

On the Reactions of N-substituted Alkyltriaminosilanes. V

LEWI TANSJÖ

Department of Organic Chemistry, University of Lund, Lund, Sweden

The reactions of N-substituted alkyltriaminosilanes with water, alcohols, phenol, acetic acid, acetic anhydride and hydrogen halides are described. On the reaction with hydrogen fluoride observations were made which indicate the existence of compounds containing the alkyl- or arylpentafluorosilicate ion, RSiF_5^{2-} , analogous to the hexafluorosilicate ion, SiF_6^{2-} , in which silicon uses two of its five *d*-orbitals for bonding.

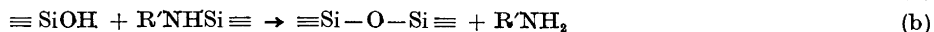
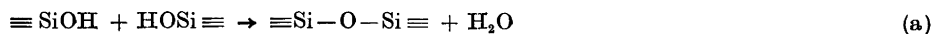
In this paper will be described some reactions of N-substituted alkyltriaminosilanes the preparations of which were previously published¹⁻⁴. This purpose was partly anticipated in Parts II² and IV⁴ of this work where their reactions with amines and their intermolecular condensations were investigated. Some of the reactions below are well known from the field of dialkyl- and trialkylamino-silanes (Ref.⁵, Chapter 11) and can be treated briefly here.

When brought into solution, by adding an alcohol, for example, N-substituted *n*-propyltriaminosilanes, $n\text{-C}_3\text{H}_7\text{Si}(\text{NHR}')_3$, react with water to give high polymeric "*n*-propylsiliconic acid", but the sensitivity of hydrolysis is markedly governed by the size of the groups on the nitrogen atoms being greatest for *n*-propyltri-(methylamino)-silane and successively less for compounds with larger R' groups. *n*-Propyltri-(*tert.*-butylamino)-silane and *n*-propyltri-(diethylamino)-silane, for example, are rather stable to 90 % alcohol, in which the corresponding methylamine and ethylamine compounds react vigorously. In acidic medium, however, even the sterically-hindered compounds above are immediately hydrolyzed which is demonstrated by the fact that they can be directly titrated with standard hydrochloric acid which involves the breaking of the Si-N bonds.

1.5 molar equivalents of water is sufficient to give complete hydrolysis of a triamino-silane according to the equation



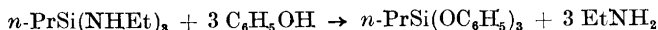
Two types of condensation reactions may be involved in building up the polymeric $\text{RSiO}_{1.5}$, namely



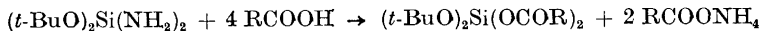
It was found that even if the hydrolysis was performed with less than 1.5 molar equivalents of water in ether solution, *n*-propyltri-(ethylamino)-silane gave very poor yields of distillable, partially hydrolysed products. This indicates that when some of the ethylamino groups are removed the intermediate hydrolysis products are much more susceptible than the remaining triaminosilane to further attack of water and/or to intermolecular condensation of the type (b) above.

n-Propyltri-(methylamino)-silane reacted spontaneously with ethanol and benzyl alcohol and complete alcoholysis was obtained on heating the reaction mixtures to reflux temperature for a short time giving the trialkoxy compounds in good yields. With the bulky *tert.*-butanol, however, only one of the methyl amino groups was replaced after prolonged heating with excess of the alcohol and the ethylamine compound was still more resistant to this alcohol.

n-Propyltri-(ethylamino)-silane reacted with phenol in a manner analogous to the reaction with alcohols to give *n*-propyltriphenoxysilane in good yield:



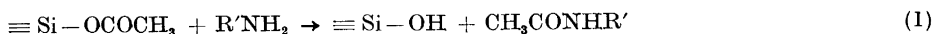
Miner *et al.*⁶ stated that *tert.*-alkoxyaminosilanes react with organic acids to form the corresponding acyloxysilanes: *e.g.*



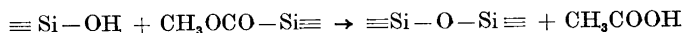
but no experiments were described to authorize this course of reaction. Organosilicon compounds have been supposed to react in an analogous way with organic acids (Ref.⁵, p. 347). It is therefore noteworthy that no alkyltriacetoxysilane could be isolated after the reaction of N-substituted alkyltriaminosilanes with acetic acid. *n*-Propyltribenzylaminosilane, for example, reacted readily with acetic acid to give a reaction mixture containing benzylamine hydroacetate, N-benzylacetamide and polysiloxanes. In another experiment ethyltriacetoxysilane was shown to react with benzylamine hydroacetate with the formation of N-benzylacetamide and acetic acid. These observations make the following course of the reaction between a N-substituted alkyltriaminosilane and acetic acid plausible: First alkyltriacetoxysilane is formed according to the equation



which then reacts with R'NH₂, liberated by a small degree of dissociation of the hydroacetate:

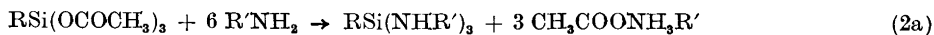


That not all of the hydroacetate is used up to give silanol and amide according to eqn. (1) may be explained as a result of intermolecular condensation of silanol and acetoxysilane:



According to eqn. (1) alkyltriacetoxysilanes would act as acylating agents, the carbonyl carbons of the silyl ester being attacked by the nucleophilic R'NH₂. But the silicon atom of organosilicon compounds is normally very

susceptible to attack by nucleophilic agents so there would exist two possibilities for a nucleophilic replacement in an alkyltriacetoxysilane as represented in the equations (2a) (attack on the silicon) and (2b) (attack on the carbonyl carbons):



In excess of amine (2a) and (2b) can both be expected to considerably lower the free energy of the system (and (2b), which includes the formation of "silicic acid", can be predicted to give the lowest one). Then the reaction which is represented by the lowest energy of the transition state would first occur. If the silicon atom is more susceptible to nucleophilic attack than the carbonyl carbons Fig. 1a would give a rough picture of the energy-profiles of the reactions — curve T_1 representing reaction (2a) and curve T_2 representing (2b). According to Fig. 1b the carbonyl carbons would be more electrophilic than the silicon atom.

