ACTA CHEMICA SCANDINAVICA 13 (1959) 35—39

N-Substituted Alkyltriaminosilanes

III. On the Preparation of Some Sterically-Hindered Compounds

LEWI TANSJÖ

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

n-Propyltribromosilane and *n*-propyltriiodosilane were shown to react more readily than *n*-propyltrichlorosilane with *tert.*-butylamine and diethylamine.

Some N-substituted alkyltriaminosilanes which could not be prepared by the direct treatment of halosilanes with the bulky amines in question could be obtained from the corresponding amine magnesium halogenides.

The preparation of fifteen compounds which have not earlier been reported is described.

Part 1. In a previous paper [1] it was shown that only two chlorine atoms are replaced when *n*-propyltrichlorosilane reacts with *tert.*-butylamine, diethylamine and N-methylaniline. This was ascribed to the steric hindrance exerted by the bulky groups in these amines, for the remaining chlorine atom could readily be exchanged by ammonia and amines with less bulky groups, such as ethylamine and even *iso*propylamine.

Thus the reactivity of the Si—Cl bond is not sufficient to give the N-substituted *n*-propyltriaminosilanes with the amines above even on prolonged reflux. In order to obtain these triaminosilanes, two other methods have been tried, both giving the desired result.

A. From the fact that in general the reactivity of halosilanes increases in the order F, Cl, Br, I, it could be expected that *n*-propyltribromosilane and *n*-propyltriiodosilane would give a better yield of the triaminosilanes than *n*-propyltrichlorosilane does in their reaction with the amines in question. This assumption was verified by the fact that *n*-propyltriiodosilane reacted completely with *tert.*-butylamine and *n*-propyltribromosilane gave a good yield of *n*-propyltri-(diethylamino)-silane. N-Methylaniline, however, replaced only two bromine atoms in *n*-propyltribromosilane; the second one not readily.

Previously [1] it has also been reported that di-*iso*propylamine only exchanged one chlorine atom in *n*-propyltrichlorosilane. Now it was shown that even in *n*-propyltribromosilane only one halogen atom was replaced by di-*iso*propylamine, illustrating the great steric requirement of this amine.

B. Breederveld and Waterman [2-3] used *tert.*-butylamine magnesium bromide and diethylamine magnesium bromide for the preparation of tetra-*tert.*-butylaminosilane and the corresponding diethylamine compound, and this method was successful also in this work. Thus *n*-propyltri-(*tert.*-butylamino)-silane was obtained in good yield by heating a mixture of *n*-propyldi-(*tert.*-butylamino)-chlorosilane and *tert.*-butylamine magnesium bromide at about 160°C for several hours, and the corresponding diethylamine compound was obtained in an analogous way from diethylamine magnesium bromide. *n*-Propyltri-(N-methylanilino)-silane was prepared directly from *n*-propyltrichlorosilane and N-methylaniline magnesium iodide. Prolonged heating of a mixture of *n*-propyl-(di-*iso*propylamino)-dichlorosilane and di-*iso*propylamine magnesium bromide seems to make possible the exchange of two chlorine atoms in *n*-propyltrichlorosilane, but no pure compound was isolated in this case.

Part 2. Whereas *n*-propyltrichlorosilane gives N-substituted *n*-propyldiaminochlorosilanes with *tert.*-butylamine and diethylamine and practically no triaminosilanes, silicon tetrachloride reacts with these amines to give the N-substituted triaminosilanes in good yield [4-5]. It must be concluded, therefore, that the reactivity of the compounds $(t\text{-}C_4H_9NH)_2SiClX$ and $[(C_2H_5)_2N]_2SiClX$ is much greater for X = Cl than for X = n-C_3H_7 in the reaction

$$(t\text{-}C_4H_9NH)_2SiClX + 2t\text{-}C_4H_9NH_2 \longrightarrow (t\text{-}C_4H_9NH)_3SiX + t\text{-}C_4H_9NH_3Cl \quad (1)$$

and the analogous reaction for diethylamine. The influence on the reactivity for some different X in the reaction above has now been qualitatively investigated in the following way. Compounds of the type $(t\text{-}C_4H_9NH)_2SiClX$ and $[(C_2H_5)_2N]_2SiClX$ were prepared with X = n-C_3H_7, C_2H_5, CH_3, H and Cl, and

Table 1. $(t-C_4H_9NH)_2SiClX + t-C_4H_9NH_2$.

