

## N-Substituted Alkyltriaminosilanes

### I. On the Reaction of *n*-Propyltrichlorosilane with Primary and Secondary Amines

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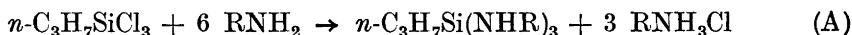
As a part of an investigation on aminosilanes the synthesis of N-substituted *n*-propyltriaminosilanes from *n*-propyltrichlorosilane and various primary and secondary amines was studied.

Observations were made which indicate a probable influence by the steric and electric properties of the amines on the reaction between *n*-propyltrichlorosilane and amines.

The preparation of thirty compounds which have not earlier been reported in the literature is described.

During the last ten years a great number of organosilicon compounds in which silicon is bound to one or more amino-nitrogen atoms have been described in the literature. Among these, however, there are only a few<sup>1-3</sup> with three silicon-nitrogen bonds and one silicon-carbon bond. In this work there will be reported the synthesis of some new aminosilanes of this type, containing the trifunctional silicon group  $n\text{-C}_3\text{H}_7\text{Si}\equiv$ .

It is well known that the silicon-chlorine bond reacts readily with ammonia and primary and secondary amines. If all the chlorine atoms in *n*-propyltrichlorosilane are exchanged, the reaction in the case of a primary amine takes part according to the formula



Amine hydrochlorides containing silicon were not obtained, and tertiary amines (trimethylamine, triethylamine, and pyridine) did not react with *n*-propyltrichlorosilane to give quaternary salts. Nor did they under the conditions employed give addition compounds,  $n\text{-C}_3\text{H}_7\text{SiCl}_3 \cdot x\text{R}_3\text{N}$ , of the type which was proposed by Trost<sup>4</sup> to be formed between silicon tetrachloride and tertiary amines.

When *n*-propyltrichlorosilane in ether or benzene solution reacted with an amine with a small R-group, the above reaction proceeded rapidly with

evolution of considerable heat, giving the calculated amount of hydrochloride which could be filtered from the reaction mixture.

However, when an ether or benzene solution of *n*-propyltrichlorosilane was added to an excess of *tert.*-butylamine or diethylamine in ether or benzene, only two chlorine atoms — and in the case of di-*isopropylamine* or di-*cyclohexylamine* only one chlorine atom — were replaced even after several hours at the boiling point of the reaction mixture. Even on prolonged heating of the compounds in a steel-bomb at 160°C, with excess of amine, no more amine hydrochloride was formed. This illustrates the great resistance against further replacement of chlorine atoms. It is most likely due to the steric effects of the bulky groups in these amines, since the residual chlorine atoms reacted readily with ammonia and after refluxing even with *isopropylamine*.

Aniline gave after refluxing for some hours in benzene or ether solution complete reaction with the chlorine in *n*-propyltrichlorosilane, but it did not react so readily as *cyclohexylamine*, thus indicating that not only the size but also the electric properties of the amine influences reaction (A). The fact that *N*-methylaniline in ether or benzene reacted even with the second chlorine atom only to a small extent then may be explained as a result of both the steric properties and the low base strength of *N*-methylaniline as compared to aliphatic amines. The influence of the electric properties of the amine on reaction (A) is also supported by the fact that diphenylamine did not react at all with *n*-propyltrichlorosilane at room temperature, while di-*isopropylamine* and di-*cyclohexylamine* under the same conditions readily reacted with one of the chlorine atoms. This is in agreement with observations made on the reaction of silicon tetrachloride with diphenylamine and di-*isopropylamine* <sup>5</sup>.

It is interesting to note that while diethylamine reacted with only two chlorine atoms in *n*-propyltrichlorosilane even after prolonged heating in benzene solution, piperidine after refluxing for about 5 h in the same solvent gave total replacement. This difference in behaviour between these two amines can hardly be explained by the small difference in base strength (for piperidine  $K_b = 16 \times 10^{-4}$  at 25°C, and for diethylamine  $K_b = 12.6 \times 10^{-4}$  at 25°C). It may, however, be caused by the difference in free rotation around the carbon-nitrogen bonds: in diethylamine the free rotation is not hindered, but in the case of piperidine it is prevented because of the ring structure of this amine. This difference must obviously diminish the steric requirement of piperidino groups as compared to that of diethylamino groups. The observed difference between the reactivity of diethylamine and piperidine is in full analogy with the fact that diethylamine in benzene solution reacted with only three chlorine atoms in silicon tetrachloride, while piperidine gave total replacement <sup>6</sup>.

