

N-Substituted Alkyltriaminosilanes

II. On the Reaction of N-Substituted *n*-Propyltriaminosilanes with Amines

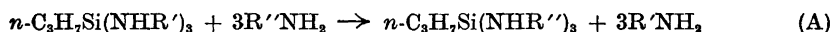
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As a part of an investigation on aminosilanes the reaction between N-substituted *n*-propyltriaminosilanes and some amines was studied. These reactions are apparently catalyzed by hydrogen ion and observations were made which indicate influence by the steric properties of the reagents.

The preparation of *n*-propyltri-(*n*-amylamino)-silane, *n*-propyltri-(*n*-hexylamino)-silane and *n*-propyltri-(benzylamino)-silane is described.

In Part I¹ of this work the author described the reaction of *n*-propyltrichlorosilane with various primary and secondary amines to give N-substituted *n*-propyltriaminosilanes. The great reactivity of the Si—N bonds in these compounds has now been used for the preparation of some compounds of this type by an exchange reaction according to the formula



The method has earlier been extensively used for the preparation of N-substituted trialkylaminosilanes, dialkyldiaminosilanes and diphenyldiaminosilanes²⁻⁸.

As it can be assumed that reaction (A) is reversible, it is desirable — in order to obtain good yields — to employ an excess of R'NH₂ and to choose R' so that liberated R'NH₂ can be easily removed from the reaction mixture. Of the compounds described in Part I, therefore, only *n*-propyltri-(methylamino)-silane and *n*-propyltri-(ethylamino)-silane were used. They reacted on heating with an excess of *n*-butylamine, *n*-amylamine, *n*-hexylamine, benzylamine, cyclohexylamine and aniline to give the following compounds

- I $n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_4\text{H}_9\text{-}n)_3$
 II $n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_6\text{H}_{11}\text{-}n)_3$
 III $n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_6\text{H}_{13}\text{-}n)_3$
 IV $n\text{-C}_3\text{H}_7\text{Si}(\text{NHCH}_2\text{C}_6\text{H}_5)_3$
 V $n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_6\text{H}_{11})_3$
 VI $n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_6\text{H}_5)_3$

II—IV have not earlier been reported in the literature. Their physical constants and analyses are given in Table 1. I, V and VI were earlier prepared in Part I of this work.

Table 1. Physical constants and analyses of $n\text{-C}_3\text{H}_7\text{Si}(\text{NHR}')_3$

No.	M	B.p. °C	Pressure mm Hg	n_D^{20}	d_4^{20}	MR_D	% Si		Equiv.wt.	
							found	calc.	found	calc.
II	329.64	164—65	3	1.4503	0.8516	104.08	8.6	8.5	110.2	109.9
III	371.72	182—83	2	1.4527	0.8507	118.04	7.6	7.6	123.6	123.9
IV	389.60	216—18	1	1.5665	1.0503	121.09	7.2	7.2	131.5	129.9

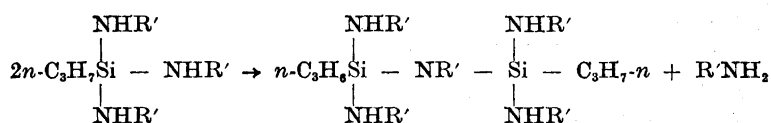
n -Propyltri-(methylamino)-silane and n -propyltri-(ethylamino)-silane both failed to react with N -methylaniline, which may be ascribed to the steric requirement of the bulky groups in this amine. That reaction (A) is influenced by steric effects is also supported by the fact that *cyclohexylamine* which reacted with n -propyltri-(ethylamino)-silane failed to react with n -propyltri-(*isopropylamino*)-silane.

Addition of a proton donor to the reaction mixture considerably accelerated reaction (A). Thus with a small amount of ammonium chloride or ammonium sulfate present, there was in all reactions a pronounced increase in the rate of liberation of $R'\text{NH}_2$. In the presence of one of these proton donors *cyclohexylamine* reacted readily even with n -propyltri(*iso*-propylamino)-silane. With still more bulky groups around the silicon atom, however, as in n -propyltri(*tert.*-butylamino)-silane, the reaction with *cyclohexylamine* seemed to be quite impeded even in the presence of these accelerators. With a small amount of ammonium sulfate added, even N -methylaniline liberated some ethylamine from n -propyltri-(ethylamino)-silane, but complete reaction was not obtained even on prolonged heating of the reaction mixture. In general ammonium sulfate was found to be more convenient as proton donor than amine hydrochlorides which during the course of the reactions partly sublimed into the reflux condenser.

