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Alkoxysilanes. III. Preparation of Alkoxysiloxyaminosilane and Some of Its Reactions

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Bis(tri-*t*-butoxysiloxy)diaminosilane was prepared by the reaction of the corresponding dichlorosilane with ammonia. It was also obtained by the reaction of silicon tetrachloride with tri-*t*-butoxysilanol in the presence of pyridine as a dehydrochloric acid agent, followed by the subsequent reaction of the mixture with ammonia. The alcoholysis, transamination reaction, hydrolysis, and acetolysis of this compound with *n*-butyl alcohol, phenol, aniline, *n*-butylamine, water, and acetic acid led to the formation of the corresponding bis(tri-*t*-butoxysiloxy)silane derivatives. In these reactions, the measurement of the ammonia evolved made it possible examine the relative reactivity of the reactants. An attempt to isolate the triaminosilane by the reaction of tri-*t*-butoxysiloxytrichlorosilane with ammonia resulted in the formation of tetraaminocyclotetrasilazane and a polymeric substance containing the silicon-nitrogen bond.

It has been previously established that the hydroxy or amino group attached to the silicon atom in alkoxy or alkylsilanes is apt to be susceptible to condensation to form a siloxane or silazane bond,[1] but these groups are stabilized in the silicon com-

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[1] P. Fessenden and J. S. Fessenden, *Chem. Revs.*, **61**, 316 (1961).

pounds containing two or three secondary or tertiary alkyl groups.[2,3]

We have reported that the hydroxy group can be stabilized remarkably by introducing the tributoxysiloxy group into silicon compounds; thus silanediol and even-triol can be obtained.[4] Therefore, it was also expected that the introduction of this substituent into silicon compounds would stabilize the amino groups and permit the isolation of di- or triaminosilane with tributoxysiloxy groups.

In the present work, the preparation of the aminosilanes and its reactions with alcohols, amines water, and acetic acid were investigated.

Results and Discussion

Bis(tri-*t*-butoxysiloxy)diaminosilane was prepared in about an 80% yield by the reaction of bis(tri-*t*-butoxysiloxy)dichlorosilane with ammonia. The same compound was also obtained in about a 65% yield by the reaction of silicon tetrachloride with tri-*t*-butoxysilanol in the presence of pyridine, followed by treatment of the reaction mixture with ammonia;

$$[(Bu^tO)_3SiO]_2SiCl_2 \xrightarrow{NH_3} [(Bu^tO)_3SiO]_2Si(NH_2)_2$$

$$SiCl_4 + 2(Bu^tO)_3SiOH + 2C_5H_5N \xrightarrow{NH_3} [(Bu^tO)_3SiO]_2Si(NH_2)_2 + 2C_5H_5NHCl$$

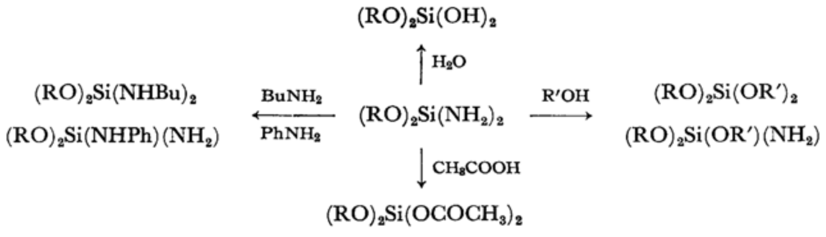
It could be distilled as a white crystalline solid without condensation, and it had a low melting point (55—57°C) and a high solubility in common organic solvents.

The diaminosilane reacted easily with water and acetic acid to give the corresponding silanediol and diacetoxysilane. However, alcoholysis and transamination reaction appear to occur step by step, for the reaction of the diaminosilane with phenol and *n*-butyl alcohol afforded only monobutoxy and monophenoxy derivatives when *n*-hexane was used as a solvent, whereas diphenoxy and dibutoxy derivatives were obtained by the reaction at the boiling point of each reactant. Similar results were obtained from transamination; the reaction of the diaminosilane with *n*-butylamine and aniline under the reflux of each reactant gave di-*n*-butylaminosilane and monoanilinosilane, but the further replacement of the amino group by aniline was difficult under the present conditions (Scheme 1).

