silane (204 g., 1.8 moles), and 0.1 ml. of 0.2 *M* chloroplatinic acid. The vessel was closed and heated to 100° for 3 hr. The products were found to be methyltrichlorosilane (135.5 g., 0.91 mole), butylmethyldichlorosilane, 53 g., 0.31 mole, b.p. 57° at 29 mm., n^{25}_D 1.4340, and 3-chlorobutylmethyldichlorosilane, 124 g., 0.60 mole, 33% yield, b.p. 96° at 30 mm., n^{25}_D 1.4559, d^{25}_4 1.1572, R_D 0.2339.

Anal. Calcd. for $Cl_2CH_3SiC_4H_8Cl$: Si, 13.7; neut. equiv., 102.8. Found: Si, 13.8; neut. equiv., 104.1, 103.3.

Part of the 3-chlorobutylmethyldichlorosilane obtained in the first experiment above was converted to 3-chlorobutyltrimethylsilane in 59% yield with excess methylmagnesium bromide. The sample had: b.p. 69° at 28 mm., n^{25}_D 1.4289, d^{25}_4 0.8654, R_D 0.2987, calcd. R_D 0.2972.

Part of the product from the second experiment was treated with hot saturated potassium hydroxide to form methylcyclopropane identified by infrared absorption spectrum.

These data all indicate that both 3-chlorobutene-1 and 4-chlorobutene-2 form the same adduct, *i.e.*, 3-chlorobutylmethyldichlorosilane. The chlorobutyltrimethylsilane prepared from the adducts of either reagent also had identical infrared spectra and identical retention times in vapor chromatograms.

3,4-Dichlorobutene-1 (105 g., 0.84 mole) and 0.08 ml. of 0.1 *M* chloroplatinic acid solution in isopropyl alcohol were heated to 120° and methyldichlorosilane (106 g., 0.92 mole) was added dropwise.

The liquid products were distilled to give: methyltrichlorosilane (67 g., 0.45 mole); 3,4-dichlorobutene-1 (28 g., 0.22 mole); butylmethyldichlorosilane (5 g., 0.03 mole); 1,4-dichlorobutene-2 (11.5 g., 0.09 mole); 3-chlorobutylmethyldichlorosilane (6.5 g., 0.03 mole); and 3,4-dichlorobutylmethyldichlorosilane (80 g., 0.33 mole, 59% yield), b.p. 131° at 30 mm., n^{25}_D 1.4805, d^{25}_4 1.2902, R_D 0.2204, calcd. R_D 0.2204.

Anal. Calcd. for $Cl_2CH_3SiC_4H_7Cl_2$: Si, 11.7; neut. equiv., 120.0. Found: Si, 12.1; neut. equiv., 121.5.

A portion of this product was methylated with methylmagnesium bromide to give 3,4-dichlorobutyltrimethylsilane in 63% yield, b.p. 101° at 31 mm., n^{25}_D 1.4530, d^{25}_4 1.026, R_D 0.2696, calcd. R_D 0.2701.

Anal. Calcd. for $C_7H_{16}Cl_2Si$: Si, 14.1; Cl, 35.6. Found: Si, 14.1; Cl, 35.4, 35.9.

The infrared spectra of these products is consistent with the assigned 3,4-dichlorobutyl structure which seems like the only likely one consistent with the properties and origin of the compounds.

1,4-Dichlorobutene-2 (876 g., 7 moles), methyldichlorosilane (1310 cc., 12.7 moles) containing 0.35 ml. of 0.2 *M* chloroplatinic acid were mixed in a stainless steel pressure vessel. The olefin was pumped into the chlorosilane maintained near 100° for several hours. Distillation of the products resulted in the following analysis: methyldichlorosilane (149 g., 10.2% of that charged); methyltrichlorosilane (883 g., 5.9 moles); 3,4-dichlorobutene-2 (68.7 g., 0.55 mole); butylmethyldichlorosilane (66.7 g., 0.39 mole); 1,4-dichlorobutene-2 (145 g., 1.16 moles); 3-chlorobutylmethyldichlorosilane (123 g., 0.60 mole, 8.6% yield); and 4-chlorobutylmethyldichlorosilane (697 g., 47.2 yield); b.p. 109° at 30 mm., n^{25}_D 1.4608, d^{25}_4 1.171, R_D 0.2343, calcd. R_D 0.2339.

