichloroethyltrichlorosilane as being α-chlorovinyltrichlorosilane.[23,25] Treatment of α-chlorovinyltrichlorosilane with methylmagnesium bromide gave α-chlorovinyltrimethylsilane in 60% yield.

$$CH_2{=}CClSiCl_3 + 3MeMgBr \longrightarrow CH_2{=}CClSiMe_3$$

α-Chlorovinyltrichlorosilane on standing at room temperature gave a gradually increasing deposit of a flocculent white solid. Irradiation with ultraviolet light accelerated the process to the point where virtually complete solidification occurred in 32 hours. α-Chlorovinyltrimethylsilane gave virtually no solid product on standing at room temperature in the presence or absence of ultraviolet light. While the white solid from α-chlorovinyltrichlorosilane is probably a vinyl-type polymer, absolute proof is not available at present.

β-Styryltrimethylsilane.—As a further example of vinylsilanes having a substituent at the vinyl grouping, β-styryltrimethylsilane has been synthesized.[26]

$$C_6H_5CH{=}CHMgBr + Me_3SiCl \longrightarrow C_6H_5CH{=}CHSiMe_3$$

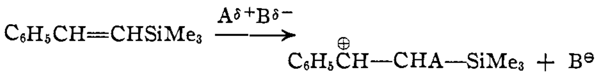
Sulfuric acid, bromine and catalytic hydrogenation gave the reactions

$$C_6H_5CH{=}CHSiMe_3 + H_2SO_4 \longrightarrow \text{polystyrene} + Me_3SiOSO_3H \xrightarrow{H_2O} Me_3SiOSiMe_3$$

$$C_6H_5CH{=}CHSiMe_3 + Br_2 \longrightarrow C_6H_5CH{=}CHBr + Me_3SiBr$$

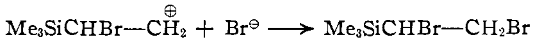
$$C_6H_5CH{=}CHSiMe_3 + H_2 \xrightarrow[\text{Ni}]{\text{Raney}} C_6H_5CH_2CH_2SiMe_3$$

The above reactions with sulfuric acid and bromine to give cleavage of the β-styryl group from silicon are reasonably formulated, in terms of the modern theory of the addition of electrophilic reagents to olefins, as involving initial formation of a β-carbonium ion or its equivalent π-complex.



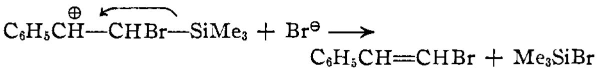
$$C_6H_5CH{=}CHSiMe_3 \xrightarrow{A^{\delta+}B^{\delta-}} C_6H_5\overset{\oplus}{C}H{-}CHA{-}SiMe_3 + B^{\ominus}$$

Addition of the positive part of the attacking reagent to the α-carbon, with consequent formation of a β-carbonium ion, is undoubtedly facilitated in the present case by the usual resonance stabilization of a positive charge on a carbon atom linked to a phenyl group. The formed carbonium ion can satisfy its electron deficiency in one of two ways. Firstly, it may unite with the negative part of the attacking reagent to give the addition product, as was found for the reaction of vinyltrimethylsilane with bromine, *viz.*



$$Me_3SiCHBr{-}\overset{\oplus}{C}H_2 + Br^{\ominus} \longrightarrow Me_3SiCHBr{-}CH_2Br$$

Secondly, it may undergo carbon–silicon cleavage by a mechanism similar to the E_1 eliminations of ordinary halides in which Me_3Si is eliminated instead of β-hydrogen, *viz.*[14b]



$$C_6H_5\overset{\oplus}{C}H{-}CHBr{-}SiMe_3 + Br^{\ominus} \longrightarrow C_6H_5CH{=}CHBr + Me_3SiBr$$

This type of β-elimination involving silicon, which comprises electron-release from silicon to electronically deficient β-carbon, is a very common reaction with a variety of organo-functional silanes capable of giving β-carbonium ion with electrophilic reagents, *e.g.*, allyltrimethylsilane,[10] 1-trimethylsilylindene,[27] β-haloalkylsilanes of the formula $ClCH_2CH_2SiR_2X$, where X is fluorine or chlorine, and $ClCH_2CH_2SiR_3$.[14b,28] The failure of β-chloroethyltrichlorosilane to give β-elimination involving silicon with aluminum chloride, which made possible the use of this halide in a Friedel–Crafts reaction,[8] in our view constitutes evidence that the above type β-eliminations with electrophilic reagents involve formation of a siliconium ion in the rate-determining step followed by a fast step comprising reaction of the siliconium ion with a negative ion.[29]

