Studies on Unsaturated Organosilicon Compounds. II. Reactions and Properties of Vinyltrimethylsilane*

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In a previous paper,[1] the syntheses of organovinylsilanes and addition of trichlorosilane to the double bond of these compounds were discussed. The present paper reports three types of reactions of vinyltrimethylsilane, that is, addition, cleavage, and polymerization. Vinyltrimethylsilane is of much theoretical interest because it is one of the simplest unsaturated organosilicon compounds and it has a silicon atom directly bonded to the C=C double bond.

Addition Reactions to the Double Bond.[2]—Vinyltrimethylsilane is thought to be one of the monosubstituted ethylenes; thus to this ethylenic double bond many compounds may be added as to ordinary unsaturated organic compounds.

The hydrogenation of unsaturated organosilicon compounds was first reported by Sommer and his coworkers on allyltrimethylsilane[3] and recently on β-styryltrimethylsilane[4] by the same author. These reactions were carried out under hydrogen pressure with Raney nickel catalyst. In the present study vinyltrimethylsilane was found to be easily hydrogenated under normal conditions with platinum oxide as catalyst in glacial acetic acid solution. The catalytic hydrogenation under normal conditions with platinum or palladium catalyst seems to be useful for the analytical determination of the number of unsaturated

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*) This work was presented in the 7th. annual meeting of the Chemical Society of Japan in April, 1954, at Tokyo.

1) M. Kanazashi, This Bulletin, **26**, 493 (1953).

2) Most of the experimental results of this section were presented in the 6th. annual meeting of the Chemical Society of Japan in April, 1953.

3) L.H. Sommer, L.J. Tyler and F.C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948).

4) L.H. Sommer, D.L. Bailey, G.M. Goldberg, C.E. Buck, T.S. Bye, F.J. Evans and F.C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).

bonds in organosilicon compounds within an error of about 2%.

The addition of halogen to the double bond of vinyltrimethylsilane was reported by the author[2] and very recently by Sommer and his coworkers[4]. It was found that chlorine and bromine easily add to the double bond of vinyltrimethylsilane, as they do in the case of vinyltrichlorosilane,[5,6,7,8] giving α, β-dihalogenoethyltrimethylsilane as reported by Sommer and his coworkers[4]. Especially the addition of bromine was found also to be useful for the analytical determination of the number of unsaturated bonds of organosilicon compounds by normal methods, i.e. reaction of a sample with carbon tetrachloride solution of bromine followed by a back titration with standard solution of sodium thiosulfate.

The addition of hydrogen halides to the double bond of vinylsilanes was first reported by Larsson[9] on vinyltriethylsilane with hydrogen chloride and bromide in the presence of hydroquinone or benzoyl peroxide. In all cases β-halogenoethyltriethylsilanes were obtained contrary to the well known Markownikoff rule. A similar result was obtained by Wagner and his coworkers[8] in the aluminum chloride catalyzed addition of hydrogen chloride to vinyltrichlorosilane. The present author also found this non-Markownikoff addition to vinyltrimethylsilane of hydrogen bromide and of hydrogen iodide in the presence and absence of a peroxide or an antioxidant, and independently from the above two reports. These results were reported orally in April 1953[2] but it was decided to postpone the publication in a journal until more detailed data for discussion of the reaction mechanism had been obtained.

Recently Sommer and others[4] reported the same results on vinyltrimethylsilane with hydrogen bromide in the presence of benzoyl peroxide and with hydrogen iodide. They found that hydrogen bromide did not add to vinyltrimethylsilane in the absence of a peroxide catalyst during a reasonable time. Contrary to this result, in the present study hydrogen bromide added easily to vinyltrimethylsilane in the absence of a peroxide catalyst or in the presence of catechol as an antioxidant, by a slight warming for ten minutes followed by cooling to −70° and saturating with hydrogen bromide.