*Cyclohexylamine* reacted more readily than *sec.*-butylamine with *n*-propyltrichlorosilane. This difference may be explained as a result of the difference in free rotation around the carbon-carbon bonds in these amines, but, of course, the difference in this case was much less.

The following compounds have been prepared (the Arabic figures refer to the numbering in the experimental part):

I	(1)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHCH}_3)_3$
II	(2)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{CH}_3)_2]_3$
III	(3)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_2\text{H}_5)_3$
IV	(4)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_3\text{H}_7\text{-}n)_3$
V	(5)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_3\text{H}_7\text{-}i)_3$
VI	(6)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}n)_3$
VII	(7)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}i)_3$
VIII	(8)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}s)_3$
IX	(9)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_6\text{H}_{11})_3$
X	(10)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_6\text{H}_5)_3$
XI	(11)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{CH}_2)_5]_3$
XII	(13)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}t)_2\text{NH}_2$
XIII	(14)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}t)_2(\text{NHC}_2\text{H}_5)$
XIV	(15)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}t)_2(\text{NHC}_3\text{H}_7\text{-}i)$
XV	(19)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_2\text{H}_5)_2]_2\text{NH}_2$
XVI	(20)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_2\text{H}_5)_2]_2(\text{NHC}_3\text{H}_7\text{-}i)$
XVII	(31)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2(\text{NHC}_3\text{H}_7\text{-}i)$
XVIII	(17)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}t)(\text{NHC}_3\text{H}_7\text{-}i)_2$
XIX	(22)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_2\text{H}_5)_2](\text{NHC}_3\text{H}_7\text{-}i)_2$
XX	(24)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_2\text{H}_7\text{-}i)_2](\text{NHC}_3\text{H}_7\text{-}i)_2$
XXI	(26)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_6\text{H}_{11})_2](\text{NHC}_3\text{H}_7\text{-}i)_2$
XXII	(29)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5)](\text{NHC}_3\text{H}_7\text{-}i)_2$
XXIII	(12)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}t)_2\text{Cl}$
XXIV	(18)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_2\text{H}_5)_2]_2\text{Cl}$
XXV	(30)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2\text{Cl}$
XXVI	(16)	$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}t)\text{Cl}_2$
XXVII	(21)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_2\text{H}_5)_2]\text{Cl}_2$
XXVIII	(23)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_3\text{H}_7\text{-}i)_2]\text{Cl}_2$
XXIX	(25)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{C}_6\text{H}_{11})_2]\text{Cl}_2$
XXX	(28)	$n\text{-C}_3\text{H}_7\text{Si}[\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5)]\text{Cl}_2$

The assigned structural formulas for these compounds have been based on the way of the syntheses (amount of amine hydrochloride formed), and the silicon content and neutralization equivalents have been determined to confirm the composition of the expected compounds.

The prepared compounds are all colourless, water-insoluble liquids, soluble in organic solvents. Some of their reactions will be described in a later part of this work. Physical constants and analyses are given in Tables 1 and 2.

The author wishes to thank Professor E. Larsson for his kind interest in this work.

#### EXPERIMENTAL

The *n*-propyltrichlorosilane used for the syntheses was a sample of technical grade from Hopkins and Williams Ltd., England, which was fractionated before use (B.p. 123°C).

All experiments were performed with carefully dried reagents and solvents and precautions were taken to exclude moisture from the reaction vessels.

The aminosilanes were distilled at reduced pressure in a glass-helix packed column of a length of 15 cm.

#### Analyses

Silicon analyses were performed according to Smith <sup>7</sup>.

The equivalent weights of the compounds containing three aliphatic or alicyclic amino groups could be determined by direct titration with standard hydrochloric acid using methyl red as the indicator, if a weighed sample was dissolved in a water-alcohol mixture

Table 1. Physical constants and analyses of compounds with three silicon-nitrogen bonds.

