Cyanoethylation of Trichlorosilane. II. α-Addition[1]

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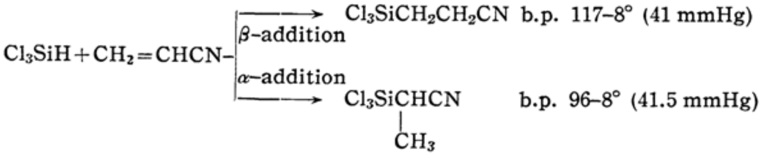
In the previous paper[2] the authors reported the cyanoethylation of trichlorosilane in the presence of organic bases, benzoyl peroxide, or of platinized asbestos. These addition reactions which were carried out in sealed glass tubes gave exclusively the β-adduct, β-cyanoethyltrichlorosilane.

In an attempt to bring about this reaction in a large scale with an autoclave made from 18–8 stainless steel in the presence of pyridine or platinized asbestos, there was obtained, curiously enough, an α-addition product instead of the expected β-adduct:



$$Cl_3SiH + CH_2{=}CHCN - \left| \begin{array}{ll} \xrightarrow{\phantom{\alpha\text{-addition}}} Cl_3SiCH_2CH_2CN & \text{b.p. } 117\text{–}8^\circ\ (41\ \text{mmHg}) \\ \beta\text{–addition} & \\ \alpha\text{–addition} & \\ \xrightarrow{\phantom{\alpha\text{-addition}}} \underset{\displaystyle CH_3}{\underset{|}{Cl_3SiCHCN}} & \text{b.p. } 96\text{–}8^\circ\ (41.5\ \text{mmHg}) \end{array} \right.$$

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

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

Since this is a new example where trichlorosilane reacted with olefin according to the Markownikow's rule, we performed a more detailed research concerning this unusual reaction. In this paper, we describe the details of the characteristic features of the above reaction, the structural proof of the product, and some discussions on the reaction mechanisms.

Cyanoethylation of Trichlorosilane in an Autoclave

The typical experiment of the cyanoethylation which was carried out in an autoclave is shown in Fig. 1. The reaction started at a temperature ranging from 150 to 170°C. As the reaction was exothermic, the pressure rose rapidly with the simultaneous elevation of the temperature, and dropped also very quickly, and at last settled on a constant value in the course of about ten minutes.

In the absence of the catalyst, the initiation of a reaction could be observed at a somewhat higher temperature than that of the reaction using catalyst, but no distillable product was obtained.

Another feature was a yield of a considerable amount of nonvolatile distillation residue. It was also noticeable that any fraction which distilled in the range of boiling point of the β-isomer was not obtained at all.

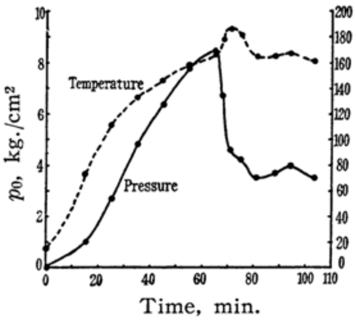
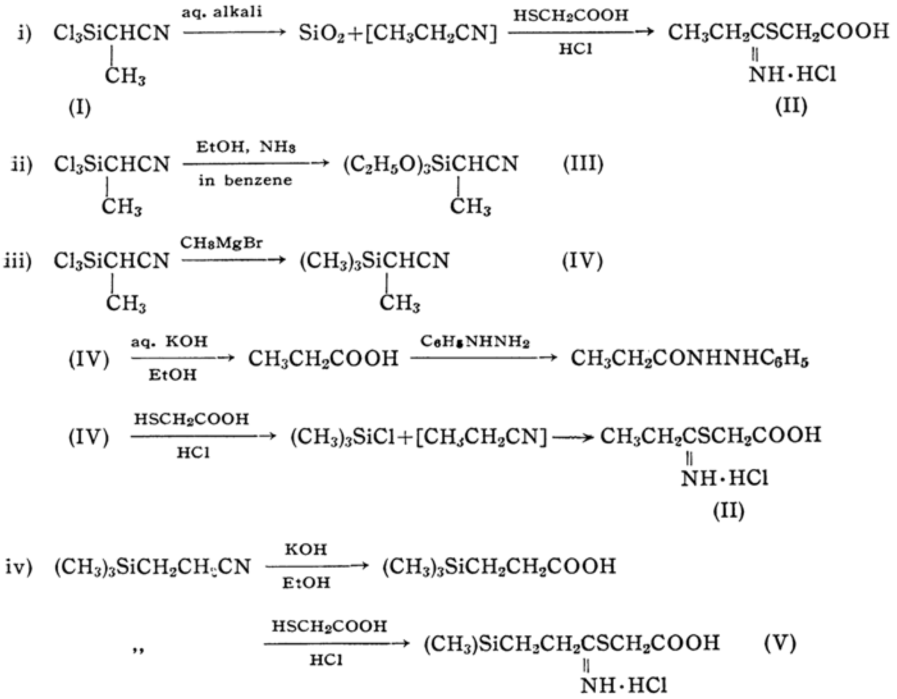