The β-halogenoethyltrimethylsilanes obtained by these addition reactions were found to be very unstable. β-Iodoethyltrimethylsilane fumed in air and slowly decomposed to give free iodine, and β-bromoethyltrimethylsilane decomposed even at room temperature by a catalytic action of the surface of unglazed porcelain or ground glass, giving trimethylbromosilane and ethylene.

$$(CH_3)_3SiCH_2CH_2Br \longrightarrow (CH_3)_3SiBr+CH_2=CH_2$$

This β-halogen in α, β-dihalogeno-or β-halogeno-ethyltrimethylsilane could be titrated by dilute alkali solution as reported by Sommer and his coworkers[10].

$$(CH_3)_3SiCH_2CH_2X \xrightarrow{OH^-} (CH_3)_3SiOH+CH_2=CH_2+X^-$$

$$(CH_3)_3SiCHXCH_2X \xrightarrow{OH^-} (CH_3)_3SiOH+CH_2=CHX+X^-$$

Cleavage Reaction of Vinyl-Silicon Bond.—The vinyl-silicon bond in vinyltrimethylsilane was cloven by concentrated sulfuric acid giving ethylene and trimethylsilyl sulfate similarly to the allyl-silicon bond in allyltrimethylsilane[3]. But the reaction was slow compared with that of allyltrimethylsilane. In these reactions a proton seems to add to α-carbon leaving a β-carbonium cation, which undergoes cleavage involving electron-release from silicon to the electronically deficient β-carbon. The resulting trimethylsilyl cation unites with sulfate anion.

$$H_2SO_4 \longrightarrow H^++HSO_4^-$$

$$(CH_3)_3SiCH=CH_2+H^+ \longrightarrow (CH_3)_3Si-CH_2-CH_2^+$$

$$(CH_3)_3Si\text{-}CH_2-CH_2^+ \longrightarrow (CH_3)_3Si^++CH_2=CH_2$$

$$2(CH_3)_3Si^++SO_4^{--} \longrightarrow [(CH_3)_3Si]_2SO_4.$$

Cleavage of the vinyl-silicon bond was also attempted by methanolic potassium hydroxide. But contrary to allyltrimethylsilane[3], the expected evolution of ethylene as a reaction product was hardly detected, and starting materials were recovered, indicating that almost no reaction had occurred. In this case, the nucleophilic attack on the electropositive silicon is prevented by the mutual action between the trimethylsilyl and the directly bonded C=C double bond as will be discussed later.

Consideration on the Reaction Mechanisms.—At present it is postulated[11] for the mechanism of the ionic addition to the C=C

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5) L.H. Sommer, *U.S.P.*, 2,605,273 (1952).

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

7) C.L. Agre and W. Hilling, *J. Am. Chem. Soc.*, **74**, 3895, 3899 (1952).

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

9) E. Larsson, *Trans. Chalmers Univ. Technol.*, No. **115**, 25 (1951).

10) L.H. Sommer, E.H. Dorfman, G.M. Goldberg and F.C. Whitmore, *J. Am. Chem. Soc.*, **68**, 488 (1946); ibid., **68**, 1083 (1946).

11) Dewar, "The Electronic Theory of Organic Chemistry", (1949), p. 143.

double bond that a positive part of the reagent makes a complex with π-electron pair and then combines to electron-rich carbon, forming a carbonium cation which unites with a negative part of the reagent. Both these results of the non-Markownikoff addition of hydrogen halides to vinyltrimethylsilane and cleavage reactions of this compound by concentrated sulfuric acid described above, provide clear evidence for the addition of a proton to α-carbon forming a β-carbonium cation intermediately. This addition of proton to α-carbon is thought to result from electronic polarization of vinyltrimethylsilane as follows.

$$(CH_3)_3Si-\overset{\delta-}{CH}=\overset{\delta+}{CH_2}$$

But such an electronic polarization is inconsistent with an established inductive effect of electron-release, relative to alkyl for trimethylsilyl, Me_3Si[12,13].

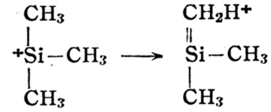
Larsson[9] pointed out the similarity between vinyltriethylsilane and acrylic acid toward hydrogen chloride or bromide. Hydrogen halide adds to α, β-unsaturated carbonyl compounds such as acrylic acid to give β-halogeno-compounds in the absence or presence of a peroxide catalyst. And this is explained by the limit formula of resonance hybrids of these compounds as follows.

$$-CH=CH-C=O \longleftrightarrow -\overset{+}{C}H-CH=C-\overline{\underline{O}}|^{-}$$

For the resonance hybrids of vinyl and allyl silicon compounds, the following limit formulae may be considered (left for vinyl and right for allyl compounds).