Experimental

Reactions of Vinyltrimethylsilane. A. With Bromine.—In a trap immersed in a bath of Dry Ice and acetone, there was placed 25 g. (0.25 mole) of vinyltrimethylsilane. To this there was added drop by drop with shaking 38 g. (0.24 mole) of dry liquid bromine. The bromine color was absorbed by the vinyltrimethylsilane and toward the end of the reaction white crystals of the dibromide were observed. Fractionation of the crude product gave 55 g. (0.21 mole) of α,β-dibromoethyltrimethylsilane, b.p. 74–75° (8 mm.), $n^{20}D$ 1.5095, d^{20} 1.5497, m.p. −9 to −11°, a yield of 89%.

Anal. Calcd. for $C_5H_{12}SiBr_2$: Br, 61.5; neut. equiv., 260. Found: Br, 61.1; neut. equiv., 263.

In order to further characterize the above compound, 23 g. of α,β-dibromoethyltrimethylsilane was added to a solution of 20 g. of potassium hydroxide in 180 cc. of 50% methanol–water during 10 minutes. Gas was evolved during the addition and after refluxing the reaction mixture for several minutes, 6.5 g. of material was collected in a Dry Ice trap and identified as vinyl bromide, b.p. 16° at 736 mm., mol. wt. (vapor density method) 108, a 69% yield.

B. With Chlorine.—In a trap immersed in a bath of Dry Ice and acetone there was placed 35 g. (0.35 mole) of vinyltrimethylsilane. By means of a flowmeter the theoretical amount of chlorine gas was passed into the trap and absorbed by the vinyl compound. Upon warming to room temperature, the crude dichloride evolved hydrogen chloride indicating that a considerable amount of substitution may also have taken place. Fractionation gave 31 g. (0.18 mole) of α,β-dichloroethyltrimethylsilane, b.p. 61° (14 mm.), $n^{20}D$ 1.4617, d^{20} 1.0573, m.p. −14.5 to −15.5°, a yield of 52%.

Anal. Calcd. for $C_5H_{12}SiCl_2$: Cl, 41.45; neut. equiv., 171. Found: Cl, 41.49; neut. equiv., 171.5.

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[25] C. Tamborski and H. W. Post, *J. Org. Chem.*, **17**, 1397 (1952).

[26] For the synthesis of β-styryltriphenylsilane and cleavage of this compound with hydrogen chloride in acetic acid solution see H. Gilman and J. F. Nobis, THIS JOURNAL, **72**, 2629 (1950).

[27] L. H. Sommer and N. S. Marans, *ibid.*, **73**, 5135 (1951).

[28] For examples of this type of β-elimination with compounds giving a β-carbonium ion by an intramolecular rearrangement process see L. H. Sommer, D. L. Bailey, J. R. Gould and F. C. Whitmore, *ibid.*, **76**, 801 (1954).

[29] *Cf.* L. H. Sommer, W. P. Barie and J. R. Gould, *ibid.*, **75**, 3765 (1953).

By the procedure described above for α,β-dibromoethyltrimethylsilane, the reaction of α,β-dichloroethyltrimethylsilane with potassium hydroxide in methanol–water gave vinyl chloride, b.p. −14 to −15° at 729 mm., mol. wt. (vapor density method) 64, 68% yield.

C. With Hydrogen Bromide.—In a large test-tube equipped with a gas inlet tube and a reflux condenser, and immersed in a salt–ice-bath, there was placed 16 g. (0.16 mole) of vinyltrimethylsilane and 0.1 g. of benzoyl peroxide catalyst. Dry hydrogen bromide was passed into the compound and after a few minutes marked absorption of the hydrogen bromide was observed. Addition of hydrogen bromide was continued until no further absorption was noted. Fractionation gave 23 g. (0.13 mole) of β-bromoethyltrimethylsilane, b.p. 64–65° (39 mm.), n^{20}D 1.4575, d^{20} 1.1499, a yield of 79%.

Anal. Calcd. for $C_5H_{13}SiBr$: Br, 44.1; neut. equiv., 181. Found: Br, 43.9; neut. equiv., 181.5.