Anal. Calcd. for $Cl_2CH_3SiC_4H_8Cl$: Si, 13.7; neut. equiv., 102.8. Found: Si, 14.3; neut. equiv., 102.7, 104.0.

The next fraction was identified as 3,4-dichlorobutylmethyldichlorosilane (96 g., 0.4 mole, 5.7% yield), b.p. 130° at 30 mm., n^{25}_D 1.4799, d^{25}_4 1.1287, R_D 0.2202, calcd. R_D 0.2204.

Anal. Calcd. for $Cl_2CH_3C_4H_7Cl_2$: Si, 11.7; neut. equiv., 120.0. Found: Si, 11.9, 120.0; neut. equiv., 121.

A portion of this compound was methylated with excess methylmagnesium bromide in ether to form 4-chlorobutyltrimethylsilane in 76% yield, b.p. 79° at 31 mm., n^{25}_D 1.4314, d^{25}_4 0.8715, R_D 0.2972, calcd. R_D 0.2972.

Anal. Calcd. for $C_7H_{17}ClSi$: Si, 17.1; Cl, 21.5. Found: Si, 17.2; Cl, 22.1.

These compounds have been assigned the structure of 4-chlorobutyl derivatives in view of their origin because they clearly are not 3-chlorobutylsilanes whose structures are thought to be quite certain. 2-Chloroalkylsilanes are so easily hydrolyzed as to be titratable.[12] 1-Chlorobutylsilanes cannot rigorously be said to be impossible, but they do seem extremely unlikely. The infrared spectra of the compounds are consistent with those expected of 4-chlorobutylsilanes.

A series of experiments were carried out in sealed Pyrex tubes with analyses accomplished by vapor phase chromatography. Data gathered in this way are compiled in Table I. These experiments all used 10^{-6} mole of chloroplatinic acid per mole of olefin and were heated to 135° overnight. The analyses in Table I are considered as approximations only. They are shown as area per cent as taken from the chromatograms, but area per cent is not synonymous with molar per cent in these mixtures.

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[12] L. H. Sommer and F. C. Whitmore, *J. Am. Chem Soc.*, **68**, 485 (1946).

Base-Catalyzed Additions of Trichlorosilane to Hydrocarbon Olefins

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Received November 16, 1961

Tertiary amines and tertiary phosphines catalyze the addition of trichlorosilane to hydrocarbon olefins in the presence of a nitrile solvent. Without solvent, or in less polar solvents such as benzene, little or no addition occurs. Trichlorosilane adds to terminal olefins using base–nitrile catalysts to give the same adducts obtained with platinum or peroxide. With nonterminal olefins such as pentene-2, branched chain alkyltrichlorosilanes similar to peroxide additions are obtained, in contrast to platinum-catalyzed additions which give straight chained adducts. Characterization of the chlorosilanes prepared by addition of trichlorosilane to hexyne-1 and phenylacetylene show that with the base–nitrile solvent system, trichlorosilane adds predominantly *cis* to give the corresponding *trans* adducts.

Preparation of organosilicon compounds by the peroxide[1b] or platinum[2,3] catalyzed addition of silicon-hydrogen bonds to unsaturated hydrocarbons is

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[1b] C. A. Burkhard and R. H. Krieble, *J. Am. Chem. Soc.*, **69**, 2687 (1947); L. H. Sommer, F. W. Pietrusza, and F. A. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947); J. L. Speier, R. Zimmerman, and J. A. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956).

[2] J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

TABLE I

ADDITION OF TRICHLOROSILANE TO HYDROCARBON OLEFINS WITH BASE CATALYST IN NITRILE SOLVENTS[a]

