Addition of Trichlorosilane to Acetylene and to Vinyltrichlorosilane[1]

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The addition of trichlorosilane to acetylene is one of the well-known methods for the preparation of organosilicon compounds, and is known to be accelerated in the presence of peroxides or platin catalyst[2].

$$HSiCl_3 + CH{\equiv}CH \longrightarrow CH_2{=}CHSiCl_3$$

$$CH_2{=}CHSiCl_3 + HSiCl_3 \longrightarrow Cl_3SiCH_2CH_2SiCl_3$$

In the course of our study on the additional reactions of trichlorosilane to various vinyl compounds, it was observed in the previous paper[3] that cyanoethylation of trichlorosilane took place easily in the presence of organic bases as well as platin or benzoylperoxide. All these catalysts resulted in the formation of β-cyanoethyltrichlorosilane. On the contrary, when the reactions were carried out either in the presence of pyridine in an autoclave, or in the presence of tetrapyridine nickel (II) chloride in sealed glass tubes, the reversal of the orientation of addition was observed[4].

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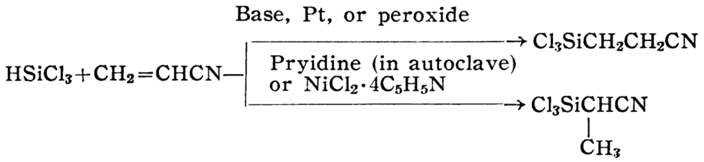
[1] Paper VI in a series on the study of organosilicon compounds.

[2] G.H. Wagner and C.O. Strother, Brit. Pat. 670, 617, Apr. 23, 1952; *C.A.*, **46**, 8894c.

[3] S. Nozakura and S. Konotsune, This Bulletin, **29**, 322 (1956).

[4] S. Nozakura and S. Konotsune, ibid., **29**, 326 (1956).



$$HSiCl_3+CH_2{=}CHCN-\begin{cases} \xrightarrow{\text{Base, Pt, or peroxide}} Cl_3SiCH_2CH_2CN \\ \xrightarrow[\text{or } NiCl_2\cdot 4C_5H_5N]{\text{Pryidine (in autoclave)}} Cl_3Si\underset{\underset{\displaystyle CH_3}{|}}{C}HCN \end{cases}$$

The present work was undertaken to see if the same base catalyst could hold its effect in the above reaction, i. e., the reaction between acetylene and trichlorosilane, and to see if the reverse orientation of addition would also take place in this case. In fact, the reverse addition took place, and there obtained 1, 1-di(trimethylsilyl) ethane which otherwise would not be obtainable.

Addition of Trichlorosilane to Acetylene. —For the comparison of the reactions, the reaction in an autoclave was carried out in the first place according to the procedure described by Wagner and Strother[2]. Thus, in the presence of platinized asbestos, the reaction started at about 170°C. When an excess amount of trichlorosilane over acetylene was used, the principal product was found to be di(trichlorosilyl) ethane. On the other hand, when a sufficient amount of acetylene was supplied to the reaction system, the main product was vinyltrichlorosilane. These results confirmed the description of Wagner and Strother.

In the presence of a catalytic amount of pyridine, on the contrary, the reaction was observed to be initiated at temperatures as high as 180-185°C. Since it was rather tedious to handle the reaction mixture directly, the chlorine atoms attached to silicon atoms were replaced by methyl groups and the mixture of silico-hydrocarbons thus obtained were fractionally distilled through the fractionating column of the Stedman type. Two main fractions were obtained being accompanied with a considerable amount of distillation residue. The physical properties of these main fractions were listed in Table I. Although the data for the first main fraction of molecular weight, analysis, and molar refraction were in good agreement with that of di(trimethylsilyl)ethane, those of boiling point, density, and refractive index showed marked differences from that of 1, 2-di(trimethylsilyl)ethane (151-2°C, 0.7565, and 1.4199, respectively[5]). This discrepancy is thought to be due to the presence of the isomeric mixture, which will be shown later on in this paper. The second main fraction was considered to be di(trimethylsilyl)butene, but the structural proof was not undertaken. In any way, the occurrence of this compound might be explained to be due to the presence of vinylacetylene which might be produced under the reaction condition.