Experiments were performed in which ethyltriacetoxysilane was added to excess of benzylamine in benzene. A precipitate of benzylamine hydroacetate was formed immediately. In different experiments it was, however, always found that the weight of hydroacetate corresponded to 50 % of the weight calculated for the reaction (2a). N-Benzylacetamide and polysiloxanes were also found in the reaction mixture. Leaving out of consideration the possibility that the silicon atom and the carbonyl carbons would be equally susceptible to nucleophilic attack the following hypothesis can be proposed on the course of reaction:

First reaction (2a) occurs establishing very rapidly an equilibrium the composition of which corresponds to a high per cent of aminosilane. The acetoxy groups left on the silicon atom react in a slower reaction according to eqn. (2b)

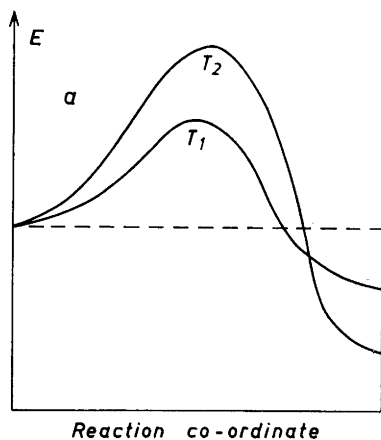


Fig. 1a.

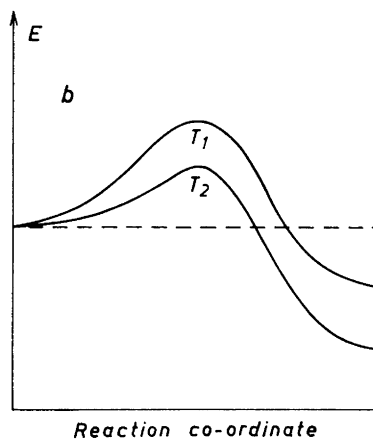
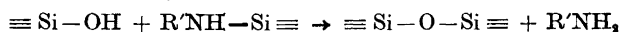
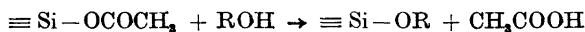


Fig. 1b.

to give silanol, and more $\equiv \text{SiOCOCH}_3$ groups are produced (by the reversal of 2a), which again are consumed according to (2b). The Si—OH groups formed will immediately condense intermolecularly with Si—N bonds:



and in this way just 50 % of the hydroacetate calculated for reaction (2a) will be left. This hypothesis is supported by the fact that reaction (2a) was found to be reversible. Thus *n*-propyltri-(benzylamino)-silane in benzene dissolved in a few minutes an equivalent amount of benzylamine hydroacetate with the formation of *N*-benzylacetamide. The fact that the weight of hydroacetate obtained when the reaction between ethyltriacetoxysilane and benzylamine was performed at -80° corresponded to more than 50 %, also gives some support to the proposed reaction pattern which is also in agreement with the finding of Dolgov *et al.*⁷⁻⁸ on the reaction of acyloxysilanes with alcohols. They found that acetoxy-silanes react with alcohols to give alkoxy-silanes if the liberated acid is removed at reduced pressure:

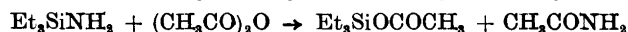


but silanols and the esters of acetic acid are obtained if the reaction mixtures are heated:

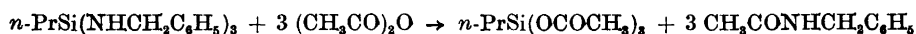


It can therefore be concluded with some certainty that the silicon atom is more susceptible to nucleophilic attack than the carbonyl carbons in alkyltriacetoxysilanes (Fig. 1a) and the acylating ability of these compounds would then be the result only of the low energy of the products obtained after reaction at the carbonyl carbons.

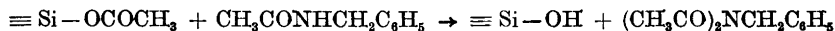
In organosilicon chemistry, acetic anhydride has been used to bring about the conversion of Si—N bonds into Si—OCOCH₃ ones⁹: *e.g.*



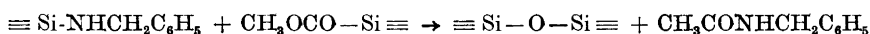
Acetic anhydride was added to the appropriate aminosilane and on distillation of the reaction mixtures 62, 56, and 32 %, respectively, of the acetoxy-silanes were obtained. Now it was found that only a very poor yield of alkyltriacetoxysilane was obtained from the reaction mixture when acetic anhydride was added to a benzene solution of a *N*-substituted alkyltriaminosilane. Thus *n*-propyltri-(benzylamino)-silane and excess of acetic anhydride gave less than 5 % of *n*-propyltriacetoxysilane on distillation of the reaction mixture at reduced pressure. However, at $158-62^\circ/11$ mm a fraction was obtained most of which consisted of diacetylbenzylamine. It could therefore be suspected with some reason that there had first been formed *n*-propyltriacetoxysilane according to the equation



which in a secondary reaction acetylated the amide:



