Addition of Trichlorosilane to Styrene, 2 Vinylpyridine, Allylcyanide and Octene-1[1]

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It is a well-known fact that trichlorosilane is added to olefinic double bonds in the presence of radical catalysts such as organic peroxides or ultraviolet light. In the previous papers the author has reported that in addition to the typical radical catalysts, organic bases and nickel complex compounds could also effect the reaction. Thus, addition of trichlorosilane to acrylonitrile took place in the presence of organic bases (β-addition)[2] and of nickel complex compound (α-addition)[3]. The reaction between trichlorosilane and acetylene (or vinyltrichlorosilane)[4] was also catalysed by tetrapyridine nickel (II) chloride, and led to the formation of a mixture of two isomeric addition products, i.e., 1,1- and 1-2-di (trichlorosilyl) ethanes.

The objectives of the work to be reported below are to study the effectiveness of such catalysts for the other vinyl compounds, and to establish the structures of the resulting addition products.

Styrene, 2-vinylpyridine, allylcyanide, octene-1 were tried as the representatives of vinyl compounds. All the addition reactions were carried out in sealed glass tubes. The reaction conditions and results are summarized in Table I.

Styrene.—Addition of trichlorosilane to styrene was attempted first by Burkhard[5] in the presence of peroxide, resulting in the formation of only a non-volatile telomeric product. Wagner and coworkers[6] succeded in the preparation of β-phenylethyltrichlorosilane by the reaction using platinized charcoal as the catalyst at 200°C.

In the present work, when trichlorosilane and styrene were heated at 160°C in the presence of pyridine, no addition product was obtained except for a non-volatile viscous polymer. But in the presence of tetrapyridine nickel chloride, about 30 percent of addition product was obtained accompanied with a considerable amount of non-volatile product. This non-volatile product may probably be a telomeric one taking into consideration the fact that it has a moderate chlorine content of 13 percent.

The phenylethyltrichlorosilane thus obtained was methylated by methylmagnesium bromide and distilled fractionally into two components. These are the isomers of phenylethyltrimethylsilane (Table II). Although the direct confirmation was not undertaken, the lower boiling isomer may be considered to be α-phenylethyltrimethylsilane by analogy

TABLE I

THE ADDITION REACTIONS BETWEEN TRICHLOROSILANE AND VINYL COMPOUNDS

	Styrene		2-Vinylpyridine	Allylcyanide				Octene-1	
$HSiCl_3$, g.	16.4	20.4	20.5	20.4	20.0	21.9	21.0	19.8	22.0
Vinyl Compound, g.	18.1	17.2	16.0	11.1	10.9	11.1	11.4	16.4	18.2
Catalyst, g.	C_5H_5N, 0.1	$NiCl_2 \cdot 4C_5H_5N$, 0.1	—	C_5H_5N, 0.2	$(C_2H_5)_3N$, 0.1	$NiCl_2 \cdot C_5H_5N$, 0.1	$NiCl_2 \cdot 4C_5H_5N$, 0.1	C_5H_5N, 0.1	$NiCl_2 \cdot 4C_5H_5N$, 0.1
Reaction Temp., °C	160	160	160	160	160	180–5	160	160	180
Reaction time, hr.	5.0	4.2	5.0	7.2	5.0	5.3	1.5	4.6	7.0
B.p. of the Product, °C (mmHg)	—	130–5 (40)	—	100–2 (27)	100–3 (26)	116–25 (41)	117–30 (41)	—	115–24 (24)
Yield, %[a]	0	30[b]	Farely good[c]	10	19	16	26	0	17

a) Yields are based on trichlorosilane used.

b) The chlorine content of the distillation residue was found to be 13%.

c) The reaction product was a crystalline mass and was methylated directly. M.p. (ca. 164°) and b.p. (ca. 190° at 24 mmHg) are measured with the sample obtained from the other run.