I	$CH_2=CH-Si$	$CH_2=CH-CH_2-Si$
II	$\dot{C}H_2-\dot{C}H-Si$	$\dot{C}H_2-\dot{C}H-CH_2-Si$
III	$CH_2^{+}-CH^{-}-Si$	$CH_2^{+}-CH^{-}-CH_2-Si$
IV	$CH_2^{-}-CH^{+}-Si$	$CH_2^{-}-CH^{+}-CH_2-Si$
V	$CH_2=CH^{-}\ Si^{+}$	$CH_2=CH-CH_2^{-}\ Si^{+}$
VI	$CH_2=CH^{+}\ Si^{-}$	$CH_2=CH-CH_2^{+}\ Si^{-}$
VII	$CH_2^{+}-CH=Si^{-}$	$CH_2=CH^{+}\ CH_2=Si^{-}$

Among the last three formulae involving the interaction with silicon atom, V is considered to make a larger contribution to the structures of the compounds than VI, due to the smaller electro-negativity of silicon relative to carbon[14], and a possibility of hyperconjugation of three methyl groups in the resulting trimethylsilyl cation as follows[15].



$$\begin{array}{c}CH_3\\ |\\ {}^{+}Si-CH_3\\ |\\ CH_3\end{array} \longrightarrow \begin{array}{c}CH_2H^{+}\\ \|\\ Si-CH_3\\ |\\ CH_3\end{array}$$

Further, V seems to make a larger contribution to the structures of allyl compounds than to those of vinyl compounds for its allylic resonance as shown below.

$$CH_2=CH-CH_2^{-} \longleftrightarrow C\overset{-}{H_2}-CH=CH_2$$

VII corresponds to the structures of α, β-unsaturated carbonyl compounds and it is considered that the silicon has the tendency to expand its valence shell by the interaction of the 3d orbitals of silicon with π-electrons of $C=C$ double bond and to place ten electrons around it. But this interaction is prevented by the shielding effect of a methylene group between silicon and $C=C$ double bond in allyl silicon compounds, and contribution of VII to the structures of allyl silicon compounds seems therefore to be small.

It is explained by these two structures, i.e. V and VII, that a proton adds to α-or γ-carbon for vinyl or allyl compounds respectively and give β-carbonium cation. It unites with a halogen anion to give β-halogeno-compound as an addition product, or it undergoes cleavage involving electron-release from silicon to electronically deficient β-carbon by the stronger action of the sulfate anion than the halogen anion, then the resulting trimethylsilyl cation unites with sulfate anion to give trimethylsilyl sulfate and ethylene as cleavage products.

In the case of the reaction with potassium hydroxide, the nucleophilic attack on electropositive silicon having a tendency to expand its valence shell is postulated[3]. This nucleophilic attack on silicon is accelerated by structure V, but prevented by structure VII because of the electronegative silicon whose valence shell is already expanded in this structure. It seems to be the reason why vinyltrimethylsilane did not react with methanolic potassium hydroxide contrary to allyltrimethylsilane, because the contribution of V is smaller and that of VII is larger in vinyl than allyl compounds.

Sommer and his coworkers reported that hydrogen chloride added to isopropenyltrimethylsilane to give α-chloroisopropyltrimethylsilane as an addition product[4], and isopropenyltrimethylsilane reacted with concentrated sulfuric acid to give *tert*-butyldimethylsilanol hemi-hydrate after treatment with water, as an intramolecular rearrangement product[16], both indicating addition of

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[12] H. Gilman and G. E. Dunn, *Chem. Res.*, 52, 77 (1953).

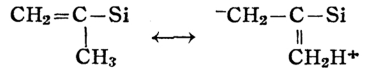
[13] (a) L.H. Sommer, J.R. Gold, C.M. Goldberg and N.S. Marans, *J. Am. Chem. Soc.*, 71, 1509 (1949); (b) L.H. Sommer and J. Rockett, ibid., 73, 5130 (1951).

[14] Pauling, "The Nature of the Chemical Bond", (1940), p. 58→70.

[15] A similar hyperconjugation was proposed by Yakubovich, et. al., (*Uspekhi Khim. S.S.S.R.*, 18, 46 (1949)) to explain the C—Si bond distance in methylchlorosilanes.

