SYNTHESIS AND PROPERTIES OF SILACYCLOBUTYLSILAZANES

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Ammonolysis of silacyclobutanes $(CH_2)_3SiRCl$ (R=Cl, CH₃) gives silacyclobutane di- and polysilazanes.

Reaction of the disilazane $[(CH_2)_3SiCH_3]_2NH$ with 1-chloro-1-methyl-1-silacyclobutane at 20-80° gives

a trisilyl-substituted amine $[(CH_2)_3SiCH_3]_3N$. Trisilyl-substituted amines with one silacyclobutyl group,

are obtained by reacting silacyclobutanes $(CH_2)_3SiRCl$ (R=CH₃, C₆H₅). with sodium or potassium silyl-
amides prepared from hexamethyldisilazane. It is shown that it is possible to obtain silylamides by react-
ing disilazanes directly with potassium metal at 90-100°.

The present work, a continuation of previous research on synthesizing Si-substituted 1-silacyclobutanes [1-5], deals
with the preparation of previously unknown silacyclobutane silazane derivatives.

Investigation of ammonolysis of 1-chloro-1-methyl-1-silacyclobutane and 1, 1-dichloro-1-silacyclobutane by way
of models, showed that the reaction is analogous to that with alkylchlorosilanes [6], and can be used for preparative pur-
poses in the synthesis of linear and cyclic silazanes of the type
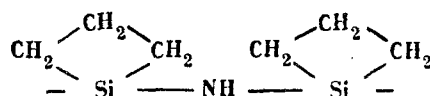
The possibility of obtaining trisilyl-substituted amines with silacyclobutane groups was also investigated.

It is known [6] that trisilyl-substituted amines of the type $(R_3Si)_3N$, where R is a hydrocarbon group, cannot be pre-
pared from ammonia and a trialkylchlorosilane or from disilazanes and trialkylchlorosilanes. For example [7], hexa-
methyldisilazane and trimethylchlorosilane do not react even when heated together in a sealed tube at 550°, in the pres-
ence of pyridine as a hydrogen chloride acceptor. It proved possible to synthesize trisilyl-substituted amines by using sil-
ylamides $(R_3Si)_2NM$ (M=Na, K, Li) [8], or by reacting triorganochlorosilanes R_3SiCl (R=CH₃), with sodamide [9]. In the
latter case the reaction products contain not only disilazane and silylamide, but also trisilylamine. Trisilylamine is
formed in high yield by reacting organochlorosilanes with lithium azide [10].

It was unexpected to find that, unlike the above examples, disilazanes and chlorosilanes of the silacyclobutane
series react with one another even at room temperature. In boiling benzene solution the yield of trisilyl-substituted
amine reaches 56%. The reaction can be represented by the following equation:
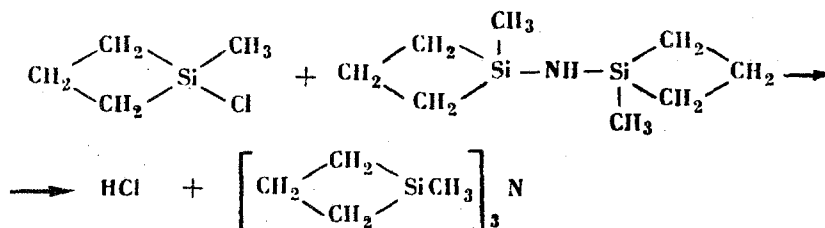
It is known [6, 7] that hydrogen chloride readily reacts with silylamines, and in the present case the reaction is
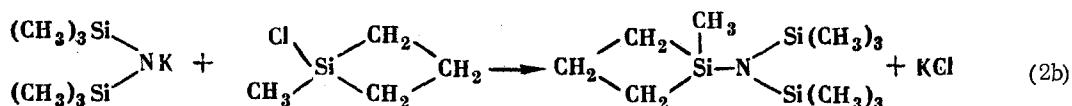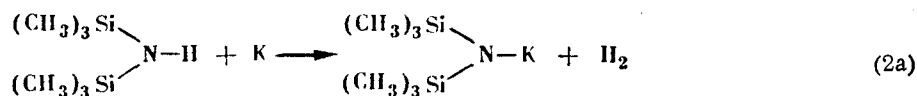apparently:
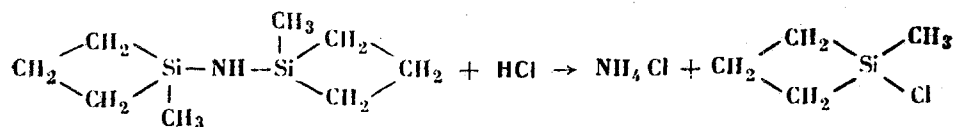
Consequently, in similar reactions, it is possible to use additional acceptors for the hydrogen chloride liberated at the
first stage of reaction (1a).