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

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

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

[4] S. Nozakura, ibid., 29, 660 (1956).

[5] C.A. Burkhard and R.H. Krieble, *J. Am. Chem. Soc.*, 69, 2687 (1947).

[6] Wagner et al., *Ind. Eng. Chem.*, 45, 367 (1953).

TABLE II

PHYSICAL AND ANALYTICAL DATA OF THE METHYRATED ADDITION PRODUCTS

Compound	α-Trimethylsilylethylbenzene	β-Trimethylsilylethylbenzene	2-β-Trimethylsilylethylpyridine	β-Trimethylsilylbutyronitrile	γ-Trimethylsilylbutyronitrile	Trimethylsilyl-sec-octylsilane[a)]	Trimethylsilyl-*n*-octylsilane
B. p., °C (mmHg)	103.0–4.5 (32)	112.0–2.2 (32)	106–7 (21)	91.0–2.5 (30)	97.0–8.0 (30)	99.0–100.0 (30)	107 (29)
d_4^{25}	0.8747	0.8603	0.8982	0.8326	0.8227	0.7667	0.7584
n_D^{25}	1.4958	1.4851	1.4843	1.4292	1.4258	1.4308	1.4241
C%, Found	74.13	74.44	—	—	—	71.37	70.62
Calcd.	74.09	74.09	—	—	—	70.86	70.86
H%, Found	10.12	10.12	—	—	—	13.38	13.79
Calcd.	10.18	10.18	—	—	—	14.05	14.05
N%, Found	—	—	8.09	9.67	9.47	—	—
Calcd.	—	—	7.82	9.92	9.02	—	—
Mol. Wt., Found	174	173	175	145	141	185	188
Calcd.	178.3	178.3	179.3	141.3	141.3	186.4	186.4
MR_D, Found	59.56	59.41	57.20	43.75	43.45	62.90	62.72
Calcd.	59.30	59.30	56.77	43.72	43.72	62.69	62.69

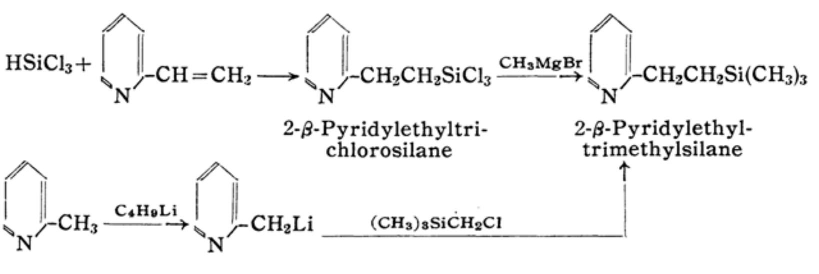
a) This sample is considered to be somewhat impure.

to the assignment of Wagner and coworkers, i. e., they assigned the lower boiling phenylethyltrichlorosilane to be α-isomer.

2-Vinylpyridine.—The addition reaction between trichlorosilane and 2-vinylpyridine took place very easily at about 160°C without the addition of any catalyst, but the product obtained is very difficult to be handled directly because of its high hygroscopicity. The product, pyridylethyltrichlorosilane, has a high melting point and it is probably due to an intermolecular attractive force exerted between silicon atoms and nitrogen atoms.

Pyridylethyltrichlorosilane is hydrolyzed by water giving a clear aqueous solution. When the solution is made alkaline by adding aqueous ammonia, an amorphous precipitate appears which is considered to be pyridylethylpolysiloxane. And this polysiloxane dissolved again in dilute hydrochloric acid.

The structure of the addition product was established by methylating it and comparing the resulting product with the sample which was synthesized by the other route from α-picoline in the following manner:

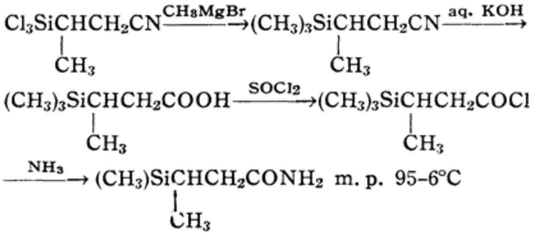


These two samples are proved to be identical in their infrared spectra, and moreover to give the same picrate.