However, a mixture of ethyltriacetoxysilane and N-benzylacetamide after standing overnight could be separated by distillation at reduced pressure without any noteworthy reaction. The only explanation of the observed reaction course would then be that during the addition of acetic anhydride to the alkyltriaminosilane a condensation between new-formed Si—OCOCH₃ groups and unreacted Si—N bonds had occurred:



The possibility of such a reaction was confirmed by the fact that ethyltriacetoxysilane and ethyltri-(benzylamino)-silane in petroleum ether immediately gave a precipitate of N-benzylacetamide. The appearance of diacetylbenzylamine in the reaction mixture above would then be the result of acetylating — not by *n*-propyltriacetoxysilane but by acetoxysiloxanes with a few silicon atoms produced in a condensation reaction according to the last equation and/or by the excess of acetic anhydride¹⁰. Therefore a good yield of alkyltriacetoxysilane can only be expected if the aminosilane is added to excess of acetic anhydride and not *vice versa*. This was confirmed by the fact that a yield of almost 80 % of *n*-propyltriacetoxysilane was obtained when *n*-propyltri-(benzylamino)-silane in benzene was added to excess of acetic anhydride.

When anhydrous hydrogen chloride, bromide or iodide was passed into the ether or benzene solution of an alkyltriaminosilane, amine hydrohalide precipitated as rapidly as the gas was introduced and the appropriate alkyltrihalosilane was left in the solution. The halosilanes obtained could again be readily converted into aminosilanes by treatment with amines. These reactions point to a general method of replacing the halogen of an alkyltrihalosilane for another one and it has been used to prepare a range of alkyltriiodosilanes from the corresponding chlorosilanes¹¹⁻¹².

In contrast to the other hydrogen halides the fluoride gave no ether soluble products when passed into the solution of a N-substituted alkyltriaminosilane or phenyltriaminosilane. Presumably the appropriate trifluorosilane was first formed according to the equation



but was then absorbed by the precipitated amine hydrofluoride to give insoluble products, approximately corresponding to the composition $\text{RSiF}_3 \cdot 3\text{R}'\text{NH}_3\text{F}$. Such an absorption is somewhat surprising in view of the finding of Booth and co-workers¹³⁻¹⁴, that sodium fluoride did not coordinate to alkyltrifluorosilanes even on prolonged contact. The supposed reaction pattern, however, is strongly supported by the fact that amine hydrofluorides absorbed *cyclohexyltrifluorosilane* and *phenyltrifluorosilane* to an extent roughly corresponding to the formation of $\text{RSiF}_3 \cdot 2\text{R}'\text{NH}_3\text{F}$. These addition compounds are white, non-hygroscopic quite stable powders insoluble in common organic solvents. They dissolved in water to give acidic solutions which soon became turbid due to hydrolysis. Probably because of unfavorable conditions of reaction between

Table 1. Physical constants and analyses of the compounds I–VIII.

No.	M	B.p. °C	Pressure mm Hg	n_D^{20}	d_4^{20}	MR _D	% Si		Equiv. wt.	
							found	calc.	found	calc.
I	217.42	110	13	1.4381	0.8523	66.98	13.0	12.9	72.8	72.5
II	231.45	114–15	10	1.4429	0.8572	71.57	12.1	12.1	77.3	77.2
III	273.53	153	11	1.4459	0.8541	85.39	10.2	10.3	91.0	91.2
IV	375.58	250–52	4	1.5715	1.0614	116.35	7.4	7.5	125.7	125.2
V	202.41	95	11	1.4384	0.8329	63.84	13.9	13.9	101.7	101.2
VI	285.54	166–67	10	1.4672	0.9011	87.96	9.7	9.8	95.2	95.2
VII	279.49	169–70	12	1.4942	0.9358	86.98	9.8	10.0	93.0	93.2
VIII	173.37	68	11	1.4335	0.8047	56.05	16.2	16.2	174.5	173.4

the solid salts and the liquid fluorosilanes, their compositions were rather ill-defined. Yet it seems plausible to interpret them as salts containing a RSiF_5^{2-} ion analogous to the hexafluorosilicate ion, SiF_6^{2-} , in which 3 sp^3d^2 hybridization of the silicon orbitals is supposed to produce six equivalent bonds constituting an octahedral arrangement of the fluorine atoms about the central silicon atom¹⁵.

In sharp contrast to the triaminosilanes, N-substituted dialkyldiaminosilanes and trialkylaminosilanes revealed no tendency to six-coordination. Thus on passing anhydrous hydrogen fluoride into an ether solution of triethyl (*n*-propylamino)-silane or diethyldi(*n*-propylamino)-silane the corresponding fluorosilanes were obtained from the ether solution and no silicon was found in the precipitated amine hydrofluoride. Nor was there observed any increase in weight of amine hydrofluorides after prolonged treatment with tri- and dialkylfluorosilanes.

EXPERIMENTAL

Of the aminosilanes employed in the reactions below the following have not been described before:

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

They were prepared as described for *n*-propylaminosilanes from the appropriate organosilicon chloride and excess of amine, the yields lying between 75 and 90 %. Their physical constants and analyses are given in Table 1. In the table are also given the data of triethyl(*n*-propylamino)-silane, VIII, which is previously described¹⁶ to have n_D^{20} 1.4332, d_4^{20} 0.8038.

Ethyltriacetoxysilane. This compound was prepared according to Dolgov *et al.*⁸ from ethyltrichlorosilane and acetic anhydride. B.p. 108–09°/10 mm Hg, n_D^{20} 1.4123, d_4^{20} 1.1440, MR_D 50.99 (lit. values⁸: b.p. 107.5–108.5/8 mm, n_D^{20} 1.4123, d_4^{20} 1.1428, MR_D 51.04). (Found: Si 11.8; equiv. wt. 77.7. Calc. for $\text{C}_2\text{H}_5\text{Si}(\text{OCOCH}_3)_3$: Si 12.0; equiv. wt. 78.1).