Addition of Trichlorosilane to Vinyltrichlorosilane.—In the course of the addition of trichlorosilane to acetylene leading to the formation of di(trichlorosilyl)ethane, vinyltrichlorosilane may be considered to be an indispensable intermediate. To make the situation simpler, vinyltrichlorosilane was used as the starting material instead of using acetylene and the reaction was carried out in glass tubes according to the following consideration: in the case of cyanoethylation of trichlorosilane published preceedingly, the reaction in an autoclave in the presence of pyridine could be well reproduced in glass tubes in the presence of tetrapyridine nickel chloride. Therefore, the analogous phenomenon was expected to occur here in the reaction of trichlorosilane and acetylene. In fact, that was the case. The typical examples of the experiments were summarized in Table II. This reaction did not take place in the presence of pyridine alone, but in the presence of a catalytic amount of tetrapyridine nickel

TABLE I

PRODUCTS OBTAINED FROM THE REACTION OF ACETYLENE AND TRICHLOROSILANE IN AN AUTOCLAVE IN THE PRESENCE OF PYRIDINE

	Fraction No. 1	Calcd. for $[(CH_3)_3Si]_2C_2H_4$	Fraction No. 3	Calcd. for $[(CH_3)_3Si]_2C_4H_6$
B. p. °C[a]	71-2 (43 mmHg), 155-6		82-5 (24 mmHg)	
d_4^{20}	0.7699		0.7933	
n_D^{20}	1.4280		1.4440	
Mol. Wt.	175	174.4	195	200.4
C %	55.30	55.05	59.53	56.92
H %	12.57	12.72	11.89	12.07
Double bond per mol.	0	0	1	1
MR_D	58.26	58.43	67.10	67.22

a) All temperature are uncorrected.

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[5] M. Kumada and A. Habuchi, *J. Inst. Polytech., Osaka City Univ.*, 3, Ser. C, 65 (1952).

TABLE II

ADDITION OF TRICHLOROSILINE TO VINYLTRICHLOROSILANE AT 180–5°C

	Run 1	Run 2	Run 3	Run 4
$HSiCl_3$, g.	17.3	21.6	32.7	22.8
$CH_2=CHSiCl_3$, g.	22.6	24.0	38.0	25.8
Catalyst, g.	$NiCl_2\cdot C_5H_5N\cdot HCl$, 0.2	C_5H_5N 0.1	$NiCl_2\cdot C_5H_5N$ 0.1	$NiCl_2\cdot 4C_5H_5N$ 0.1
Reaction time, hr.	8.0	5.4	7.3	7.5
B. p. of product, °C (mmHg)	110–5 (54)	—	111–5 (51)	111–4 (49)
Yield, %a)	8.5	0	13	55b)

a) The yields are based on the vinyltrichlorosilane used.

b) The chlorine content of the product was 70.4. (Calcd. for $C_2H_4Si_2Cl_6$, 71.7%).

chloride, the addition was realized to the extent of about 50 percent. The reaction product was then methylated by treating with methylmagnesium bromide and subjected to fractional distillation (Fig. 1). The physical data of two main fractions (fractions No. 3 and 9) were listed in Table III. As the lower boiling fraction (No. 3) shows physical constants which correspond closely to that described by Kumada[5], this fraction can probably be assigned as 1, 2-di(trimethylsilyl)ethane. The higher boiling fraction, which has a similar composition, may be assigned as 1, 1-di(trimethylsilyl)ethane. However, as it was generally unusual that the branched isomer has a higher boiling point than the normal one, the normal compound was synthesized according to the processes of Frisch and Young[6] as follows, and thus the structure of the lower boiling isomer was established conclusively:

$$2\,C_2H_5MgBr \xrightarrow{CH\equiv CH} BrMgC\equiv CMgBr \xrightarrow{(CH_3)_3SiCl} (CH_3)_3SiC\equiv CSi(CH_3)_3 \xrightarrow{H_2,\ Pt} (CH_3)_3SiCH_2CH_2Si(CH_3)_3 \quad \text{(Table III, B)}$$

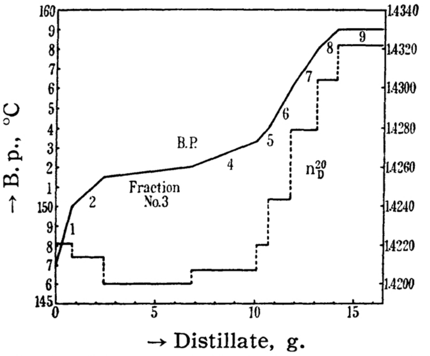


Fig. 1. Fractional distillation curve of the methylated product obtained from trichlorosilane and vinyltrichlorosilane.

