tion, there was obtained 0.40 g. (6%) of triphenylsilanol; identified by infrared spectra.

Reaction of triphenylsilyllithium with cyclopentyl chloride. A solution of triphenylsilyllithium (0.05 mole) in tetrahydrofuran was added dropwise to 5.23 g. (0.05 mole) of cyclopentyl chloride. The reaction was exothermic, but to a lesser extent than with primary halides. Color Test I was positive after addition. The reaction mixture was stirred at refluxing temperature for 18 hr. after which Color Test I was negative. Subsequent to hydrolysis, 1.2 g. (9.3%) of hexaphenyldisilane, m.p. 356–357°, was isolated. Work-up of the organic layer gave a solid residue which was chromatographed on alumina. From petroleum ether (b.p. 60–70°) as an eluant there was obtained 6.50 g. (40%) of cyclopentyltriphenylsilane, m.p. 112–116°, after recrystallization from ethanol. The product was identified by a mixed melting point determination with an authentic sample, and infrared spectra.

Reaction of triphenylsilyllithium with 1,3-dichloropropane. A solution of triphenylsilyllithium (0.05 mole) in tetrahydrofuran was added dropwise to 2.83 g. (0.025 mole) of 1,3-dichloropropane. The reaction was exothermic, and Color Test I was negative immediately after addition. Work-up gave a solid residue, which was recrystallized from petroleum ether (b.p. 60–70°), yielding 10.25 g. (73%) of 1,3-bis(triphenylsilyl)propane, m.p. 132–133.5°. Recrystallization from the same solvent raised the melting point to 133–134°. Infrared spectrum supported the structure of the product.

Anal. Calcd. for $C_{39}H_{36}Si_2$: Si, 10.02. Found: Si, 10.00, 9.92.

Reaction of triphenylsilyllithium with 1,3-dibromopropane. A solution of triphenylsilyllithium (0.04 mole) in tetrahydrofuran was added dropwise to 4.04 g. (0.02 mole) of 1,3-dibromopropane. The reaction was exothermic, and Color Test I was negative immediately after addition. Subsequent to hydrolysis, 7.4 g. (71.5%) of hexaphenyldisilane, m.p. 355–357°, was isolated. A very small amount of the residue, which was obtained after work-up of the organic layer, has failed to give any pure product.

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CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

Cyanoethylation of Trichlorosilane

JOHN C. SAAM AND JOHN L. SPEIER

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The reaction of trichlorosilane and acrylonitrile in the presence of tertiary amines has been reported by Nozakura and Konotsune[1] and also by Prober and Cooper[2] to give 3-trichlorosilylpropionitrile (I). This product has also been reported[3] to have been prepared from the same reagents in the presence of triphenylphosphine.

While evaluating various catalysts for the reaction of acrylonitrile and trichlorosilane, several amides were found to promote the formation of I. The reactants were heated to reflux for 24 hr. or longer in the presence of two mole percent of the amide. The table lists the yields of I obtained with various amides. None of these amides promoted cyanoethylation of methyldichlorosilane. The product in each case had the same melting point as that reported by Nozakura and Konotsune,[1] who related the structure of their product to the known 3-trimethylsilylpropionamide.[4] The isomeric 2-trichlorosilylpropionitrile was not detected in any of the mixtures although its properties[5] should have made its detection very easy.

Treatment of I with ethanol and pyridine gave the known 3-triethoxysilylpropionitrile (II)[1] in good yields, and 3-methyldichlorosilylpropionitrile (III)[2] was prepared from I and methyl magnesium bromide. Hydrolysis of I and III gave polysiloxane resins and fluids.

The accepted mechanism for base-catalyzed cyanoethylation reactions[6] would lead one to expect trichlorosilane, polarized as $Cl_3Si^+H^-$,[7] to yield 2-trichlorosilylpropionitrile. Contrary to such expectations, certain catalysts bring about almost exclusive formation of 3-trichlorosilylpropionitrile. These catalysts are not the strong bases used in common cyanoethylations, but have been found among special classes of compounds which form relatively stable complexes with chlorosilanes.