β-Bromoethyltrimethylsilane was further characterized by the independent synthesis of the isomeric α-bromoethyltrimethylsilane as follows:

There was prepared in the usual manner 0.66 mole of the Grignard reagent of α-chloroethyltrimethylsilane by the reaction of 127 g. (0.93 mole) of the chloride with 24 g. (1 mole) of magnesium in 500 ml. of anhydrous ether. To the Grignard reagent there was added 101 g. (0.63 mole) of dry, liquid bromine and the reaction mixture was stirred for two hours. After working up the above reaction mixture in the usual manner and removing the ether, fractionation gave 55.8 g. (0.31 mole) of α-bromoethyltrimethylsilane, b.p. 134° (736 mm.), n^{20}D 1.4509, d^{20} 1.1440, a yield of 33%.

Anal. Calcd. for $C_5H_{13}SiBr$: Br, 44.12. Found: Br, 43.81.

α-Bromoethyltrimethylsilane is fairly inert toward dilute alkali and gives no reaction on titration.

D. With Hydrogen Iodide.—In a large test-tube equipped with reflux condenser and gas inlet tube there was placed 15 g. (0.15 mole) of vinyltrimethylsilane. Hydrogen iodide was passed into the vinyltrimethylsilane for a period of four hours. Fractionation gave 22.5 g. (0.10 mole) of β-iodoethyltrimethylsilane, b.p. 76–76.5° (27 mm.), n^{20}D 1.5008, d^{20} 1.3862, a yield of 65%.

Anal. Calcd. for $C_5H_{13}SiI$: I, 55.6; neut. equiv., 228. Found: I, 55.4; neut. equiv., 231.

β-Iodoethyltrimethylsilane is quite unstable and decomposes to give free iodine as one of the decomposition products.

Iodoethyltrimethylsilane was further characterized by the independent synthesis of the isomeric α-iodoethyltrimethylsilane as follows:

In a 1-liter, round-bottom flask equipped with reflux condenser and drying tube, there was placed 46 g. (0.33 mole) of α-chloroethyltrimethylsilane, 90 g. of dry sodium iodide and 500 ml. of dry acetone. The mixture was refluxed on the steam-bath for 32 hours. After removal of most of the acetone the residual liquid was washed with water and dried. Fractionation gave 16 g. (0.07 mole) of α-iodoethyltrimethylsilane, b.p. 156° (729 mm.), n^{20}D 1.4941, d^{20} 1.3862, a yield of 20%.

Anal. Calcd. for $C_5H_{13}SiI$: I, 55.6. Found: I, 55.5.

α-Iodoethyltrimethylsilane is a stable colorless liquid, inert toward alkali at room temperature.

E. With Ozone.—In a large trap equipped with a ground-glass joint and immersed in a salt–ice-bath, there was placed 10 g. (0.1 mole) of vinyltrimethylsilane and 150 ml. of dry pentane. By means of the ground-glass joint the trap was connected to an apparatus for generating ozone. The outlet to the trap was connected to another trap immersed in Dry Ice and acetone. Ozone was bubbled through the solution of pentane and vinyltrimethylsilane until the rubber tubing connected to the outlet tube cracked. At this point a thick sirupy ozonide was observed which upon warming to room temperature showed no tendency to decompose. The ozonide was hydrolyzed in the usual manner by steam distillation from a suspension of zinc dust in water. Formaldehyde was identified as one of the products of the reaction by the preparation of the 2,4-dinitrophenylhydrazone, m.p. 162°, and dimedone derivative, m.p. 191°, from the water layer. Fractionation of the pentane layer in a column and subsequent distillation of the residual liquid gave a mixture of trimethylsilanol and hexamethyldisiloxane which upon dehydration with a drop of trimethylchlorosilane and refractionation gave 4.9 g. (0.030 mole) of hexamethyldisiloxane, b.p. 98–99°, n^{20}D 1.3780, a yield of 61%.

F. With Butyraldehyde.—In a 200-cc. three-necked flask equipped with dropping funnel, reflux condenser and thermometer there was placed 30 g., 0.42 mole, of freshly distilled butyraldehyde. After heating the butyraldehyde in the flask to reflux a solution of 1 g. of freshly prepared diacetyl peroxide in 10 g. of vinyltrimethylsilane was added through the dropping funnel over the course of one hour. The reaction mixture was then refluxed for 20 hours during which time the temperature of the solution rose from 64 to 82°. Fractionation gave 7,7-dimethyl-7-silaoctane-4-one, b.p. 53° at 4 mm., n^{20}D 1.4294, mol. wt. cryoscopically in benzene 174 (calcd. 172).