[16] L.H. Sommer and F.J. Evans, *J. Am. Chem. Soc.*, 76, 1030 (1954).

a proton to the terminal methylene group of the olefinic grouping to give α-carbonium cation intermediately. These reactions are explained by considering that a resonance structure such as V or VII is overcome by introduction of a single α-methyl having a possibility of hyperconjugation as follows.

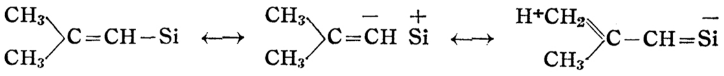


$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-Si \longleftrightarrow {}^{-}CH_2-\underset{\displaystyle CH_2H^+}{\underset{\|}{C}}-Si$$

They reported also that β-chlorovinyltrimethylsilane gave no β-elimination on titration with dilute alkali, in contrast with saturated β-halogenoalkyl compounds[4]. This evidence is explained by considering the resonance structure similar to VII as shown below.

$$Cl-CH=CH-Si \longleftrightarrow {}^{+}Cl=CH-CH=Si^{-}$$

Petrov[17] reported that hydrogen bromide added to isobutenyltrimethylsilane to give β-bromoisobutyltrimethylsilane. This is also explained by considering resonance structrures such as V or VII, and VII is further conjugated with the two methyl groups bonded to β-carbon as follows.



Many reactions of vinyl, allyl and other related organosilicon compounds are able to be explained by the two resonance structures discussed above. These two structures were postulated by several authors[18,19], but Gilman and Dunn[11] considered it unlikely that organosilicon compounds received significant contributions from resonance structures involving silicon-carbon double bond as VII.

Recently the resonance structures involving a silicon-carbon double bond as VII was postulated for nitration of trimethylsilylbenzene by Speier[20] and for Hammett's σ-values of p-trimethylsilyl-phenol, aniline and dimethylaniline by Benkeser and Krysiak[21]. Sommer and his coworkers pointed out this limited non-inductive effect of trimethylsilyl in vinyltrimethylsilane similarly to the consideration in this paper.

Further evidence for this resonance structure was obtained from infrared and Raman spectra of these compounds. Petrov and Nikishin[17] reported on a characteristic absorption band due to the $\nu_{C=C}$ vibrational mode at 1620 cm.$^{-1}$ in the infrared absorption spectra of isobutenyltrimethylsilane, and Egorov and Bazhulin[22] reported on a similar band at 1591 cm.$^{-1}$ for vinyltriethylsilane. In a previous paper[1] it was reported that the characteristic absorption band due to the $\nu_{C=C}$ vibrational mode was found at 6.29–6.30 μ (1590–1587 cm.$^{-1}$) in the infrared spectra of four vinylsilanes, i.e. vinyltrimethylsilane, divinyldimethylsilane, vinyltriethylsilane and vinyldimethylphenylsilane[23]. In the present study, the same band at 1590 cm.$^{-1}$ was also observed with Raman spectrum of vinyltrimethylsilane.

It is postulated that $\nu_{C=C}$ is primarily dependent upon the C=C streching force constant and is therefore lowered by conjugation, showing a shift of $\nu_{C=C}$ from the standard position, ca. 1650 cm.$^{-1}$, to longer wave length[24].

The observed shift of $\nu_{C=C}$ in these vinyl or isobutenyl silanes, provides a clear evidence of the presence of conjugation such as in structure VII in these compounds, as in the case of conjugated nitriles[25], ketones and esters of α, β-unsaturated acids[26]. Studies of the conjugation of vinyltrimethylsilane by electron diffraction and dipole moment measurement are under way.

Polymerization Reactions.—The four vinylsilanes synthesized in a previous study[1] did not seem to be polymerized by heating for twenty four hours at 150° in the presence of benzoyl or acetyl peroxide[2]. (For details see the experimental part of the present paper). It was already reported by Ushakov and Itenberg[27] that vinyltriethylsilane was not polymerized by heating in the presence of a peroxide catalyst.

Recently Wagner and his coworkers[8] reported polymerization of vinyltrichlorosilane and vinyl triethoxysilane at high temperature in the presence and absence of a peroxide

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[17] A.D. Petrov and G.I. Nikishin, *Doklady Akad. Nauk, S.S.S.R.*, **93**, 1049 (1953).