X	Hydrochloride g	Per cent reaction
$n-C_3H_7$	<0.2	<2
C_2H_5	1.4	13
CH_3	5.3	48
H	10.4	95
Cl	10.1	92

Table 2. $[(C_2H_5)_2N]_2SiClX + (C_2H_5)_2NH$

X	Hydrochloride g	Per cent reaction
$n-C_3H_7$	<0.2	<2
C_2H_5	0.4	4
CH_3	1.4	13
H	9.8	89
Cl	10.0	91

these were refluxed with an excess of *tert.*-butylamine and diethylamine, respectively, in benzene solution. The amount of hydrochloride precipitated after ten hours was taken as a measure of the per cent reaction. From the results presented in Tables 1 and 2, it is seen that the reactivity increases in the order n-C_3H_7, C_2H_5, CH_3, H and that X = Cl gives a greater reactivity than any alkyl group. It also appears that *tert.*-butylamine reacts more readily than diethyl amine, probably due to the difference in steric requirement between these amines.

From the compounds, prepared in part 1 and 2 the following have not been described before (the Arabic figures refer to the numbering in the experimental part):

I	(1)	n-$C_3H_7Si(NHC_4H_9$-$t)_3$
II	(2)	n-$C_3H_7Si[N(C_2H_5)_2]_3$
III	(4)	n-$C_3H_7Si[N(CH_3)(C_6H_5)]_3$
IV	(9)	$C_2H_5Si(NHC_4H_9$-$t)_3$
V	(9)	$C_2H_5Si[N(C_2H_5)_2]_3$
VI	(9)	$CH_3Si(NHC_4H_9$-$t)_3$
VII	(9)	$CH_3Si[N(C_2H_5)_2]_3$
VIII	(7)	$C_2H_5Si(NHC_4H_9$-$t)_2Cl$
IX	(7)	$C_2H_5Si[N(C_2H_5)_2]_2Cl$
X	(7)	$CH_3Si(NHC_4H_9$-$t)_2Cl$
XI	(7)	$CH_3Si[N(C_2H_5)_2]_2Cl$
XII	(7)	$HSi(NHC_4H_9$-$t)_2Cl$
XIII	(7)	$HSi[N(C_2H_5)_2]_2Cl$
XIV	(3)	n-$C_3H_7Si[N(CH_3)(C_6H_5)]_2Br$
XV	(5)	n-$C_3H_7Si[N(C_3H_7$-$i)_2]Br_2$

Their physical constants and analyses are given in Table 3.

EXPERIMENTAL

The method of the determination of the physical data of the compounds and the analyses have been previously described [1] and also the general performance of the syntheses. The preparation of n-propyltribromosilane and n-propyltriiodosilane will be described in a later paper.

1. n-*Propyltri-(*tert.-*butylamino)-silane (I). A.* 18.1 g (0.04 mole) of n-propyltriiodosilane in 50 ml of benzene were added dropwise to 21.9 g (0.3 mole) of *tert.*-butylamine in 75 ml of the same solvent, and then the mixture was refluxed for 10 h. Filtration left 24.1 g (calc. for the replacement of three halogen atoms 24.1 g) of *tert.*-butylamine hydroiodide, and fractionation of the filtrate gave 9.8 g (85 %) of I with the data given in Table 3.

B. 12.0 g (0.11 mole) of ethylbromide in 25 ml of ether were added dropwise to 2.7 g (0.11 mole) of magnesium in 15 ml of ether. After the addition the mixture was stirred for 15 min. Thereafter 8.8 g (0.12 mole) of *tert.*-butylamine in 20 ml of ether were slowly added, and the mixture was gently refluxed for 15 min. To the suspension of *tert.*-butylamine magnesium bromide formed, 25.1 g (0.1 mole) of n-propyldi(*tert.*-butyl-

Table 3. Physical constants and analyses of the compounds I–XV.

