

lene to the trimethylsilyl derivatives was carried out in a similar manner.

$C_6H_5CH=CHSi(CH_3)_3$  was obtained in 79 wt. % yield, b.p.  $155^\circ$ ,  $n_D^{25}$  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.  $42^\circ$ , (0.1 mm.),  $n_D^{25}$  1.5223,  $n_D^{30}$  1.5250. Previously reported for *trans*- $\beta$ -trimethylsilylstyrene,  $n_D^{20}$  1.5260.<sup>9</sup>

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*- $C_6H_9CH=CHSiCl_3$  (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  $160^\circ$  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.  $81^\circ$  (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 $\beta$ -Cyanoethyltrichlorosilane Using Silylamine Catalysts

ROSCOE A. PIKE<sup>1a</sup> AND RICHARD L. SCHANK

Silicones Division, Union Carbide Corp., Tonawanda, N. Y.

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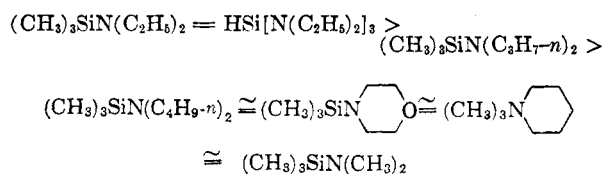
Silylamines of the type  $(CH_3)_3SiNR_2$  have been shown to be directive catalysts for the addition of trichlorosilane to acrylonitrile.  $(CH_3)_3SiN(C_2H_5)_2$ , the most effective catalyst, gave  $\beta$ -cyanoethyltrichlorosilane exclusively. The actual catalyst is probably the silylamine  $HSi(NR_2)Cl_2$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

Addition of trichlorosilane to acrylonitrile gives  $\beta$ -cyanoethyltrichlorosilane when the reaction is catalyzed with organic amine,<sup>1</sup> phosphine<sup>2</sup> and amide<sup>3</sup> 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.<sup>3</sup> 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  $\beta$ -cyanoethyltrichlorosilane are summarized in Table I. In all cases, the major product was the  $\beta$ -isomer with small amounts of  $\alpha$ -cyanoethyltrichlorosilane being formed with the less effective catalysts.

As was the case with triphenylphosphine,<sup>2</sup> 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  $140^\circ$  to  $150^\circ$  was found to vary with the structure of the silylamine as follows:



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<sup>1</sup> 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

(1a) Present address: Norton Co., Worcester 6, Mass.

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

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

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

TABLE I

EFFECT OF TEMPERATURE AND STRUCTURE OF SILYLAMINE CATALYSTS ON THE ADDITION OF  $\text{HSiCl}_3$  TO ACRYLONITRILE<sup>a</sup>

Catalyst	Temp.°	Mole % Conversion <sup>b</sup> to $\text{NCCH}_2\text{CH}_2\text{SiCl}_3$	Remarks <sup>c</sup>
$(\text{CH}_3)_3\text{SiN}(\text{C}_2\text{H}_5)_2$	115	36	Reaction mixture homogeneous
$(\text{CH}_3)_3\text{SiN}(\text{C}_2\text{H}_5)_2$	140	74	Reaction mixture homogeneous
$(\text{CH}_3)_3\text{SiN}(\text{C}_2\text{H}_5)_2$	160	66	Reaction mixture homogeneous
$(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$	135	34	Solids formed on addition of silylamine to reaction mixture
$(\text{CH}_3)_3\text{SiN}(\text{C}_3\text{H}_7-n)_2$	115	44	...
$(\text{CH}_3)_3\text{SiN}(\text{C}_3\text{H}_7-n)_2$	140	32	Less than 5 wt. % alpha adduct present
$(\text{CH}_3)_3\text{SiN}(\text{C}_4\text{H}_9-n)_2$	150	38	Less than 5 wt. % alpha adduct present
$(\text{CH}_3)_3\text{SiNC}_4\text{H}_9\text{O}$	150	36	...
$(\text{CH}_3)_3\text{SiNC}_5\text{H}_{10}$	145	34	Solids formed on addition of silylamine to reaction mixture
$\text{HSi}[\text{N}(\text{C}_2\text{H}_5)_2]_3$	145	67	Trace of solids formed on addition of silylamine to reaction mixture
$\text{HSiN}(\text{C}_3\text{H}_7-n)_2\text{Cl}_2$	150	22	Silylamine used in xylene solution
$\text{HSiN}(\text{C}_3\text{H}_7-i)_2\text{Cl}_2$	150	15	Less than 5 wt. % alpha adduct present

