Cyanoethylation of Trichlorosilane. I. β-Addition.[1]

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Since Sommer and coworkers[2] discovered the peroxide-catalyzed addition of trichlorosilane to 1-octene in 1947, a number of olefins have been found to react in the following manner[3]:

$$HSiCl_3 + CH_2 = CHR \dashrightarrow Cl_3SiCH_2CH_2R$$

Wagner and Strother[4] also reported the preparation of vinyltrichlorosilane from acetylene and trichlorosilane in the presence of catalysts such as peroxide and platinized asbestos. Thus the method gained its importance in the industrial production of vinyltrichlorosilane.

However, the olefins which have hitherto been used were generally simple olefins, and only a few reactive vinyl compounds were tried. In an attempt to effect the addition of trichlorosilane with styrene, Burkhark[3] was only able to isolate a nonvolatile telomeric product. Quite recently, in the midst of our experiments, butadiene[5] and vinyltrimethylsilane[6] were reported to react with trichlorosilane.

In this paper we describe the addition reaction of trichlorosilane and acryronitrile. Acrylonitrile among the various vinyl compounds was tried first, as we expected that the addition might take place readily and the identification of its products might also be easy.

TABLE I

CYANOETHYLATION OF TRICHLOROSILANE IN THE PRESENCE OF BENZOYLPEROXIDE AND PLATINIZED ASBESTOS

No.	Trichlorosilane, g.	Acrylonitrile, g.	Catalyst, g.	Reaction[a] temp. °C	Reaction time, hr.	Yield,[b] %
1	19.1	7.6	—	160	5.0	9.7
2	19.9	7.8	—	180	5.0	10
3	18.5	8.0	benzoylperoxide, 0.05	160	5.0	46[c]
4	19.9	7.8	〃 0.05	130	5.0	0[d]
5	19.9	7.8	〃 0.05	100	5.0	0[e]
6	19.6	7.8	benzoic acid 0.05	160	5.0	0
7	19.7	7.8	platinized asbestos 0.1	160	5.5	11
8	19.3	7.6	〃 0.1	180–200	5.8	61

a) Reaction temperatures fluctuated within ±3°C.
b) The yields are based on trichlorosilane used.
c) A pale yellow precipitate weighed 3.2 g. (Si, 5.3%)
d) Precipitate, 1.1 g. (Si, 4.01%)
e) Precipitate, 2.8 g. (Si, 1.69%)

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[1] Paper IV in a series on the study of organosilicon compound.

[2] L.H. Sommer, et. al., *J. Am. Chem. Soc.*, **69**, 188 (1947).

[3] C.A. Burkhard and R.H. Krieble, ibid., **69**, 2687 (1947); W. Pietrusza, et. al.; ibid., **70**, 484 (1948); C.L. Agre, ibid., **71**, 300 (1949); C.A. Burkhard, ibid., **72**, 1402 (1950).

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

[5] D.L. Bailey and A.N. Pines, *Ind. Eng. Chem.*, **46**, 2363 (1954).

[6] D. Seyferth and E.G. Rochow, *J. Org. Chem.*, **20**, 250 (1955).

Cyanoethylation of Trichlorosilane in the Presence of Benzoylperoxide and Platinized Asbestos

Table I shows the catalytic effects of benzoylperoxide and platinized asbestos. Benzoylperoxide was effective at above 160°C., and it produced simultaneously a considerable amount of an insoluble pale yellow precipitate which appeared to be either polyacrylonitrile or tellomeric product. Although such an insoluble precipitate was also produced at 130°C or at lower temperatures, no addition product, except the polymer, was obtained. Experiment with benzoic acid alone, which is a possible decomposition product of benzoylperoxide, had no catalytic action at all. On the other hand, platinized asbestos, which has been known to be effective in the addition of trichlorosilan to acetylene, catalyzed effectively and gave cyanoethylation product without accompanying the precipitate.