TABLE III

PHYSICAL CONSTANTS AND ANALITICAL DATA OF DI(TRIMETHYLSILYL)ETHANE OBTAINED BY VARIOUS METHODS

	C c)		A a)	B b)
	Fraction No. 3	Fraction No. 9		
B. p. °C	151.5–2.0	159	150.0–0.5	150.5–1.0
d_4^{20}	0.7539	0.7808	0.7542	0.7532
n_D^{20}	1.4200	1.4322	1.4196	1.4194
Mol. Wt. in benzene	177	176	——	——
C %	55.53	54.66	54.55	55.68
H %	12.60	12.41	12.30	12.74
MR_D	58.54	57.95	58.46	58.51

a) A is the product of the reaction between acetylene and trichlorosilane in the presence of platinized asbestos.

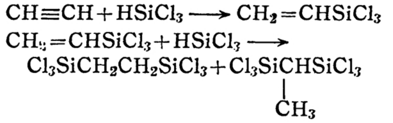
b) B is the product obtained from acetylene via di-Grignard reagent of acetylene.

c) C is the product obtained from the reaction of trichlorosilane and vinyltrichlorosilane in the presence of tetrapyridine nickel chloride.

From the comparison of these physical data, the structure of the lower boiling fraction (No. 3) is established to be 1, 2-di(trimethylsilyl)ethane. Further evidence for the identity of these compounds was obtained from the comparison of infrared spectra. Although the higher boiling compound could not be compared with the authentic sample because of the difficulty of synthesis, it may be reasonably considered to be the branched isomer. For the sake of comparison, the di(trimethylsilyl)ethane which is derived from the reaction of acetylene and trichlorosilane in the presence of platinized asbestos is also listed in Table III (A).

The author refers again to the aforementioned di(trimethylsilyl)ethane which was obtained from acetylene in the autoclave in the presence of pyridine. This compound proved to be a mixture of these two isomers through comparison of physical constants and infrared spectra. But at that time it could not be fractionated into the components, owing to its small amount.

As the results of the above experiments, the author is led to the conclusion that the main reaction in this condition may be represented as follows:



$$CH\equiv CH + HSiCl_3 \longrightarrow CH_2=CHSiCl_3$$
$$CH_2=CHSiCl_3 + HSiCl_3 \longrightarrow Cl_3SiCH_2CH_2SiCl_3 + Cl_3Si\underset{\displaystyle CH_3}{\underset{|}{C}}HSiCl_3$$

Experimental

Reaction of Trichlorosilane and Acetylene in an Autoclave.—The procedure described by Wagner and Strother[2] was followed by the author. One and a half grams of platinized asbestos[3] and 28 g. of trichlorosilane were charged into an autoclave of 100 ml. capacity. The air in the autoclave was replaced several times by acetylene, and then gradual heating was applied.

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[6] K.C. Frisch and R.B. Young, U.S. Pat. 2,671,099, Mar. 2 (1954); *C.A.* 49, 2498g.

The initial pressure of acetylene was 12 kg./cm^2 at room temperature. The reaction started at 168°C, and the pressure at that time was 27.5 kg./cm^2 and decreased smoothly to the constant value of 3.2 kg./cm^2 at 174°C within three hours. After cooling, the contents of the autoclave was washed out by dry ether, filtered, and distilled, yielding 11.5 g. of 1, 2-di(trichlorosilyl)ethane, b. p. 197–8.5°C.

In the other run, the pressure was maintained at above 15 kg./cm^2 throughout the operation by charging the acetylene intermittently, and the heating was stopped when the decrement of the pressure had amounted to 28 kg./cm^2 as a total. Distillation yielded 12.4 g. of vinyltrichlorosilane (b. p. 89.5–91.0°C) and 5.2 g. of higher boiling product.