The reaction in the presence of tetrapyridine nickel chloride was not attempted in this case.

Since the reactant itself is a base, the reaction should be base-catalyzed one just as the cyanoethylation of trichlorosilane catalyzed by bases[2)].

Allylcyanide.—The reactivity of trichlorosilane for allylcyanide was rather low in the presence of organic bases. The product may possibly be either one of two isomers, β- and γ-trichlorosilylbutylonitrile, or a mixture of them. The acid amide which was derived from the product has the melting point of 95–6°C. The manners of conversion were as follows:

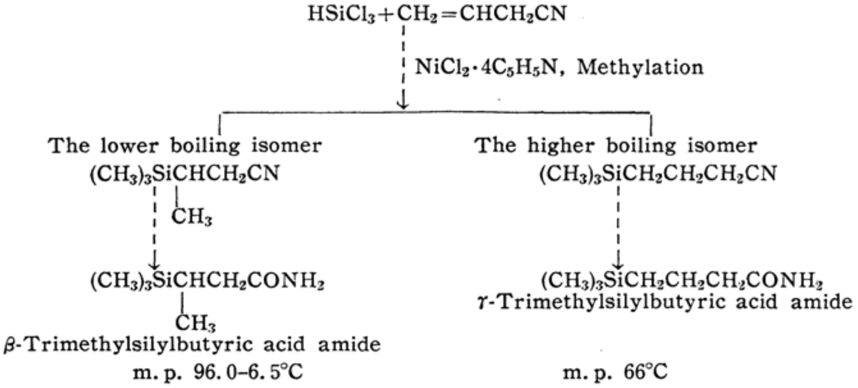


$$Cl_3Si\underset{CH_3}{CH}CH_2CN \xrightarrow{CH_3MgBr} (CH_3)_3Si\underset{CH_3}{CH}CH_2CN \xrightarrow{aq.\ KOH}$$
$$(CH_3)_3Si\underset{CH_3}{CH}CH_2COOH \xrightarrow{SOCl_2} (CH_3)_3Si\underset{CH_3}{CH}CH_2COCl$$
$$\xrightarrow{NH_3} (CH_3)Si\underset{CH_3}{CH}CH_2CONH_2 \text{ m. p. } 95\text{–}6°C$$

Since γ-trimethylsilylbutyric acid amide is known to have the melting point of 66.5–6.7°C.[5)], the product here obtained must be the other isomer, that is β-trichlorosilylbutyronitrile.

β-Trichlorosilylbutyronitrile gave on hydrolysis the corresponding polysiloxane, $NCCH_2CH(CH_3)SiO_{1.5}$.

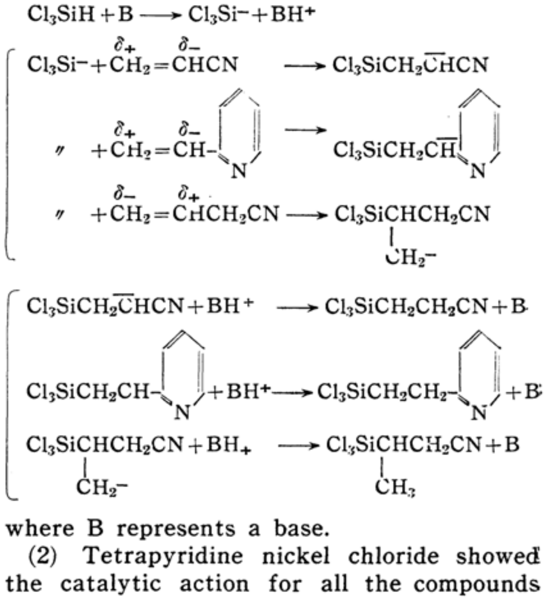
In the presence of tetrapyridine nickel chloride, the yield of the addition product was somewhat higher than the corresponding one with the pyridine catalyst (Table I). However, the product showed a very wide range of boiling point, indicating that it contained more than one component. The product was methylated and fractionally distilled into two isomers (Table II). The structures of these isomers were established by converting them into the corresponding acid amides as follows and comparing them with the specimens formerly obtained by Sommer7):