To answer the question, whether reaction (1) is characteristic only of silacyclobutane derivatives, or whether it can be extended to derivatives of other silacycloalkanes, the behaviors of the silacyclopentane derivatives $[(CH_2)_4SiCH_3]_2NH$ and $(CH_2)_4Si(CH_3)Cl$ were investigated. However, the compounds were found not to react under the conditions used for reaction (1), but if the silacyclobutane ring is present in only one component (disilazane or chlorosilane), reaction occurs, though less vigorously, though then the reaction products were more complex than would be expected from Eq. (1).
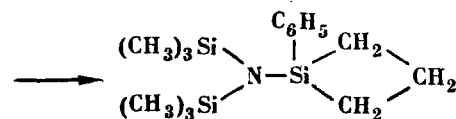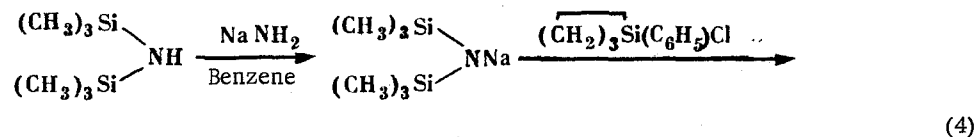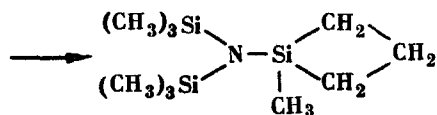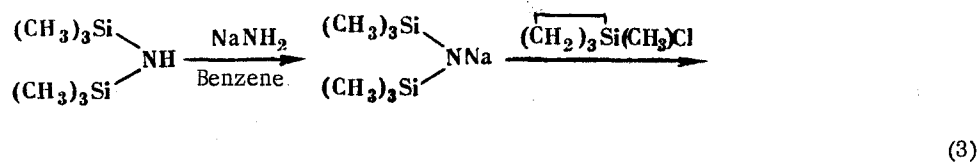
To determine the peculiarities of the course of reaction with compounds containing various substituents at the silicon atom, the reaction between hexamethyldisilazane and $(CH_2)_3Si(CH_3)Cl$ was investigated. The reaction products were uniformly found to be a high-boiling fraction, bp 180-270° (760 mm), from which it did not prove possible to isolate as an individual the expected $[(CH_3)_3Si]_2NSi(CH_2)_3$. At the same time, trimethylchlorosilane was found to be formed in an amount greater than would be expected according to Eq. (1b). If excess $(CH_2)_3Si(CH_3)Cl$ was used and the reaction carried out in flask fitted with a fractionating column, the trimethylchlorosilane formed being led off (thus shifting the equilibrium over to the side of formation of trisilyl-substituted amines), a substance was obtained with analytical data and IR spectrum identical with that of the trisilylamine $[(CH_2)_3SiCH_3]_3N$, prepared by reaction (1a).

The unsymmetrical trisilylamine $[(CH_2)_3SiCH_3]N[Si(CH_3)_3]_2$, which could not be isolated from the products of the reaction mentioned, was prepared in two steps, thus:

$$\begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} N-H \; + \; K \longrightarrow \begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} N-K \; + \; H_2 \qquad (2a)$$

$$\begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} NK \; + \; \text{[Cl-Si ring]} \longrightarrow \text{[product]} \; + \; KCl \qquad (2b)$$

It is of interest to mention that reported attempts to effect reaction (2a) have been unsuccessful [7]. Here it has been possible to carry out the reaction because tubes evacuated to 10^{-2} to 10^{-3} mm and sealed were used (apparently in a hydrogen atmosphere the reaction surface of the potassium is activated).