Cyanoethylation of Trichlorosilane in the Presence of Organic Bases

Organic and inorganic bases are known to be effective catalysts in the usual case of cyanoethylation. However, in our cases inorganic bases such as metal hydroxides were inadequate because of their strong reactivity towards trichlorosilane, and this led us to turn our attention to tertiary organic bases. The results obtained with the addition of organic bases are given in Table II. The reaction mixtures were clear in almost all the cases and colored from a light yellow to a light orange. The addition product obtained here was the same as that from peroxidecatalysed. In contrast to the latter case, there occurred no precipitate. Pyridine was also effective at a temperature as low as 130°. Catalytic activities of the bases increased in the order, dimethylaniline $\ll$ quinoline $<$ pyridine, piperidine $<$ triethylamine.

It is also of interest to note that pyridine hydrochloride, benzyltriethylammonium chloride, and piperidine have shown a moderate catalytic activity. Since piperidine has an active hydrogen, it may react with trichlorosilane to form piperidylsilicon bonds and piperidine hydrochloride. The catalytic activity of piperidine may possibly be due to the effect of the latter two compounds.

It must be taken into consideration that tertiary amine may have also changed to its hydrochloride to a certain extent prior to heating by a small amount of moisture which inevitably adhered to the sealed tube and the resulting hydrochloride acted as a catalyst. However, this is not very serious in view of the fact that the catalytic activity of pyridine was found to be higher than its hydrochloride as clearly demonstrated in the experiment No. 8 and 9 (Table II).

Structural Proof of Addition Products

The addition product was proved to consist almost exclusively of β-cyanoethyltrichlorosilane, which was identified by the process described below. Cyanoethyltrichlorosilane was converted to the corresponding trimethylsilylpropionic amide (IV), m.p. 95–6°C.

TABLE II

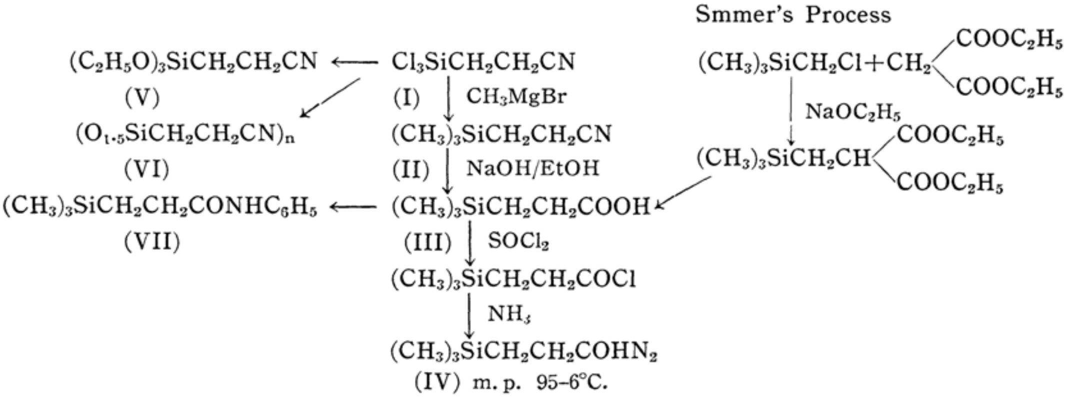
CYANOETHYLATION OF TRICHLOROSILANE IN THE PRESENCE OF ORGANIC BASES

No.	Trichlorosilane, g.	Acrylonitrile, g.	Catalyst, g.	Reaction temp. °C	Reaction time, hr.	Yield, b) %
1	19.9	8.7	pyridine, 0.1	185	5.0	67
2	27.8	13.0	〃 0.1	160	5.0	69
3	19.9	8.7	〃 0.1	130	6.0	14
4	18.6	8.0	triethylamine, 0.1	160	5.0	76
5	20.1	8.7	piperidine, 0.1	160	5.0	69
6	20.2	8.7	quinoline, 0.1	160	5.0	40
7	20.5	7.9	dimethylaniline, 0.1	160	5.0	0
8	20.0	7.8	pyridine, 0.05	160	5.0	59
9	19.8	7.8	pyridine hydrochloride a)	160	5.0	35
10	20.5	8.9	benzyltriethylammonium chloride, 0.1	160	5.0	70

a) The pyridine hydrochloride was prepared in the reaction tube by interacting 0.05 g. of pyridine and an excess of concd. hydrochloric acid and by drying in vacuo.

b) The yields are based on trichlorosilane used.