Fig. 1. An example of the cyanoethylation of trichlorosilane in an autoclave. (Trichlorosilane, 32.5 g., acrylonitrile, 19.1 g., and pyridine, 0.2 g.)

The Structural Proof of the Product obtained in an Autoclave

Several derivatives of the addition product was prepared, and their chemical and physical properties were compared with those of the derivatives of the known β-cyanoethyltrichlorosilane. The reactions involved are as follows:



$$\text{i)}\ \mathrm{Cl_3Si\underset{CH_3}{C}HCN}\ \xrightarrow{\text{aq. alkali}}\ \mathrm{SiO_2+[CH_3CH_2CN]}\ \xrightarrow[\mathrm{HCl}]{\mathrm{HSCH_2COOH}}\ \mathrm{CH_3CH_2\underset{NH\cdot HCl}{C}SCH_2COOH}$$

(I) (II)

$$\text{ii)}\ \mathrm{Cl_3Si\underset{CH_3}{C}HCN}\ \xrightarrow[\text{in benzene}]{\mathrm{EtOH,\ NH_3}}\ \mathrm{(C_2H_5O)_3Si\underset{CH_3}{C}HCN}\qquad \text{(III)}$$

$$\text{iii)}\ \mathrm{Cl_3Si\underset{CH_3}{C}HCN}\ \xrightarrow{\mathrm{CH_3MgBr}}\ \mathrm{(CH_3)_3Si\underset{CH_3}{C}HCN}\qquad \text{(IV)}$$

$$\text{(IV)}\ \xrightarrow[\mathrm{EtOH}]{\text{aq. KOH}}\ \mathrm{CH_3CH_2COOH}\ \xrightarrow{\mathrm{C_6H_5NHNH_2}}\ \mathrm{CH_3CH_2CONHNHC_6H_5}$$

$$\text{(IV)}\ \xrightarrow[\mathrm{HCl}]{\mathrm{HSCH_2COOH}}\ \mathrm{(CH_3)_3SiCl+[CH_3CH_2CN]}\longrightarrow \mathrm{CH_3CH_2\underset{NH\cdot HCl}{C}SCH_2COOH}$$

(II)

$$\text{iv)}\ \mathrm{(CH_3)_3SiCH_2CH_2CN}\ \xrightarrow[\mathrm{EtOH}]{\mathrm{KOH}}\ \mathrm{(CH_3)_3SiCH_2CH_2COOH}$$

$$\text{,,}\qquad \xrightarrow[\mathrm{HCl}]{\mathrm{HSCH_2COOH}}\ \mathrm{(CH_3)SiCH_2CH_2\underset{NH\cdot HCl}{C}SCH_2COOH}\qquad \text{(V)}$$