Triethylfluorosilane. This compound was prepared according to Eaborn¹⁷ from triethylchlorosilane and 48 % hydrofluoric acid containing alcohol to ensure a homogenous system. B.p. 110°, n_D^{20} 1.3902, d^{20} 0.8391 (lit. values: b.p. 109.5°¹⁷, n_D^{20} 1.3910¹⁷, d^{20} 0.8380¹⁸). Equiv. wt.: Found 135.0; calc. 134.3.

Diethyldifluorosilane was obtained according to Marans *et al.*¹⁹ from diethyldichlorosilane and 48 % hydrofluoric acid. B.p. 63–64°, n_D^{20} 1.3400, d^{20} 0.9343 (lit. values: b.p. 62°¹⁷, n_D^{23} 1.3393²⁰, d_4^{20} 0.9348¹⁹). Equiv. wt.: Found 61.8; calc. 62.1.

Phenyltrifluorosilane was prepared according to Pearlson *et al.*²¹ by agitating a mixture of phenyltrichlorosilane and anhydrous hydrogen fluoride at 0°. B.p. 103–04°, n_D^{20} 1.4110, d^{20} 1.211 (lit. values: b.p. 101–02°²¹, n_D^{22} 1.4103²³, d_4^{17} 1.212²²). Equiv. wt.: Found 54.0; calc. 54.1.

Cyclohexyltrifluorosilane was obtained in the way described for phenyltrifluorosilane. B.p. 106°, n_D^{20} 1.3700, d^{20} 1.106 (lit. values²⁰: b.p. 106°, n_D^{25} 1.3680, d^{25} 1.1012). Equiv. wt.: Found 55.8; calc. 56.1.

The equivalent weights of these fluorosilanes were determined by dissolving the compounds in excess of standard potassium methoxide. After a few minutes water was added and the excess of alkali back-titrated with standard hydrochloric acid using thymolblue as the indicator.

Hydrolysis experiments (a) *n*-Propyltri-(methylamino)-silane and *n*-propyltri-(ethylamino)-silane were vigorously hydrolyzed in contact with liquid water and gave insoluble granular and generally intractable solids containing no nitrogen. Compounds with larger groups on the nitrogen atoms gave a liquid mixture with only a very slow reaction occurring at the interface when poured into water. This is apparently a consequence of their water insolubility for upon addition of ethanol to the amine-water mixture a homogeneous solution resulted accompanied by rapid hydrolysis of the compounds. However, the most sterically hindered compounds, *i.e.* *n*-propyltri-(*tert*-butylamino)-silane and the corresponding diethylamine compound were remarkably stable to the action of water. 5.8 g (0.02 mole) of *n*-propyltri-(*tert*-butylamino)-silane (n_D^{20} 1.4427, equiv. wt. 96.7) was dissolved in 45 ml of 90 % ethanol. After standing for 2 h the solvent was evaporated at reduced pressure leaving a residue with n_D^{20} 1.4430 and equiv. wt. 99.0 from which more than 90 % of the aminosilane could be recovered by distillation.

(b) 20.3 g (0.1 mole) of *n*-propyltri-(ethylamino)-silane in 200 ml of dry ether were stirred rapidly and 200 ml of ether containing 0.90 g (0.05 mole) of water were added during one hour. After standing overnight the ether was removed by distillation. In the distillate was found 0.1 mole of ethylamine indicating that the intermolecular condensation had proceeded quantitatively. 12.2 g (60 %) of unreacted aminosilane were recovered by distillation. From the residue only 0.5 g of partial hydrolysis products, equiv. wt. about 200, was obtained. The remainder, 2.7 g, rapidly gelled to an insoluble resin typical of cross-linked structures and contained only traces of nitrogen.

(c) In the same way 1.35 g (0.075 mole) of water in 200 ml of ether liberated 0.15 mole of ethylamine from 15.3 g (0.075 mole) of *n*-propyltri-(ethylamino)-silane in 100 ml of absolute ether. 4.0 g (26 %) of unreacted aminosilane were recovered by distillation and a residue of 4.75 g of a high-polymeric resin containing less than 1 % nitrogen were left.

Reactions with alcohols. (a) 8.1 g (0.05 mole) of *n*-propyltri-(methylamino)-silane and 11.3 g (0.25 mole) of ethanol were mixed and gave a spontaneous reaction with evolution of methylamine. The reaction mixture was heated to reflux temperature until no more methylamine was liberated (2 h.). On distillation 8.0 g (77 %) of *n*-propyltriethoxysilane was obtained, b.p. 169–70° (1 atm), n_D^{20} 1.3969, d^{20} 0.8891, MR_D 55.88, calc. 55.73 (according to Smith²⁴) (lit. values²⁵: 170–72°, n_D^{20} 1.3956, d^{20} 0.8916). (Found: Si 13.5. Calc. for $C_3H_{22}O_3Si$: Si 13.6).

(b) In the same way 4.8 g (0.03 mole) of *n*-propyltri-(methylamino)-silane and 13.0 g (0.12 mole) of benzylalcohol gave 9.4 g (80 %) of *n*-propyltribenzyloxysilane, b.p. 220–22°/2 mm, n_D^{20} 1.5408, d^{20} 1.0750, MR_D 114.71, calc. 114.59. Smith does not give the group refractivity r -SiOCH₂C₆H₅, but from his value of the group refractivity r -SiOCH₃ and the atomic and structural constants of H (in CH₂) and C₆H₅ given by Vogel²⁶, the group refractivity r -SiOCH₂C₆H₅ was calculated to 32.61 ml. (Found: Si 7.1. Calc. for $C_{24}H_{28}O_3Si$: Si 7.2).