Olefin	Solvent	Base	Product (Mole % Yield)[h]	B.P. (mm.)
Styrene	Acetonitrile	n-$(C_4H_9)_3N$	β-Phenylethyltrichlorosilane (42)[e]	110 (8)
Styrene	Benzene	n-$(C_4H_9)_3N$	Phenylethyltrichlorosilane (2.5)	...
Styrene	Acetonitrile	Pyridine	β-Phenylethyltrichlorosilane (40.8)[e]	85 (2.5)
Octene-1	Acetonitrile	n-$(C_4H_9)_3N$	n-Octyltrichlorosilane (41.5)	107 (24)
Octene-1	Adiponitrile[b]	n-$(C_4H_9)_3N$	n-Octyltrichlorosilane (43.3)	103 (20)
Pentene-1	Acetonitrile[c]	$(C_8H_5)_3P$	n-Pentyltrichlorosilane (42.3)	79 (40)
Pentene-2	Acetonitrile[c]	$(C_6H_5)_3P$	2- and 3-Pentyltrichlorosilane (24.4)	81 (42)
Pentene-2	Acetonitrile	n-$(C_4H_9)_3N$	2- and 3-Pentyltrichlorosilane (14.7)	26–27 (1.0)
Acetylene	Adiponitrile[d]	$(C_6H_5)_3P$	Bistrichlorosilylethane (49)	199 (760)
Hexyne-1	Acetonitrile	n-$(C_4H_9)_3N$	Hexenyltrichlorosilane (13.4)[f]	54 (3.5)
Phenylacetylene	Acetonitrile	$(C_4H_9)_3N$	β-Phenylethenyltrichlorosilane (17.7)[g]	74 (1.0)

[a] Reactions carried out using 0.5 mole of trichlorosilane and olefin in a stainless steel pressure vessel at 150–160° for 2 hr.; 0.5 mole of solvent used except where indicated. Catalyst concentration 2 wt. % of total reaction mixture. [b] 0.25 mole of solvent. [c] Run at 200°. [d] Carried out in steam-jacketed 800-cc. pressure vessel. [e] Infrared spectra show α-phenylethyltrichlorosilane present, 1 mole % or less. [f] Shown on conversion to trimethylsilyl derivative to be a mixture of the *trans* isomer and a silane containing a methylene group. [g] Shown on conversion to trimethylsilyl derivative to be the *trans* isomer. [h] Yield based on olefin used. In all cases except with the acetylenic compounds unchanged olefin was recovered.

widely used and has been extensively covered in the chemical and patent literature.

In contrast, only two examples of organic base-catalyzed silanic hydrogen additions have been reported. Trichlorosilane adds to acrylonitrile using tertiary amine,[4,5] tertiary phosphine,[4] or substituted amide[6] catalysts to give β-cyanoethyltrichlorosilane and to vinylpyridine, without additional catalyst, to give β-pyridylethyltrichlorosilane.[7] Attempted use of organic bases as catalysts for the addition of trichlorosilane to other olefins has been unsuccessful. Pyridine did not catalyze the addition of trichlorosilane to styrene, octene-1, or vinyltrichlorosilane.[7]

This paper describes the results obtained in the base-catalyzed addition of trichlorosilane to hydrocarbon olefins in the presence of a nitrile solvent. Structural differences in the products resulting from base-, platinum-, or peroxide-catalyzed additions of trichlorosilane are also discussed.

The addition of trichlorosilane to a variety of hydrocarbon olefins using a tertiary amine or phosphine catalyst in the presence of a nitrile solvent is illustrated in Table I. The type of nitrile used had little effect on the yield of adduct. For example, essentially the same yield of n-octyltrichlorosilane was obtained in the addition of trichlorosilane to octene-1 using acetonitrile or adiponitrile as solvent. However, replacement of the nitrile with a solvent of lower polarity such as benzene, gave only a trace of adduct as shown using styrene and trichlorosilane. This is in accord with the results previously obtained using no solvent and pyridine catalyst.[7] In general, equimolar amounts of solvent and trichlorosilane were used. However, as little as one-tenth mole of solvent per mole of silane was found to be effective for the addition reaction.

The phosphine and amine catalysts appeared to be equally effective in promoting the addition reaction. However, a higher temperature was generally used with triphenylphosphine to obtain yields comparable to the amine-catalyzed reactions. Amines of different structure had little effect on the yield of adduct as illustrated in the runs with styrene. Tri-n-butylamine or pyridine in acetonitrile gave equivalent yields of β-phenylethyltrichlorosilane. Differences in effectiveness of the amines might be more noticeable at lower reaction temperatures. Only a small amount of the alpha adduct was formed as determined by the infrared spectrum of the product. In contrast, tetrapyridine nickel (II) chloride catalyst gave predominantly α-phenylethyltrichlorosilane.[7] A study of varying reaction conditions for these additions was not carried out. Undoubtedly, improved yields could be obtained if optimum times and temperatures were used as has been illustrated for the base-catalyzed addition of trichlorosilane to acrylonitrile.[4]