The structure of the latter compound was already proved by Sommer[7] through a series of reactions. Mixed melting point test of our addition product with that synthesized showed no depression. Therefore, the compound (I) was assigned to be β-cyanoethyltrichlorosilane.



The examination of the compound (II) by infra red spectrum proved it to be identical with that derived from β-trimethylsilylpropionic amide according to Sommer's method.

The following new compounds were prepared and characterized; β-cyanoethyltriethoxysilane (V), β-cyanoethylpolysiloxane (VI), and β-trimethylsilylpropionic anilide (VII).

The Effect of Solvent on the Base-catalyzed Cyanoethylation of Trichlorosilane

Although a more accurate measurement of reaction rate must be done for a detailed discussion, we carried out here an approximate comparison of three solvents, acetonitrile, chlorobenzene, and benzene, dielectric constants of which being 37.5, 5.61, and 2.29 respectively. The effect of the solvents on the base-catalyzed addition reaction are summarized in Table III. When the reactions were carried out in the presence of the strongest catalyst such as triethylamine, there were no detectable differences among the solvents studied. However, when a weaker base catalyst such as pyridine was used, a marked difference was observed among them.

Discussion of Reaction Mechanisms

The peroxide-catalyzed cyanoethylation may be regarded as a radical chain reaction as Sommer and others have suggested in the case of other olefins. Tne base-catalyzed cyanoethylation of trichlorosilane does not seem to be a radical reaction. Although there

TABLE III

CYANOETHYLATION OF TRICHOLOROSILANE IN VARIOUS SOLVENTS AT 160°C

No.	Trichlorosilane, g.	Acrylonitrile, g.	Catalyst, g.	Solvent, ml.	Reaction time, hr.	Yield b) %
1	22.2	9.6	triethylamine, 0.1	acetonitrile, 26	5.0	64
2	21.8	9.4	〃, 0.1	benzene, 45	5.0	59
3	20.4	8.8	pyridine, 0.1	acetonitrile, 40	1.0	39
4	16.8	7.3	〃, 0.07	〃 34	2.0	59
5	20.4	8.8	〃, 0.1	benzene, 40	1.0	0
6	17.1	7.5	〃, 0.07	〃, 34	2.0	0
7	18.8	8.1	〃, 0.1	〃, 38	5.0	0
8	20.0	8.7	〃, 0.1	chlorobenzene, 40	5.0	0
9	16.8	7.3	〃, 0.07	nitrobenzene, 34	2.0	—a)

a) The colour of the reaction mixture was brownish black and its distillation was difficult due to decomposition.

b) The yields are based on trichlorosilane used.

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[7] L.H. Sommer, et. al., *J. Am. Chem. Soc.*, 73, 5130 (1951); 76, 1609 (1954).

has not yet been reported an example in which the fission of silicon-hydrogen bond and addition of it to a double bond may be explained in terms of ionic mechanism, we believe that ionic mechanism involved in our case. The following three pieces of evidence may support such an ionic mechanism. First, base catalysts are effective. Second, no appreciable amount of precipitates of polyacrylonitrile is produced in the base-catalyzed reactions in contrast to the case of peroxide-catalyzed. Third, solvents give a considerable effect in some cases as mentioned above. The deficiency of the influence of the solvents in the case of triethylamine catalyst is probably due to the much higher catalytic activity of triethylamine than that of pyridine.