(c) A mixture of 8.1 g (0.05 mole) of *n*-propyltri-(methylamino)-silane and 14.8 g (0.2 mole) of *tert*-butanol was heated to reflux temperature for 30 h. On distillation of the

reaction mixture 6.6 g of a product with equiv. wt. 87.3 were obtained, apparently a mixture of *n*-propyltri-(methylamino)-silane (equiv. wt. 53.8) and *n*-propyl*tert*-butoxydi-(methylamino)-silane (equiv. wt. 102.2). 11 g of *tert*-butanol were added to the product and the mixture was again heated to reflux temperature for 40 h. On distillation 6.0 g of a product boiling at 76–77°/10 mm were obtained, n_D^{20} 1.4273, d_4^{20} 0.8748, MR_D 60.02, equiv. wt. 105.6, Si 13.4. Calc. for $n\text{-C}_3\text{H}_7\text{Si}(\text{NHCH}_3)_2(\text{OC}_4\text{H}_9\text{-}t)$: equiv. wt. 102.2, Si 13.7, MR_D 59.98, using the bond refractivities $r\text{-SiC}_3\text{H}_7\text{-}n$ and $r\text{-SiOC}_4\text{H}_9\text{-}t$ given by Smith²⁴ and the mean value 10.42 ml for $r\text{-SiNHMe}$ obtained from three alkyltri-(methylamino)-silanes.^{1,4}

(d) 10.2 g (0.05 mole) of *n*-propyltri-(ethylamino)-silane and 22.2 g (0.3 mole) of *tert*-butanol were heated to reflux temperature for 25 h. Only a small amount of ethylamine was liberated and on distillation more than 8 g of the triaminosilane were recovered. In another experiment a mixture of 10.2 g (0.05 mole) of *n*-propyltri-(ethylamino)-silane and 22.2 g (0.3 mole) of *tert*-butanol containing one g of sodium was heated to reflux temperature for 90 h. After filtration of the reaction mixture distillation gave 8.0 g of a product boiling at 90–100°/10 mm with equiv. wt. 83.7, apparently a mixture of *n*-propyltri-(ethylamino)-silane (equiv. wt. 67.8) and *n*-propyl*tert*-butoxydi-(ethylamino)-silane (equiv. wt. 116.2).

Reaction with phenol. 4.6 g (0.023 mole) of *n*-propyltri-(ethylamino)-silane and 8.5 g (0.09 mole) of phenol were mixed and gave a spontaneous reaction with evolution of heat. The reaction mixture was heated to reflux temperature for 4 h. On distillation 6.0 g (74 %) of *n*-propyltriphenoxysilane were obtained, b.p. 192°C/2 mm, n_D^{20} 1.5518, d_4^{20} 1.1056, MR_D 101.26, calc. 101.10 (from the observed MR_D 91.84 for methyltriphenoxysilane²⁷ and the group refractivities $r\text{-SiCH}_3$ and $r\text{-SiC}_3\text{H}_7\text{-}n$ given by Smith). (Found: Si 8.0. Calc. for $\text{C}_{21}\text{H}_{22}\text{O}_3$, Si: Si 8.0.)

Reactions with glacial acetic acid. (a) 5.2 g (0.0133 mole) of *n*-propyltri-(benzylamino)-silane in 30 ml of benzene were added dropwise to 6.0 g (0.1 mole) of glacial acetic acid. Reaction immediately occurred with evolution of much heat. The solvent and excess of acetic acid were removed at reduced pressure from the homogeneous reaction mixture. On distillation 3.5 g of a viscous oil were obtained at 99°C/10 mm. Benzene was added to the residue in the distillation flask and the high-polymeric silicones (1.2 g) which had precipitated under the distillation were removed by filtration. When petroleum ether was added to the filtrate 2.4 g of *N*-benzylacetamide, m.p. 60–61° (lit.²⁸ 60–61°) precipitated. (Found: C 72.7; H 7.5. Calc. for $\text{C}_9\text{H}_{11}\text{NO}$: C 72.5; H 7.4). The oil obtained on distillation crystallized on cooling. It melted without definite melting point between 50 and 80°, dissolved in water to give acidic solution and contained no silicon. (Found: C 60.2; H 7.7. Calc. for $\text{CH}_3\text{COONH}_2\text{CH}_2\text{C}_6\text{H}_5$: C 64.6; H 7.8 and for $\text{CH}_3\text{COONH}_2\text{CH}_2\text{C}_6\text{H}_5$; CH_3COOH : C 58.1; H 7.5). When a mixture of benzylamine and excess of acetic acid was distilled, a viscous oil was also obtained at 99–100°/10 mm with the same properties and approximately the same analyses apparently consisting of acidic benzylamine hydroacetate of ill-defined composition.

(b) 4.0 g (0.0146 mole) of ethyltri-(*n*-butylamino)-silane and 7.5 g (0.125 mole) of acetic acid in the same way reacted exothermically to give a homogeneous reaction mixture and on distillation high polymeric silicones precipitated in the distillation flask. At 92°/10 mm 4.0 g of a viscous oil, $n_D^{20} = 1.4365$, were obtained, apparently consisting of acidic *n*-butylamine hydroacetate (Found: C 50.5; H 10.4. Calc. for $\text{CH}_3\text{COONH}_2\text{C}_4\text{H}_9$; CH_3COOH : C 49.7; H 9.9). A viscous oil ($n_D^{20} = 1.4365$, C 50.2; H 10.2) also distilled from a mixture of *n*-butylamine and excess of acetic acid at 92°/10 mm.