For preparing unsymmetrical trisilyl-substituted amines with one silacyclobutane group in the molecule, sodium silylamides were also used, these being prepared by a known method [8] from disilazanes using sodamide:

$$\begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} NH \xrightarrow[\text{Benzene}]{NaNH_2} \begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} NNa \xrightarrow{(CH_2)_3Si(CH_3)Cl}$$

$$\qquad (3)$$

$$\longrightarrow \begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} N-Si \text{[ring CH}_2\text{]}$$

$$\begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} NH \xrightarrow[\text{Benzene}]{NaNH_2} \begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} NNa \xrightarrow{(CH_2)_3Si(C_6H_5)Cl}$$

$$\qquad (4)$$

$$\longrightarrow \begin{array}{c}(CH_3)_3Si \\ \diagdown \\ \diagup \\ (CH_3)_3Si\end{array} N-Si \text{[ring CH}_2\text{, C}_6H_5\text{]}$$

The properties of the products obtained by reactions 2b and 3, were identical.

Neither the trisilylamines containing a silacyclobutane group, prepared in the course of the present work, nor the tris(trimethylsilyl)amine were titrated with 0.1 N HCl by the method [11], used for determining nitrogen in disilazanes.

Investigation of the resistance to hydrolysis of some silazane derivatives of silacyclobutane by a method previously reported [12], showed that on hydrolysis in toluene − 0.3 N aqueous NH_4Cl at the boiling point of the mixture, the sila-

Compound no.	Structural formula	Bp, °C (Pressure mm)	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calculated [1]	Molecular formula	Found, % C	H	Si	N*	Calculated, % C	H	Si	N	M (Cryoscopic in benzene) Found	Calc.	Yield, %
I	(cyclic) CH_2–CH_2–Si(CH_3)–NH–Si(CH_3)(CH_2–CH_2) with CH_2 bridge	91—92(14)	1.4810	0.9200	57.28	57.23	$C_8H_{19}Si_2N$	52.59	10.71	29.8	7.4	51.83	10.33	30.28	7.66	185	185	60
II	[silacyclopentane–CH_3]$_3$N	111—113(2)	1.5013	0.9568	82.99	83.13	$C_{12}H_{27}Si_3N$	53.41	10.11	31.49	5.0	53.47	10.1	31.28	5.128	264	269	56
III	Si(CH_3)[$Si(CH_3)_3$]–N–$Si(CH_3)_3$ cyclic	97—99(8)	1.4660	0.8875	76.61	77.13	$C_{10}H_{27}Si_3N$	48.91	10.94	34.32	5.7	48.9	11.1	34.3	5.7	246	245.5	30—41
IV	Si(C_6H_5)[$Si(CH_3)_3$]–N–$Si(CH_3)_3$ cyclic	155—157(7)	1.5170	0.9645	96.30	96.90	$C_{15}H_{29}Si_3N$	59.02	9.26	26.85	4.87	58.51	9.52	27.4	4.57	303	307.6	18.5
V	[silacyclopentane–SiNH]$_3$	Mp 110—112°**			—	—	$C_{29}H_{21}Si_3N_3$	42.17	8.48	33.23	15.97	42.3	8.26	33.0	16.44	254	255.5	40.0
VI	Si(CH_3)–NH–Si with two silacyclopentane rings and CH_3	111—112(6)	1.4833	0.9283	65.55	65.49	$C_{10}H_{23}Si_2N$	—	—	25.28	6.6	—	—	26.3	6.57	213	213.3	60
VII	silacyclopentane Si(C_6H_5)Cl	103.5—105.5(7)	1.5476	1.0919	53.11	52.73	$C_9H_{11}SiCl$	Cl content 19.4				Cl content 19.45				181.5	182.87	20
VIII	Cl–$CH_2CH_2CH_2CH_2$Si(C_6H_5)Cl_2	142.5—143.5(4)	1.5367	1.2504	63.36	63.46	$C_9H_{11}SiCl_3$	Cl content 28.1				Cl content 28.0				—	253.76	40

*Nitrogen content determined by titration, or indirectly by hydrolysis followed by titration of the ammonia liberated.