No.	M	B.p. °C	Pressure mm Hg	n_D^{20}	d^{20}	MR_D	% Si		Equiv.wt.	
							found	calc.	found	calc.
I	287.56	119–20	11	1.4427	0.8452	90.14	9.8	9.8	96.7	95.9
II	287.56	136–37	10	1.4599	0.8752	89.97	9.9	9.8	96.1	95.9
III	389.60	227–29	2–3				7.2	7.2	130.0	129.9
IV	273.53	115–16	14	1.4414	0.8459	85.46	10.2	10.3	92.6	91.2
V	273.53	133–34	14	1.4595	0.8773	85.32	10.3	10.3	92.3	91.2
VI	259.51	96–97	12	1.4370	0.8413	80.81	10.9	10.8	86.5	86.5
VII	259.51	115–16	12	1.4515	0.8672	80.65	10.9	10.8	87.0	86.5
VIII	236.86	95–96	12	1.4465	0.9280	68.13	11.8	11.9	236.3	236.9
IX	236.86	100–01	12	1.4517	0.9395	67.97	11.8	11.9	238.0	236.9
X	222.84	81–82	12	1.4419	0.9259	63.68	12.6	12.6	222.4	222.8
XI	222.84	84–85	12	1.4453	0.9343	63.52	12.6	12.6	223.7	222.8
XII	208.81	74–75	12	1.4379	0.9261	59.18	13.6	13.5	210.2	208.8
XIII	208.81	77–78	11	1.4433	0.9354	59.20	13.6	13.5	209.9	208.8
XIV	363.38	205–06	10	1.5770	1.2126	99.31	7.6	7.7	358.6	363.4
XV	331.19	114–15	10				8.6	8.5	335.1	331.2

amino)-chlorosilane were added. The ether was distilled off, and then the mixture was heated for 14 h at 125°C. On distillation 15 g of a liquid were obtained between 114° and 116°C at 10 mm Hg with a neutralization equivalent of 106 (calc. for I 95.9) and n_D^{20} = 1.4437; d^{20} = 0.8572. To complete the reaction this product was again heated with a small quantity of *tert.*-butylamine magnesium bromide for 14 h at 160°C. Distillation now gave 12.0 g (42 %) of a compound freed from chlorine and with the same data as the compound obtained in A.

2. n-*Propyltri-(diethylamino)-silane (II).* *A.* 9.3 g (0.03 mole) of *n*-propyltribromosilane in 40 ml of benzene were added to 16.1 g (0.22 mole) of diethylamine in 75 ml of benzene. The mixture was refluxed for 4 h. Filtration left 12.3 g diethylamine hydrobromide on the filter (calc. for complete reaction 13.9 g). 10 g of diethylamine were added to the filtrate, and the mixture was then refluxed overnight. Filtration now left 1.5 g of hydrobromide. Fractionation gave 5.0 g (58 %) of II with the data given in Table 3.

B. 25.1 g (0.1 mole) of *n*-propyldi-(diethylamino)-chlorosilane were added to diethylamine magnesium bromide obtained in the same way as the corresponding *tert.*-butylamine compound. After evaporation of the ether the mixture was heated for 4 h at 130°C. Distillation at 9 mm Hg gave three fractions: 110–120°C, 4 g, n_D^{20} = 1.4560; 120–127°C, 4 g, n_D^{20} = 1.4575; 127–135°C, 10 g, n_D^{20} = 1.4590. After a new treatment with about 0.05 mole of diethylamine magnesium bromide for 10 h at 160°C, 9.1 g (32 %) of II and 6 g of a first fraction with E = 103 were obtained.

3. n-*Propyldi-(N-methylanilino)-bromosilane (XIV).* 9.3 g (0.03 mole) of *n*-propyltribromosilane in 40 ml of benzene were added to 22.5 g (0.21 mole) of N-methylaniline in 50 ml of benzene. After the addition some hydrobromide had precipitated, but on warming this was quantitatively dissolved. The solution was refluxed overnight, and the hydrobromide precipitated after cooling was filtered off. The benzene and the excess of N-methylaniline were distilled off. On fractionation of the residue, 3.3 g (30 %) of XIV were obtained. 4.5 g of a product distilled between 160° and 180°C at 10 mm Hg and presumably contained *n*-propyl-(N-methylanilino)-dibromosilane. Only a small residue was left in the distillation flask, showing that *n*-propyltri-(N-methylanilino)-silane cannot be obtained in this way.

4. n-*Propyltri-(N-methylanilino)-silane (III).* 8.9 g (0.05 mole) of *n*-propyltrichlorosilane in 25 ml of ether were slowly added to N-methylaniline magnesium iodide obtained from 3.9 g (0.16 mole) of magnesium, 22.7 g (0.16 mole) of methyliodide and 21.4 g (0.2 mole) of N-methylaniline. After refluxing for 30 min, the ether was distilled off and

the residual mixture was heated for 6 h at 130°C. Fractionation gave 7.0 g (36 %) of III as a very viscous syrup and a first fraction of about 6 g between 160° and 200°C at 2—3 mm Hg.