(c) 1.2 g (0.0072 mole) of benzylamine hydroacetate dissolved in less than one minute when added to 1.4 g (0.006 mole) of ethyltriacetoxysilane in 12 ml of benzene. The solvent and the acetic acid formed in the reaction were removed at reduced pressure and the residue was again dissolved in 10 ml of benzene. When 20 ml of petroleum ether were then added 0.7 g of *N*-benzylacetamide, m.p. 61–62°, precipitated.

(d) 3.5 (0.015 mole) of ethyltriacetoxysilane in 10 ml of benzene were added dropwise to a stirred solution of 10.7 g (0.1 mole) of benzylamine in 40 ml of benzene. Reaction immediately occurred with formation of a heavy precipitate. The reaction mixture was heated to 50° for one hour, cooled to 0° and filtered. 3.8 g (calc. for reaction (2a): 7.5 g) of benzylamine hydroacetate were left on the filter, m.p. 99–100° (lit.²⁹ 96.3–97.1°). (Found: C 64.6; H 7.8. Calc. for $\text{C}_9\text{H}_{13}\text{NO}_2$: C 64.6; H 7.8). The salt proved to be insoluble in benzene. When petroleum ether was added to the filtrate 2.4 g of a mixture of *N*-

benzylacetamide and high-polymeric silicones precipitated. The silicones were removed by heating the mixture with 75 ml of petroleum ether and 15 ml of benzene to reflux temperature. On filtration the silicones were left on the filter and N-benzylacetamide, m.p. 61–62°, precipitated from the filtrate on cooling.

(e) In another experiment 3.5 g (0.015 mole) of ethyltriacetoxysilane in 10 ml of benzene were rapidly added to an ice-cooled solution of 10.7 g (0.1 mole) of benzylamine in 40 ml of benzene. The reaction mixture was stirred at 0° for 5 min and then filtered. 3.7 g of benzylamine hydroacetate, m.p. 99–100°, was left on the filter and polysiloxanes and N-benzylacetamide were again found in the filtrate.

(f) 3.5 g (0.015 mole) of ethyltriacetoxysilane in 10 ml of toluene were slowly added to a stirred solution of 10.7 g (0.1 mole) of benzylamine in 40 ml of toluene, cooled to –80°. Thereafter the reaction mixture was stirred at the same temperature for 10 min and filtered. During the filtration the temperature increased almost to room temperature. 4.7 g of benzylamine hydroacetate, m.p. 98.5–100° – corresponding to 63% of the amount calc. for reaction (2a) – were now left on the filter and silicones and N-benzylacetamide were found in the filtrate.

(g) 1.7 g (0.01 mole) of benzylamine hydroacetate dissolved in a few minutes when added to 3.9 g (0.01 mole) of *n*-propyltri-(benzylamino)-silane in 15 ml of benzene. 35 ml of petroleum ether were added and after standing overnight N-benzylacetamide, m.p. 61–62°, had precipitated.

Reactions with acetic anhydride (a) 21.3 g (0.21 mole) of acetic anhydride were added dropwise to an ice-cooled solution of 20.0 g (0.051 mole) of *n*-propyltri-(benzylamino)-silane in 100 ml of benzene. Reaction immediately occurred with evolution of much heat. The solvent and the excess of acetic anhydride were removed at reduced pressure. On distillation of the residue only about 0.5 g was obtained at 100–125°/11 mm where *n*-propyltriacetoxysilane can be expected to distil. 11.8 g of a viscous oil containing no silicon distilled at 158–62°. It was re-distilled and gave at 155–57°/10 mm (lit.¹⁰ 176–78°/30 mm) 7.0 g of diacetylbenzylamine. (Found: C 68.6; H 6.9. Calc. for C₁₁H₁₃NO₃: C 69.1; H 6.9). When petroleum ether was added to the residue 8.0 g of N-benzylacetamide, m.p. 61–62°, precipitated.

In the same way acetic anhydride added to *n*-propyltri-(cyclohexylamino)-silane, ethyltri-(*n*-butylamino)-silane, and ethyltri-(benzylamino)-silane only gave traces of the expected triacetoxysilanes.

(b) 15.6 g (0.04 mole) of *n*-propyltri-(benzylamino)-silane in 25 ml of benzene was added dropwise to a stirred, ice-cooled solution of 20.4 g (0.2 mole) of acetic anhydride in 50 ml of benzene. The solvent and the excess of acetic anhydride were removed at reduced pressure. On distillation of the residue 7.8 g (79 %) of *n*-propyltriacetoxysilane were obtained at 117–118°/10 mm (lit.³⁰ 127–31°/20 mm) with n_D^{20} 1.4148; d_4^{20} 1.1157; MR_D 55.71 (Found: Si: 11.2; equiv. wt. 82.6. Calc. for *n*-C₃H₇Si(OCOCH₃)₃: Si: 11.3; equiv. wt. 82.8). N-benzylacetamide was left in the distillation flask.

(c) 7.0 g (0.03 mole) of ethyltriacetoxysilane were mixed with 8.0 g (0.054 mole) of N-benzylacetamide. After standing overnight 6.1 g of ethyltriacetoxysilane could be recovered by distillation at 12 mm Hg.