The accelerating effect of protons on the reactions of aminosilanes with amines has been reported in the literature prior to this work. Thus Langer, Conell and Wender⁸ recently demonstrated a pronounced catalytic effect by hydrogen or ammonium ion on the reaction between hexamethyldisilazane and primary amines, and Speier, Zimmerman and Webster⁹ recognized this catalysis in the preparation of allylaminotrimethylsilane from hexamethyldisilazane and allylamine.

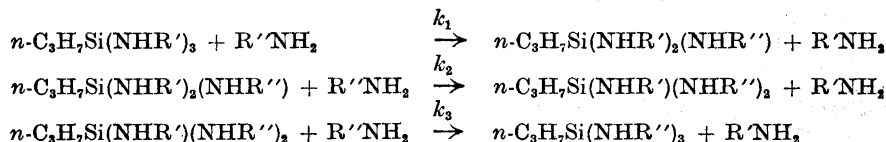
In the presence of a proton donator the initial step in reaction (A) seems to be the formation of an ion, $\text{Si}-\overset{+}{\text{N}}\text{H}_2\text{R}'$, which on the following nucleophilic attack from $\text{R}''\text{NH}_2$ splits off $\text{R}'\text{NH}_2$. The fact that aminosilanes do not give hydrochlorides with hydrogen chloride but are spontaneously converted to chlorosilanes by this reagent demonstrates clearly the great reactivity of the $\text{Si}-\overset{+}{\text{N}}$ bond.

n-Propyltri-(methylamino)-silane and *n*-propyltri-(ethylamino)-silane could both be refluxed for several hours without any liberation of methylamine or ethylamine, which indicates that the rate of the intermolecular condensation reaction, the first step of which would be



is very low. Thus it is evident that such a reaction will not accompany reaction (A) to any great extent. As can be expected, however, also the condensation reaction is catalyzed by hydrogen ion. This will be further described in a later part of this work.

Reaction (A) can be considered as the sum of three consecutive competitive reactions:



Therefore, if the reaction is performed with a mole ratio $\text{R}''\text{NH}_2 : n\text{-C}_3\text{H}_7(\text{NHR}')_3$ less than 3:1, a mixture of four compounds will result. The relative amounts of these compounds will depend on the ratio $k_1:k_2:k_3$ between the rate constants of the competitive reactions above. This was demonstrated in the case of *n*-hexylamine and *n*-propyltri-(ethylamino)-silane, which were mixed in the mole ratio 1:1 and heated in the presence of some ammonium chloride giving a mixture containing all the expected compounds.

The conceivable redistribution between two aminosilanes of the type $n\text{-C}_3\text{H}_7\text{Si}(\text{NHR}')_3$ with different R' -groups was studied in the case of *n*-propyltri-(ethylamino)-silane and *n*-propyltri-(*n*-amylamino)-silane. These compounds could be refluxed together for several hours without any noteworthy change. In the presence of some ammonium sulfate, however, heating to reflux temperature for a few hours caused redistribution resulting in a mixture of the expected four compounds.

EXPERIMENTAL

The method of the determination of the physical data of the compounds and the analyses have been previously described¹. The preparation of *n*-propyltri-(*tert.*-butylamino)-silane will be described in the next part of this work.

n-Propyltri-(*n*-butylamino)-silane (I). A mixture of 3.2 g (0.02 mole) of *n*-propyltri-(methylamino)-silane and 5.9 g (0.08 mole) of *n*-butylamine was heated to reflux temperature for one hour in the presence of 0.1 g of ammonium chloride. Distillation of the reaction mixture gave 4.0 g (70 %) of I, b.p. 159–161°/12 mm, $n_D^{20} = 1.4472$, $d_4^{20} = 0.8525$, equiv. wt. 96.0 (calc. 95.9).

n-Propyltri-(*n*-amylamino)-silane (II). A mixture of 3.2 g (0.02 mole) of *n*-propyltri-(methylamino)-silane and 8.7 g (0.1 mole) of *n*-amylamine was heated in a flask equipped with thermometer and reflux condenser. Liberated methylamine was titrated with standard hydrochloric acid using methyl red as the indicator. Sixty five per cent of the expected amount of methylamine escaped from the reaction vessel during a period of 1.5 h, and during that time the reflux temperature rose from 108 to 122°. After cooling about 0.1 g of methylamine hydrochloride was added to the reaction mixture. On heating methylamine evolution began below 100° and the expected amount of it was liberated within 15 min. Distillation of the reaction mixture gave 4.9 g (74 %) of II.