No.	<i>M</i>	B.p. °C	Pressure mm Hg	$n_D^{20}$	$d^{20}$	<i>MR</i> <sub>D</sub>	% Si		Equiv. wt.	
							found	calc.	found	calc.
I	161.33	101	50	1.4427	0.8884	48.11	17.5	17.4	54.6	53.8
II	203.40	72-74	13	1.4423	0.8695	61.93	13.8	13.8	69.1	67.8
III	203.40	90	12	1.4380	0.8545	62.49	13.8	13.8	68.4	67.8
IV	245.48	120	11	1.4436	0.8545	76.25	11.5	11.4	82.3	81.8
V	245.48	101-02	12	1.4339	0.8332	76.69	11.4	11.4	82.1	81.8
VI	287.56	117-19	2	1.4474	0.8527	90.17	9.8	9.8	96.8	95.9
VII	287.56	140-41	12	1.4424	0.8466	89.94	9.8	9.8	96.5	95.9
VIII	287.56	130-31	12	1.4436	0.8473	90.08	9.9	9.8	96.2	95.9
IX	365.67	187-89	2	1.4916	0.9478	111.85	7.8	7.7	122.3	121.9
X	347.52	235	3				8.0	8.1	115.4	115.8 <sup>a</sup>
XI	323.58	172-75	2	1.5007	0.9696	98.27	8.6	8.7	109.5	107.9
XII	231.46	104	15	1.4414	0.8539	71.64	12.0	12.1	78.0	77.2
XIII	259.51	109-10	12	1.4415	0.8471	80.98	10.8	10.8	86.5	86.5
XIV	273.53	118-19	14	1.4404	0.8430	85.58	10.2	10.3	93.4	91.2
XV	231.46	108-09	15	1.4489	0.8684	71.48	12.1	12.1	77.7	77.2
XVI	273.53	125-26	15	1.4494	0.8595	85.43	10.2	10.3	93.0	91.2
XVII	341.56	204-05	10	1.5608	1.0155	108.89	8.2	8.2	113.2	113.9 <sup>a</sup>
XVIII	259.51	105-07	11	1.4375	0.8385	81.16	10.8	10.8	86.6	86.5
XIX	259.51	111-12	13	1.4412	0.8469	80.95	10.7	10.8	87.8	86.5
XX	287.56	131-32	15	1.4480	0.8564	89.89	9.7	9.8	96.3	95.9
XXI	367.68	188-89	8	1.494			7.5	7.6	126.0	122.6
XXII	293.52	153	10	1.5030	0.9352	92.78	9.6	9.6	96.8	97.8 <sup>a</sup>
									148.0	146.8

a) In non-aqueous medium

containing sufficient alcohol to give a homogeneous system throughout the titration (about 25 ml 96 % alcohol were used for 10 ml 0.1 N hydrochloric acid). With considerably less alcohol the solution became turbid during the titration and too high an equivalent weight resulted. In such a case an excess of hydrochloric acid had to be added and after digesting for several hours back-titration with standard base gave the expected equivalent weight, *i.e.*,  $M/3$  ( $M$  = molecular weight).

In an analogous way compounds of the types  $n\text{-C}_3\text{H}_7\text{Si}(\text{NHR})_2\text{Cl}$  and  $n\text{-C}_3\text{H}_7\text{Si}(\text{NHR})\text{Cl}_2$  gave equivalent weights =  $M$ , the first type with standard hydrochloric acid and the second type with standard base.

For the trianilino compound (X) a titration in a non-aqueous solvent had to be used. A weighed sample was dissolved in glacial acetic acid and titrated with standard perchloric acid in glacial acetic acid using methyl violet (violet to blue green) as the indicator giving an equivalent weight =  $M/3$ .

Compounds with aromatic amino groups and unexchanged chlorine atoms (XXV and XXX) were titrated in water. After agitating a weighed sample of the compounds in an excess of base and digesting for some hours back-titration with standard hydrochloric acid gave the expected equivalent weights.

For compounds with both aliphatic and aromatic amino groups (XVII and XXII) titration in water-alcohol mixture with standard hydrochloric acid and methyl red indicator gave equivalent weights corresponding to the aliphatic amino groups =  $M$  or  $M/2$ , and a non-aqueous titration as above gave equivalent weights =  $M/3$ , corresponding to the sum of amino groups.

Beside the analyses the following data are given in the tables: Boiling points, refractive indices (determined with an Abbe refractometer), densities (determined with an Ostwald-Sprengler pycnometer of a volume of 1.5 ml) and molecular refractivities (calculated from Lorenz-Lorentz formula).

Table 2. Physical constants of compounds containing silicon-chlorine bonds.