[18] J.D. Roberts, E.A. McElhill and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 2923 (1949).

[19] H. Soffer and T. De Vries, ibid., **73**, 5817 (1951).

[20] J.S. Speier, ibid., **75**, 2930 (1953).

[21] R.A. Benkeser and H.R. Krysiak, ibid., **75**, 2421 (1953).

[22] Yu. P. Egorov and P.A. Bazhulin, *Doklady Akad. Nauk S.S.S.R.*, 88, 647 (1953).

[23] The characteristic bands at 9.94—9.99 μ, and 10.50—10.54 μ in the spectra of the four vinylsilanes reported in a previous paper[1], are considered to be assigned to the out-of-plane bending vibrational mode of H in the ethylene group according to the results of Davison and Bates[24].

[24] W.H.T. Davison and G.R. Bates, *J. Chem. Soc.*, **1953**, 2607.

[25] Sheppard and Sutherland, ibid., **1947**, 453; Kitson and Griffith, *Anal Chem.*, **24**, 334 (1952).

[26] Hartwell, Richards and Thompson, *J. Chem. Soc.*, **1948**, 1436.

[27] S.N. Uschakow and A.M. Itenberg *Zhr. Obshchei Khim. S.S.S.R.*, **7**, 2495 (1937).

catalyst or a Friedel-Crafts type catalyst such as aluminum chloride. There was obtained a low molecular weight polymer consisting mainly of tetramers, by heating at 290° without a catalyst or by heating 50–90° with a Friedel-Crafts type catalyst. But with a peroxide catalyst the formation of polymer was very small. And a high molecular weight polymer was not obtained in all cases.

In view of the conflicting evidence as to the ability of vinylsilanes to polymerize, it seemed of importance to reinvestigate the subject. In the present study, therefore, the radical polymerization of vinyltrimethylsilane with peroxide or α, α'-azodiisobutyronitrile as a catalyst and the cationoid polymerization of the same compound with a Friedel-Crafts type catalyst were investigated. Contrary to vinyltrichlorosilane, vinyltrimethylsilane gave no polymer by the cationoid polymerization and gave a small amount of low molecular weight polymer by the radical polymerization. No high molecular weight polymer was obtained from vinyltrimethylsilane.

The absence of high molecular weight polymers in the product from vinyltrichloro- or vinyltrimethyl-silane seems to result from the steric hindrance of the large trisubstituted silyl group in the structural unit of the polymer, $-\mathrm{CH_2}\underset{\mathrm{SiX_3}}{\underset{|}{\mathrm{CH_2}}}-$ (X=Cl, Me, Et), as shown in Fig. 1. The presence of a polymer of relatively high molecular weight in the product from vinyltriethoxysilane seems to be explained by the free rotation of the ethoxy group around Si—O bond as shown in Fig. 2.[28]

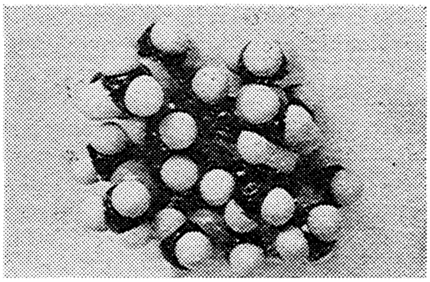

Fig. 1. A growing (pentameric) chain of polymerizing vinyltrimethylsilane. Further addition seems to be very difficult.

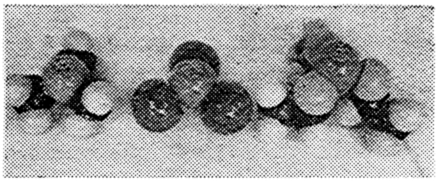

Fig. 2. Comparison of steric effect of tri-substituted silyl group. (left to right: trimethylsilyl, trichlorosilyl and triethoxysilyl group).

The extent of a group bonded to silicon in the neighboring space around silicon is able to be made the smallest in triethoxysilyl by the free rotation of the ethoxy group around Si-O bond.

Further studies on polymerization and other reactions of vinylsilanes are being continued now in this laboratory.

Experimental

Addition Reactions.—Products of addition reactions to the double bond of vinyltrimethylsilane are listed in Table I.