<sup>a</sup> 1:1 mole ratio of reactants; 2 hr. at temperature; 2 wt. 3% catalyst, in 100-ml. stainless steel vessel. <sup>b</sup> Based on acrylonitrile. <sup>c</sup> Identification of alpha and beta adducts was made by infrared as described in ref. 2.

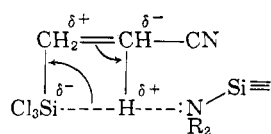
TABLE II

PHYSICAL CONSTANTS OF SILYLAMINE CATALYSTS<sup>a</sup>

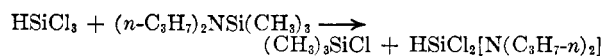
Silylamine	B.P. (mm.)	$n_D^{25}$	Analysis
$(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2^b$	84(760)	1.3950	Calcd. for $\text{C}_7\text{H}_{19}\text{NSi}$ : Si, 19.2; N, 9.66. Found: Si, 19.0; N, 9.9
$(\text{CH}_3)_3\text{SiN}(\text{C}_2\text{H}_5)_2$	31(47)	1.4110	Neut. equiv.: theory, 154.2; found: 151
$(\text{CH}_3)_3\text{SiN}(\text{C}_3\text{H}_7-n)_2$	76-78(35)	1.4209	Calcd. for $\text{C}_9\text{H}_{23}\text{NSi}$ : Si, 16.2; N, 8.1. Found: Si, 16.0; N, 8.2
$(\text{CH}_3)_3\text{SiN}(\text{C}_4\text{H}_9-n)_2$	90(49)	1.4757	Neut. equiv.: Calcd. for $\text{C}_{11}\text{H}_{27}\text{NSi}$ : 201.4. Found: 205
$(\text{CH}_3)_3\text{SiNC}_4\text{H}_9\text{O}^c$	160(760)	1.4407	Calcd. for $\text{C}_7\text{H}_{17}\text{SiNO}$ : N, 8.8. Found: N, 8.6
$(\text{CH}_3)_3\text{SiNC}_5\text{H}_{10}^d$	156(760)	1.4398	Neut. equiv.: Calcd. for $\text{C}_9\text{H}_{19}\text{NSi}$ : 157.2. Found: 160
$\text{HSi}[\text{N}(\text{C}_2\text{H}_5)_2]_3$	62-65(1)	1.4445	Calcd. for $\text{C}_{12}\text{H}_{31}\text{N}_3\text{Si}$ : N, 17.1. Found: N, 16.8

<sup>a</sup> Silylamines prepared by treating the chlorosilane with organic amine in petroleum ether or diethyl ether solvent. Yield of product greater than 50 wt. % in all preparations. <sup>b</sup> Amine contaminated with some solvent. <sup>c</sup>  $\text{C}_4\text{H}_9\text{O}$  = morpholino. <sup>d</sup>  $\text{C}_5\text{H}_{10}$  = piperidino.

different silylamines can best be explained on the basis of a four-centered cyclic transition state similar to that proposed for the organic base-catalyzed addition of trichlorosilanes to hydrocarbon olefins.<sup>4</sup>



The actual catalyst in the reaction is probably not  $N,N$ -dialkyltrimethylsilylamine. It is known that silylamines redistribute with alkylchlorosilanes the amine group going to the silicon atom having the greater functionality.<sup>5</sup> A redistribution between trichlorosilane and the  $N,N$ -dialkyltrimethylsilylamines was shown to take place by mixing  $(\text{CH}_3)_3\text{SiN}(\text{C}_3\text{H}_7-n)_2$  with trichlorosilane in xylene followed by immediate distillation of trimethylchlorosilane.



The hydrogenchlorosilylamine which results could

(4) R. A. Pike, *J. Org. Chem.*, **27**, 2186 (1962).