In view of these facts we may suggest the following reaction mechanism, which is similar to the ordinary cyanoethylation:

$$Cl_3SiH+B \longrightarrow Cl_3Si^-+HB^+$$
$$Cl_3Si^-+CH_2=CHCN \longrightarrow Cl_3SiCH_2CH^-CN$$
$$Cl_3SiCH_2CH^-CN+HB^+ \longrightarrow Cl_3SiCH_2CH_2CN+B$$

where B represents organic bases.

Organic salts, such as pyridine hydrochloride and benzyltriethylammonium chloride, are soluble in the reaction mixture and we considered that their catalytic effect is probably due to a salt effect.

Experimental

General Procedure for Cyanoethylation of Trichlorosilane.—Trichlorosilane (b.p. 31.5–32.0°C) and freshly distilled acrylonitrile) b.p. 76.5–77°C) were charged into a hard glass reaction ampule of about a 100 ml. capacity and 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 equipped with an automatic controller. After cooling, the reaction tube was opened and the precipitate if any was filtered. The precipitate was washed with dry benzene and absolute alcohol, dried in a desiccater, and analyzed for silicon.

A mixture of the solvent and the unreacted starting material of the filtrate was distilled under atmospheric pressure, and then the product was distilled from a Claisen flask under reduced pressure.

Catalyst.—Platinized asbestos was prepared according to the following directions. Three grams of purified asbestos was mixed with 0.06 g. of chloroplatinic acid, H_2PtCl_6, and an appropriate quantity of water. After being dried on the water bath, the mixed asbestos was heated in a glass tube at 200°C in a stream of air for one hour and then reduced with dry hydrogen at 200°C for three hours.

β-Cyanoethyltrichlorosilane (I).—After the purification by redistillation, the physical constants of β-cyanoethyltrichlorosilane were determined. B.p. 109° (30 mmHg), m.p. 34.6–35.1°C.

Anal. Found: Cl, 56.25. Calcd. for $C_3H_4NSiCl_3$: Cl, 56.43%.

β-Cyanoethylpolysiloxane (VI).—β-cyanoethyltrichlorosilane (I) was poured into a large quantity of water to give a homogeneous solution. When the solution was neutralized with 6N aqueous ammonia, β-cyanoethylpolysiloxane (VI) precipitated as a white amorphous powder. After filtration and washing with water the precipitate was dried at 100°C over phosphorous pentoxide.

Anal. Found: Si, 26.38; N, 13.22. Calcd. for $C_3H_4NO_{1.5}Si$: Si, 26.42; N, 13.21%.

β-Cyanoethyltriethoxysilane (V).—In a 200 ml. three-necked flask equipped with a mercury-sealed stirrer, a dropping funnel, and a calcium chloride tube, a mixture of 9.8 g. of absolute ethanol and 9.8 g. of dry benzene was placed. A solution of 12 g. of β-cyanoethyltrichlorosilane in an equal quantity of dry benzene was added dropwise through the dropping funnel under vigorous stirring. The temperature of the reaction mixture was kept below 0°C by the external cooling with ice-salt bath. After the addition was completed stirring was continued for one and a half hours. Then a slight excess of dry ammonia was introduced into the reaction mixture under cooling. An excess amount of ammonia was driven off by dry air, and the resulting ammonium chloride was filtered off. Vacuum distillation of the filtrate gave 9.0 g. of the crude β-cyanoethyltriethoxysilane (V), b.p. 121–130°C (20 mmHg) (65%). Redistillation yielded the pure compound, b.p. 111.5–112.5° (10 mmHg), d_4^{25}, 0.9699; n_D^{25}, 1.4103.

Anal. Found: Si, 12.58; N, 5.8; MR_D, 55.55. Calcd. for $C_9H_{19}NO_3Si$: Si, 12.92; N, 6.4%; MR_D, 55.26.