Anal. Calcd. for $C_9H_{20}OSi$: Si, 16.3. Found: Si, 16.2.

A semicarbazone was prepared, m.p. 72–73°.

Anal. Calcd. for $C_{10}H_{23}ON_3Si$: Si, 12.2. Found: Si, 11.9.

Reaction of Isopropenyltrimethylsilane with Hydrochloric Acid.—Isopropenyltrimethylsilane, 15 g., 0.131 mole, was stirred with 150 ml. of concd. hydrochloric acid at 50° for 17 hours. At the end of this time, when stirring was stopped, two liquid layers formed. However, on standing with external cooling, a mass of white crystals formed in the upper layer. When cold, the crystals were filtered, washed with three 25-ml. portions of water and then dissolved in 50 ml. of ether. The ether solution was dried over calcium chloride. The ether was then evaporated and the crystals were sublimed. These crystals were white and waxy and sublimed slowly at room temperature in fern-like patterns. A total of 6.9 g., 0.046 mole, of α-chloroisopropyltrimethylsilane, m.p. 95–97°, a 35% yield was obtained. This relatively low yield is likely due to incomplete reaction, since isopropenyltrimethylsilane does not react at all with concd. hydrochloric acid at room temperature after a reasonable time.

Titration of α-chloroisopropyltrimethylsilane with dilute alkali gave no reaction at all.

Anal. Calcd. for $C_6H_{15}SiCl$: Si, 18.6; Cl, 23.6. Found: Si, 18.6; Cl, 23.5.

Sulfuryl Chloride Chlorinations. A. Diethyldichlorosilane.—In a 1-liter round-bottomed flask fitted with a Hopkins condenser there were placed 255 g., 1.62 moles, of diethyldichlorosilane, 219 g., 1.62 moles of sulfuryl chloride, and 1 g. of benzoyl peroxide. The flask was heated on the steam-bath and an evolution of gas began almost at once. After two hours of heating, gas evolution had slowed considerably and an additional 0.5 g. of benzoyl peroxide was added. Two more 0.5-g. additions of benzoyl peroxide were required before the loss in weight of the contents of the flask reached 151 g., 1.51 moles, of sulfur dioxide and hydrogen chloride. Fractionation gave 96 g., 0.6 mole, of recovered diethyldichlorosilane, b.p. 128° at 731 mm., Cl, 45.0 (calcd., Cl, 45.1); α-chloroethylethyldichlorosilane, 28.8 g., 0.15 mole, b.p. 76° at 43 mm., neut., equiv. 95.2 (calcd. for reaction of the two chlorine atoms linked to silicon, 95.8); and β-chloroethylethyldichlorosilane, 47.0 g., 0.25 mole, b.p. 92° at 42 mm., neut. equiv. 64.1 (calcd. for reaction of the two chlorine atoms linked to silicon plus the chlorine atom bound to β-carbon, 63.9).

Anal. Calcd. for $C_4H_9SiCl_3$: Si, 14.6. Found: Si, 14.7 (for the α-compound) and 14.6 (for the β-compound).

B. **α-Chloroethyltrichlorosilane**.—Following essentially the procedure described above, 554 g., 2.84 moles, of α-chloroethyltrichlorosilane was chlorinated with 388 g., 2.84 moles, of sulfuryl chloride in the presence of 1 g. of benzoyl peroxide. Fractionation gave 130 g., 0.66 mole, 23% recovery of α-chloroethyltrichlorosilane, b.p. 138° at 732 mm.; α,α-dichloroethyltrichlorosilane, 158 g., 0.68 mole, b.p. 152° at 734 mm., m.p. 112–114°, and α,β-dichloroethyltrichlorosilane, 160 g., 0.69 mole, b.p. 99° at 58 mm., 182° at 739 mm.

Anal. Calcd. for $C_2H_3SiCl_5$: Cl, 76.3; neut. equiv. (for reaction of chlorine attached only to silicon), 77.5. Found: Cl, 76.3; neut. equiv., 77.5. Calcd. for $C_2H_3SiCl_5$: Cl, 76.3; neut. equiv. (for reaction of three chlorine atoms attached to silicon plus one chlorine linked to β-carbon), 58.1. Found: Cl, 76.8; neut. equiv., 58.0.