Tertiary amines,[8,9] phosphines,[9] arsines,[9] and amides[10] form complexes involving the *d*-orbitals of silicon. These complexes are the probable reactive intermediates leading to 3-trichlorosilylpropionitrile.

To see if the amine hydrochlorides formed by decomposition of amide complexes[11] were catalyt-

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

[2] M. Prober and C. D. Cooper, Fr. Patent **1,116,726** (1956).

[3] R. A. Pike and D. L. Bailey, Abstracts of the 134th meeting of the American Chemical Society, 49P, September 1958.

[4] L. H. Sommer and J. Rockett, *J. Am. Chem. Soc.*, **73**, 5130 (1951).

[5] S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, **29**, 326 (1956).

[6] J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, New York, 1956, p. 221.

[7] L. Pauling, *The Nature of the Chemical Bond*, 2nd ed., Cornell University Press, Ithica, 1940, pp. 58–69.

[8] A. B. Burg, *J. Am. Chem. Soc.*, **76**, 2674 (1954). V. Wannagot, R. Schwartz, H. Voss, and K. G. Knauff, *Z. anorg. u. allgem. Chem.*, **277**, 73 (1954).

[9] B. J. Aylett, H. J. Emeleus, and A. G. Maddock, *J. Inorg. & Nuclear Chem.*, **1**, 187 (1955).

[10] T. S. Piper and E. J. Rochow, *J. Am. Chem. Soc.*, **76**, 4318 (1954). Yu. Volnov, *Sbornik Statei Obshchei Khim., Akad. Nauk. S.S.S.R.*, **2**, 979 (1953).

[11] E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 4852 (1954).

ically active species, diethylamine hydrochloride and aniline hydrochloride were tested, but they had no catalytic effect under these conditions.

EXPERIMENTAL

3-Trichlorosilylpropionitrile (I). A mixture of 106 g. (2 moles) of acrylonitrile, 271 g. (2 moles) of trichlorosilane, and 7.2 g. (0.1 mole) of dimethylformamide was refluxed for 24 hr. During this period the temperature increased from 37° to 83°.[12] Then an additional 135.5 g. of trichlorosilane was slowly added to the refluxing mixture over a period of 48 hr. The final reflux temperature was 105°. The lower boiling components were distilled from the mixture before the product was distilled at reduced pressure to give 272 g. (72%) of 3-trichlorosilylpropionitrile, m.p. 32–33°, b.p. 78–84° at 7–8 mm.

Anal. Calcd. for $C_3H_4NCl_3Si$: Si, 14.90; Neut. Equiv., 62.9. Found: Si, 15.3; neut. equiv., 62.6.

The amides listed in the table were evaluated as catalysts by refluxing equimolar amounts of trichlorosilane and acrylonitrile for 24 hr. in the presence of 2 mole % of the amide. The product was then distilled from the mixture in the yields shown.

CATALYSTS FOR THE CYANOETHYLATION OF TRICHLORISOLANE

Amide	% Yield in 24 Hr.
Dimethylformamide	42
N,*N*-Diethylbenzamide	38
N,*N*-Dibutylacetamide	38
N,*N*-Diethyldecanamide	42
p-Acetotoluide	43
Acetanilide	21
N,*N*-Dibutylbutyramide	35
N,*N*-Diethylpropionamide	34

3-Triethoxysilylpropionitrile (II).[1] A solution of 94 g. (0.5 mole) of I in 150 ml. of hexane was slowly added with stirring to a solution of 158 g. (2 moles) of pyridine, 92 g. of ethanol (2 moles), and 400 ml. of hexane. The mixture was cooled, filtered, and devolatilized. The residue was distilled at reduced pressure to give 86.7 g. (80%) of II, b.p. 108–110° at 10 mm., n_D^{22} 1.4121.