**Substance not recrystallized.

cyclobutane disilazane [(CH$_2$)$_3$SiCH$_3$]$_2$NH hydrolyzes 17.5 times faster than hexamethyldisilazane*. In homogeneous medium, using acetone-water or tetrahydrofuran-water, silacyclobutane disilazane hydrolyzes somewhat slower than hexamethyldisilazane. The trisilyl-substituted amines [(CH$_3$)$_3$Si]$_3$ and [(CH$_2$)$_3$SiCH$_3$]$_3$ also hydrolyzes in the homogeneous acetone — 0.3 N NH$_4$Cl medium. However, there the trisilylamine [(CH$_2$)$_3$SiCH$_3$]$_3$N hydrolyzes considerably slower than tris(trimethylsilyl)amine. At the present time a detailed study is being made of hydrolysis of silazane derivatives of silacyclobutane, and information will be published later.

The table gives physical constants and analytical data for the compounds synthesized.

In every case the IR spectra of the compounds confirm the presence of the indicated structural groups.

With the disilazane VI the frequencies 860, 1025, 1076, and 1155 cm^{-1} characterize the 1,1-substituted silacyclobutane ring [15], and the band at 1256 cm^{-1} is connected with vibrations of the Si—CH$_3$ group, while the group ≡SiNHSi≡ is characterized by frequencies 934, 1175, and 3385 cm^{-1}.

With compounds I, V, VII the frequencies 920-923, 1120-1122, and 1180-1190 cm^{-1} indicate the presence of a 1,1-substituted silacyclobutane ring [15]. The frequencies 700, 998, 1480, and 1585 cm^{-1} for VII are characteristic of the Si—C$_6$H$_5$ bond. The 1254 cm^{-1} band in disilazane I is due to vibrations of the Si—CH$_3$ group. Regarding the absorption band of the group ≡SiNHSi≡ , in I it is connected with bands at 942, 1165, and 3380 cm^{-1}, and in V with bands at 954, 1179, and 3389 cm^{-1} [16].

In compounds II, III, and IV, the frequencies of the 1,1-substituted silacyclobutane ring are 910-925, 1122-1129, and 1184-1185 cm^{-1}; Si—C$_6$H$_5$ absorbs at 701, 998, 1111, 1488, and 1588 cm^{-1}; the absorption at 1250-1265 cm^{-1} is characteristic of the Si—CH$_3$ group. The absorption of the [≡Si]$_3$N group is characterized by a very intense band in the region 940-950 cm^{-1}.

Experimental

Starting materials

1-Chloro-1-methyl-1-silacyclobutane (bp 102.4°; Cl 29.6%), 1,1-dichloro-1-silacyclobutane (bp 112.4°, Cl 50.6%), and also 1-chloro-1-phenyl-1-silacyclobutane**, synthesized for the first time, were prepared by the method of [1]. 1-chloro-1-methyl-1-silacyclopentane (bp 128.5°, Cl 26.5%) was prepared by the method of [13]. Hexamethyldisilazane (bp 125-126° · n$_D^{20}$ 1.4070), and tris(trimethylsilyl)amine (bp 78° (13 mm), mp 70-71°) were prepared by the methods of [8, 14].

I. Dry ammonia gas was passed at the rate of 500 ml/min for 6 hr through a well-stirred solution of 25 g (0.2 mole) (CH$_2$)$_3$Si(CH$_3$)Cl in dry ether cooled to 3-5°, in a 3-necked flask fitted with a reflux condenser. The precipitate of NH$_4$Cl was filtered off, and washed with ether. The ether was distilled off from the filtrate, and the product vacuum-distilled, to give 11 g of the disilazane I.

V. Synthesized in a way similar to that described above. 60.0 g (0.42 mole) (CH$_2$)$_3$SiCl$_2$, gave 14.4 g (0.056 mole) V.

VI. Prepared similarly to V, from 38 g (0.18 mole) (CH$_2$)$_4$SiCH$_3$Cl , yield 23.4 g (0.11 mole).

II was prepared from [(CH$_2$)$_3$SiCH$_3$]$_2$NH and (CH$_2$)$_3$Si(CH$_3$)Cl by two methods:

a) A mixture of 7.4 g (0.04 mole) [(CH$_2$)$_3$SiCH$_3$]$_2$NH and 5.0 g (0.042 mole) (CH$_2$)$_3$SiCH$_3$Cl was heated for 15 hr in a sealed tube at 110-140° in a silicone bath. The white precipitate of NH$_4$Cl was filtered off; vacuum-distillation gave 3 g (0.011 mole) trisilylamine II, a transparent viscous liquid.

b) A mixture of 80 ml dry benzene, 19 ml (0.1 mole) [(CH$_2$)$_3$SiCH$_3$]$_2$NH , and 6.2 g (0.051 mole) (CH$_2$)$_3$Si(CH$_3$)Cl , was heated for 18 hr in a flask fitted with a reflux condenser and thermometer. Ammonium chloride was liberated during heating, sublimed along with solvent, and appeared on the condenser walls. Vacuum distillation gave 11.5 g (0.043 mole) II.

