Studies on Unsaturated Organosilicon Compounds. I.*
Syntheses of Organovinylsilanes by Wurtz-Fittig Reaction

By Motonori KANAZASHI

(Received July 2, 1953)

Vinyl silicon compounds have been prepared by the elimination of hydrogen halides from haloethylsilanes,[1,2] and by the high temperature interaction of vinyl chloride and silicon in the presence of a catalyst such as copper or tin.[2,5] Recently Wagner[6] prepared vinyltrichlorosilane from acetylene and trichlorosilane at a high temperature and under pressure with platinized asbestos as a catalyst.

In this work, vinyl chloride and organohalosilanes were allowed to react with metallic sodium (in the shape of finely divided particles) in ethyl ether, to form organovinylsilanes. Trimethylchlorosilane, dimethyldichlorosilane, triethylbromosilane, and dimethylphenylchlorosilane were used as the organohalosilane.

The infrared spectra of these vinylsilanes are given in Fig. 1. From the spectra of cyclic tri- and tetra-siloxane,[7] it was found that the characteristic absorption bands for methyl, ethyl, and phenyl linked to silicon are remarkably constant in many compounds in the wave length shorter than about 11.0μ, that is 3.38, 7.08, and 7.94 μ for the methyl group, 6.84, 7.08, 7.26, 8.05, 9.9, and 10.4 μ for

---

[*] This paper was presented in the sixth annual meeting of the Chemical Society of Japan in April, 1953, at Kyoto.

[1] S. N. Uschakov and A.M. Itenberg, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 2495 (1947).

[2] D. T. Hurd, *J. Am. Chem. Soc.*, **67**, 1813 1945), U.S.P., 2,420,912 (1947).

[3] *Brit. P.* 618,608 (1949).

[4] C. D. Strother and G. H. Wagner, *U.S.P.*, 2,532,430 (1950).

[5] D. T. Hurd and G. F. Roedel, *Ind. Eng. Chem.*, **40**, 2078 (1948).

[6] G. H. Wagner and C. O. Strother, *Brit. P.*, 670,617 (1952).