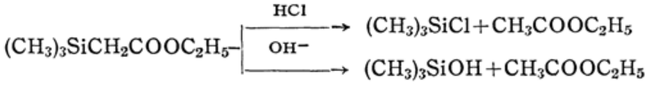
i) When the product (I) was hydrolyzed in a large excess of water and neutralized with an aqueous solution of ammonia, there was precipitated an amorphous silica as the result of the cleavage of the silicon-carbon bond. The organic fragment, propionitrile, was separated out and identified as the thioglycolic acid adduct (II). In contrast with this, the β-isomer did not result in the cleavage of the silicon-carbon bond but gave the corresponding β-cyanoethylpolysiloxane.

ii) The alcoholysis of the compound (I) was carried out according to an usual manner which contains the treatment with absolute alcohol in benzene and with dry ammonia. The low yield (37%) of the alcoholysis may be partly due to the cleavage of the silicon-carbon bond during the reaction. The physical constants of the compound (III) were also quite different from that of the β-isomer.

iii) The hydrolysis of α-cyanoethyltrimethylsilane (IV) by an aqueous solution of alkali resulted in the cleavage of the silicon-carbon bond. The fission product, propionic acid, was identified as its phenylhydrazide. The reaction of the compound (IV) with thioglycolic acid in the presence of dry hydrogen chloride also gave the fission product (II).

iv) On the other hand, the hydrolysis and the reaction with thioglycolic acid of the β-cyanoethyltrimethylsilane yielded β-trimethylsilylpropionic acid and silicon-containing thioglycolic acid adduct (V), respectively. This is the marked difference from the case of the α-isomer.

The fission of the silicon-carbon bonds shown in these reactions is reasonably explainable by assigning α-cyanoethyltrichlorosilane to the structure of this addition product. Sommer and Marans[3] also reported the fission of ethyltrimethylsilylacetate by acid or alkali:



$$(CH_3)_3SiCH_2COOC_2H_5 \begin{cases} \xrightarrow{HCl} (CH_3)_3SiCl + CH_3COOC_2H_5 \\ \xrightarrow{OH^-} (CH_3)_3SiOH + CH_3COOC_2H_5 \end{cases}$$

The ease of fission of α-cyanoethylsilyl derivatives may be interpreted by the similar situation of its electronic configuration to that of ethyltrimethylsilylacetate, that is, in both cases an electronically negative atom

TABIE I

α-CYANOETHYLATION OF TRICHLOROSILANE IN SEALED TUBES AT 160°C[a]

No.	Catalysts, g.		Reaction time, hr.	Yield of α-adduct, %[b]	Appearance after heating
1	$AlCl_3$,	0.1	5.0	0	light brown
2	$FeCl_3$,	0.1	5.0	0	light yellow
3	stainless foil, pyridine	2.0 0.1	5.0	0	characteristic deep brownish black
4	Fe powder pyridine,	1.5 0.1	5.0	trace	light brown
5	Ni powder pyridine,	2.0 0.1	5.0	7	characteristic deep brownish black
6	Cr powder pyridine,	2.0 0.1	5.0	12	brown, mainly β-addition[c]
7[d]	stainless foil, pyridine,	2.0 0.1	3.0	0	light yellow
8[e]	stainless foil, pyridine,	2.0 0.1	5.0	31	characteristic deep brownish black
9	$NiCl_2$,	0.2	5.0	trace	colorless
10	$NiCl_2 \cdot C_5H_5N \cdot HCl$,	0.2	5.0	22	characteristic deep brownish black[f]
11	$NiCl_2 \cdot C_5H_5N$,	0.1	2.0	17	,, [g]
12	$NiCl_2 \cdot 4C_5H_5N$,	0.1	5.0	7	,, [h]

a) About 20 g. of trichlorosilane and 1.1 times equivalents of acrylonitrile were used.

b) Considering from their boiling points, the contamination by β-adduct if any is probably very small. The yields are based on trichlorosilane.

c) b.p. 97–101° (30 mmHg).

d) Benzene (40 ml.) was used as solvent.

e) Acetonitrile (40 ml.) was used as solvent.

f) Distillation residue, 5 g.

g) Residue, 7 g.

h) Reaction temp., 160–70°C. Residue, 8 g. Hydrolyzable Cl, 32.1 %.