Reaction of Trichlorosilane and Acetylene in an Autoclave in the Presence of Pyridine.—A half gram of pyridine and 55.8 g. of trichlorosilane (0.41 mol.) were charged into an autoclave of 240 ml. capacity, and treated in a similar manner as mentioned above. The reaction started at 184C° and 0.21 mol. of acetylene was consumed within 8.3 hr. Upon distilling the unreacted trichlorosilane, there remained 46 g. of a higher boiling product (Cl, 58.6%). The product was methylated in the usual manner with methyl magnesium bromide prepared from 23 g. of magnesium, and fractionally distilled through a Stedman column of about thirty theoretical plates, giving the following fractions: (1) b. p. 72°(70 mm.)–63°(27 mm.), 3.5 g.; (2) b. p. 59–76°C(23 mm.), 1.3 g.; (3) b. p. 76–88°C(23 mm.), 1.3 g.; (4) residue, 3.5 g. The first main fraction (No. 1) was purified by shaking it with concentrated sulfuric acid to remove the higher boiling unsaturated compound and by redistilling. The physical data of the purified compound are listed in Table I. The second main fraction (No. 3) was redistilled and its physical constants are also given in Table I.

Reaction of Trichlorosilane and Vinyltrichlorosilane.—Vinyltrichlorosilane was the product of Linde Air Products Co. and distilled at 89–90°C.

The reactions were carried out in sealed glass tubes and its procedure was as follows: trichlorosilane (b. p. 31.5–32.0°C), a vinylcompound, and catalyst were charged into a hard glass reaction ampoule of about 100 ml. capacity and cooled in an ice salt bath, and then the open end of the ampoule was sealed after the air had been replaced by dry nitrogen. Heating was carried out in an electric furnace equipped with an automatic controller. After cooling, the reaction tube was opened, the content was washed out with dry benzene, and the precipitate, if any, was filtered. The unreacted starting material and the solvent in the filtrate was distilled under atmospheric pressure, and then the product was distilled from a Claisen flask under reduced pressure. The results are summarized in Table II.

The product of several runs are combined (35.4 g.) and methylated in the usual manner with methylmagnesium bromide prepared from 20.0 g. of magnesium, yielding 14.5 g. of di(trimethylsilyl)ethane, b. p. 150–8°C (70%). It (19.2 g.) was then distilled fractionally through a Stedman column (Fig. 1). The physical data of two main fractions (No. 3 and 9) are given in Table III.

Di(trimethylsilyl)ethyne.—This compound was synthesized according to the description of Frisch and Young[6]. Into the ethereal solution of ethylmagnesium bromide prepared from 30 g. of magnesium, dry acetylene was bubbled slowly for about six hours at room temperature. After boiling for a short time and then cooling, 1 g. of cuprous chloride was added, and stirred until the gas evolution settled down. Then, 30 g. of trimethylchlorosilane was added, stirred for half an hour, and refluxed for two and a half hours. After cooling, the reaction mixture was treated with ice and diluted hydrochloric acid, and the ether layer was separated, washed with water, and dried with calcium chloride. After filtration the ether solution was distilled through a Stedman column, yielding 2.1 g. of di(trimethylsilyl)ethyne, b. p. 136.0°C; d_4^{25}, 0.7578; n_D^{25}, 1.4231; MR_D, 57.25 (calcd. 56.82).

1, 2-Di(trimethylsilyl)ethane.—A solution of 2.84 g. of di(trimethylsilyl)ethyne in 10 ml. of alcohol was reduced catalytically in the presence of palladium charcoal. The amount of hydrogen absorbed was quantitative. After the removal of the catalyst by filtration, 50 ml. of water was added, and the separating oily layer was extracted with ether. The ether extract was washed with a small amout of water and dried over calcium chloride. Distillation of the ether solution yielded 1.8 g. of the crude product. The crude product was shaken twice with about equal volume of concentrated sulfuric acid and then distilled, yielding 1.0 g. of the pure 1, 2-di(trimethylsilyl)ethane, b. p. 150.5–151.0°C. The physical constants and analytical data are shown in Table III (B).

Summary

The addition reactions of trichlorosilane and acetylene in an autoclave were carried out in the presence of platinized asbestos or of pyridine. In the case of the former catalyst, 1, 2-di(trichlorosilyl)ethane was obtained exclusively. In the case of the latter, on the other hand, the principal product proved to be a mixture of 1, 2- and 1, 1-di(trichlorosilyl)ethane.

The addition of trichlorosilane to vinyltrichlorosilane in the presence of tetrapyridine nickel(II) chloride in glass tubes also led to the formation of a mixture of two isomers. Therefore, it might be considered that the reaction processes in the autoclave in the presence of pyridine was reproduced by the reactions in glass tubes. This situation seems to be analogous to that in the case of cyanoethylation of trichlorosilane which was previously reported.

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