No.	M	B.p. °C	Pressure mm Hg	$n_D^{20}$	$d^{20}$	$MR_D$	% Si		Equiv. wt.	
							found	calc.	found	calc.
XXIII	250.89	118-19	15	1.4468	0.9153	72.89	11.1	11.2	251.5	250.9
XXIV	250.89	121	17	1.4530	0.9323	72.74	11.0	11.2	253.0	250.9
XXV	318.92	195-97	11	1.5675			8.8	8.8	319.9	318.9
XXVI	214.22	73-74	11				13.0	13.1	217.0	214.2
XXVII	214.22	86-88	17				13.1	13.1	213.9	214.2
XXVIII	242.26	105	15	1.4557	1.0192	64.58	11.5	11.6	244.0	242.3
XXIX	322.39	180-81	10	1.499			8.7	8.7	326.0	322.4
XXX	248.23	125	11				11.4	11.3	123.0	124.1

## Syntheses

All the reactions were performed in a three-necked flask equipped with a mechanical stirrer, a dropping funnel and a reflux condenser. The amine hydrochloride formed was filtered from the mixture on a fine-porous glass-filter in an atmosphere of dry air and was carefully washed with the solvent and dried before the weighing. The complete separation of amine hydrochloride sometimes caused considerable difficulty. If it was not completely removed, it contaminated the aminosilanes, subliming with them during the distillation. After the filtration the filtrate and wash-liquid were combined, and the solvent was removed at atmospheric pressure before distillation of the aminosilane at reduced pressure.

1. *n*-Propyltri-(methylamino)-silane (I). To an ice-cooled, vigorously stirred solution of about 30 g (1.0 mole) of methylamine in 150 ml of ether a solution of 17.8 g (0.1 mole) of *n*-propyltrichlorosilane in 50 ml of ether was added dropwise. After all had been added the stirring was continued, and the temperature was slowly raised by the removal of the ice-bath. Finally the stirred mixture was heated to reflux temperature for 2 h to remove the excess of methylamine. Filtration of the cooled mixture left 20.2 g (calc. 20.3 g) of methylamine hydrochloride on the filter. Distillation of the filtrate gave 14.2 g (88 %) of I.

2. *n*-Propyltri-(dimethylamino)-silane (II). Under exactly the same conditions as above 45 g (1.0 mole) of dimethylamine and 17.8 g (0.1 mole) of *n*-propyltrichlorosilane gave only 23.6 g (calc. 24.5 g) of dimethylamine hydrochloride, and 18 g of a product with an equivalent weight of 74 (calc. for II 67.8) was obtained. When this was again heated for 2 h in benzene containing dimethylamine, more amine hydrochloride was obtained; distillation gave 15.0 g (74 %) of II with the data given in Table 1. The observed difference in reactivity between dimethylamine and methylamine must be ascribed to the greater steric requirement of the former one.

3. *n*-Propyltri-(ethylamino)-silane (III). As described for the methylamine compound 44.4 g (0.25 mole) of *n*-propyltrichlorosilane in 50 ml of ether and about 90 g (2.0 moles) of ethylamine in 250 ml of the same solvent gave 61.2 g (calc. 61.2 g) of ethylamine hydrochloride and 47.2 g (93 %) of III.

4. *n*-Propyltri-(*n*-propylamino)-silane (IV). 17.8 g (0.1 mole) of *n*-propyltrichlorosilane in 50 ml of benzene were added to 53 g (0.9 mole) of *n*-propylamine in 100 ml of benzene. The mixture was refluxed for 2 h. Thereafter the excess of *n*-propylamine was distilled off. Filtration left 28.7 g (calc. 28.7 g) of *n*-propylamine hydrochloride on the filter, and fractionation of the filtrate gave 22.1 g (90 %) of IV.

5. *n*-Propyltri-(isopropylamino)-silane (V). In the same way 8.9 g (0.05 mole) of *n*-propyltrichlorosilane in 50 ml of ether and 30 g (0.5 mole) of isopropylamine in 75 ml of the same solvent gave 14.4 g (calc. 14.4 g) of isopropylamine hydrochloride and 10.5 g (86 %) of V.

6. *n*-Propyltri-(*n*-butylamino)-silane (VI). 8.9 g (0.05 mole) of *n*-propyltrichlorosilane in 75 ml of benzene were added to 37 g (0.5 mole) of *n*-butylamine in 100 ml of the same solvent. After refluxing for 2 h and cooling, filtration left 16.0 g (calc. 16.4 g) of *n*-butylamine hydrochloride on the filter; fractionation of the filtrate gave 11.1 g (77 %) of VI.