β-Cyanoethyltrimethylsilane (II).—Eleven gram (0.058 Mol.) of β-cyanoethyltrichlorosilane (I) was methylated in the usual manner with the ether solution of methylmagnesiumbromide prepared from 6.2 g. (0.25 Atom) of magnesium and the reaction gave 5.8 g. of β-cyanoethyltrimethylsilane (II)., b.p. 98.5–101.8° (75 mmHg) (78%).

In order to remove a possible impurity of β-trimethylsilylmethylketone, the crude product was shaken with a saturated solution of sodium bisulfite. After washing with the water and drying over calcium chloride, it was subjected again to vacuum distillation, b.p. 98°–97.5° (65–64 mmHg), d_4^{25}, 0.8226; n_D^{25}, 1.4202.

The infra red spectrum of the compound (II) was identical with that of the standard sample prepared according to the method described by Sommer⁷⁾.

Anal. Found: Si, 21.67; N, 10.7; Mol. Wt. (in benzene), 127; MR_D, 39.09. Calcd. for $C_6H_{13}NSi$; Si, 21.92; N, 11.0%; Mol. Wt., 127; MR_D, 39.07.

β-Trimethylsilylpropionic Acid (III).—A mixture of 3.0 g. of β-cyanoethyltrimethylsilane, 10 ml. of 50% aqueous sodium hydroxide and 10 ml. of alcohol was refluxed for three and half hours until the evolution of ammonia ceased. The reaction mixture was concentrated by an aspirator on a water bath to a slushy state. It was dissolved in a small portion of water and extracted with ether in order to remove the unreacted nitrile. The water layer was acidified with concentrated hydrochloric acid and the separating oil was extracted again with ether. The ether solution was dried with sodium sulfate, filtered, and distilled under vacuum to yield 1.0 g. of β-trimethylsilylpropionic acid. (III), b.p. 114–6° (20 mmHg) (49%). n_D^{25}, 1.4257 (in literature7); n_D^{20}, 1.4282).

Anal. Found: Si, 18.85; Mol. Wt., (from titration), 142. Calcd. for $C_6H_{14}O_2Si$: Si, 19.19%; Mol. Wt., 145.

β-Trimethylsilylpropionic Amide (IV) and Anilide (VII).—When 0.9 g. of thionylchloride was added to 0.2 g. of β-trimethylsilylpropionic acid (III), a vigorous reaction took place instantly. After refluxing for a half hour, an excess of thionylchloride was evaporated in vacuo. To the ice-cold residual oil 20 ml. of ether saturted with dry ammonia was poured in. After standing for about a half hour, an excess ammonia was driven off with a stream of dry air. The precipitating ammonium chloride was separated by filtration and the filtrate was evaporated to yield 0.2 g. of β-trimethylsilylpropionic amide (IV), m.p. 95–6°C (recrystallised from petroleum benzine).

Anal. Found: Si, 19.23. Calcd. for $C_6H_{15}NOSi$: Si, 19.34%.

The mixed melting point test of the compound (IV) with the standard sample prepared according to Sommer7) showed no depression.

β-Trimethylsilylpropionic anilide (VII) was prepared by heating in a sealed tube the mixture of 0.1 g. of the acid (III) and 0.2 g. of aniline at 180°C for eight hours. The reaction mixture was digested with 4 ml. of 2N hydrochloric acid and the insoluble oil crystallised in large needles after standing for a long time, m.p. 87–8°C. (recrystallised from alcohol)

Anal. Found: Si, 12.99. Calcd. for $C_{12}H_{19}NOSi$: Si, 12.68%.

Summary

1. Cyanoethylation of trichlorosilane was found to be catalysed by organic bases, benzoylperoxide, or platinized asbestos at about 160°C. The catalytic activities of organic bases increased in the order, dimethylaniline $\ll$ quinoline $<$ pyridine, piperidine $<$ triethylamine. Pyridine hydrochloride and benzyltriethylammonium chloride has also catatytic effects.

2. The orientation of the addition reaction was found to be almost exclusively of the β-position.

3. An ionic mechanism was suggested for the organic base-catalysed addition reaction.

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