5. n-*Propyl-(di-*iso*propylamino)-dibromosilane (XV).* 31.1 g (0.1 mole) of *n*-propyltribromosilane in 100 ml of benzene were added dropwise to 50.6 g (0.5 mole) of di-*iso*propylamine in 100 ml of the same solvent. The mixture was then refluxed for 4 h. Filtration left 18.9 g (calc. for the replacement of one bromine atom 18.2 g) of di-*iso*-propylamine hydrobromide on the filter. Further refluxing of the filtrate for 30 h gave only 0.3 g more hydrobromide, so it is seen that the diaminosilane cannot be obtained in reasonable yield by this method. The yield of XV was 22.5 g (68 %). It is immediately hydrolyzed in contact with moist air and was never quite freed from hydrobromide.

6. 24.2 g (0.1 mole) of *n*-propyl-(di-*iso*propylamino)-dichlorosilane were heated for 22 h at 150°C with di-*iso*propylamine magnesium bromide obtained from 2.7 g (0.11 mole) of magnesium, 12.0 g (0.11 mole) of ethylbromide and 12.1 g (0.12 mole) of di-*iso*propyl-amine. On fractionation of the mixture at 9 mm Hg most of the dichlorosilane was recovered, but at 120—135°C there were obtained 5.1 g of a product which consumed acid to an extent corresponding to about 75 % *n*-propyldi-(di-*iso*propylamino)-chloro-silane and 25 % of the dichlorosilane. No further attempts were made to isolate a pure compound from this fraction.

7. The compounds VIII—XIII used for the investigation in part 2 were all prepared by addition dropwise of 59 g (0.8 mole) of *tert.*-butylamine or diethylamine in 100 ml of ether to 0.2 mole of the appropriate trihalosilane in 100 ml of the same solvent and refluxing for 2 h. The amine hydrochlorides precipitated (43.8 ± 0.5 g; calc. 43.8 g) were filtered off. The yields of diamino compounds ranged from 55 to 70 %.

The preparation of *n*-propyldi-(*tert.*-butylamino)-chlorosilane and the corresponding diethylamine compound, which were also used in part 2, has been earlier described [1]. Di-(*tert.*-butylamino)-dichlorosilane and di-(diethylamino)-dichlorosilane have been prepared by Breederveld and Waterman [4-5]. Here they were prepared in the same way as VIII—XIII, and the data of the compounds obtained were in good agreement with those given in Refs.[4-5].

8. The experiments in part 2 were performed by refluxing a mixture of 0.10 mole of the compounds $(t\text{-BuNH})_2SiClX$ or $[(C_2H_5)_2N]_2SiClX$ with 21.9 g (0.3 mole) of *tert.*-butyl-amine respectively diethylamine in 100 ml of benzene for 10 h. After cooling, the precipitated amine hydrochloride was separated from the reaction mixture, carefully washed with benzene and dried. The appropriate filtrates were used for the syntheses below.

9. As is seen from Tables 1 and 2 the direct treatment of ethyltrichlorosilane or methyltrichlorosilane with *tert.*-butylamine or diethylamine will not give the compounds IV—VII in good yields. These compounds were more easily obtained according to method B in part 1:

Ethyltri-(tert.-*butylamino)-silane (IV).* After the benzene had been distilled off from the filtrate, mentioned in 8, the residue was added to 0.1 mole of *tert.*-butylamine magnesium bromide and the mixture was heated for 12 h at 160°C. On the following fractionation 10.2 g (37 %) of IV were obtained.

Ethyltri-(diethylamino)-silane (V) (9.8 g; 36 %), *methyltri-*(tert.-*butylamino)-silane* (VI) (10.5 g; 40 %) and *methyltri-(diethylamino)-silane* (VII) (9.6 g; 37 %) were obtained in exactly the same way as IV.

The author is indebted to Professor E. Larsson for his kind interest in this work.

REFERENCES

1. Tansjö, L. *Acta Chem. Scand.* **11** (1957) 1613.
2. Breederveld, H. and Waterman, H. I. *Research London* **6** (1953) s. 48.
3. Breederveld, H. and Waterman, H. I. *Research London* **6** (1953) s. 1.
4. Breederveld, H. and Waterman, H. I. *Research London* **6** (1953) s. 43.
5. Breederveld, H. and Waterman, H. I. *Research London* **5** (1952) 537.

Received September 30, 1958.