C. **β-Chloroethyltrichlorosilane**.—Chlorination of β-chloroethyltrichlorosilane, 200 g., 1 mole, with sulfuryl chloride, 135 g., 1 mole, and 1 g. of benzoyl peroxide gave after fractionation β-chloroethyltrichlorosilane, 50.4 g., 0.255 mole, 25.5% recovery, b.p. 150° at 739 mm., and 126.8 g., 0.55 mole, 72% yield of β,β-dichloroethyltrichlorosilane, b.p. 172° at 739 mm., and no α,β-dichloroethyltrichlorosilane.

Anal. Calcd. for $C_2H_3SiCl_5$: Cl, 76.3; neut. equiv. (for reaction of three chlorine atoms attached to silicon plus one chlorine linked to β-carbon), 58.1. Found: Cl, 76.5; neut. equiv., 57.9.

β-Chlorovinyltrichlorosilane.—In a 100-ml. round-bottomed flask there were placed 46 g., 0.20 mole, of β,β-dichloroethyltrichlorosilane and 30 g., 0.24 mole, of quinoline. The flask was placed under a column and heated to 130°. Here, a vigorous reaction took place. The heat was removed and the flask temperature increased to 145° before the reaction subsided. The flask was then heated and 38.3 g. of material boiling 53–137° was distilled from the quinoline. Fractionation of the distillate gave β-chlorovinyltrichlorosilane, b.p. 135° at 735 mm. (lit.[23] b.p. 133–135° at 738 mm.), 20.7 g., 0.10 mole, 50% yield.

Anal. Calcd. for $C_2H_2SiCl_4$: Si, 14.3; Cl, 72.4; neut. equiv.) (for reaction of only the three chlorine atoms attached to silicon), 65.3. Found: Si, 14.4; Cl, 72.3; neut. equiv., 65.3.

α-Chlorovinyltrichlorosilane.—From treatment of 35 g., 0.15 mole, of α,α-dichloroethyltrichlorosilane with 25 g., 0.20 mole, of quinoline by the procedure given above there was obtained α-chlorovinyltrichlorosilane, b.p. 124° at 750 mm. (lit.[23] b.p. 124° at 724 mm.), 17 g., 0.09 mole, 58% yield.

Anal. Calcd. for $C_2H_2SiCl_4$: Si, 14.2; Cl, 72.4; neut. equiv. (for reaction of only the three chlorines attached to silicon), 65.3. Found: Si, 14.3; Cl, 72.4; neut. equiv., 64.6.

Treatment of α,β-dichloroethyltrichlorosilane obtained from chlorination of α-chloroethyltrichlorosilane, with quinoline gave α-chlorovinyltrichlorosilane, b.p. 124° at 741 mm., in 80.5% yield.

α-Chlorovinyltrimethylsilane.—In a 3-liter round-bottomed flask equipped in the usual way for Grignard reactions there was prepared 1.28 moles of methylmagnesium bromide in 550 ml. of dry ether. To the methylmagnesium bromide, which was chilled in an ice-bath, there was added dropwise over a period of 2.5 hours 56.8 g., 0.34 mole, of α-chlorovinyltrichlorosilane. After the addition was completed, the reaction mixture was stirred for two hours at ice-bath temperature and then for about 16 hours at room temperature. This was followed by refluxing for 3.5 hours. After hydrolysis at ice temperature and addition of dilute hydrochloric acid the product was extracted with ether and dried with potassium carbonate. Fractionation gave α-chlorovinyltrimethylsilane, b.p. 104° at 730 mm., $n^{20}D$ 1.4299, d^{20} 0.8875, MRD 39.14 (calcd. 39.28), 29.3 g., 0.216 mole, 64% yield.

Anal. Calcd. for $C_5H_{11}SiCl$: Si, 20.9. Found: Si, 20.7.

Polymerization of α-Chlorovinylsilanes.—On standing at room temperature α-chlorovinyltrichlorosilane gave a gradually increasing deposit of a white (presumably) polymeric solid during a period of several months. This behavior is not characteristic of α-chlorovinyltrimethylsilane or vinyltrichlorosilane. Further, on irradiation with ultraviolet light a 1.0-g. sample of α-chlorovinyltrichlorosilane became almost completely solid after 32 hours. Similar treatment of α-chlorovinyltrimethylsilane gave virtually no solid product.