[7] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

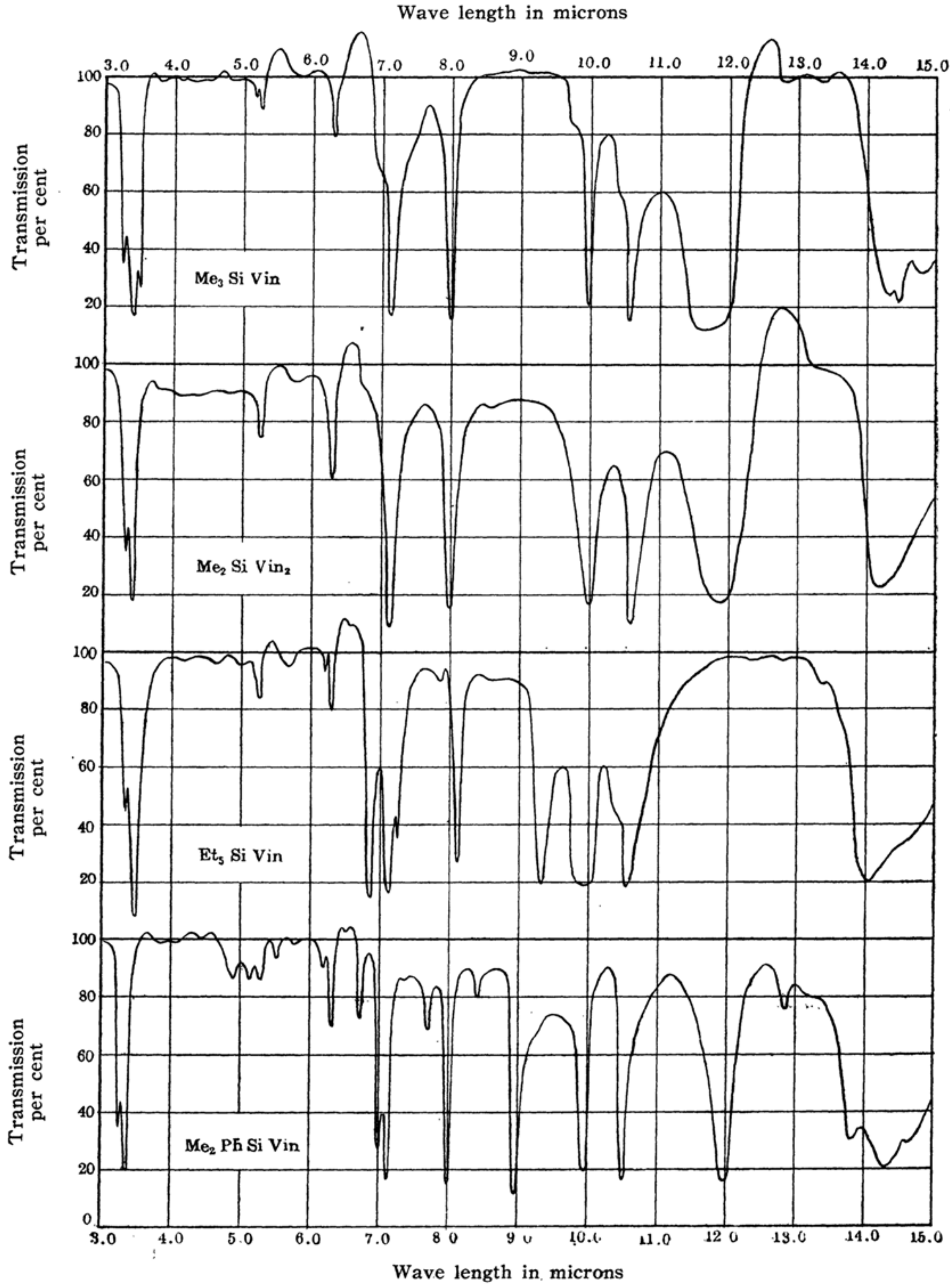

Fig. 1. The infrared spectra of organovinylsilanes

the ethyl group, and 6.28, 6.7, 6.98, 8.4, 8.9, 9.7, and 10.04 μ for the phenyl group, and allow a ready determination of the presence of these groups.

These bands are found at 3.39~3.43, 7.13~7.14, and 8.00~8.03 μ for methyl group in trimethylvinylsilane, dimethyldivinylsilane and dimethylphenylvinylsilane; 6.88, 7.12, 7.27, 8.11, 9.87 (not separated from 9.99 μ band) and 10.4 μ for ethyl group in triethylvinylsilane; and 6.21, 6.72, 7.01, 8.40, and 8.99 μ for phenyl group (9.7 and 10.04 μ bands were not found) in dimethylphenylvinylsilane.

The remaining bands common to four compounds are 5.27~5.28, 6.29~6.30. 9.94~9.99, and 10.50~10.54 μ. Of these, the bands at 6.29~6.30 and 10.50~10.54 μ were also found in vinyl siloxanediols at 6.2~6.3 and 10.3~10.4 μ and were assigned to C=C double bond and the vinyl group linked to silicon respectively, by Frisch and others.[8] The band at 5.28 μ in dimethyldivinylsilane is about twice as intense as in the other three compounds similar to the band at 6.3 μ, and it is doubtless due to the vinyl group linked to silicon. Probably the band at 9.95 μ is also believed to be assigned to the vinyl group.

Trichlorosilane was found to be added to these vinylsilanes in the presence of diacetyl peroxide like as to vinyltrichlorosilane, and the corresponding β-trichlorosilylethylsilanes were prepared.

Other réactions and properties of organovinylsilanes are under investigation in this laboratory.

Experimental

All yields reported are based on the amount of organohalosilanes or organovinylsilanes used.

Syntheses of Organovinylsilanes.