The terminal olefins, octene-1 and pentene-1, gave the same n-alkyltrichlorosilanes with the base catalyst obtained in the corresponding platinum- or peroxide-catalyzed additions. Pentene-2, however, gave a mixture of branched chain alkyltrichlorosilanes, tentatively identified as 2-pentyl- and 3-pentyltrichlorosilane in a ratio of 1:2. This is essentially the same result obtained using peroxide catalyst for the addition of trichlorosilane to pentene-2.[8] In contrast, n-pentyltrichlorosilane was the only product isolated when platinum was used for the same addition reaction.[2]

The stereospecificity of peroxide- and platinum-catalyzed silanic hydrogen additions has been established by determination of the geometric isomers

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(3) G. H. Wagner, U. S. Patent 2,637,738, May 5, 1953; G. H. Wagner and C. O. Strother, U. S. Patent 2,632,013, March 17, 1953; D. L. Bailey, Abstract of Papers, 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

(4) R. A. Pike, D. L. Bailey, J. E. McMahon, V. B. Jex, and W. T. Black, *J. Org. Chem.*, **24**, 1939 (1959).

(5) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, **29**, 322 (1956).

(6) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 427 (1959).

(7) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, **29**, 784 (1956).

(8) J. L. Speier and J. A. Webster, *J. Org. Chem.*, **21**, 1044 (1956).

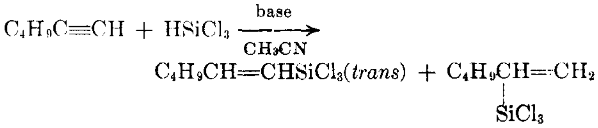
formed on addition of trichlorosilane to aryl- and alkylacetylenes.[9] The chlorosilane adducts were converted to the trimethylsilyl derivatives for ease of identification. In order to obtain samples and reference spectra of *cis* and *trans* adducts, the peroxide addition of trichlorosilane to hexyne-1 was carried out as described.[9] After reaction of the resulting hexenyltrichlorosilane with methylmagnesium chloride, a product containing two isomers was obtained. Separation by gas chromatography gave pure *cis*-1-trimethylsilyl-1-hexene (77 wt. %) characterized by a band in the infrared spectrum at 775 cm.$^{-1}$ with no bands in the 990-cm.$^{-1}$ region and *trans*-1-trimethylsilyl-1-hexene, (23 wt. %) with bands at 990 cm.$^{-1}$ and 1584 cm.$^{-1}$. These results are the same as those previously reported,[9] except that no actual measurement of the *cis-trans* ratio was made, and verify the stereospecificity of the peroxide addition as being predominantly *trans* addition to give a *cis* isomer.

The base-catalyzed addition of trichlorosilane to hexyne-1 and phenylacetylene in acetonitrile was carried out in an attempt to establish the stereospecific course of the reaction. In each case the yield of mono adduct was low, similar to the peroxide catalyzed additions, due to a second addition which gave saturated compounds.

$$RC{\equiv}CH + HSiCl_3 \xrightarrow[CH_3CN]{base} RCH{=}CHSiCl_3 + RC_2H_4(SiCl_3)_2$$

The resulting *n*-hexenyltrichlorosilane and phenylethenyltrichlorosilane reacted with methylmagnesium chloride to give the corresponding trimethylsilyl derivatives. Comparison of the infrared spectrum of $C_6H_5CH{=}CHSi(CH_3)_3$ with the spectra obtained in the peroxide addition using hexyne-1 showed the product of the addition reaction was *trans*-β-phenylethenyltrichlorosilane. The spectrum was characterized by a strong band at 990 cm.$^{-1}$ in conjunction with a band at 1584 cm.$^{-1}$. It seems likely therefore that the product was formed by a *cis* addition. The addition of trichlorosilane to hexyne-1 was not as specific. The spectrum of the hexenyltrimethylsilane showed characteristic bands due to the *trans* isomer and also a strong band at 921 cm.$^{-1}$ indicating the presence of a terminal methylene (=CH_2) group.[10] Complete separation of the two isomers by gas chromatography was not possible. The isomers, *trans* and terminal methylene were formed in equal amounts.