TABLE I

Reagent	Catal.	Product Me$_3$Si-	Yield %	m.p. °C	b.p.		d_4^{20}	n_D^{20}	Mol. ref.		Titratable halogen %	
					°C	mm.			Calcd.	Found	Calcd.	Found
H_2	Pt	CH_2CH_3 a)	70		62–4	760	0.6839	1.3821	34.91	34.80		
Cl_2		$CHClCH_2Cl$ b)	76	−16	67–9	20	1.0586	1.4608	44.59	44.37	20.72	21.2 j)
Br_2		$CHBrCH_2Br$ c)	90	−7	62–3	4	1.5321	1.5062	50.27	50.45	30.73	33.5 j)
$HSiCl_3$	Ac_2O_2	$CH_2CH_2SiCl_3$ d)	90	−18	94–6	50	1.1062	1.4473	57.32	56.96	45.13	45.0
HBr		CH_2CH_2Br e)	65		50–2	21	1.1481	1.4562	42.59	42.91	44.11	44.1
HBr	Ac_2O_2	CH_2CH_2Br e)	72		49	19	1.1489	1.4556	42.59	42.86	44.11	44.6 j)
HBr	Bz_2O_2	CH_2CH_2Br e)			35–45 g)	20	1.1483	1.4560	42.59	42.89	44.11	45.4 j)
HBr	Catechol	CH_2CH_2Br e)			33–47 g)	20	1.150	1.4568	42.59	42.88	44.11	44.5 j)
HI		CH_2CH_2I f)			53–5	10	1.3976	1.4950	47.77	47.61	55.62	57.3 j)

(a) b.p. 62°C (760 mm.), d_4^{20} 0.6849, n_D^{20} 1.3820.[29] (b) b.p. 61°C (14 mm.), d_4^{20} 1.0537, n_D^{20} 1.4617, m.p. −15°C.[4,30] (c) b.p. 74–5°C (8 mm.), d_4^{20} 1.5497, n_D^{20} 1.5095, m.p. −9–11°C.[4] (d) Reported in a previous paper.[1] (e) b.p. 64–5°C (39 mm.), d_4^{20} 1.1499, n_D^{20} 1.4575.[4] (f) b.p. 76–76.5°C (27 mm.), d_4^{20} 1.3862, n_D^{20} 1.5008.[4] (g) Decomposition occurred. (h) To a solution of the sample in methanol, there was added N/5 NaOH aq. solution and back titrated by N/10 HCl with phenol phthalein as an indicator. (i) Calculated for a halogen bonded to β-carbon or silicon. (j) This high halogen value seems to result from decomposition during distillation or preservation.

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[28] B.A. Arbuzov and T.G. Shavsha, *Doklady Akad. Nauk S.S.S.R.*, 68, 859 (1949); C. A., 44, 886 (1950).

[29] F.C. Whitmore, L.H. Sommer, et. al., *J. Am. Chem. Soc.*, 68, 475 (1946).

[30] L.H. Sommer, U.S.P., 2,605,273 (1952).

1. Hydrogenation.—A solution of 6.84 g. of vinyltrimethylsilane in 150 cc. of glacial acetic acid was shaken with hydrogen for two hours in the presence of 0.1 g. of platinum oxide catalyst. The absorption of hydrogen took about two hours, being very fast during the middle period of twenty minutes. At the end the volume of absorbed hydrogen was 1444 cc. (including 18 cc. used for reduction of the catalyst), corresponding to 1.013 mole per mole of vinyltrimethylsilane. The reaction product was separated from the catalyst by filtration, then a fraction boiling up to 90° was collected upon fractionation. Twenty grams of toluene was added to the fraction and washed with 10% sodium bicarbonate solution and water. After drying over calcium chloride, the fractionation of the product gave ethyltrimethylsilane as shown in Table I.

2. Halogenation.—Ten grams (0.1 mol.) of vinyltrimethylsilane was cooled to −70° in a bath of dry ice and acetone, then a theoretical amount of bromine was added drop by drop or a theoretical amount (from weight increase) of chlorine was bubbled with shaking. Toward the end of the reaction white crystals of the product were observed. Upon warming to room temperature, the product was fractionated and α, β-dibromo- or dichloro-ethyltrimethylsilane was obtained as shown in Table I.