Reaction of [(CH$_3$)$_3$Si]$_2$NH with (CH$_2$)$_3$Si(CH$_3$)Cl.

A mixture of 9 g (0.056 mole) hexamethyldisilazane, 15 g (0.125 mole) (CH$_2$)$_3$SiCH$_3$Cl , and 30 ml dry benzene was placed in a flask fitted with a fractionating column with a glass packing (packing height 30 cm). Soon after wetting of the packing, the vapor temperature fell to 66° and stayed there for 0.5 hr, after which take-off of reflux was

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*For 50% conversion.

**Prepared from Cl(CH$_2$)$_3$Si(C$_6$H$_5$)Cl$_2$. The table gives the properties and analytical data of these compounds.

begun. It was continued so long as the temperature did not rise to 80°, and did not fall when take-off was interrupted. Repeated distillation of a 60-80% cut gave 9.4 g (0.086 mole, or 77%) of pure trimethylchlorosilane. Vacuum distillation of the still residue gave 3.85 g (0.014 mole, 35%) $[(CH_2)_3SiCH_3]_3N$.

III. A 0.5 l three-necked flask, fitted with bubbler, stirrer, and reflux condenser, was charged with 78.8 g (0.49 mole) hexamethyldisilazane, 18.5 g (0.475 mole) $NaNH_2$, and 300 ml benzene dried over sodium. The solution was vigorously stirred and refluxed while a stream of dry argon was passed to carry off the liberated ammonia. Heating was continued so long as ammonia continued to be evolved (12 hr). Then 57 g (0.47 mole) $\overline{(CH_2)_3}Si(CH_3)Cl$ was added (precipitate formed) over 30 mins, the mixture then stirred for 5 hr without heating, the benzene distilled off, and the residue vacuum distilled to give 35 g (0.14 mole) III.

IV was prepared similarly to III. 16.1 g (0.1 mole) hexamethyldisilazane and 3.9 g (0.1 mole) $NaNH_2$ gave silylamide, to which 18.25 g (0.1 mole) $\overline{(CH_2)_3}Si(C_6H_5)Cl$ was added, and the mixture heated for a further 6 hr, after which the precipitate was filtered off, and the filtrate vacuum distilled to give 5.6 g (0.018 mole) IV. 1.8 g (0.012 mole) diphenyl, bp 255°, mp 70°, was also isolated from the reaction products.

$[(CH_3)_3Si]_2NK$. 5 g (0.031 mole) hexamethyldisilazane and 1 g (0.023 mole) potassium metal were charged to a 50 ml glass ampul, which was then evacuated to 10^{-2} to 10^{-3} mm (until vigorous evolution of gas bubbles ceased on thawing) and sealed. The tube was heated for 15-20 hr in a silicone bath at 95-100°, when the potassium reacted and a bulky yellowish precipitate appeared. Excess pressure was observed when the tube was opened (hydrogen). To remove excess hexamethyldisilazane the tube was continuously evacuated for 2 hr at 1 mm.

III. The 8 g (0.04 mole) $[(CH_3)_3Si]_2NK$ obtained from two runs was dissolved in 200 ml dry benzene, and introduced into a flask fitted with stirrer, reflux condenser, dropping funnel, and gas inlet tube for introducing an inert gas. 4.8 g (0.04 mole) $\overline{(CH_2)_3}Si(CH_3)Cl$ was then added with stirring, when a finely divided crystalline substance precipitated. After 10 hr heating the precipitate was filtered off, and the filtrate vacuum distilled to give 4.0 g (0.0163 mole, or 41%) III.

The IR spectra of the compounds prepared were recorded with a UR-10 recording spectrophotometer in the region 400-3500 cm^{-1}. Liquids were measured with a 0.004 cm thick layer, and also in a capillary layer, while the solids were tabletted with KBr (weight of compound 0.0015 g per 2 g KBr) or investigated as CCl_4 solutions.

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