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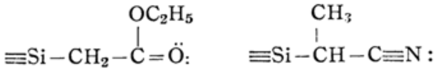
[3] L.H. Sommer and N.S. Marans, *J. Am. Chem. Soc.*, 72, 1935 (1950).

(oxygen or nitrogen) having the unshared electrons is situated at the β-position to silicon by an unsaturated bond.



$$\equiv Si-CH_2-\overset{\overset{OC_2H_5}{|}}{C}=\ddot{O}: \qquad \equiv Si-\overset{\overset{CH_3}{|}}{CH}-C\equiv N:$$

Cyanoethylation of Trichlorosilane in sealed Tubes

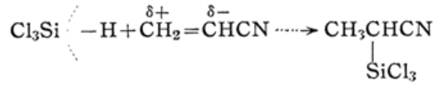
In order to find out what catalysed the α-cyanoethylation in an autoclave, we carried out the reaction in a sealed glass tube in the presence of one of several possible catalysts taking it into consideration that the wall of the autoclave might have some catalytic influences. Experimental results are given in Table I. The Friedel-Crafts type catalyst, anhydrous ferric chloride and aluminum chloride, showed no effect. Only nickel metal among the constituent metals of 18–8 stainless steel of the autoclave seemed te be responsible for a catalytic effect for the α-addition in the presence of pyridine, but in this case the yield of the product was very low and the distillation residue amounted to a considerable quantity. Anhydrous nickel (II) chloride also showed only a poor catalytic activity. Mono- and tetrapyridine nickel (II) chloride, $NiCl_2 \cdot C_5H_5N$, $NiCl_2 \cdot 4C_5H_5N$, and nickel chloride pyridine hydrochloride complex compound, $NiCl_2 \cdot C_5H_5N \cdot HCl$, were found to show the marked catalytic effect for the α-addition.

In all the α-addition reactions, as we mentioned above, the comparatively large amount of distillation residue was observed. This may have a close correlation with the fact that α-cyanoethyltrichlorosilane was found to be easily decomposed by heating in the presence of tetrapyridine nickel chloride. When α-cyanoethyltrichlorosilane was heated along with a catalytic amount of tetrapyridine nickel chloride in a sealed tube at 160°C., only 43% of the starting chlorosilane was recovered from the deep brownish black reaction mixture by distillation in vauco. The distillation residue was about 19% of the starting material, and therefore the total weight loss during the procedure amounted to about 38% of the starting material. Thus, the large weight loss and the considerable amount of the residue suggest us the decomposition of the α-adduct. Therefore, it seems to be probable that the low yield of the α-cyanoethyltrichlorosilane is partly due to the secondary degradation reaction, and the yield of the primary addition product may be much higher than the observed value.

Reaction Mechanism

In view of the above results it appears to be that either nickel chloride pyridine hydrochloride complex, mono- or tetrapyridine nickel chloride is one of the probable catalyst for the reaction in an autoclave. The mechanism of the catalytic action of these compounds still remains to be ambiguous.

As both the peroxide- and base-catalyzed additions are known to lead to the β-addition, one of the possible interpretations of the α-addition is the intermediate ionization of a silicon-hydrogen bond to a siliconium cation and a hydride anion.



$$Cl_3Si-H+\overset{\delta+}{CH_2}=\overset{\delta-}{C}HCN \longrightarrow CH_3\underset{\underset{SiCl_3}{|}}{C}HCN$$

These ionic mechanism is supported in part by the effect of solvents, which is shown in experiment No. 7 and 8 in Table I.

Experimental

Catalysts.—The preparation of the platinized asbestos was described in the preceding paper[2].

Mono- and tetra-pyridine nickel chlorides and nickel chloride pyridine hydrochloride complex were prepared according to the method of Reizenstein[4].

Iron powder was the commercial product, and nickel and chrom powder were prepared from the electrolyzed metals.

