TRANSSILYLATION OF DISILAZANES WITH 1-CHLORO-1-METHYL-1-SILACYCLOBUTANE AND OTHER TRIORGANYLCHLOROSILANES

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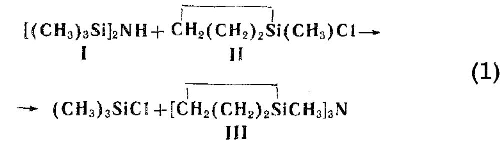
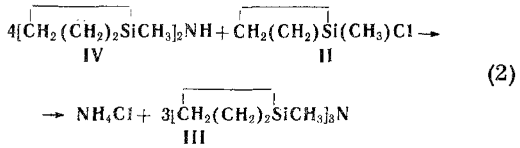
The first stage of the reaction of hexamethyldisilazane with 1-chloro-1-methyl-1-silacyclobutane gives 1, 3, 3, 3-tetramethyl-1, 1-trimethylenedisilazane $CH_2(CH_2)_2Si(CH_3)NHSi(CH_3)_3$, and after that 1, 3-dimethyl-1, 3-bis(trimethylene)disilazane $[CH_2(CH_2)_2SiCH_3]_2NH$ is formed. The latter reacts with 1-chloro-1-methyl-1-silacyclobutane to give tris[methyl(trimethylene)silyl] amine $[CH_2(CH_2)_2SiCH_3]_3N$. From a large number of examples it is shown that transsilylation of disilazanes with chlorosilanes is a general reaction.

We previously showed [1] that hexamethyldisilazane (I) reacts with excess 1-methyl-1-chloro-1-silacyclobutane (II), to give basically the corresponding trisilylamine (III):



$$\underset{I}{[(CH_3)_3Si]_2NH} + \underset{II}{CH_2(CH_2)_2Si(CH_3)Cl} \to (CH_3)_3SiCl + \underset{III}{[CH_2(CH_2)_2SiCH_3]_3N} \quad (1)$$

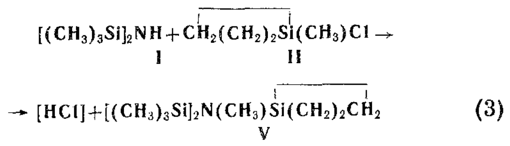
III is also obtained by reacting II with the disilazane IV:



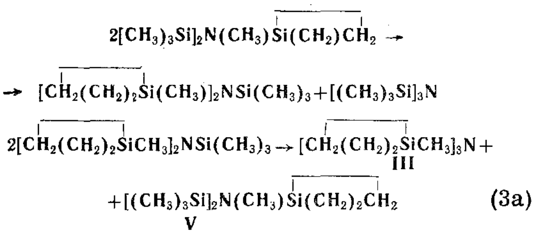
$$4\underset{IV}{[CH_2(CH_2)_2SiCH_3]_2NH} + \underset{II}{CH_2(CH_2)Si(CH_3)Cl} \to NH_4Cl + 3\underset{III}{[CH_2(CH_2)_2SiCH_3]_3N} \quad (2)$$

It was of interest to investigate reaction 1 in greater detail, and to obtain information about the stages involved in formation of III.

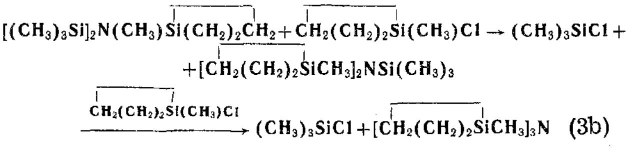
It could be postulated that III is formed from the trisilyl-substituted amine V, which is transsilylated by II* or disproportionated:



$$\underset{I}{[(CH_3)_3Si]_2NH} + \underset{II}{CH_2(CH_2)_2Si(CH_3)Cl} \to [HCl] + \underset{V}{[(CH_3)_3Si]_2N(CH_3)Si(CH_2)_2CH_2} \quad (3)$$



$$2[(CH_3)_3Si]_2N(CH_3)Si(CH_2)CH_2 \to [CH_2(CH_2)_2Si(CH_3)]_2NSi(CH_3)_3 + [(CH_3)_3Si]_3N$$
$$2[CH_2(CH_2)_2SiCH_3]_2NSi(CH_3)_3 \to \underset{III}{[CH_2(CH_2)_2SiCH_3]_3N} + \underset{V}{[(CH_3)_3Si]_2N(CH_3)Si(CH_2)_2CH_2} \quad (3a)$$