Thus, the melting point of the acid amide derived from the higher boiling isomer is in good agreement with that of γ-trimethylsilylbutyric acid amide reported by Sommer7). Therefore, it is concluded that the lower boiling alternative may be β-trimethylsilylbutyronitrile and the higher one may be γ-isomer.

Octene-1.—The reaction of trichlorosilane and octene-1 did not take place at all in the presence of catalytic amount of pyridine, but it took place to a small extent (17%) in the presence of tetrapyridine nickel chloride catalyst at 180°C (Table I). As the product obtained showed a rather wide range of boiling point, it was methylated as usual and was subjected to fractional distillation. Two isomers of trimethyloctylsilanes were isolated and their physical constants are listed in Table II. As the higher boiling one has the physical constants which coincide fairly well with those of *n*-octyltrimethylsilane described by Pietrusza and coworkers8), the higher boiling one could be assigned to be *n*-octyltrimethylsilane. Although the lower boiling fraction is considered to be mainly composed of sec-octyltrimethylsilane, its purity is rather doubtful considering from its analytical data and infrared spectrum, which showed unexpected weak bands at $1622^{-\text{cm.}}$ and $2116^{-\text{cm.}}$. Further purification may be necessary.

General Conclusion.—The experimental results of all these additional experiments are summarized in Table III including the results of the previous paper. The following conclusions are deduced: (1) In the reactions between trichlorosilane and vinyl compounds, organic bases such as pyridine showed the catalytic action in some special cases (acrylonitrile, allylcyanide, and 2-vinylpyridine). 2-Vinylpyridine may be classified into this group because of its own basicity. The orientation of the addition could be well explained by the base-catalyzed ionic mechanism as follows:



where B represents a base.

(2) Tetrapyridine nickel chloride showed the catalytic action for all the compounds

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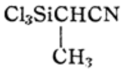
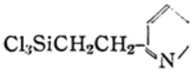
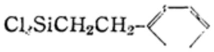
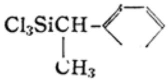
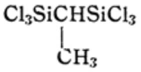
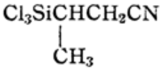
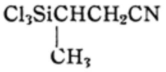
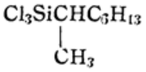
7) L.H. Sommer, U.S.P., 2, 610, 198, Sept. 9 (1952); *C.A.*, 47, 9346 b (1953).

8) E.W. Pietrusza et al., *J. Am. Chem. Soc.*, 70, 484 (1948).

TABLE III

ADDITION OF TRICHLOROSILANE TO VINYL COMPOUNDS IN THE PRESENCE OF PYRIDINE OR TETRAPYRIDINE NICKEL(II) CHLORIDE

Vinyl Compound	The Product in the Presence of Pyridine	The Product in the presence of $NiCl_2 \cdot 4C_5H_5N$
Acrylonitrile	$Cl_3SiCH_2CH_2CN$	 $Cl_3SiCH(CH_3)CN$
2-Vinylpyridine		Not attempted
Styrene	No addition	 
Vinyltrichlorosilane	No addition	$Cl_3SiCH_2CH_2SiCl_3$  $Cl_3SiCH(CH_3)SiCl_3$
Allylcyanide	 $Cl_3SiCH(CH_3)CH_2CN$	$Cl_3SiCH_2CH_2CH_2CN$  $Cl_3SiCH(CH_3)CH_2CN$
Octene-1	No addition	$Cl_3SiCH_2CH_2C_3H_{13}$  $Cl_3SiCH(CH_3)C_6H_{13}$

examined, and the addition products were found to be generally the mixtures of normal and branched compounds.