3. Addition of Hydrogen Bromide.—In a test-tube equipped with gas inlet and outlet tubes, there was placed 10 g. (0.1 mol.) of vinyltrimethylsilane. Hydrogen bromide gas dried with phosphorus pentoxide was introduced in the first experiment, but 0.1 g. of peroxide or catechol was added prior to the introduction of HBr in the other three experiments. The reaction mixture was warmed slightly for ten minutes to initiate the reaction and cooled to −70° in a bath of dry ice and acetone, then saturated with a theoretical amount of HBr. Standing overnight up to room temperature, the reaction mixture was fractionated giving β-bromoethyltrimethylsilane as shown in Table I.

Decomposition of β-Bromoethyltrimethylsilane.—The β-bromoethyltrimethylsilane thus obtained was very unstable and decomposed by slight heating in distillation or other treatment, and with a catalytic action of a surface of unglazed porcelain or ground glass it decomposed even at room temperature. In a flask fitted with a reflux condenser and a gas outlet tube at the top, containing a few small pieces of unglazed porcelain such as boiling chips, there was added β-bromoethyltrimethylsilane. At once a vigorous reaction occurred and almost half of the sample was lost. Then the remaining liquid was heated slowly on a water bath, a reaction occurred at 40–45°, and ethylene gas was evolved. Ethylene was identified by convertion to ethylene dibromide, n_D^{15} 1.5392. The residue was fractionated and trimethylbromosilane boiling at 80.5–81.0° was obtained, this was converted to disiloxane, n_D^{17} 1.3784.

4. Addition of Hydrogen Iodide.—In a test-tube equipped with gas inlet and outlet tubes, there was placed 10 g. (0.1 mol.) of vinyltrimethylsilane. Hydrogen iodide gas dried with phosphorus pentoxide was introduced in the test-tube cooled to −30° in a bath of dry ice and acetone. After a theoretical increase in weight had taken place, the reaction mixture was allowed to be warmed slowly to room temperature and it was fractionated, giving β-iodoethyltrimethylsilane as shown in Table I.

Cleavage Reactions 1. With Concentrated Sulfuric Acid.—In a test-tube equipped with a gas outlet tube, there was placed 3 g. of vinyltrimethylsilane and 1.5 g. of conc. H_2SO_4 and cooled to −20° in a bath of dry ice and acetone. But almost no reaction occurred at this temperature. Then the reaction mixture was warmed to room temperature (15–20°) with shaking, the reaction proceeding slowly with the evolution of ethylene gas. The ethylene was absorbed by carbon tetrachloride solution of bromine. The reaction became rapid gradually, and the upper layer of vinyltrimethylsilane decreased, while the lower layer of sulfuric acid increased conversely. The reaction became more and more vigorous and the temperature rose to about 40° in the course of four hours, toward the end of which the reaction mixture became homogeneous. It was cooled to 10° and gradually warmed up to 20°. After about six hours the reaction came to the end and no more ethylene was evolved. The carbon tetrachloride solution was fractionated and 3 g. of ethylene dibromide was obtained, n_D^{15} 1.5410 (after washing with H_2O and drying with $CaCl_2$), about 50% yield. The residue was solidified by cooling and melted at 46–51°; it therefore seems to be crude trimethylsilyl sulfate, of which the melting point of a pure specimen is reported to be 56–58°[31].

2. With Methanolic Potassium Hydroxide.—In a 50 cc. flask equipped with a reflux condenser and a gas outlet tube at the top, there were placed 10 g. (0.1 mol.) of vinyltrimethylsilane, 12 g. (ca. 0.2 mol.) of KOH and 10 g. of methanol. The mixture was heated at the reflux temperature for 15 hrs., but the evolution of a gaseous product was hardly detected. The reaction mixture was distilled rapidly at a reduced pressure. Upon fractionation of the distillate, 9.5 g. of an azeotrope of methanol and vinyltrimethylsilane, b.p. 44.3° n_D^{20} 1.3865, and a mixture of methanol and vinyltrimethylsilane, b.p. 46–60°, n_D^{20} 1.3350, were obtained. Neither trimethylmethoxysilane (in an azeotrope with methanol) nor trimethylsilanol was obtained. The azeotrope was further characterized by an independent preparation as follows. A mixture of 5 g. of vinyltrimethylsilane and 5 g. of methanol was distilled through a distillation column of about 10 theoretical plates. A fraction boiling at 44.3°, n_D^{20} 1.3860 was obtained, but the ratio of

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[31] L.H. Sommer, et. al., *J. Am. Chem. Soc.*, 68, 156 (1946). Sommer, et. al.[3] reported m.p. 49—52° for a crude one.

two components was not determined.