The formation of a *cis* isomer (by *trans* addition) followed by isomerization to the *trans* isomer is a possibility in these reactions. To determine if such a rearrangement did occur the mixture of *cis* and *trans* isomers of hexenyltrichlorosilane, prepared by peroxide addition of trichlorosilane to hexyne-1, was heated with pyridine–acetonitrile under the conditions used for the addition reactions. No change in the *cis-trans* ratio was found to take place.

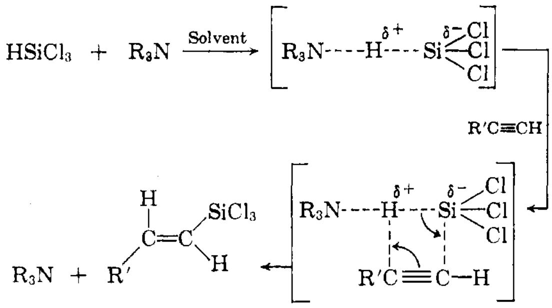


$$C_4H_9C{\equiv}CH + HSiCl_3 \xrightarrow[CH_3CN]{base} C_4H_9CH{=}CHSiCl_3(trans) + C_4H_9\underset{\underset{SiCl_3}{|}}{C}H{=}CH_2$$

These results show that the base-catalyzed addition of trichlorosilane to olefins is predominantly a *cis* addition, as is the platinum-catalyzed reaction, and is characterized by the necessity of using a polar solvent. The addition does not proceed without the polar solvent unless the olefin contains a polar group as does acrylonitrile. In adding to terminal olefins the silicon atom normally adds to the primary carbon, with non-terminal olefins the silicon adds to a secondary carbon similar to peroxide-catalyzed reactions. No isomerization occurs as is the case with platinum.[2]

The results obtained can tentatively be explained on the basis of a solvated four-centered transition state in which the SiH bond is polarized as $Si^{\delta-}$----$H^{\delta+}$.

Similar transition states have been used to explain the reactions of organosilicon halides with Grignard reagents, alcoholysis of silicon halides, and disproportionation reactions of hydrogen containing halogenosilanes.[11,12] The solvated transition state could be pictured as follows:



Because of steric arrangement the silicon atom would tend to orient away from R'. However, a strong inductive or resonance effect which would polarize the unsaturated bond so that the terminal carbon was highly negative could cause the reverse orientation and lead to formation of an adduct with the silicon atom on a secondary carbon. The products obtained with octene-1, pentene-1, styrene, and phenylacetylene represent systems in which the steric factor is predominant. With hexyne-1 the formation of some adduct containing a terminal methylene group may be due to addi-

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(9) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1958, p. 51. In asymmetric disubstituted ethylenes, $R_1R_2C{=}CH_2$, the double bond frequency usually occurs at 892–887 cm.$^{-1}$. If R_1 and R_2 are other than hydrocarbon groups there is a shift to higher frequencies for the unsaturation, 900–945 cm.$^{-1}$.

(11) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp. 109, 110, 184.

(12) G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4815, 4825 (1959).

tion resulting from polarization of the triple bond as $RC^{\delta +}\equiv CH^{\delta -}$. With olefins containing polar groups, such as acrylonitrile, which due to inductive effect as well as steric arrangement orient R′ opposite to the trichlorosilyl group, addition would proceed to give only a beta isomer exclusively as has been shown.

Experimental

Tributylamine-Catalyzed Addition of Trichlorosilane to Olefins.—In a 300-cc. stainless steel pressure vessel was charged 55. g. (0.5 mole) octene-1, 67.8 g. (0.5 mole) trichlorosilane, 2.3 g. tri-*n*-butylamine, and 20.5 g. (0.5 mole) of acetonitrile. The vessel was sealed and heated in a rocking furnace for 2 hr. at 160°. The vessel was then cooled and discharged to give 144 g. of liquid product. Distillation through a Vigreux column gave 31.5 g. (25.7 mole % conversion) of *n*-octyltrichlorosilane, b.p. 106–108° (24 mm.). Also recovered was 21 g. of unchanged octene-1. Yield of product, based on octene-1 was 41.5 mole %.

A similar run was carried out using adiponitrile as solvent, 0.25 mole per 0.5 mole octene-1. The yield of adduct based on octene-1 was 46.4 mole %, b.p. 102° (20 mm.), $n^{25}\text{D}$ 1.4458. Hydrolyzable chlorine: Calcd., 43.3; Found, 42.5.