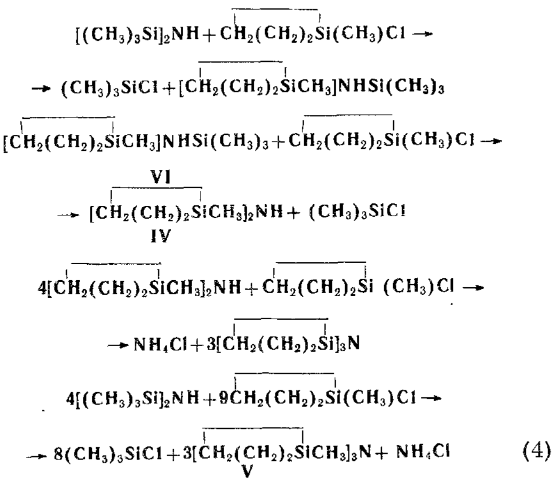
$$[(CH_3)_3Si]_2N(CH_3)Si(CH_2)_2CH_2 + CH_2(CH_2)_2Si(CH_3)Cl \to (CH_3)_3SiCl + [CH_2(CH_2)_2SiCH_3]_2NSi(CH_3)_3 \xrightarrow{CH_2(CH_2)_2Si(CH_3)Cl} (CH_3)_3SiCl + [CH_2(CH_2)_2SiCH_3]_3N \quad (3b)$$

To check on whether the reaction of Eq. 3a takes place, we ran a control in which V, specially synthesized as described in [1], was heated at 145–150° in a sealed tube, in the presence of 5% by weight of ammonium chloride. It was shown that 4 hours heating left V unchanged, so that Eq. 3a was excluded.

Evidently reaction 3b is also excluded, since, as a control showed, tris(trimethylsilyl)amine does not react with II.

Thus though formation of V in the first stage is also possible, to postulate by analogy with reaction 2, subsequent formation of III from it, is improbable.

Another route to III can be transsilylation of I:



$$[(CH_3)_3Si]_2NH + CH_2(CH_2)_2Si(CH_3)Cl \to (CH_3)_3SiCl + [CH_2(CH_2)_2SiCH_3]NHSi(CH_3)_3$$
$$\underset{VI}{[CH_2(CH_2)_2SiCH_3]NHSi(CH_3)_3} + CH_2(CH_2)_2Si(CH_3)Cl \to \underset{IV}{[CH_2(CH_2)_2SiCH_3]_2NH} + (CH_3)_3SiCl$$
$$4[CH_2(CH_2)_2SiCH_3]_2NH + CH_2(CH_2)_2Si(CH_3)Cl \to NH_4Cl + 3[CH_2(CH_2)_2Si]_3N$$
$$4[(CH_3)_3Si]_2NH + 9CH_2(CH_2)_2Si(CH_3)Cl \to 8(CH_3)_3SiCl + 3\underset{V}{[CH_2(CH_2)_2SiCH_3]_3N} + NH_4Cl \quad (4)$$

To determine the possibility of a reaction taking place in accordance with Eq. 4, I was reacted with II, using a mole ratio 2:1. 1,3,3,3-tetramethyl-1,1-trimethylenedisilazane VI and 1,3-dimethyl-1,I,3,3-bis-(trimethylene)disilazane (IV).

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*Transsilylation of silazanes is known, but little investigated. Thus it has been established [2] that I reacts with tetrachlorosilane according to the equation $[(CH_3)_3Si]_2NH + SiCl_4 \to (CH_3)_3SiNHSiCl_3 + (CH_3)_3SiCl$. A similar reaction of trisilylamines has been described, but instead of chlorosilanes, BCl_3 was used [3]: $(H_3Si)_3N + BCl_3 \to H_3SiCl + (H_3Si)_2NBCl_2$.

Table 1

Physicochemical Constants, Yields, Analytical Data, and Molecular Weights for the Disilazanes Synthesized