Polymerization Reactions 1. Polymerization of vinylsilanes on a small scale.—A half gram of each three vinylsilanes, i.e. trimethylvinylsilane, dimethyldivinylsilane, and dimethylphenylvinylsilane, was heated at 100° or 150° for 24 hours in a sealed glass tube in the presence of 10 mg. of acetyl or benzoyl peroxide. But neither solidification nor increase of viscosity was found even in the case of divinyldimethylsilane, indicating that no polymerization occurred.

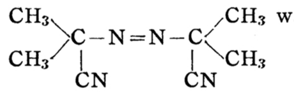
2. Polymerization of Vinyltrimethylsilane.—The conditions of polymerization of vinyltrimethylsilane and properties of the polymers are shown in Table II.

TABLE II

POLYMERIZATION OF VINYLTRIMETHYLSILANE

Catalyst	Yield %	Fraction	Polymer B.p. °C.	mm.	n_D^{20}	Mol.[c] Weight	Analytical Data C% Calcd.[d]	Found	H% Calcd.[d]	Found
Bz_2O_2-Ac_2O_2	15	I.	100–104	8–9	1.4593	360	59.91	61.20	12.07	11.86
		II.	120–140	3	1.4698	460	59.91	61.12	12.07	11.69
		residue			1.4780	550	59.91	60.25	12.07	11.76
Azonitrile[a]	10	I.	80–100	3–10	1.4474	400	59.91	61.01	12.07	11.73
		II.	100–130	2	1.4568	350	59.91	63.63	12.07	12.07
		residue			1.4763	1000				
$AlCl_3$	2									
BF_3[b]	0									

a) α, α'-Azodiisobutyronitrile



$(CH_3)_2C(CN)-N=N-C(CN)(CH_3)_2$

was used. b) used as an addition compound with diethylether. c) obtained by Rast method, but these values are very rough. d) calculated for $(C_5H_{12}Si)n$

With Acetyl Peroxide and Benzoyl Peroxide Mixture.—In a sealed glass tube there were placed 20 g. (0.2 mol.) of vinyltrimethylsilane, 0.12 g. (0.5 mol.%) of diacetyl peroxide, and 0.24 g. (0.5 mol.%) of dibenzoyl peroxide. The tube heated at 150–5° for 24 hours. Unreacted vinyltrimethylsilane was recovered at atmospheric pressure. The precipitated crystals of benzoic acid were filtered, recrystalized, m.p. 117–8°, mixed m.p. to be 117.5–9.0°. The filtrate was fractionated under reduced pressure to give fractions as shown in Table II.

With Other Catalysts.—Similarly to the case with the peroxide catalyst, all catalyst were used in amount of 1 mole % to vinylsilanes. But heating at 150° for boron trifluoride and 120° for α, α'-azodiisobutyronitrile and aluminum chloride was employed. As in the case of azonitrile, tetramethylsuccinonitrile was isolated as a decomposition product of the catalyst, m.p. 165.5–6.5°, mixed m.p. 165.5–7.0°. In the case with boron trifluoride and aluminum chloride almost no polymer was obtained.

Summary

1) Addition reactions to the double bond of vinyltrimethylsilane were studied with hydrogen, bromine, chlorine, hydrogen bromide and iodide, and the properties of the products were given.

2) Vinyl-silicon bond was cloven by concentrated sulfuric acid but no reaction occurred with methanolic potassium hydroxide.

3) Reaction mechanisms of the above two reactions of vinyl, allyl or related unsaturated organosilicon compounds were discussed. A conjugated structure involving silicon-carbon double bond in which the silicon atom has an expanded valence shell was postulated for some of these reactions. Such a structure was further confirmed by the shift of $\nu_{C=C}$ in the absorption spectra of vinyltrimethylsilane.

4) Polymerization reactions of this compound were studied and the steric hindrance by a large trimethylsilyl group in the structural unit of the polymer was discussed, particularly concerning the absence of a high molecular weight polymer in the reaction product.

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