(d) 1.5 g (0.0064 mole) of ethyltriacetoxysilane in 6 ml of petroleum ether were added to 2.4 g (0.0064 mole) of ethyltri-(benzylamino)-silane in 8 ml of petroleum ether. Precipitation immediately occurred. After standing for 2 h the mixture was filtered and left 0.8 g of N-benzylacetamide, m.p. 59–61°, on the filter.

n-Propyltrichlorosilane. 7.4 g (0.03 mole) of *n*-propyltri-(*n*-propylamino)-silane in 100 ml of absolute ether was placed in a 250 ml three-necked flask equipped with a reflux condenser, mechanical stirrer and gas inlet tube. When dry hydrogen chloride was passed into the reaction mixture amine hydrochloride was immediately formed. After excess of hydrogen chloride had been added the reaction mixture was heated to reflux temperature for 30 min. On filtration 8.6 g (calc. 8.6 g) of *n*-propylamine hydrochloride was left on the filter. Distillation of the filtrate gave 4.2 g (79 %) of *n*-propyltrichlorosilane boiling at 122–123° (1 atm) (lit.¹ 123°). Equiv. wt. 59.9; calc. 59.3.

n-Propyltribromosilane. 53.3 g (0.3 mole) of *n*-propyltrichlorosilane in 150 ml of benzene were added dropwise to an ice-cooled, vigorously stirred solution of about 90 g of ethylamine in 200 ml of benzene. After all had been added the stirring was continued for 2 h and thereafter the excess of ethylamine was removed by distillation. Filtration of the cooled mixture left 73.2 g (calc. 73.4 g) of ethylamine hydrochloride on the filter.

Hydrogen bromide which had been carefully dried over phosphorus pentoxide was then passed into the filtrate as described for the preparation of *n*-propyltrichlorosilane above. Filtration of the reaction mixture gave 112 g (calc. 113 g) of ethylamine hydrobromide on the filter. Distillation of the filtrate gave 78.0 g (83 %) of *n*-propyltribromosilane boiling at 179–81° (1 atm) lit.³¹ 179–80/754 mm). Equiv. wt. 104.0 calc. 103.6 The assigned structure of the product which was a colourless liquid, fuming extensively in moist air, was confirmed by its reaction with diethylamine to give *n*-propyltri-(diethylamino)-silane³.

n-Propyltriiodosilane. A small excess of hydrogen iodide which had been carefully dried over phosphorus pentoxide was passed into 15.3 g (0.075 mole) of *n*-propyltri-(ethylamino)-silane in 200 ml of benzene as described above. On filtration 38.7 g (calc. 38.9 g) ethylamine hydroiodide were left on the filter. Distillation of the filtrate gave 27.0 g (80 %) of *n*-propyltriiodosilane boiling at 118–19°/10 mm (lit.¹² 142–43°/20 mm). Equiv. wt. 151.0, calc. 150.7. The assigned structure of the product which was a colourless liquid fuming in moist air was confirmed by its reaction with *tert*-butylamine to give *n*-propyltri-(*tert*-butylamino)-silane³.

Reactions with hydrogen fluoride. In Table 2 are reported the results of six experiments in which dry gaseous hydrogen fluoride was passed into an ice-cooled, stirred solution of 0.02 mole of a *N*-substituted alkyltriaminosilane or phenyltriaminosilane in 100 ml of ether. In all cases a white solid immediately precipitated. The introduction of hydrogen fluoride was stopped just when no more solid precipitated to avoid the formation of acidic amine hydrofluorides. Thereafter the reaction mixture was stirred for 30 min and the temperature raised to room-temperature before filtering. The products left on the filter, which were much less hygroscopic than amine hydrofluorides, were all found to contain silicon and no silicon was observed in the filtrates. The amounts obtained were considerably greater than the amounts calculated for the formation of amine hydrofluorides according to eqn. (3) but corresponded to the composition $\text{RSiF}_3 \cdot 3\text{R}'\text{NH}_2\text{F}$. They dissolved in water to give acidic solutions which soon became turbid, apparently due to hydrolysis products. Their amine content (E_1 in the table) was determined by back-titrating an acid fixed condensate from a boiling solution containing the compound in excess of standard base using methylred as the indicator, and their fluorine content (E_2 in the table) was determined by back-titrating the excess of base with standard acid using phenolphthalein or thymolblue as the indicator.

When the same reaction was performed with triethyl-(*n*-propylamino)-silane or diethyldi-(*n*-propylamino)-silane the precipitates left on the filter were found to be neutral *n*-propylamine hydrofluoride containing no silicon. From the filtrates, triethylfluorosilane and diethyldifluorosilane respectively were obtained on distillation.

Table 2. *N*-substituted triaminosilanes and hydrogen fluoride.

	Yield, g		E_1		E_2	
	found	calc. ^a	found	calc.	found	calc.
<i>n</i> -C ₃ H ₇ Si(NHC ₂ H ₅) ₃ , 4.1 g	6.3	6.5	118	108	52.5	53.9
CH ₃ Si(NHC ₃ H ₇ - <i>n</i>) ₃ , 4.3 g	6.8	6.8	116	112	55.4	56.2
C ₆ H ₅ Si(NHC ₃ H ₇ - <i>n</i>) ₃ , 4.6 g	6.8	7.0	120	117	56.8	58.6
<i>n</i> -C ₃ H ₇ Si(NHC ₃ H ₇ - <i>n</i>) ₃ , 4.9 g	7.1	7.3	126	122	62.3	60.9
C ₆ H ₁₁ Si(NHC ₃ H ₇ - <i>n</i>) ₃ , 5.7 g	7.7	8.1	135	135	69.0	67.6
C ₆ H ₅ Si(NHC ₃ H ₇ - <i>n</i>) ₃ , 5.6 g	8.2	8.0	141	133	63.5	66.6

^a calc. for the formation of $\text{RSiF}_3 \cdot 3\text{R}'\text{NH}_2\text{F}$.

The co-ordination of amine hydrofluorides to fluorosilanes. When phenyltrifluorosilane or cyclohexyltrifluorosilane was added to samples of amine hydrofluorides (ethyl-, *n*-propyl-, or *n*-butylamine hydrofluoride) exothermic reactions always occurred and the liquid was absorbed by the solid salt to give a dry powder.