Trimethylvinylsilane I.—Ninety two grams (4.0 mole) of finely divided metallic sodium, 217 g. (2.0 mole) of trimethylchlorosilane (presented by the Shin-etsu Chem. Ind. Co.), and 250 cc. of ethyl ether were placed in a 1-l. three necked flask fitted with a mercury-sealed stirrer, a gas inlet tube and a 30 cm. Dimroth reflux condenser with a condenser sermounted with a cold finger, 4×15 cm., filled with a dry ice-aceton mixture.

Vinyl chloride gas, dried with phosphorus pentoxide, was introduced to the reaction mixture with stirring, at a rate of 10~20 l. per hour. About ten minutes after, 2 cc. of ethyl acetate was added to catalyze the reaction. When the reaction started the introduction of vinyl chloride was controlled so that a gentle reflux of ether was maintained. The reaction approached to the end in six hours then the introduction of vinyl chloride gas was stopped, and the reaction mixture was heated gently with stirring for one hour. The reaction mixture was allowed to stand overnight; then the ether layer was decanted and the residue was washed with ether and filtered. These ether solutions were mixed up and washed twice with water. After drying overnight over calcium chloride, the ether solution was fractionated through a 1-m. distillation column of about 30 theoretical plates. One hundred and fifty five grams of trimethylvinylsilane, boiling 53~56° at 767 mm. were isolated. Yield 77.5%.

The trimethylvinylsilane obtained in three runs was redistilled and the middle cut, b.p. 55.5° at 767 mm. was taken for analysis and determination of physical constants. See Table I.

Dimethyldivinylsilane II.—Ninety two grams (4 mole) of finely divided metallic sodium, 129 g. (1.0 mole) of dimethyldichlorosilane (presented by the Shin-etsu Chem. Ind. Co.), and 200 cc. of ethyl ether in a 1-l. flask reacted with vinyl chloride as indicated above, dimethyldivinylsilane were isolated, b.p., 80.8~81.6° at 760 mm., 26 g. yield 24%.

Triethylvinylsilane III.—Triethylbromosilane used in this synthesis was prepared from trichlorosilane *via* triethylsilane by the method of Whitmore and others[9] and Ladenberg,[10] and fractionated through a 30 cm. column, b.p., 78~79° at 50 mm.

Twelve grams of metallic sodium, 41 g. of triethylbromosilane and 100 cc. of ethyl ether in a 500 cc. flask reacted with vinyl chloride as outlined above, fractionation of the product through a 30 cm. column, gave triethylvinylsilane, b.p., 143.2° at 755 mm., 13.2 g., yield 45%.

---

[8] K. C. Frisch, P. A. Goodwin and R. E. Scott, *J. Am. Chem. Soc.*, **74**, 4584 (1952).

[9] F. C. Whitmore, E. W. Pietruza and L. H. Sommer, *J. Am. Chem. Soc.*, **69**, 2108 (1947).

[10] Ladenberg, *Ann.*, **164**, 300 (1872).

TABLE I

THE PPOPERTIES OF ORGANOVINYLSILANES

Compound	b.p.		d_4^{20}	n_D^{20}	Molar ref.		Si %	
	°C	mm.			Calcd.	Obsd.	Calcd.	Found
I	55.5	767	0.6910	1.3914	34.44	34.50	28.02	27.8
II	80.8~81.6	760	0.7337	1.4176	38.60	38.52	25.03	24.9
III	143.2	755	0.7847	1.4330	48.33	47.47	19.60	19.6
IV	82.0	20	0.8919	1.5048	54.26	53.96	17.31	17.4

Dimethylphenylvinylsilane IV. — Dimethylphenylchlorosilane used in this synthesis was prepared from dimethyldichlorosilane and phenylmagnesium bromide in ether, and was fractionated through a 30 cm. column, b.p., 84～85° at 20 mm.

Twenty three grams (1 mole) of metallic sodium, 85 g. (0.5 mole) of dimethylphenylchlorosilane, and 100 cc. of ethyl ether in a 500 cc. flask reacted with vinyl chloride as outlined above, fractionation of the product through a 30 cm. column, gave 29.2 g. of dimethylphenylvinylsilane, b,p., 82.0° at 20 mm., yield 36%.

The physical constants and analytical data of these organovinylsilanes are given in Table I.