7. *n*-Propyltri-(*isobutylamino*)-silane (VII). In the same way 8.9 g (0.05 mole) of *n*-propyltrichlorosilane in 75 ml of benzene and 37 g (0.5 mole) of *isobutylamine* in 100 ml of the same solvent gave 16.4 g (calc. 16.4 g) of *isobutylamine* hydrochloride and 11.7 g (81 %) of VII.

8. *n*-Propyltri-(*sec*-butylamino)-silane (VIII). 7.1 g (0.04 mole) of *n*-propyltrichlorosilane in 50 ml of ether were added to 21.9 g (0.3 mole) of *sec*-butylamine in 50 ml of the same solvent. After refluxing for 1.5 h and cooling, filtration left 11.1 g (calc. 13.2 g) of *sec*-butylamine hydrochloride on the filter. A little more *sec*-butylamine was added to the filtrate, and the mixture was refluxed for 6 h. On cooling, filtration left 2.0 g of amine hydrochloride; distillation gave 7.8 g (68 %) of VIII.

9. *n*-Propyltri-(*cyclohexylamino*)-silane (IX). In exactly the same way 29.8 g (0.3 mole) of *cyclohexylamine* gave already after refluxing for 1 h the calculated amount of *cyclohexylamine* hydrochloride (16.3 g). From the filtrate 11.3 g (77 %) of IX were obtained.

10. *n*-Propyltrianilinosilane (X). 17.8 g (0.1 mole) of *n*-propyltrichlorosilane in 50 ml of ether were added dropwise to 70 g (0.75 mole) of aniline in 125 ml of the same solvent. The mixture was refluxed for 2 h. After cooling, filtration left 34.2 g (calc. 38.9 g) of aniline hydrochloride on the filter. After removal of the ether from the filtrate by distillation, the residual mixture was heated at about 100°C for 2 h. On cooling and addition of 150 ml of ether, filtration left another 4.6 g of amine hydrochloride on the filter. Fractionation gave 29.5 g (85 %) of X as a colourless, very viscous syrup, which soon achieved the yellow tint, which aniline usually has.

In another experiment the reactivity of aniline and *cyclohexylamine* was studied as follows. A mixture of 1.78 g (0.01 mole) of *n*-propyltrichlorosilane and 5.59 g (0.06 mole) of aniline in 25 ml of benzene was agitated for 15.0 min at room temperature and filtered. 1.95 g of aniline hydrochloride were left on the filter, which makes 50.1 % of the calculated amount according to formula (A). After standing for 12 h, 1.05 g more aniline hydrochloride were obtained, yielding a total of 77.1 %.

5.95 g (0.06 mole) of *cyclohexylamine* under exactly the same conditions gave 3.38 g (82.3 %) of *cyclohexylamine* hydrochloride and after 12 h 0.59 g. This makes a total of 97.5 % of the calculated amount. Therefore it must be concluded that *cyclohexylamine* reacts more readily than aniline with *n*-propyltrichlorosilane.

11. *n*-Propyltripiperidinosilane (XI). 17.8 g (0.1 mole) of *n*-propyltrichlorosilane in 50 ml of benzene were added to 60 g (0.7 mole) of piperidine in 100 ml of the same solvent, and the mixture was refluxed for 5 h. Filtration of the cooled mixture left 34.0 g (calc. 36.5 g) of piperidine hydrochloride. The filtrate was again refluxed for 5 h, and filtration then gave 2.3 g more amine hydrochloride. From the filtrate 22.0 g (68 %) of XI were obtained.

12. *n*-Propyl-di-(*tert*-butylamino)-chlorosilane (XXIII). In the same way 17.8 g (0.1 mole) of *n*-propyltrichlorosilane and 55 g (0.75 mole) of *tert*-butylamine after refluxing for 2 h gave 22.5 g of *tert*-butylamine hydrochloride. This is in agreement with the calculated amount for the replacement of only two of the chlorine atoms in *n*-propyltrichlorosilane (21.9 g). The filtrate did not give more amine hydrochloride even when refluxed for 10 h. On fractionation of the mixture 20.5 g (81 %) of XXIII were obtained.

12.5 g (0.05 mole) of XXIII were heated with 11 g (0.15 mole) of *tert*-butylamine and 50 ml of benzene in a steel-bomb at about 160°C for 8 h. Only traces of amine hydrochloride were formed, and XXIII could be recovered by distillation. Thus it must be concluded that *n*-propyltri-(*tert*-butylamino)-silane cannot be obtained in this way.