To establish the effect of a small amount of solvent a run using 55 g. (0.5 mole) of octene-1, 67.8 g. (0.5 mole) of trichlorosilane, 2 g. acetonitrile (0.048 mole), and 2.3 g. tri-*n*-butylamine was carried out in a rocking furnace at 160° for 2 hr. The vessel was cooled and discharged to give 128 g. of crude product which was concentrated and distilled under reduced pressure through a 30-cm. glass helix-packed column. There was obtained 22.5 g. (17.6 wt. % conversion) of *n*-octyltrichlorosilane, b.p. 68° (1.6 mm.), $n^{25}\text{D}$ 1.4450.

The additions of trichlorosilane to styrene and pentene-1 using tri-*n*-butylamine were carried out in a similar manner.

Addition to Pentene-2.—In a 300-cc. pressure vessel was charged 67.5 g. (0.5 mole) of trichlorosilane, 35 g. (0.5 mole) pentene-2, 20.5 g. of acetonitrile, and 2.5 g. tri-*n*-butylamine. The vessel was sealed and heated in a rocking furnace at 175° for 2 hr. The vessel was then cooled and discharged. The crude reaction product was concentrated and distilled under reduced pressure through a Vigreux column to give 8.0 g. of adduct, b.p. 26–27° (1.0 mm.), $n^{25}\text{D}$ 1.4465. The distilled adduct was passed through a gas chromatograph column using an Apiazon L packing. At 60 v., one third of the material appeared after 38 min., two thirds after 41 min. At 75 v., one third appeared in 16.5 min., two thirds in 17.5 min. From the infrared spectrum the sample appears to be a mixture of 2-pentyltrichlorosilane and 3-pentyltrichlorosilane.

Addition to Acetylene.—In an 800-cc. steam-jacketed steel pressure vessel was charged 145 g. (1.07 moles) of trichlorosilane, 55 g. of dry adiponitrile, and 4 g. of triphenylphosphine. The vessel was sealed and placed in a rocking furnace and purged three times with 50 p.s.i.g. acetylene before adding acetylene to 150 p.s.i.g. The furnace was started rocking and immediately an exothermic reaction occurred raising the temperature from 25° to 105° and the pressure to 300 p.s.i.g. The vessel was heated to 155° and at this temperature the pressure fell from 370 to 190 p.s.i. After 2.5 hr. the vessel was cooled and discharged to give 194 g. of liquid product. The liquid was distilled at atmospheric pressure through a Vigreux column to give 49 g., b.p. 199–200° of bistrichlorosilylethane, (49 mole %). Hydrolyzable chlorine: Calcd., 69.5; Found, 70.1. Also isolated was 15 g. of a lower boiling compound b.p. 64–66° (755 mm.), identified as impure vinyldichlorosilane by infrared spectrum. A total of 41 g. of silicon tetrachloride was also recovered along with 71 g. of high-boiling residue.

Effect of Solvent and Amine on the Addition of Styrene to Trichlorisilane.—In a 300-cc. stainless steel pressure vessel was charged 52 g. (0.5 mole) of styrene, 67.8 g. (0.5 mole) of trichlorosilane, 45 g. of benzene, 2.4 g. tri-*n*-butylamine, and 1.0 g. of Ionol. The vessel was sealed and heated in a rocking furnace at 150° for 2 hr. The vessel was cooled and discharged and the resulting product distilled at atmospheric pressure through a glass helix-packed column. There was obtained 95 g. of material with b.p. less than 85°. An attempt was made to distill the viscous residue under reduced pressure. There was obtained 4.5 g. of styrene b.p. 35° (5 mm.), and 3.0 g. (2.5 mole %) of impure phenylethyltrichlorosilane, b.p. 81–85° (5 mm.). The material in the distillation flask had gelled.

To determine the effect of a different amine on the addition a run was made in a 300-cc. stainless steel pressure vessel using 52 g. (0.5 mole) of styrene, 67.8 g. (0.5 mole) of trichlorosilane, 45 g. of acetonitrile, and 2.4 g. of pyridine. The vessel was sealed and heated in a rocking furnace for 2 hr. at 150°. The vessel was cooled and the product discharged. Distillation of the material through a glass helix-packed column gave 3 g. of unchanged styrene and 46 g., 40.8 mole % yield, b.p. 84–86° (2.5 mm.), of β-phenylethyltrichlorosilane.