β-Styryltrimethylsilane.—A solution of β-styrylmagnesium bromide, 0.38 equivalent, in 285 ml. of ether was prepared in 73% yield from β-bromostyrene essentially according to the procedure of Gilman.[30] To this was added 60 ml. of dry benzene and ether was distilled until the temperature of the flask contents reached 55°. After cooling, trimethylchlorosilane, 49.5 g. (0.46 mole), was rapidly added with stirring and the reaction mixture was then heated at reflux temperature for two days. After hydrolysis with ice and hydrochloric acid, separation of the ether layer, and ether extraction of the water layer, fractionation gave 35.5 g., 0.20 mole, of β-styryltrimethylsilane, b.p. 98° (10.5 mm.), $n^{20}D$ 1.5270, d^{20} 0.888, 53% yield.

Anal. Calcd. for $C_{11}H_{16}Si$: Si, 15.94; mol. wt., 176. Found: Si, 15.86; mol. wt. (cryoscopically in benzene), 176.

Reactions of β-Styryltrimethylsilane. A. With Sulfuric Acid.—β-Styryltrimethylsilane, 12.3 g. (0.07 mole) was added with stirring to 25 ml. of concentrated sulfuric acid cooled in an ice-bath. The first drop gave an orange solid which continued to form during the entire addition. After the addition was complete (30 minutes), the reaction mixture was stirred for ten additional minutes and then poured onto ice. Addition of ether dissolved all of the solid. After separating layers, the water layer was neutralized and extracted with ether. The combined ether solution of the product was washed with water, twice with 10% sodium bicarbonate solution, and finally with water. After drying fractionation gave 3.95 g., 0.025 mole, of hexamethyldisiloxane, b.p. 99°, $n^{20}D$ 1.3772, 69% yield. A residue of 6.59 g. which gave no test for silicon consisted of polystyrene, 90% yield. Addition of a sample of styrene to concentrated sulfuric acid gave an orange precipitate identical in appearance with that obtained from β-styryltrimethylsilane.

B. **With Bromine.**—In a 200-ml. three-necked flask fitted with a dropping funnel, mechanical stirrer, and reflux condenser, and protected from moisture by a Gilman sulfuric acid trap, there was placed 16.0 g., 0.09 mole, of β-styryltrimethylsilane. The flask was cooled in a Dry Ice–acetone-bath, and 13.6 g., 0.085 mole, of bromine was added over a period of 30 minutes. After standing overnight at room temperature, the reaction product was fractionated. There was obtained 8.11 g., 0.53 mole, of trimethylbromosilane, b.p. 78.5° at 735 mm.,[31] Br, 52.3 (calcd. Br, 52.4), 58.5% yield, and β-bromostyrene, 5.5 g., 35% yield, having unreacted β-styryltrimethylsilane as a contaminant, b.p. 98° at 13 mm., $n^{20}D$ 1.5775.

C. **With Hydrogen.**—A solution of β-styryltrimethylsilane in 150 cc. of anhydrous ether was shaken with hydrogen at 43.3 lb./sq. in. for 22 hours in the presence of 2 g. of Raney nickel catalyst. At the end of this time, the drop in hydrogen pressure indicated 92.5% hydrogenation and the reaction was stopped. After removal of the ether by distillation, the product was added to 50 ml. of cold concentrated sulfuric acid in order to remove any unhydrogenated β-styryltrimethylsilane. After washing with 10% sodium bicarbonate solution and water, the product was dried over anhydrous sodium sulfate and fractionated. There was obtained 22.2 g., 0.126 mole, of β-phenylethyltrimethylsilane, b.p. 78° at 8.5 mm., $n^{20}D$ 1.4863, d^{20} 0.8629, 84% yield. A substance with identical properties was prepared in 80% yield from the reaction of β-phenylethylmagnesium bromide with trimethylchlorosilane.

Anal. Calcd. for $C_{11}H_{18}Si$: Si, 15.8. Found: Si, 15.9.

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(30) H. Gilman, *et al.*, *Rec. trav. chim.*, **54**, 584 (1935).

(31) W. F. Gilliam, R. N. Meals and R. O. Sauer, THIS JOURNAL, **68**, 1161 (1946).