Experimental

The General Procedure for the Reaction between Trichlorosilane and Vinylcompounds.—All the reactions were carried out in sealed glass tubes. Trichlorosilane (b. p. 31.5–32.0°C), a vinyl compound, and catalyst were charged into a hard glass ampoule of about 100 ml. capacity which had been cooled in an ice salt bath, and 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 and the temperature was kept constant automatically within the range of of ±3°C. After cooling the ampoule was opened, the content was washed out with dry benzene, and the catalyst was filtered. The unreacted starting material and the solvent in the filtrate was distilled under atmospheric pressure, and the product was distilled from a Claisen flask under reduced pressure.

Mono- and tetra-pyridine nickel chlorides are prepared according to the method of Reizenstein[9].

Methylation of Phenylethyltrichlorosilane.—The products of two runs are combined and redistilled, yielding 15.9 g. of phenylethyltrichlorosilane, b. p. 127–36°C (31.5 mmHg).

Anal. Found: Cl, 44.2. Calcd. for $C_8H_9SiCl_3$: Cl, 44.46%.

Phenylethyltrichlorosilane (15.9 g.) was methylated by treating with methylmagnesium bromide prepared from 5.8 g. of magnesium. Phenylethyltrimethylsilane was then fractionally distilled through the Stedman column of about thirty theoretical plates. The following fractions were obtained at the pressure of 32 mmHg: (1) b. p. 102.5–3.0°C, 0.05 g. (2) b. p. 103.0–4.5°, 2.6 g. (3) 104.5–5.5°, 2.6 g. (4) b. p. 105.5–111.0°, 1.1 g. (5) b. p. 111.0–112.0°, 0.6 g. (6) 112.0–112.2°, 0.8 g. (7) residue, 1.1 g. The physical and analytical data of fraction No. 2 and 6 are listed in Table II.

2-β-Trichlorosilylethylpyridine and its Methylation.—2-β-Trichlorosilylethylpyridine which was obtained from trichlorosilane and 2-vinylpyridine* was purified by distillation in vacuum, b. p. ca. 190°C (24 mm.); m. p., ca. 164°C. Analysis was made by potentiometric titration using Beckman Model G of an aqueous solution. An aqueous solution of 0.08085 g. of the sample in 20 ml. of water was titrated with 0.0966 N aqueous sodium hydroxide. Found for the neutralization point of 2Cl, 6.91 ml. (pH, 3.76) and for 3Cl, 10.48 ml. (pH, 7.70). Calcd. for $C_7H_8SiCl_3$, 6.95 and 10.43 ml., respectively.

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9) F. Reizenstein, *Z. anorg. Chem.*, **11**, 254 (1896); **18**, 264 (1898).

* 2-Vinylpyridine was kindly supplied by M. Yoshida at Osaka Prefectural University. B.p. 82°(55 mmHg).

The product obtained from the reaction described in Table I was directly methylated as follows: the crystalline mass of the crude 2-β-trichlorosilylethylpyridine and 50 ml. of ether were placed in a three necked flask equipped with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser which was connected to a calcium chloride tube. The ethereal solution of methylmagnesium bromide which was obtained from 13.2 g. of magnesium was dropped into it through the funnel within about forty minutes so as to keep the solution gently refluxing. And then the refluxing was continued for four hours. After cooling, the reaction mixture was treated with ice-water and an excess of hydrochloric acid. The aqueous layer was separated, and made alkaline by an excess of aqueous sodium hydroxide, and then subjected to steam distillation. The distillate was extracted with ether and the extract was dried with unhydrous sodium sulfate. After filtration, the ether solution was distilled, yielding 13.3 g. of 2-β-trimethylsilylethylpyridine, b. p. 106–7°C (21 mmHg). The overall yield calculated from trichlorosilane used was 49 percent. The analytical and physical data are given in Table II.