13. *n*-Propyl-di-(*tert*-butylamino)-aminosilane (XII). 10.0 g (0.04 mole) of XXIII in 50 ml of ether were added dropwise to about 50 ml of liquid ammonia, cooled in a dry ice and acetone bath. The temperature was slowly raised to room temperature, and the mixture was at last refluxed for 1 h to remove the excess of ammonia. Filtration left 2.1 g (calc. 2.1 g) of ammonium chloride on the filter, and distillation of the filtrate gave 6.5 g (70 %) of XII.

14. *n*-Propyl-di-(*tert*-butylamino)-(ethylamino)-silane (XIII). 5.0 g (0.02 mole) of XXIII dissolved in 15 ml of ether were added to an ether solution containing excess of ethylamine. After stirring at room temperature for about half an hour, the excess of ethylamine was removed. Filtration left 1.6 g (calc. 1.6 g) of ethylamine hydrochloride on the filter, and on fractionation of the filtrate 4.6 g (89 %) of XIII were obtained.

15. *n*-Propyl-di-(tert.-butylamino)-(isopropylamino)-silane (XIV). 10.0 g (0.04 mole) of XXIII in 25 ml of benzene were added to 7 g (0.12 mole) of isopropylamine in 40 ml of the same solvent. No amine hydrochloride precipitated until the mixture had been heated for a while. After refluxing for 1.5 h and removal of the excess of isopropylamine, filtration left only 1.8 g (calc. 3.8 g) of isopropylamine hydrochloride on the filter. 7 g of isopropylamine were added to the filtrate, and the mixture was refluxed for 15 h. The excess of isopropylamine was again distilled off. Filtration now left another 1.9 g, and from the filtrate 8.0 g (73 %) of XIV were obtained.

*n*-Propylamine and *n*-butylamine gave immediately a heavy precipitate of amine hydrochloride when XXIII, dissolved in benzene, was added to their benzene solutions. The low reactivity of isopropylamine may be attributed to its steric properties.

16. *n*-Propyl-(tert.-butylamino)-dichlorosilane (XXVI). This compound was obtained by the addition dropwise of 36.5 g (0.5 mole) of tert.-butylamine in 75 ml of ether to 44.4 g (0.25 mole) of *n*-propyltrichlorosilane in 75 ml of the same solvent and refluxing for 1.5 h. Filtration left 27.3 g (calc. 27.4 g) of tert.-butylamine hydrochloride, and distillation of the filtrate gave 36.0 g (67 %) of XXVI.

17. *n*-Propyl-(tert.-butylamino)-di-(isopropylamino)-silane (XVIII). 10.7 g (0.05 mole) of XXVI in 50 ml of benzene were added to 15 g (0.25 mole) of isopropylamine in 50 ml of the same solvent. After refluxing for 1.5 h and removal of the excess of isopropylamine, filtration left 9.6 g (calc. 9.6 g) of isopropylamine hydrochloride. Thus it is seen that the chlorine is more easily replaced by isopropylamine in XXVI than in XXIII. From the filtrate 9.9 g (76 %) of XVIII were obtained.

18. *n*-Propyl-di-(diethylamino)-chlorosilane (XXIV). 17.8 g (0.1 mole) of *n*-propyltrichlorosilane in 50 ml of benzene were added to 59 g (0.8 mole) of diethylamine in 75 ml of the same solvent. Thereafter the mixture was refluxed for 4.5 h. After the excess of diethylamine had been removed by distillation, filtration left 22.4 g of diethylamine hydrochloride on the filter. This corresponds with the calculated amount for the replacement of only two chlorine atoms in *n*-propyltrichlorosilane (21.9 g), and no more amine hydrochloride precipitated on further refluxing with diethylamine in benzene. Fractionation gave 18.5 g (73 %) of XXIV. The resistance of this compound against further reaction with diethylamine was illustrated in the same way as for XXIII.

19. *n*-Propyl-di-(diethylamino)-aminosilane (XV). This substance was prepared as described for XII from 5.0 g (0.02 mole) of XXIV giving 1.1 g (calc. 1.1 g) of ammonium chloride and 3.2 g (69 %) of XV.