In another experiment a mixture of 2.0 g (0.01 mole) of *n*-propyltri-(ethylamino)-silane and 4.4 g (0.05 mole) of *n*-amylamine was heated to reflux temperature for one hour. Only about 30 % of the calculated amount of ethylamine were liberated. On addition of 10 mg of ammonium sulfate to the reaction mixture, however, the rest of the ethylamine disappeared within 30 min.

n-Propyltri-(*n*-hexylamino)-silane (III). 3.1 g (0.015 mole) of *n*-propyltri-(ethylamino)-silane and 7.6 g (0.075 mole) of *n*-hexylamine were heated at about 125° for one hour. The liberated amount of ethylamine during that period corresponded to only 20 % of the expected amount. After addition of 50 mg of ammonium sulfate to the reaction mixture gas evolution began at about 100° and the rest of the ethylamine disappeared within 25 min. Distillation of the reaction mixture gave 4.2 g (75 %) of III.

n-Propyltri-(benzylamino)-silane (IV). A mixture of 2.0 g (0.01 mole) of *n*-propyltri-(ethylamino)-silane, 4.3 g (0.04 mole) of benzylamine and 20 mg of ammonium sulfate gave upon heating to reflux temperature for 45 min the expected amount of ethylamine. On distillation of the reaction mixture 3.0 g (77 %) of IV were obtained.

n-Propyltri-(cyclohexylamino)-silane (V). 7.9 g (0.08 mole) of cyclohexylamine liberated on heating to reflux temperature for one hour about 30 % of the expected amount of ethylamine from 4.1 g (0.02 mole) of *n*-propyltri-(ethylamino)-silane. On addition of 50 mg of ammonium sulfate to the reaction mixture complete reaction was obtained after reflux for one hour. Distillation gave 6.1 g (83 %) of V, b.p. 192–93°/3 mm, $n_D^{20} = 1.4918$, $d_4^{20} = 0.9479$, equiv. wt. 121.6 (calc. 121.9).

n-Propyltri(aminosilane (VI). 3.2 g (0.02 mole) of *n*-propyltri-(methylamino)-silane and 7.4 g (0.08 mole) of aniline were heated to reflux temperature for one hour. About 50 % of the expected amount of methylamine were evolved. On addition of 50 mg of ammonium sulfate the rest of the methylamine evolved in 20 min on heating to reflux temperature. Distillation gave 5.4 g (78 %) of VI, b.p. 220°/2 mm, equiv. wt. 115.3 (calc. 115.8).

Reaction with N-methylaniline. A mixture of *n*-propyltri-(methylamino)-silane and *N*-methylaniline did not react after 6 h of reflux. In another experiment 3.1 g (0.015 mole) of *n*-propyltri-(ethylamino)-silane and 8.0 g (0.075 mole) of *N*-methylaniline were heated to reflux temperature for 8 h without reaction. On addition of 50 mg of ammonium sulfate to the reaction mixture 50 % of the amount of the ethylamine, calculated for complete reaction, were liberated on heating to reflux temperature for 6 h. On fractionation of the mixture most of the *N*-methylaniline was recovered. Between 160 and 200° at 10 mm Hg 2.0 g of a substance was obtained which contained *N*-methylaniline and may have been a mixture of *n*-propyl-(*N*-methylanilino)-di-(ethylamino)-silane and *n*-propyldi-(*N*-methylanilino)-(ethylamino)-silane. It is probable that the evolution of ethylamine was partly due to an intermolecular condensation of *n*-propyltri-(ethylamino)-silane.