In one experiment excess of phenyltrifluorosilane (4.5 g; 2.8×10^{-2} mole) was added to 1.006 g (1.27×10^{-2} mole) of *n*-propylamine hydrofluoride in 35 ml of ether. The mixture was heated to reflux temperature for 3 h. After cooling, the solid was separated by filtration, carefully washed with the solvent and dried. The gain in weight was found to be 0.832 g (corresponding to 0.51×10^{-2} mole of phenyltrifluorosilane); calc. for the formation of $C_6H_5SiF_3 \cdot 2n-C_3H_7NH_3F$: 1.003 g. The amine content (E_1) of the product was determined as described above but methanol was used as the solvent for the alkaline solution to ensure a homogeneous system. After the amine had been distilled off, water was added to the residue and the excess of alkali back-titrated using thymolblue as the indicator. (Found: E_1 153; E_2 62. Calc. for $C_6H_5SiF_3 \cdot 2n-C_3H_7NH_3F$: E_1 160; E_2 64).

The gain in weight of 0.478 g (0.60×10^{-2} mole) of *n*-propylamine hydrofluoride after contact with excess of cyclohexyltrifluorosilane as described for phenyltrifluorosilane above was 0.398 g; calc. for the formation of $C_6H_{11}SiF_3 \cdot 2n-C_3H_7NH_3F$: 0.508 g. (Found: E_1 158; E_2 62. Calc. for $C_6H_{11}SiF_3 \cdot 2n-C_3H_7NH_3F$: E_1 163; E_2 65).

Similar experiments were performed under varying conditions but well-defined products were never obtained.

When triethylfluorosilane or diethyldifluorosilane were added to samples of amine hydrofluorides the solid was immediately wet and no evolution of heat was observed. Nor was there found any gain in weight of the solid after prolonged contact with these fluorosilanes.

REFERENCES

1. Tansjö, L. *Acta Chem. Scand.* **11** (1957) 1613.
2. Tansjö, L. *Acta Chem. Scand.* **13** (1959) 29.
3. Tansjö, L. *Acta Chem. Scand.* **13** (1959) 35.
4. Tansjö, L. *Acta Chem. Scand.* **14** (1960) 2097.
5. Eaborn, C. *Organosilicon Compounds*, Butterworths Scientific Publications, London 1960 (Chapter 11).
6. Miner, C. S., Bryan, L. A., Holysz, R. P. and Pedlov, G. W. *Ind. Eng. Chem. (Indust.)* **39** (1947) 1368.
7. Dolgov, B. N., Davydova, V. P. and Voronkov, M. G. *Zhur. Obschchei Khim.* **27** (1957) 921.
8. Dolgov, B. N., Davydova, V. P. and Voronkov, M. G. *Zhur. Obschchei Khim.* **27** (1957) 1593.
9. Larsson, E. *Trans. Chalmers Univ. Technol. Gothenburg* No. **115** 1951.
10. Holmes, L. and Ingold, C. K. *J. Chem. Soc.* **127** (1925) 1820.
11. Anderson, H. H., Seaton, D. L. and Rudnicki, R. P. T. *J. Am. Chem. Soc.* **73** (1951) 2144.
12. Anderson, H. H. *J. Am. Chem. Soc.* **73** (1951) 2351.
13. Booth, H. S. and Carnell, P. H. *J. Am. Chem. Soc.* **68** (1946) 2650.
14. Booth, H. S. and Martin, W. F. *J. Am. Chem. Soc.* **68** (1946) 2655.
15. Keteelar, J. A. A. *Z. Krist.* **92** (1935) 155.
16. Dolgov, B. N., Kharitonov, N. P. and Voronkov, M. G. *Zhur. Obschchei Khim.* **24** (1954) 678.
17. Eaborn, C. *J. Chem. Soc.* **1952** 2846.
18. Bailey, D. L., Sommer, L. H. and Whitmore, F. C. *J. Am. Chem. Soc.* **70** (1948) 435.
19. Marans, N. S., Sommer, L. H. and Whitmore, F. C. *J. Am. Chem. Soc.* **73** (1951) 5127.
20. Sowa, F. J. *U. S. Pat.* 2,477,704; *C. A.* **44** (1950) 3008.
21. Pearlson, W. H., Brice, T. J. and Simons, J. H. *J. Am. Chem. Soc.* **67** (1945) 1769.
22. Emeleus, H. J. and Wilkins, C. J. *J. Chem. Soc.* **1944** 454.
23. Spialter, L. *Tetrahedron Letters* **1960** No. 5, 11.

24. Smith, B. *Kiselorganiska studier* (Diss.) Chalmers University of Technology, Gothenburg 1951.
25. Larsson, E. *Kgl. Fysiograf. Sällskap. Lund Handl. (N.F.)* **63** (1952) No. 12.
26. Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd Ed. Longmans, Green and Co., London 1956.
27. George, P. D. and Newkirk, A. E. *U.S. Pat.* 2,837,552; *C.A.* **52** (1958) 17181.
28. Dermier, O. C. and King, J. *J. Org. Chem.* **8** (1943) 168.
29. Buehler, C. A., Carson, L. and Edds, R. *J. Am. Chem. Soc.* **57** (1935) 2181.
30. MacKenzie, C. A. and Schoffman, M. *U.S. Pat.* 2,537,073; *C.A.* **45** (1951) 3410.
31. Nametkin, N. S., Topchiev, A. V. and Kartasheva, L. I. *Doklady Akad. Nauk S.S.S.R.* **101** (1955) 885.

Received April 18, 1961.