The Reaction of Trichlorosilane and Acrylonitrile.—A mixture of trichlorosilane, acrylonitrile, and a catalyst was charged into a 18–8 stainless steel autoclave of 100 ml. capacity. The air in the autoclave was replaced by nitrogen, and then the gradual heating was applied. (Fig. 1). A sudden exothermic reaction started at a temperature between 150 and 170°C in the presence of either pyridine or platinized asbestos. The heating was stopped in about thirty minutes after the rapid decrease of the pressure had ceased. The color of the reaction mixture was always a deep brownish black which was characteristic to the α-cyanoethylation of trichlorosilane. The reaction mixture was then washed out by benzene, and after the removal of benzene by distillation at an atmospheric pressure, the remaining product was distilled in vacuo. The yield of α-cyanoethyltrichlorosilane was 21–39% (to trichlorosilane used) and approximately equal volume of nonvolatile distillation residue was produced.

Without catalyst, the reaction started at about 190°C, the yield of addition product was null, and a resin-like distillation residue of about 30 weight % was obtained.

The purified α-cyanoethyltrichlorosilane boils at 96–8° (41.5 mmHg).

Anal. Found: Hydrolyzable Cl, 56.3. Calcd. for $C_3H_4NSiCl_3$: Cl, 56.5%.

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

The procedure for the reaction of trichlorosilane and acrylonitrile in sealed glass tubes was similar to that of the preceding paper.

Degradation of α-Cyanoethyltrichlorosilane.—A mixture of 27 g. of α-cyanoethyltrichlorosilane (b.p. 99–102° (50 mmHg)) and 0.1 g. of tetrapyridine nickelchloride sealed in glass reaction tube was heated at 160°C. for six hours. The reaction mixture was colored to a deep brownish-black. Distillation gave 11.6 g. (43%) of the recovered chlorosilane (b.p. 101–5° (51 mmHg)), and 5.0 g. of a resin-like distillation residue (hydrolyzable Cl, 32.3%).

Hydrolysis of α-Cyanoethyltrichlorosilane (I).—When a small portion of α-cyanoethyltrichlorosilane was poured onto a large amount of water, it dissolved clearly with the evolution of heat. By neutralizing the acidic solution with an excess of 6 N aqueous solution of ammonia, the gellation took place. The gelled silica was filtered, washed with water, and dried in vacuo at 100°C.

Anal. A qualitative test for N was negative. Found: Si, 44.15. Calcd. for SiO_2: Si, 46.65%.

When 2.5 g. of trichlorosilane (I) was added dropwise to 10 ml. of 6 N aqueous sodium hydroxide, the once precipitated silica dissolved clearly into the solution. The alkaline solution was extracted twice with 20 ml. of ether. The ether layer was dried with calcium chloride, filtered, 1.0 g. of thioglycolic acid was added, and it was saturated with dry hydrogen chloride under the ice-cooling. After standing over night in ice-water, the thioglycolic acid adduct of propionitrile (II) crystallised in fine needles. The crystal was filtered, washed with ether, and dried in desiccater over phosphorous pentoxide, the yield was 0.5 g. (20%), m.p. 124°.

Anal. Found: Cl, 19.38. Calc. for $C_5H_{10}NO_2SCl$: Cl, 19.33%.

α-Cyanoethyltriethoxysilane (III).—The reaction procedure was analogous to that of β-cyanoethyltriethoxysilane in the preceding paper. From 16.6 g. (0.088 mol.) of α-cyanoethyltrichlorosilane and 13.0 g. (0.28 mol.) of absolute alcohol, 1.4 g. of ethylorthosilicate (b.p. 76–8° (26 mmHg)) and 7.1 g. of the crude α-cyanoethyltriethoxysilane (III) (b.p. 115–9° (26 mmHg)) was obtained. (37%). The compound (III) was purified by redistillation, b.p. 119–120° (26.5 mmHg) d_4^{25}, 0.9630; n_D^{25}, 1.4070.

Anal. Found: N, 6.45; Si, 12.73. MR$_D$, 55.46. Calcd. for $C_9H_{19}NO_3Si$: N, 6.45; Si, 12.91%. MR$_D$, 55.26.