(5) H. Grosse-Ruyken and K. Schaarschmidt, *Chemische Technik*, **11**, 451 (1959).

function as the active catalyst for the addition reaction. The xylene solution containing  $\text{HSiCl}_2\text{N}(\text{C}_3\text{H}_7-n)_2$  catalyzed the addition of trichlorosilane to acrylonitrile and gave  $\beta$ -cyanoethyltrichlorosilane containing a small amount of alpha isomer, as did  $N,N$ -di- $n$ -propyltrimethylsilylamine, but at a somewhat lower conversion.

More conclusive evidence that silylamines containing SiH bonds are active catalysts was obtained using  $\text{HSi}[\text{N}(\text{C}_2\text{H}_5)_2]_3$  which was added as a pure compound to the reactants. The silylamine reacted exothermically with the trichlorosilane-acrylonitrile mixture, however, only a small amount of solid was formed. The yield of  $\beta$ -cyanoethyltrichlorosilane obtained was similar to that using  $N,N$ -diethyltrimethylsilylamine.

## Experimental

**Preparation of  $N,N$ -Diethyltrimethylsilylamine.**—In a 2-l., three-necked flask fitted with a thermometer, reflux condenser, dropping funnel, and mechanical stirrer, was charged 217 g. (2 moles) of trimethylmonochlorosilane dissolved in 700 ml. of anhydrous diethyl ether. To this solution was added dropwise with vigorous stirring 402 g. (4.14 moles) of diethylamine over the course of 1 hr. The mixture was stirred an additional hour, and the amine hydrochloride which formed was filtered using a fritted glass filter. The salt was washed with 700 ml. of diethyl ether and these washings were combined with the original filtrate. The combined ether solution was concentrated and the residue

distilled through a 20-cm. Vigreux column to give 218 g. (75.5 mole %) b.p. 31° (47 mm.)  $n_{25}^D$  1.4110 of *N,N*-diethyltrimethylsilylamine.

The silylamines listed in Table II were prepared using similar procedures.

**Addition of Trichlorosilane to Acrylonitrile Using *N,N*-Diethyltrimethylsilylamine Catalyst.**—In a 300-cc. stainless steel pressure vessel was charged 53.0 g. (1 mole) of acrylonitrile, 135.5 g. (1 mole) of trichlorosilane, and 3.8 g. (2 wt. %) of *N,N*-diethyltrimethylsilylamine. The vessel was sealed and heated in a rocking furnace at 140° for 1.75 hr. The maximum pressure obtained was 200 p.s.i.g. The vessel was cooled and discharged to give 186 g. of liquid product. Distillation through a 20-cm. Vigreux column gave 139.5 g. (74 wt. % yield) b.p. 76–77° (5 mm.) of  $\beta$ -cyanoethyltrichlorosilane.

*Anal.* Calcd. for  $C_4H_9SiCl_3$ : Hydrolyzable chlorine, 56.4%; Found: 56.2%.

An infrared spectrum of the product verified the compound as the beta isomer. Table I lists the addition reactions carried out in a similar manner using the various silylamine catalyst.

**Reaction of *N,N*-Di-*n*-propyltrimethylsilylamine with Trichlorosilane.**—In a 250-ml. flask was charged 50 ml. of xylene, 43.5 g. (0.25 mole) of *N,N*-di-*n*-propyltrimethylsilylamine, and 33.9 g. (0.25 mole) of trichlorosilane. The flask was quickly attached to a 30-cm. glass helix-packed fractionating column. The temperature of the solution rose rapidly to 63° when the materials were mixed. Gentle heat was applied to the flask after the reaction subsided and 28.4 g. of material, b.p. 56–57° identified as trimethylchlorosilane containing a trace of trichlorosilane as indicated by hydrolyzable chlorine. As described above, 3.9 g. of the remaining xylene solution was used to catalyze the addition of trichlorosilane and acrylonitrile. The reaction was run 2 hr. at 150°. On distillation,  $\beta$ -cyanoethyltrichlorosilane, containing a small amount of the alpha isomer was obtained in 22 mole % conversion.

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## *p*-Phenylenediphosphine and Related Compounds<sup>1,2</sup>

EARL M. EVLETH, JR., LEVERN D. FREEMAN, AND ROSS I. WAGNER<sup>3</sup>

Whittier Research Laboratory, American Potash & Chemical Corp., Whittier, Calif.