Peroxide Addition of Trichlorosilane to Hexyne-1.—The addition was carried out as previously described[9] to give $C_4H_8CH{=}CHSiCl_3$ b.p. 97–99° (30 mm.), $n^{25}\text{D}$ 1.4572. Titrated for hydrolyzable chlorine. Calcd. for $C_6H_{11}SiCl_3$: Cl, 49.2. Found: Cl, 49.3.

Addition of Trichlorosilane to Phenylacetylene and Hexyne-1 with Tributylamine in Acetonitrile.—In a 300-ml. stainless steel pressure vessel was charged 67.5 g. (0.5 mole) of trichlorosilane, 51.2 g. (0.5 mole) of phenylacetylene, 25 g. of acetonitrile, and 2.1 g. of tributylamine. The vessel was sealed and heated in a rocking furnace 4 hr. at 148°. The vessel was cooled and discharged to give a homogeneous, dark brown liquid which was concentrated at atmospheric pressure. The crude product was distilled at reduced pressure through an alumina (8 × 10 mesh)-packed column to give 21.0 g. (17.7 mole %) of $C_6H_5CH{=}CHSiCl_3$, b.p. 74–75° (1.0 mm.). Titrated for hydrolyzable chlorine. Calcd. for $C_8H_7SiCl_3$: Cl, 44.3. Found: Cl, 44.7. Also obtained was 29.5 g. $C_6H_5C_2H_2(SiCl_3)_2$ b.p. 88–90° (1.0 mm.), $n^{25}\text{D}$ 1.5355. Titrated for hydrolyzable chlorine. Calcd. for $C_8H_7Si_2Cl_6$: Cl, 55.2. Found: Cl, 55.1.

Similarly carried out was a reaction using 67.8 g. (0.5 mole) of trichlorosilane, 41 g. (0.5 mole) of hexyne-1, 2.3 g. of tributylamine, and 30 g. of acetonitrile. The reaction time was 3.0 hr. at 160°. On distillation there was obtained 8.0 g. b.p. 53–54° (3.5 mm.) of $C_4H_9CH{=}CHSiCl_3$. The remainder of the material, 67 g., was found to be the diadduct $C_4H_9(CH_2)_2(SiCl_3)_2$ b.p. 131–135° (2.5 mm.). At a reaction temperature of 155–160° for 8 hr. using the same ratio of starting materials 14.5 g. of the hexenyltrichlorosilane was obtained.

Reaction of $RCH{=}CHSiCl_3$ with Methylmagnesium Chloride.—The unsaturated chlorosilanes were converted to the corresponding trimethylsilyl derivatives as previously described[9] except that a 3.0 *M* solution of methylmagnesium chloride in tetrahydrofuran was used as the Grignard reagent.

$C_4H_9CH{=}CHSiCl_3$ prepared by the peroxide addition was obtained in 98% yield, b.p. 156–157° (740 mm.). $n^{25}\text{D}$ 1.4268–1.4271.

Anal. Calcd. for $C_{10}H_{20}Si$: Si, 16.8. Found: Si, 17.0.

The gas chromatographic analysis was carried out on a 2.5-m. chromosorb W column impregnated with Apiezon L at 200°. Helium was used as a carrier gas at a flow rate of 60 ml./min. Two peaks were obtained. Part of the sample, 23 wt. %, had a retention time of 13 min. while 77 wt. % of the sample had a retention time of 17 min.

Conversion of the adducts obtained by the base-catalyzed addition of trichlorosilane with hexyne-1 and phenylacetylene to the trimethylsilyl derivatives was carried out in a similar manner.

$C_4H_9CH{=}CHSi(CH_3)_3$ was obtained in 79 wt. % yield, b.p. 155°, $n^{25}D$ 1.4261.

Anal. Calcd. for $C_{10}H_{20}Si$: C, 59.6; Si, 16.8. Found: C, 59.5; Si, 16.5.

$C_6H_5CH{=}CHSi(CH_3)_3$ was obtained in 60.2 wt. % yield, b.p. 42°, (0.1 mm.), $n^{25}D$ 1.5223, $n^{20}D$ 1.5250. Previously reported for *trans*-β-trimethylsilylstyrene, $n^{20}D$ 1.5260.[9]

Anal. Calcd. for $C_{11}H_{16}Si$: C, 75.0; H, 9.1; Si, 15.9. Found: C, 73.6; H, 9.0; Si, 15.8.