Formula	Mole ratio $[(CH_3)_3Si]_2NH : R_3SiCl$ —	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	M (cyroscopic in benzene)		MR_D		Molecular Formula	N, %		Yield, %
					Found	Calculated	Found	Calculated		Found	Calculated	
$[\overline{CH_2(CH_2)_2Si}(CH_3)]_2NH$*	1 : 2	54.5—66 (3—4)	1.4810	0.9210	185.0	185.36	57.2	57.23	$C_8H_{19}NSi_2$	7.4	7.57	48.5
$[\overline{CH_2(CH_2)_2Si}(C_2H_5)]_2NH$	1 : 4	108—108.5 (7)	1.4860	0.9292	215.3	213.4	65.98	66.25	$C_{10}H_{23}NSi_2$	6.2	6.57	75.0
$\overline{CH_2(CH_2)_2Si}(CH_3)NHSi(CH_3)_3$	1 : 0.5 1 : 2	68—72 (19)	1.4466	0.8498	176.0	173.4	54.41	54.23	$C_7H_{19}NSi_2$	7.6	8.07	24.2 29.4
$[\overline{CH_2(CH_2)_3Si}(CH_3)]_2NH$**	1 : 2.0	87—89 (4)	1.4838	0.9291	213.0	213.4	65.4	65.49	$C_{10}H_{23}NSi_2$	6.6	6.57	56.0
$[CH_2{=}CH(CH_3)_2Si]_2NH$	1 : 2.5	162—163 (760)	1.4405	0.8186	184	185.36	59.65	59.55	$C_8H_{19}NSi_2$	7.42	7.57	77.3
$[CH_2{=}CHCH_2(CH_3)_2Si]_2NH$	1 : 2.5	62.5—63.(4—5)	1.4510	0.8342	217.7	213.4	69.0	69.17	$C_{10}H_{23}NSi_2$	6.10	6.57	56.3
$[n\text{-}C_3H_7(CH_3)_2Si]_2NH$	1 : 2.0	67—69 (5)	1.4320	0.8115	226	217.4	69.5	69.85	$C_{10}H_{27}NSi_2$	6.08	6.44	57.2
$[ClCH_2(CH_3)_2Si]_2NH$	1 : 2.5	95.5 (7)	1.4685	1.0543	228.2	230.25	60.77	60.91	$C_6H_{17}NCl_2Si_2$	5.86	6.09	87,0
$[C_6H_5(CH_3)_2Si]_2NH$***	1 : 2.5	156—158 (6)	1.5360	0.9866	277	285.47	90.4	90.87	$C_{16}H_{23}NSi_2$	4.80	4.91	69.0
$[C_6H_5(CH_3)_2Si]NHSi(CH_3)_3$	1 : 0.5	84.5—85 (5)	1.4862	0.9031	219	223,4	71.06	71.05	$C_{11}H_{21}NSi_2$	5.90	6.27	54.0

The literature gives: * 91—92° (14mm); n_D^{20} 1.4810; d_4^{20} 0.9200[1]; **111—112° (6mm); n_D^{20} 1.4833; d_4^{20} 0.9283[1]; *** 128—129° (2—3mm); n_D^{20} 1.5384; d_4^{20} 0.9850[4].

Table 2

Starting Triorganylchlorosilanes

Compound	Bp, °C (pressure, mm)	n_D^{20}	Cl, %	
			Found	Calculated
$\overline{\mathrm{CH_2(CH_3)_2Si}}\mathrm{(CH_3)Cl}$	102—103 (760)	1.4482	29.6	29.43
$\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(C_2H_5)Cl}$	133.5 (760)	1.4567	26.7	26.4
$\overline{\mathrm{CH_2(CH_2)_3Si}}\mathrm{(CH_3)Cl}$	129 (760)	1.4537	26.5	26.4
$\mathrm{ClCH_2(CH_3)_2SiCl}$	114—116 (760)	1.4370	25.10	24.85
$\mathrm{C_6H_5(CH_3)_2SiCl}$	73—75 (9—10)	1.5095	20.9	20.8
$\mathrm{CH_2{=}CH(CH_3)_2SiCl}$	82—83 (760)	1.4140	29.85	29.5
$\mathrm{CH_2{=}CH_2{-}CH_2(CH_3)_2SiCl}$	113—115 (760)	1.4295	26.3	26.35
$n\text{-}\mathrm{C_3H_7(CH_3)_2SiCl}$	111.5—113 (760)	1.4127	26.0	26.0

When reaction 4 was run using a 1:1 mole ratio of I:II, the products were III, IV, and VI. The reaction of I with 1-chloro-1-ethyl-1-silacyclobutane (mole ratio of reactants and reaction conditions the same as for I) also confirms that III is formed by Eq. 2. Because of the large volume of the group $\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{C_2H_5}$ compared with that of $\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{CH_3}$ it could be assumed that reaction 4 would lead primarily or solely to the disilazane $[\underline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{C_2H_5}]_2\mathrm{NH}$, and this was found experimentally to be the case.

Transsilylation can be extended to many triorganochlorosilanes with alkyl, aryl, chlormethyl and other substituents at the silicon atom:

$$[(\mathrm{CH_3})_3\mathrm{Si}]_2\mathrm{NH}+\mathrm{RR_2'SiCl}\rightarrow(\mathrm{CH_3})_3\mathrm{SiCl}+[\mathrm{RR_2'Si}]_2\mathrm{NH}$$
$$\mathrm{R{=}CH_2{=}CH};\quad \mathrm{CH_2{=}CH{-}CH_2};\quad \mathrm{C_6H_5};$$
$$\mathrm{ClCH_2};\quad n\text{-}\mathrm{C_3H_7};\quad \mathrm{R'{=}CH_3};$$

or
$$\mathrm{RR_2'Si{=}}\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(CH_3)};\quad \overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(C_2H_5)};$$
$$\overline{\mathrm{CH_2(CH_2)_3Si}}\mathrm{(CH_3)} \qquad (5)$$