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Application of the reaction of organometallic reagents with dialkylaminohalophosphines has provided a practical synthesis for aromatic diphosphorus compounds. The syntheses of the first primary and secondary aromatic diphosphines as well as the derivatives, *P,P,P',P'*-tetrakis(dimethylamino)-*p*-phenylenediphosphine, *P,P,P',P'*-tetrachloro-*p*-phenylenediphosphine, and *p*-phenylenebis(methylphosphinic acid), are reported. From a number of infrared spectra of a variety of dimethylaminophosphines a characteristic strong absorption at 980–950  $cm^{-1}$  has been assigned to the P—N(CH<sub>3</sub>)<sub>2</sub> group. The acid strengths of *p*-phenylenebis(methylphosphinic acid) ( $pK_a$  2.67) and methylphenylphosphinic acid ( $pK_a$  2.96) have been measured.

Primary and secondary aromatic diphosphines have not been reported previously in the chemical literature.<sup>4</sup> We now wish to report the preparation of *p*-phenylenediphosphine<sup>5</sup> (I) and *P,P'*-dimethyl-*p*-phenylenediphosphine (II) as well as the new

aromatic diphosphorus compounds, *P,P,P',P'*-tetrakis(dimethylamino)-*p*-phenylenediphosphine (III), *P,P,P',P'*-tetrachloro-*p*-phenylenediphosphine (IV), and *p*-phenylenebis(methylphosphinic acid) (V).

The synthetic sequence outlined below was selected from a number of preliminary reactions, described later, which indicated that treatment of organolithium reagents with a bis(dialkylamino)halophosphine<sup>6,7</sup> would be a practical synthetic route to trivalent diphosphorus compounds.

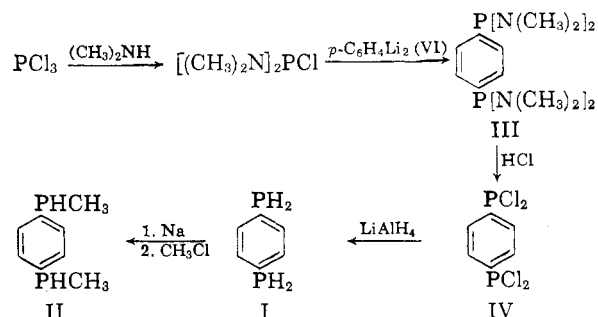
(1) This research was supported in part by the United States Air Force under Contracts AF 33(616)-3506, 5433, 6913, and 7810, monitored by the Materials Laboratory, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

(2) Presented in part at the Pacific Southwest Regional Meeting of the American Chemical Society, October 25, 1958.

(3) To whom inquiries should be addressed.

(4) During the course of this investigation, the preparation of a tertiary aromatic diphosphine was reported by F. A. Hart and F. G. Mann, *J. Chem. Soc.*, **1957**, 3939 and subsequently other aromatic tertiary di- and triphosphines have been reported by F. Ramirez and D. Rhum, *J. Org. Chem.*, **24**, 894 (1959); A. F. Clifford and R. R. Olsen, Abstracts of 135th American Chemical Society Meeting, April, 1959, p. 16M; F. A. Hart, *J. Chem. Soc.*, **1960**, 3324; D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961); and R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961).

(5) All of the trivalent phosphorus compounds discussed in this paper have been named as derivatives of phosphine to emphasize their relationship to the parent compound and to each other rather than to employ the less frequently used "Index Compounds" of Chemical Abstracts. For convenience the names (and *Chem. Abstr.* indexing names) are listed for the parent compounds: H<sub>2</sub>NPH<sub>2</sub>, aminophosphine (phosphinous amide); H<sub>2</sub>PCH<sub>3</sub>, chlorophosphine (phosphinous chloride); HP(NH<sub>2</sub>)<sub>2</sub>, diaminophosphine (phosphonous diamide); HPCL<sub>2</sub>, dichlorophosphine (phosphonous dichloride); and H<sub>2</sub>NPClH, aminochlorophosphine (no index name listed by *Chem. Abstr.*).



(6) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).