Results similar to our findings that alcoholysis takes place step by step had been reported by Miner *et al.*,[2] who investigated the reaction of di-*t*-butoxydiaminosilane with alcohols and suggested that the reaction depends on the steric effect of the alkyl group of the alcohol. Therefore, the formation of mono-substituted derivatives when *n*-hexane is used as the solvent seems attributable to the steric effect of the *n*-butyl or phenyl group. Figure 1 shows the relative rates of transamination and alcoholysis determined by measuring the ammount of ammonia evolved. Apparently the reaction rate of *n*-butyl amine is faster than that of aniline, but the readiness of alcoholysis is not always in the phenol $>$ *n*-butyl alcohol order since the reaction temperatures are not taken into consideration.

In order to obtain tri-*t*-butoxysiloxytriaminosilane, the reaction of the corresponding trichlorosilane with ammonia was carried out. This reaction afforded, instead of the desired compound, a cyclosilazane containing a free amino group, which was identified as tetraaminotetra(tri-*t*-butoxysiloxy)cyclotetrasilazane $[(Bu^tO)_3SiOSi(NH_2)(NH)]_4$. Identification was made on the basis of the evidence from elemental analysis, the molecular-weight determination, and the infrared absorption peaks at 3450 and 3350 (ν_{NH}), 1530 (δ_{NH2}), 1050 ($\nu_{Si-O-Si}$), and 950 ($\nu_{Si-N-Si}$) cm^{-1}.

In general, the reaction between trichlorosilane and ammonia leads to the formation of silsesquiazene;[5] nevertheless, in this case the cyclosilazane containing free amino groups was obtained.



$$\begin{tikzcd}
 & (RO)_2Si(OH)_2 & \\
\begin{matrix}(RO)_2Si(NHBu)_2 \\ (RO)_2Si(NHPh)(NH_2)\end{matrix} & (RO)_2Si(NH_2)_2 \arrow[l, "BuNH_2"', "PhNH_2"] \arrow[u, "H_2O"] \arrow[r, "R'OH"] \arrow[d, "CH_3COOH"] & \begin{matrix}(RO)_2Si(OR')_2 \\ (RO)_2Si(OR')(NH_2)\end{matrix} \\
 & (RO)_2Si(OCOCH_3)_2 &
\end{tikzcd}$$

where $R=(BuO)_3Si$ and $R'=Bu$ or Ph

Scheme 1

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2) C. S. Miner, L. A. Bryan, R. P. Holysz and G. W. Pedlow, *Ind. Eng. Chem.*, **39**, 1368 (1947).

3) J.E. Wright, R.O. Bolt, A. Goldschmidt and A.D. Abbott, *J. Am. Chem. Soc.*, **80**, 1733(1951); C. R.(1951). Morgan, W. F. Olds and A. L. Rafferty, *ibid.*, **73**, 5193

4) Presneted at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

5) U. Wannagat, E. Bogush and F. Hofler, *J. Organometal. Chem.*, **7**, 203 (1967); K. A. Andrianov and G. V. Kotrelev, *ibid.*, **7**, 217 (1967).

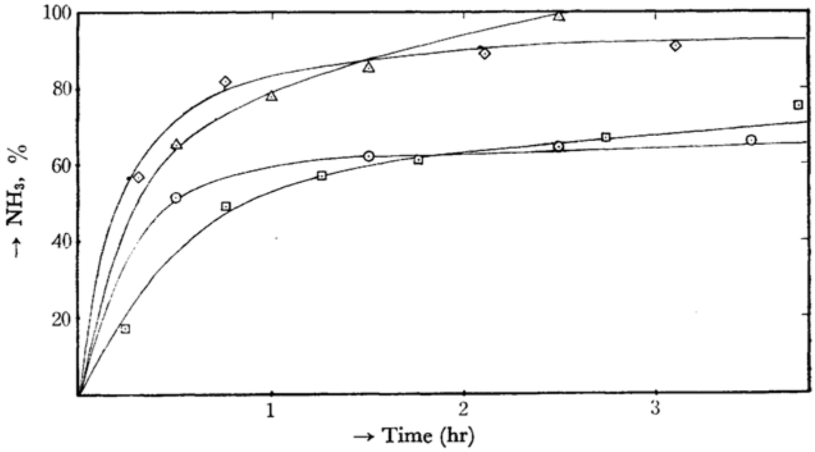
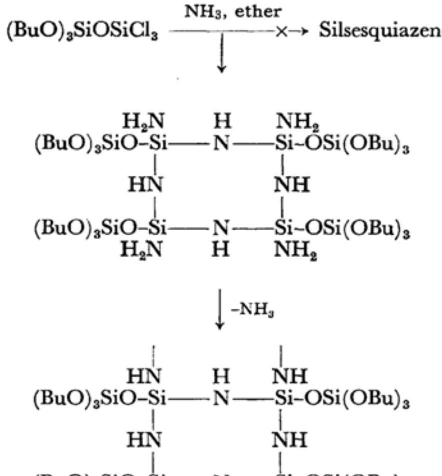