Reaction of cyclohexylamine with n-propyltri-(isopropylamino)-silane and n-propyltri-(tert.-butylamino)-silane. No isopropylamine distilled from the reaction mixture when

7.9 g (0.08 mole) of cyclohexylamine and 4.9 g (0.02 mole) of *n*-propyltri-(isopropylamino)-silane were heated to 125° for 4 h. On addition of 50 mg of ammonium sulfate to the reaction mixture more than 90 % of the calculated amount of isopropylamine distilled over on heating to 115° for one hour. From *n*-propyltri-(*tert.*-butylamino)-silane, however, under the same conditions no liberation of *tert.*-butylamine occurred on prolonged heating to 125°, even in the presence of some ammonium sulfate.

n-Propyltri-(ethylamino)-silane and *n*-hexylamine. 30.5 g (0.15 mole) of *n*-propyltri-(ethylamino)-silane and 15.2 g (0.15 mole) of *n*-hexylamine were heated for 2 h to reflux temperature in the presence of about 0.1 g (0.002 mole) of ammonium chloride. The calculated amount of ethylamine (0.15 mole) was liberated, most of this during the first 45 min. The precipitate was filtered from the reaction mixture. On distillation at 11 mm Hg the following fractions were obtained:

A:	90—95°	7.2 g	equiv.wt. = 68.1
B:	95—135	1.9 g	» = 82.7
C:	135—137	11.1 g	» = 86.3
D:	137—180	3.1 g	» = 89.7
E:	180—182	9.3 g	» = 105.3
F:	182—200	1.8 g	» = 111.3
G:	dist. residue	2.2 g	» = 179

The following compounds, E_i = equiv.wt., can be expected to be present in the reaction mixture:

$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_2\text{H}_5)_3$	$E_1 = 67.8$
$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_2\text{H}_5)_2(\text{NHC}_6\text{H}_{13}\text{-}n)$	$E_2 = 86.5$
$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_2\text{H}_5)(\text{NHC}_6\text{H}_{13}\text{-}n)_2$	$E_3 = 105.2$
$n\text{-C}_3\text{H}_7\text{Si}(\text{NHC}_6\text{H}_{13}\text{-}n)_3$	$E_4 = 123.9$

The found equivalent weights of the fractions seem to indicate that:

A = E_1
B = E_1 (0.3 g) and E_2 (1.6 g)
C = E_2
D = E_2 (2.5 g) and E_3 (0.6 g)
E = E_3
F = E_3 (1.1 g) and E_4 (0.7 g)

If it is further assumed that G is a mixture of E_4 (1.5 g) and products of total hydrolysis (0.7 g) the following compounds seem to have been formed:

7.2 + 0.3	= 7.5 g of $E_1 = 0.037$ mole
11.1 + 1.6 + 2.5	= 15.2 g » $E_2 = 0.059$ »
9.3 + 0.6 + 1.1	= 11.0 g » $E_3 = 0.035$ »
and about 2 g	» $E_4 = 0.005$ »
	<hr/> Sum: 0.136 mole

If $k_1:k_2:k_3$ is 3:2:1, *i. e.*, if the difference in steric and polar properties of the species are neglected, it can be shown¹⁰ that $E_1:E_2:E_3:E_4$ would be 8:12:6:1. For 0.15 mole of starting material this makes $E_1 = 0.044$; $E_2 = 0.067$; $E_3 = 0.033$ and $E_4 = 0.006$ mole.

Fraction C, which was assumed to be E_2 , had $n_D^{20} = 1.4455$; $d^{20} = 0.8532$; $MR_D = 81.02$; E, which was assumed to be E_3 , had $n_D^{20} = 1.4499$; $d^{20} = 0.8521$; $MR_D = 99.51$.

Redistribution. 11.8 g (0.058 mole) of *n*-propyltri-(ethylamino)-silane and 15.3 g (0.041 mole) of *n*-propyltri-(*n*-amylamino)-silane were heated to reflux temperature for 3 h. On distillation most of the starting materials were recovered. Less than one g of substance was obtained between 100—200° at 12 mm Hg, so it is evident that redistribution had occurred only to a very small extent. In another experiment, however, 8.1 g (0.04 mole) and 13.2 g (0.04 mole), respectively of the compounds were heated to reflux

temperature for 3 h in the presence of 20 mg of ammonium sulfate. Now distillation of the reaction mixture gave: 92–127°: 1.0 g, E = 72.3; 127–136°: 2.4 g, E = 82.2; 136–162°: 2.7 g, E = 86.5; 162–170°: 4.3 g, E = 95.0; 170–185°: 2.8 g, E = 98.2; 185–205°: 2.4 g, E = 100.1, and distillation residue 3.0 g, so it is evident that under these conditions redistribution had occurred. Some ethylamine was liberated during the course of reaction, which seems to indicate that the reaction was accompanied by an intermolecular condensation reaction.

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