20. *n*-Propyl-di-(diethylamino)-isopropylaminosilane (XVI). 8.3 g (0.033 mole) of XXIV were refluxed with 12 g (0.2 mole) of isopropylamine in 50 ml of benzene for 20 h, and then the excess of isopropylamine was removed. Filtration left 3.1 g (calc. 3.2 g) of isopropylamine hydrochloride on the filter, and from the filtrate 5.8 g (64 %) of XVI were obtained.

21. *n*-Propyl-(diethylamino)-dichlorosilane (XXVII). This substance was prepared as described for XXVI from 35.5 g (0.2 mole) of *n*-propyltrichlorosilane in 90 ml of benzene and 30 g (0.41 mole) of diethylamine in 100 ml of the same solvent. Filtration left 21.4 g (calc. 21.9 g) of diethylamine hydrochloride and 31.0 g (72 %) of XXVII were obtained.

22. *n*-Propyl-(diethylamino)-di-(isopropylamino)-silane (XIX). As described for the preparation of XVIII, 10.7 g (0.05 mole) of XXVII and 15 g (0.25 mole) of isopropylamine gave 9.5 g (calc. 9.6 g) of isopropylamine hydrochloride and 10.7 g (82 %) of XIX.

23. *n*-Propyl-(di-isopropylamino)-dichlorosilane (XXVIII). 60.7 g (0.6 mole) of di-isopropylamine in 75 ml of benzene were added dropwise to 53.3 g (0.3 mole) of *n*-propyltrichlorosilane in 100 ml of the same solvent. The mixture was then refluxed for 1 h. Filtration left di-isopropylamine hydrochloride on the filter, which even after ordinary washing contained some grams of a material containing silicon (total weight 45.2 g; calc. for the replacement of one of the chlorine atoms in *n*-propyltrichlorosilane 41.3 g). From the filtrate 38.3 g (53 %) of XXVIII were obtained. When this substance was refluxed for several hours with di-isopropylamine in benzene, only a very small amount of amine hydrochloride was formed.

In another experiment 18.2 g (0.075 mole) of XXVIII and 20 g (0.2 mole) of di-isopropylamine in 50 ml of benzene were heated to about 170°C for 15 h in a steel-bomb. Only 0.4 g of amine hydrochloride was formed. — Therefore it must be concluded that *n*-propyl-di-(di-isopropylamino)-chlorosilane cannot be obtained in reasonable yield in this way.

24. *n*-Propyl-(di-isopropylamino)-di-(isopropylamino)-silane (XX). 9.7 g (0.04 mole) of XXVIII and 18 g (0.3 mole) of isopropylamine in 50 ml of ether were refluxed for 1 h. Filtration of the cooled mixture left 6.0 g (calc. for total replacement 7.7 g) of isopropylamine hydrochloride. The ether was distilled off from the filtrate, and 50 ml of benzene containing about 10 g of isopropylamine were added to the rest. After refluxing for about 5 h and removal of the excess of isopropylamine, a new filtration left the expected amount of isopropylamine hydrochloride (1.6 g). From the filtrate 6.5 g (57 %) of XX were obtained.

25. *n*-Propyl-(di-cyclohexylamino)-dichlorosilane (XXIX). 35.5 g (0.2 mole) of *n*-propyltrichlorosilane in 75 ml of benzene were added dropwise to 81.6 g (0.45 mole) of di-cyclohexylamine in 100 ml of benzene. Amine hydrochloride was immediately formed. After refluxing for 5 h, filtration left 44.0 g (calc. 43.6 g) of di-cyclohexylamine hydrochloride on the filter. On fractionation of the filtrate 44.1 g (68 %) of XXIX were obtained. 16.1 g (0.05 mole) of this substance were refluxed with 22 g (0.12 mole) of di-cyclohexylamine in 100 ml of benzene for 8 h, but no more amine hydrochloride was formed. Thereafter the benzene was distilled off and the rest was heated at 180°C for 12 h, but even now only traces of amine hydrochloride were formed. Thus it is seen that *n*-propyldi-(di-cyclohexylamino)-chlorosilane cannot be obtained in reasonable yield in this way.

26. *n*-Propyl-(di-cyclohexylamino)-di-(isopropylamino)-silane (XXI). A mixture of 16.1 g (0.05 mole) of XXIX and 24 g (0.4 mole) of isopropylamine in 100 ml of benzene were refluxed for 15 h, and then the excess of isopropylamine was removed. Filtration of the cooled mixture left 9.3 g (calc. 9.6 g) of isopropylamine hydrochloride, and from the filtrate 14.0 g (77 %) of XXI were obtained.