Fig. 1. The relative rate of the reaction of diaminosilane with *n*-butyl alcohol (⊡), aniline (⊙), phenol (◇), and *n*-butylamine (△). Reaction temperature, boilling points of reagents

This unexpected result is probably due to the large steric effect of tri-*t*-butoxysiloxy groups.[6,7]

In the couse of the distillation of the cyclosilazane, a solid was obtained as a residue; it was then purified to give a white powder (mp 240—243°C). Its IR spectrum was essentially identical with that of the cyclosilazane except for the absence of the absorption peaks at 1354 and 860 cm^{-1}. This product seems, therefore, to be a polymer formed by the condensation of the amino group in the cyclosilazane.



Experimental

All the experiments were carried out in a dry atmosphere or nitrogen. The melting points and boilling points were uncorrected.

Materials. The alcohols and amines were dried on calcium oxide or sodium hydroxide and were purified by distillation. The acetic acid was purified by fractional distillation. Bis(tri-*t*-butoxysiloxy)dichlorosilane and tri-*t*-butoxysiloxytrichlorosilane were prepared by a method previously described.[4]

Preparation of Bis(tri-*t*-butoxysiloxy)diaminosilane. To a solution of bis(tri-*t*-butoxysiloxy)dichlorosilane (28 g) in 200 m*l* of benzene, dry ammonia gas was introduced at 0—5°C with stirring. After the completion of the absorption of the ammonia, the mixture was refluxed for 1 hr. This treatment was repeated, and then the ammonium hydrochloride was filtered out and washed with benzene. The solvent was reomved, and the residue was distilled under reduced pressure to give 20 g of a crystalline solid (76.5%), bp 150°C/1 mmHg, mp 55—57°C. Found: C, 49.11; H, 9.96; N, 4.48; Si, 14.32%. Calcd for $C_{24}H_{58}O_8N_2Si_3$: C, 48.48; H, 10.40; N, 4.77; Si, 14.36%.

The preparation of the diaminosilane from silicon tetrachloride and tri-*t*-butoxysilanol proceeded in the following way: to a mixture of 74.6 g (0.283 mol) of silanol, 22.4 g (0.283 mol) of pyridine, and 400 m*l* of benzene, 23.8 g (0.141 mol) of silicon tetrachloride in 100 m*l* were stirred in, drop by drop, at about 0°C. The mixture was refluxed for 1 hr. Then the combined solution was cooled at about 0°C and ammonia gas was introduced. The distillation of the filtrate gave 53.8 g (64.0%) of the diaminosilane, 154°C/1 mmHg. IR: 3400 and 3350 (doublet, w, ν_{NH}), 1535 (m, δ_{NH_2}), 1385 and 1362 (doublet, *t*-butyl group), 1065 (s, $\nu_{Si-O-Si}$) cm^{-1}.

The Reaction of Diaminosilane with *n*-Butyl Alcohol. A solution of 3.4 g of *n*-butyl alcohol in 20 m*l* of *n*-hexane was added to a solution containing 15.2 g of diaminosilane. The mixture was refluxed for 1.5 hr with stirring, and the ammonia thus evolved

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6) R. Schwarz and F. Weigel, *Z. Anorg. Allg. Chem.*, **268**, 251 (1952).

7) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York (1967), p. 146; D. N. Hunter, "Inorganic Polymers," John Willey & Sons Inc., New York (1963).

was trapped by introducing it into a sulfuric acid solution. The ratio of the recovery of ammonia was 47.4%. The removal of the solvent, followed by fractional distillation *in vacuo*, gave 14.6 g (88.1%) of a liquid; bp 156—157°C/0.6 mmHg, $n_{\rm D}^{20}$ 1.4125. Found: N, 2.07; Si, 12.93%. Calcd for $C_{28}H_{65}O_9NSi_3$: N, 2.17; Si, 13.00%. IR: 3400 and 3350 (doublet, w, $\nu_{\rm NH}$), 1530 (w, $\delta_{\rm NH_2}$) cm^{-1}.