Addition of Trichlorosilane.

β-Trichlorosilylethyltrimethylsilane V. — A mixture of 5 g. (0.05 mole) of trimethylvinylsilane, 14 g. (0.1 mole) of trichlorosilane, and 0.25 g. (0.002 mole) of diacetyl peroxide (2.0 mole % to trichlorosilane used) in a glass sealed tube was heated for ten hours at 60° in a water bath. Then distilled in a 20 cc. Claisen flask, the excess trichlorosilane was recovered at atmospheric pressure and 10.5 g. of β-trichlorosilylethyltrimethylsilane, b.p., 94～96° at 50 mm. and 1 g. of residue was obtaind, yield 90%.

Bis(β-trichlorosilylethyl)dimethylsilane VI. —Heating a mixture of 3.5 g. (0.03 mole) of dimethyldivinylsilane, 13.6 g. (0.1 mole) of trichlorosilane, and 0.2 g of diacetyl peroxide for eleven hours in a sealed glass tube at 60°, gave 8.5 g. of bis(β-trichlorosilylethyl)dimethylsilane, b.p., 119～121° at 3 mm., yield 72%.

β-Trichlorosilylethyltriethylsilane VII.—Heating a mixture of 7.1 g. (0.05 mole) of triethylvinylsilane, 13.6 g. of trichlorosilane, and 0.2 g. of diacetyl peroxide for eight hours in a sealed glass tube at 60°, gave 6 g. of β-trichlorosilylethyltriethylsilane, b.p., 122～125° at 18 mm., yield 42%.

TABLE II

THE PROPERTIES OF β-TRICHLOROSILYLETHYLSILANES

Compound	f.p. °C	b.p. °C	b.p. mm.	d_4^{20}	n_D^{20}	Molar ref. Calcd.	Molar ref. Obsd.	Cl % Calcd.	Cl % Found
V	−18	94～ 96	50	1.1062	1.4473	57.32	56.96	45.13	45.0
VI	− 4	119～121	3	1.2966	1.4838	84.36	84.52	55.52	55.4
VII		122～125	18	1.0713	1.4632	71.21	71.44	38.29	38.3
VIII		138～139	10	1.1553	1.5112	77.14	77.24	35.72	35.5

β-Trichlorosilylethyldimethylphenylsilane VIII.—Heating a mixture of 8.1 g. (0.05 mole) of dimethylphenylvinylsilane, 13.6 g. of trichlorosilane, and 0.2 g. of diacetyl peroxide for sixteen hours in a sealed glass tube at 60°, gave 3.5 g. of β-trichlorosilylethyldimethylphenylsilane, b.p., 138～139° at 10 mm., yield 24%.

The physical constants and analytical data of these β-trichlorosilyethylsilanes are given in Table 2.

Preparation of Spectra—The infrared spectra shown here were obtained using a Perkin-Elmer Model 12-C Spectrometer (rock salt prism) of Government Chemical Industrial Research Institute, Tokyo. All samples were run in potassium bromide cell, 0.1 mm. thick, as pure liquid.

Summary

1) Vinyl chloride and organohalosilanes were shown to react with finely divided metallic sodium in ethyl ether, and trimethyl-, dimethyldi-, triethyl- and dimethylphenylvinylsilanes were prepared. Of these, dimethyldi- and dimethylphenyl-vinylsilane are new compounds and their physical constants were given.

2) Infrared spectra of these four organovinylsilanes were obtained and certain characteristic absorption bands were discussed.

3) Trichlorosilane was found to add to these vinylsilanes at the presence of diacetyl peroxide and four new β-trichlorosilylethylsilanes were prepared and characterized.

The author is indebted to Mr. M. Yonemoto and Mr. S. Saeki for the spectra reported in this paper and the Shin-etsu Chem. Ind. Co. for the methylchlorosilanes used in this investigation. The author is also grateful to Dr. O. Shimamura and Dr. T. Yamada for much helpful advice in this investigation.

Electrotechnical Laboratory
Agency of Industrial Science
and Technology, Tokyo