27. *n*-Propyltrichlorosilane and diphenylamine. 8.9 g (0.05 mole) of *n*-propyltrichlorosilane in 25 ml of benzene were added to 34 g (0.2 mole) of diphenylamine in 100 ml of the same solvent. No reaction could be observed at room temperature, so it is evident that the reactivity of diphenylamine is much less than that of di-isopropylamine and di-cyclohexylamine. Since the steric properties of these amines are of about the same order, the difference may be attributed to the difference in their base strength. Even after refluxing for 8 h and cooling no solid precipitated, and on fractionation more than 8 g of the *n*-propyltrichlorosilane could be recovered.

28. *n*-Propyl-(*N*-methylanilino)-dichlorosilane (XXX). 8.9 g (0.05 mole) of *n*-propyltrichlorosilane in 25 ml of benzene were added to 27 g (0.25 mole) of *N*-methylaniline in 50 ml of benzene. The precipitate of *N*-methylaniline hydrochloride, which was first formed, dissolved on heating of the mixture to reflux. After refluxing for 4.5 h and cooling of the mixture, filtration left 6.4 g (calc. for the replacement of one of the chlorine atoms in *n*-propyltrichlorosilane 7.2 g). The filtrate was again refluxed for 20 h, and filtration now left 1.2 g of amine hydrochloride. Reflux of the filtrate for another 22 h caused the formation of only about 0.5 g of amine hydrochloride, so it is evident that the second chlorine atom in *n*-propyltrichlorosilane is difficultly replaced by *N*-methylaniline. If the benzene is distilled off and the residue is heated to reflux of the *N*-methylaniline for several hours, more amine hydrochloride is formed and *n*-propyldi-(*N*-methylanilino)-chlorosilane (XXV) can be obtained in reasonable yield from the reaction mixture.

In another experiment 43 g (0.4 mole) of *N*-methylaniline in 50 ml of ether were added dropwise to 35.5 g (0.2 mole) of *n*-propyltrichlorosilane in 100 ml of ether. After refluxing for 2.5 h, filtration of the cooled mixture left 22.9 g (calc. 23.7 g) of *N*-methylaniline hydrochloride on the filter. The ether was distilled off from the filtrate, and the residue was heated to about 100°C for 2 h. After cooling the ether was again added, and filtration now left 2.0 g of amine hydrochloride. The ether was again distilled off, and refluxing for about 5 h now left 3.1 g of amine hydrochloride on the filter (totally 23.0 g). Distillation of the filtrate gave 32.1 g (65 %) of XXX.

29. *n*-Propyl-(*N*-methylanilino)-di-(isopropylamino)-silane (XXII). 12.4 g (0.05 mole) of XXX in 50 ml of benzene were added to 24 g (0.4 mole) of isopropylamine in 50 ml of benzene. After refluxing for 8 h and removal of the excess of isopropylamine, filtration left 9.5 g (calc. 9.6 g) of isopropylamine hydrochloride on the filter. From the filtrate 12.0 g (82 %) of XXII were obtained.

30. *n*-Propyldi-(*N*-methylanilino)-chlorosilane (XXV). 21 g (0.2 mole) of *N*-methylaniline were added to 20.0 g (0.089 mole) of XXX in 100 ml of ether. After refluxing for 3 h, only traces of *N*-methylaniline hydrochloride had precipitated. Therefore the ether



was distilled off, and the residual mixture was heated to about 100°C for 8 h. When the ether was again added to the cooled mixture, 3.5 g of amine hydrochloride were obtained on filtration. After repeating the same procedure, 2.5 g of amine hydrochloride were left on the filter. On fractionation of the filtrate about 4 g of XXX and 5.1 g (20 %) of XXV were obtained.

31. *n*-Propyl-di-(*N*-methylanilino)-(isopropylamino)-silane (XVII). 4.2 g (0.013 mole) of XXV and 9 g (0.15 mole) of isopropylamine in 50 ml of benzene were refluxed for 10 h, and the excess of isopropylamine was removed. Filtration left 1.2 g (calc. 1.3 g) of isopropylamine hydrochloride, and from the filtrate 3.5 g (78 %) of XVII were obtained.

32. *n*-Propyltrichlorosilane and tertiary amines. When *n*-propyltrichlorosilane was added to absolutely dry trimethylamine, triethylamine or pyridine in ether or benzene solution, no reaction was observed in any case and the *n*-propyltrichlorosilane could be recovered by distillation.

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