Its picrate melted at 89°C.

Anal. Found: N, 13.80; Si, 6.94. Calcd. for $C_{16}H_{20}N_4O_7Si$: N, 13.73; Si, 6.85%.

Its hydrochloride has the melting point of 102–3°C. and it was not analyzed because of its extreme hydroscopicity.

Synthesis of 2-β-Trimethylsilylethylpyridine from α-Picoline.—Into the benzene solution of butyllithium prepared from 2.0 g. of lithium, 9.3 g. of *n*-butylchloride, and 60 ml. of benzene, 9.3 g. of α-picoline was added dropwise at room temperature and let stand for forty minutes. Twelve grams of chloromethyltrimethylsilane was added to this reaction mixture, and it was let stand overnight. Then the mixture was treated with a solution of 20 ml. of water and 22 ml. of concentrated hydrochloric acid. The aqueous layer was separated, 14 g. of sodium hydroxide was added, and extracted with ether. After drying with anhydrous sodium sulfate, the ether solution was distilled, yielding 4.1 g. of 2-β-trimethylsilylethylpyridine, b. p. 105–7°C (21 mmHg). n_D^{2}, 1.4845.

Anal. Found: N, 7.99. Calcd. for $C_{10}H_{17}NSi$: N, 7.82%.

The identity of this compounds with the one derived from the addition product of trichlorosilane and 2-vinylpyridine was established through comparison of their infrared spectra.

Methylation of the Addition Product Obtained from the Reactions of Trichlorosilane and Allylcyanide in the Presence of Bases, and Conversion into the Corresponding Acid Amide.—The products of two runs were combined and redistilled to yield 5.5 g. of β-trichlorosilylbutyronitrile, b. p. 105.0–6.5°C (25 mmHg) (Found: Cl, 51.4. Calcd. for $C_4H_6NSiCl_3$: Cl, 52.5%).

A few drops of β-trichlorosilylbutyronitrile was poured onto a large excess of water. When the resulting solution was neutralized with aqueous ammonia, an amorphous precipitate of β-cyanopropylpolysiloxane appeared. It was filtered, washed with water, and dried over phosphorous pentoxide.

Anal. Found: Si, 23.0. Calcd. for $C_4H_3NO_{1.5}Si$: Si, 23.3%.

β-Trichlorosilylbutyronitrile (4.9 g.) was methylated in a usual manner by methylmagnesium bromide prepared from 2.0 g. of magnesium. In order to remove the impurity of ketone the methylated product was shaken with a saturated solution of sodium bisulfite, and then distilled, yielding 1.4 g. crude β-trimethylsilylbutyronitrile, b. p. 90–93°C (34.5 mmHg), (41%).

A mixture of 1.2 g. of β-trimethylsilylbutyronitrile, 5 ml. of aqueous 50 percent sodium hydroxide, and 5 ml. of alcohol was refluxed for twenteen hours. After cooling, alcohol was evaporated in reduced pressure, 10 ml. of water was added, and then extracted with ether to remove the unreacted nitrile. The remaining aqueous layer was then acidified with hydrochloric acid, and again extracted with ether. After drying with anhydrous sodium sulfate, the ether extract was distilled to yield 0.7 g. of β-trimethylsilylbutyric acid, b. p. 106–111°C (10.5 mmHg) (51%).