α-Cyanoethyltrimethylsilane (IV).—When 19g. (0.10 mol.) of α-cyanoethyltrichlorosilane (I) was methylated in a usual manner with the ether solution of methylmagnesium bromide prepared from 10.7 g (0.44 Atom) of magnesium, 6.4 g. of crude α-cyanoethyltrimethylsilane (IV) was obtained, b.p. 95–9° (66 mmHg) (50%). In order to remove the possible impurity of α-trimethylsilylethylmethylketone, the crude product was shaken with the saturated solution of sodium bisulfite, washed with water, dried with sodium sulfate, and distilled again in vacuo, yielding 4.1 g. of pure α-cyanoethyltrimethylsilane (IV), b.p. 91.5–92.5° (58 mmHg); d_4^{25}, 0.8254; n_D^{25}, 1.4232.

Anal. Found: N, 10.50; Si, 21.09. MR$_D$, 39.19. Calcd. for $C_6H_{13}NSi$: N, 11.02; Si, 22.05%. MR$_D$, 39.09.

Reactions of β- and α-Cyanoethyltrimethylsilane (IV) with Thioglycolic Acid.—When a mixture of 0.2 g. of α-cyanoethyltrimethylsilane (IV), 0.3 g. of thioglycolic acid, and 1 ml. of dry ether, was saturated with dry hydrogenchloride under the cooling with ice water, a needlelike crystal began to appear within a half hour. After standing for one hour, the crystal was filtered and washed with ether, dried in desiccater. The yield of the thioglycolic acid adduct of propionitrile was 0.1 g., m.p. 119–120°.

Anal. Found: Cl, 19.23; Si, 0.00. Calcd. for $C_5H_{10}NO_2SCl$: Cl, 19.33; Si, 0.00%.

A mixture of 0.2 g. of β-cyanoethyltrimethylsilane, 0.3 g. of thioglycolic acid, and 1 ml. of ether was similarly treated with dry hydrogen chloride. The crystallization was completed in half an hour and 0.2 g. of the needle-like adduct was obtained, m.p. 143°.

Anal. Found: Cl, 13.98; Si, 11.03. Calcd. for $C_8H_{18}NO_2SClSi$: Cl, 13.87; Si, 10.95.

Alkaline Hydrolysis of α-Cyanoethyltrimethylsilane (IV).—When a solution of 4.0 g. of potassium hydroxide in 4 ml. of water was added to 3.1 g. of α-cyanoethyltrimethylsilane, a vigorous reaction took place. Then 10 ml. of alcohol was added to the solution and it was refluxed for five hours until the evolution of ammonia ceased. To the reaction mass 40 ml. of water was added after cooling, and extracted with 10 ml. of ether to remove the unreacted nitrile. The aqueous layer was acidified with hydrochloric acid and extracted again with ether. The ether layer, which contained the produced carboxylic acid, was dried with sodium sulfate, filtered, and distilled. The carboxylic acid thus obtained was identified as its phenylhydrazide as follows; the distillate (b.p. 65–145°, 1.3 g.) and 2.0 g. of phenylhydrazine were refluxed for a half hour on a free flame. After cooling, the crystalline mass was filtered and washed thoroughly with benzene to yield 1.0 g. of propionic phenylhydrazide as a scaly crystal, m.p. 154–5°. After recrystallization from benzene, it melted at 155–6°C (157° in literature).

Summary

Contrary to the case of β-cyanoethylation, α-cyanoethylation of trichlorosilane was found to take place in an autoclave in the presence of either pyridine or platinized asbestos.

In the reactions in sealed glass tubes, on the other hand, stainless steel and pyridine, mono- and tetrapyridine nickel chloride, and nickel chloride pyridine hydrochloride complex were effective for the α-addition. An ionic mechanism was suggested for the α-cyanoethylation.

The structural proof of α-cyanoethyltrichlorosilane was given from the comparison

of the physical constants and chemical behaviour of it to those of the β-isomer. α-Cyanoethyl-triethoxysilane and -trimethylsilane were prepared from α-cyanoethyltrichlorosilane and characterised.

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