It can also be used to synthesize unsymmetrical disilazanes:

$$[(\mathrm{CH_3})_3\mathrm{Si}]_2\mathrm{NH}+\mathrm{C_6H_5(CH_3)_2SiCl}\rightarrow$$
$$\rightarrow\mathrm{C_6H_5(CH_3)_2SiNHSi(CH_3)_3}+(\mathrm{CH_3})_3\mathrm{SiCl} \qquad (6)$$

Transsilylation proceeds readily, is characterized by high yields (up to 90%), and in a number of cases can be used as a simple preparative method for symmetrical and unsymmetrical disilazanes. We consider that it is best effected by boiling the reactants in a flask fitted with a fractionating column with slow bleed-off of the much lower boiling chlorosilane formed (trimethylchlorosilane when I is used). However transsilylation can be effected by simply distilling a mixture of disilazane and chlorosilane from a Claisen flask, as we confirmed for I and II.

Physico-chemical constants and yields of disilazanes obtained by transsilylation, as well as the mole ratios of the reactants, are given in Table 1.

EXPERIMENTAL

The starting I had bp 125—126°, n_D^{20} 1.4085, d_4^{20} 0.7750. Table 2 gives the constants of the triorganylchlorosilanes used.

The transsilylation of disilazanes with chlorosilanes was run in a flask fitted with a fractionating column with a 400 mm long glass-packed section. In the case of reaction of I with various triorganylchlorosilanes, the resultant trimethylchlorosilane was slowly distilled off at 56.5–59°. Reaction was carried out with various mole ratios of reactants (see Table 1). Benzene or toluene (150–250 ml per 1 mole of I) was the solvent when reacting chloro derivatives of 1-silacyclobutane, to prevent polymerization of the silane derivatives of 1-silacyclobutane formed.

Transsilylation of I with phenyldimethylchlorosilane. A mixture of 16.1 g (0.1 mole) I and 8.5 g (0.05 mole) phenyldimethylchlorosilane was charged to a flask fitted with a fractionating column, and heated to boiling. 5 min after start of refluxing the column head temperature settled down to 56.5°. In 30 min 4.6 g trimethylchlorosilane was taken off, bp 56.5–59° (85% yield). The residue in the flask was transferred to a Claisen flask, and excess I distilled off. Vacuum-distillation then gave 6 g (0.027 mole) 1, 1, 3, 3, 3-pentamethyl-1-phenyldisilazane and 1.9 g (0.0075 mole) 1, 3-bis(phenyldimethyl)disilazane.

Reaction of I with 1-chloro-1-methyl-1-silacyclobutane. a) A solution of 32.2 g (0.2 mole) I in 50 ml dry benzene was brought to react with 48.1 g (0.4 mole) $\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(CH_3)Cl}$ as described above. After distilling off the trimethylchlorosilane the mixture was distilled from a Claisen flask, and I and benzene vacuum-distilled off. Subsequent distillation gave 10.2 g (0.059 mole) $\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(CH_3)NHSi(CH_3)_3}$, 17.9 g (0.097 mole) $[\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(CH_3)}]_2\mathrm{NH}$ and 2.0 g (0.0074 mole) $[\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(CH_3)}]_3\mathrm{N}$.

b) A mixture of 32.2 g (0.2 mile) I and 12.05 (0.1 mole) $\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(CH_3)Cl}$ was put in a Claisen flask and distilled at atmospheric pressure. After distilling off 12 g material bp 60–115°, the residue was vacuum-distilled, to give 4.2 g (0.024 mole) $\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(CH_3)NHSi(CH_3)_3}$ and 2.8 g (0.015 mole)

$[\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{CH_3}]_2\mathrm{NH}$.

Coammonolysis of trimethylchlorosilane and 1-chloro-1-methyl-1-silacyclobutane. The method described in [1] was used to prepare, from 108.5 g (1 mole) trimethylchlorosilane and 21 g (0.17 mole) $\overline{\mathrm{CH_2(CH_2)_2Si}}\mathrm{(CH_3)Cl}$ 15 g (0.087 mole, 50%) 1, 3, 3, 3-tetramethyl-1, 1(trimethylene)disilazane, bp 71—75° (19 mm), n_D^{20} 1.4455, d_4^{20} 0.8527. Found: MR_D 54.11, M 175. Calculated MR_D 54.23, M 173.4.

REFERENCES

1. N. S. Nametkin, V. M. Vdovin, E. D. Babich,

and V. D. Oppengeim, KhGS [Chemistry of Heterocyclic Compounds], 455, 1965.

2. H. Grobe-Ruyken and K. Schaarschmidt, Chem. Techn., **11**, 1959.

3. A. B. Burg and E. S. Kuljian, J. Am. Chem. Soc., 72, 3103, 1950.

4. M. F. Shostakovskii and K. I. Kondrat'ev, Izv. AN SSSR, OKhN, 811, 1956.

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