3-Methyldichlorosilylpropionitrile (III).[2] A solution of 0.5 mole of methyl magnesium bromide in 200 ml. of ether was added over a period of 1 hr. to a stirred solution of 94.2 g. (0.5 mole) of I in 200 ml. of ether. The stirring was continued for 0.5 hr., the solution was filtered, and the precipitate was washed with dry ether. The solvent was distilled from the combined filtrates, and the residue was distilled at 79–93° at 7–9 mm. to give 64 g. of crude product. Redistillation of the crude product gave 18.3 g. of pure III, b.p. 89° at 16 mm.; n_D^{22}, 1.4560; d_4^{25}, 1.206.

Anal. Calcd. for $SiC_4H_7NCl_2$: Neut. Equiv. 84.0. Found: 83.0.

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[12] An attempt to carry out this reaction in a sealed pressure bottle on a steam bath resulted in an explosion causing considerable damage to the surroundings.

Syntheses of *N*-Vinyl-secondary-amic Acids

KIYOSHI YANAGI, CHUJI ASO, AND SABURO AKIYOSHI

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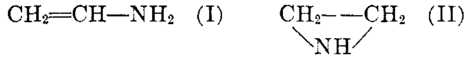
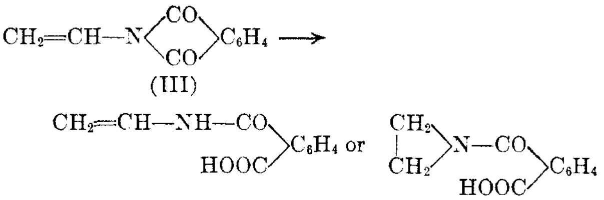
Since vinylamine (I) is unstable and is immediately isomerized into ethyleneimine (II) by the migration



$CH_2{=}CH{-}NH_2$ (I) $\quad$ $CH_2{-}CH_2$ (II) (bridged by NH)

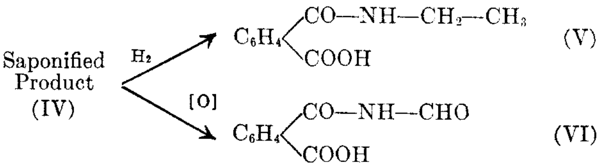
of hydrogen from nitrogen to carbon, all reactions intended to form vinylamines yield ethyleneimine.[1] On the other hand *N*-vinylimides, that is, *N*,*N*-disubstituted vinylamines such as *N*-vinylphthalimide (III), are stable. It is a matter of much interest whether the partially saponified product of III is *N*-vinylphthalamic acid (IVa) (*N*-vinyl secondary amide type structure) or *N*-(*o*-carboxybenzoyl)ethyleneimine (IVb).



(III)

(IVa) (IVb)

We attempted to saponify III with alkali under mild conditions, obtaining a product whose composition was found to be $C_{10}H_9NO_3$ by analysis. This is equivalent to IVa or IVb. Through the catalytic hydrogenation of the saponified product under ordinary pressure and at room temperature, *N*-ethylphthalamic acid (V) was obtained. By oxidizing the saponified product with dilute aqueous potassium permanganate at room temperature, *N*-(*o*-carboxybenzoyl)formamide (VI) was obtained. (The ethyleneimine ring is stable to potassium permanganate.[2]) In the infrared spectrum of the saponified product there are seen absorption bands at 3.02μ and 6.48μ which are considered to represent N—H of the secondary amide. If the saponified product were IVb, which is the tertiary imide and has no N—H group, these bands would not be expected. The absorptions at 6.02μ, 10.15μ, and 11.15μ, which are lacking in the infrared spectrum of the hydrogenated product (V), reveal the existence of a vinyl group, indi-



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[1] C. C. Howerd and W. Markwald, *Ber.*, **32**, 2036 (1899).

[2] W. Markwald, *Ber.*, **33**, 765 (1900).