Reaction of *cis*-Hexenyltrichlorosilane with Pyridine in Acetonitrile.—In a 300-cc. stainless steel pressure vessel was charged 25 g. of *cis*-$C_4H_9CH{=}CHSiCl_3$ (containing less than 10 wt. % *trans* adduct), 10 g. of dry acetonitrile, and 0.7 g. of pyridine. The vessel was sealed and heated in a rocking furnace at 160° for 2 hr. The vessel was then cooled and discharged. The product was concentrated and distilled under reduced pressure through a 25-cm. glass helix-packed column to give 17.5 g. hexenyltrichlorosilane, b.p. 81° (20 mm.). The infrared spectrum was identical with starting material and gas chromatographic analysis showed no change had occurred in the *cis-trans* ratio of the material.

Preparation of β-Cyanoethyltrichlorosilane Using Silylamine Catalysts

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Received November 16, 1961

Silylamines of the type $(CH_3)_3SiNR_2$ have been shown to be directive catalysts for the addition of trichlorosilane to acrylonitrile. $(CH_3)_3SiN(C_2H_5)_2$, the most effective catalyst, gave β-cyanoethyltrichlorosilane exclusively. The actual catalyst is probably the silylamine $HSi(NR_2)Cl_2$ formed by rearrangement of chloro and amino groups between $(CH_3)_3SiNR_2$ and trichlorosilane.

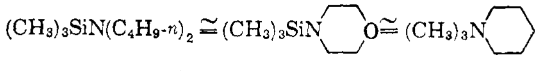
Addition of trichlorosilane to acrylonitrile gives β-cyanoethyltrichlorosilane when the reaction is catalyzed with organic amine,[1] phosphine[2] and amide[3] catalysts. The compounds which facilitate the addition are not strong bases and it has been suggested that they are effective because of their ability to form complexes with chlorosilanes.[3] Silylamines, although they cannot be considered true organic amines, complex with chlorosilanes and should be suitable replacements for organic amines in the addition of trichlorosilane to acrylonitrile.

The results of a study to determine the most effective type of silylamine for preparation of β-cyanoethyltrichlorosilane are summarized in Table I. In all cases, the major product was the β-isomer with small amounts of α-cyanoethyltrichlorosilane being formed with the less effective catalysts.

As was the case with triphenylphosphine,[2] the reaction was characterized by a temperature dependence as shown in runs using $(CH_3)_3SiN(C_2H_5)_2$ as catalyst. A different optimum temperature is required for each catalyst to obtain maximum conversion to the beta isomer.

The conversion to product at 140° to 150° was found to vary with the structure of the silylamine as follows:

$$(CH_3)_3SiN(C_2H_5)_2 = HSi[N(C_2H_5)_2]_3 > (CH_3)_3SiN(C_3H_7\text{-}n)_2 >$$



$$\cong (CH_3)_3SiN(CH_3)_2$$

The physical constants of the silylamines are listed in Table II.

The degree of effectiveness of the catalysts cannot be rationalized on the basis of base strength alone. For example, the silylamine prepared from the strongest organic base, piperidine, and the corresponding silylamine made with morpholine gave the same low yield of product. The result using the piperidine analogue was due in part to formation of an insoluble complex with trichlorosilane as evidenced by precipitation of a white solid on addition of the silylamine to the acrylonitrile–trichlorosilane solution. $(CH_3)_3SiN(CH_3)_2$ gave similar results. The remaining catalysts did not form solids, but remained clear and homogeneous when added to the reaction mixture. The marked degree of difference in the formation of product between the catalysts where R = ethyl *n*-propyl and *n*-butyl must be due to more than base strength since these silylamines should have nearly the same relative strength as the parent amines. Since in this series there is little difference in base strength, the conversion to product should have been nearly the same.

Steric hindrance might be a possible explanation of the results obtained. If the mechanism which has been proposed for the reaction[1] is correct, *i.e.*, abstraction of a proton by the base from silicon to form $B{:}H^+$ and Si^-, steric effects do not appear to be a valid argument to account for the differences between the silylamine catalysts. However, the results using the diisopropylsilylamine indicate that there is a steric factor which must be considered. It is suggested that the steric effects found with the

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