A mixture of 0.4 g. of β-trimethylsilylbutyric acid and 1.6 g. of thionyl chloride was gently refluxed for one hour. The excess of thionyl chloride was evaporated under reduced pressure. The residual oil was dissolved in 20 ml. of dry ether and saturated with dry ammonia under cooling with ice-water, and let stand for a short time. After filtration of the resulting ammonium chloride, the ether solution was evaporated to yield 0.3 g. of crude β-trimethylsilylbutyric acid amide, m. p. 93–4°C. Purification was carried out by recrystallization from petroleum benzine, m. p. 95–6°C.

Anal. Found: N, 8.68. Calcd. for $C_7H_{17}NOSi$: N, 8.79%.

The Product Obtained from the Reactions of Trichlorosilane and Allylcyanide in the Presence of Tetrapyridine Nickel Chloride.—The products of several runs (23.6 g.) were combined and methylated in the usual manner using 9.4 g. of magnesium. The methylated product was shaken with an aqueous saturated solution of sodium bisulfite, and then washed with water, dried with calcium chloride, and distilled through a Stedman column of about thirty theoretical plates. The following fractions were obtained under the pressure of 30 mmHg: (1) 87.5–91.0°, a few drops, (2) 91.0–2.5° 1.7 g., (3) 92.5–5.0°, 1.5 g., (4) 95.0–7.0°, 0.8 g., (5) 97.0–8.0°, 2.8 g., (6) residue, 3.5 g. Analytical and physical data of two main fractions (No. 2 and 5) are listed in Table II.

One gram of the fraction No. 2 (β-trimethylsilylbutyronitrile) was hydrolyzed in the same manner mentioned above, and yielded 0.5 g. of crude β-trimethylsilylbutyric acid, b. p. 108-115° (10 mmHg). The latter product was immediately treated with 2.0 g. of thionylchloride and then ammonia, yielding 0.5 g. of crude β-trimethylsilylbutyric acid amide. Recrystallization from a mixture of alcohol and water gave 0.3 g. of pure sample, m. p. 96.0–6.5°C.

Anal. Found: N, 8.47. Calcd for $C_7H_{17}NOSi$: N, 8.79%.

One and two tenth grams of fraction No. 5 (γ-trimethylsilylbutyronitrile) was treated in a similar manner, and gave 0.8 g. of γ-trimethylsilylbutyric acid (b. p. 115–7° (11 mmHg)) and then 0.5 g. of crude γ-trimethylsilylbutyric acid amide, m. p. 61.5–4.0°C. By recrystallization from *n*-heptane, the pure sample was obtained, m. p. 66.0°C.

Anal. Found: N, 8.96. Calcd. for $C_7H_{17}NOSi$: N, 8.79%.

The Product Obtained from the Reactions of Trichlorosilane and Octene-1.—The products of several runs (16.9 g.) were combined and methylated in the usual manner by methylmagnesium bromide prepared from 6.5 g. of magnesium. The methylated product was distilled through a Stedman column into the following fractions: (1) 96.0–9.0° (30 mm.), 0.4 g. (2) 99–100.0° (30 mm.), 1.7 g. (3) 100.0° (30 mm.)–103.0° (29 mm.), 2.1 g. (4) 103.0–107.° (29 mm.), 0.3 g. (5) 107° (29 mm.), 4.1 g.

Analytical and physical data of two main fractions (No. 2 and 5) are listed in Table II.

Summary

Addition reactions of trichlorosilane to styrene, 2-vinylpyridine, allylcyanide, and octene-1 were attempted in the presence of bases such as pyridine and in the presence of tetrapyridine nickel(II) chloride. The structures of the reaction products were established. In the presence of bases, trichlorosilane was added to 2-vinylpyridine and allylcyanide, yielding 2-β-trichlorosilylethylpyridine and β-trichlorosilylbutyronitrile, respectively. On the other hand, in the presence of tetrapyridine nickel chloride, the addition was effected for all the vinyl compounds examined. (2-vinylpyridine was not attempted.) In this case, however, the addition products proved to be composed of two position isomers, the occurrence of which was due to the difference in the orientation of addition, for each of the starting vinyl compounds.

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