Dibutoxy derivatives were obtained when the above reaction was carried out without any solvent; the diaminosilane (10.5 g) was heated with *n*-butyl alcohol (4.5 g) at 140—150°C for 10 hr under stirring (93%, ammonia evolved). The reaction mixture, on fractionation, gave 9.9 g (79.0%) of a pale yellow solid; bp 164—165°C/1 mmHg, mp 38—40°C (recrystallized with acetone). Found: C, 54.49; H, 11.22; Si, 12.03%. Calcd for $C_{32}H_{72}O_{10}Si_3$: C, 54.82; H, 10.30; Si, 11.87%. NMR: 8.71 (singlet, Bu^t), 6.32 (triplet, CH_2), 9.10 (doublet, CH_3) τ.

The Reaction of Diaminosilane with Phenol. To a solution of 13.4 g of diaminosilane in 50 m*l* of *n*-hexane, a solution of 4.4 g of phenol in 20 m*l* of *n*-hexane was added. The combined solution was then refluxed for 1.5 hr with stirring (45.6%, ammonia evolved). After the solvent had been removed, the residue was fractionated to give 9.9 g of a viscous liquid (75.7%); bp 182—183°C/1 mmHg, $n_{\rm D}^{20}$ 1.4361. Found: N, 1.74; Si, 12.78%. Calcd for $C_{30}H_{61}O_9NSi_3$: N, 2.16; Si, 12.80%.

The reaction was carried out without any solvent to obtain a diphenoxy derivative; a mixture of 16.0 g of diaminosilane and 7.7 g of phenol was heated at 170—180°C for 3.5 hr with stirring (94.0%, ammonia evolved). The residue was submitted to fractional distillation; this gave 15.6 g of a pale yellow solid (77.6%), bp 230—231°C/1 mmHg, mp 74—76°C (recrystallized with petroleum ether). Found: C, 57.10; H, 9.02; Si, 11.17%. IR: 1595, 1490, and 750 (m, phenyl group) cm^{-1}. NMR: 8.74 (singlet, Bu^t), 2.94 (single, phenyl protons) τ.

Hydrolysis of Diaminosilane. To 150 m*l* of a sulfuric acid solution (5%), 17.0 g of diaminosilane in 50 m*l* of *n*-hexane were added, drop by drop, at 7—8°C with agitation. The oily layer was separated, washed with a sodium bicarbonate solution and then water, and dried over anhydrous sodium sulfate. After the removal of the solvent, the residue was distilled *in vacuo*, giving 13.0 g (76.0%) of a white solid, bis(tri-*t*-butoxysiloxy)silanediol,[4] bp 154—155°C/1 mmHg.

The Reaction of Diaminosilane with Acetic Acid. Into a solution of 16.2 g of diaminosilane in 100 m*l* of *n*-hexane, a solution of 6.7 g of acetic acid in 50 m*l* of *n*-hexane was stirred, drop by drop, at 5—10°C for 45 min. The mixture was further stirred at room temperature for 1.5 hr, and then the ammonium acetate was filtered out. The removal of the solvent from the filtrate gave a solid, which was then dissolved into 20 m*l* of *n*-hexane. A white crystal was obtained from the solution when it was left standing under cooling; yield, 13.3 g (71.5%), mp 57—62°C. Found: C, 49.73; H, 9.29; Si, 12.30%. Calcd for $C_{28}H_{60}O_{12}Si_3$: C, 49.97; H, 8.98; Si, 12.52%. IR: 1734 (s, calbonyl group) cm^{-1}. NMR: 8.70 (Bu^t), 9.79 ($OCOCH_3$) τ.

Transamination Reaction of Diaminosilane with Aniline. A mixture of diaminosilane (13.7 g) and aniline (8.7 g) was heated at 140—150°C for 2.5 hr under stirring (54.5%, ammonia evolved). After the removal of the excess aniline, the mixture was distilled under reduced pressure, giving 13.0 g (80.7%) of a pale yellow liquid, bp 190.5°C/0.5 mmHg. The product partially solidified at room temperature. Found: C, 54.60; H, 10.10; N, 4.09; Si, 12.54%. Calcd for $C_{30}H_{62}O_8N_2Si_3$: C, 54.35; H, 9.42; N, 4.32; Si, 12.72%. IR: 3450 and 3350 (doublet, w, $\nu_{\rm NH}$), 1530 (w, $\delta_{\rm NH_2}$), 1487, 1590, and 750 (m, phenyl group) cm^{-1}. NMR: 8.66 (Bu^t), 5.75 (NHPh), 3.13 and 3.16 (doublet, phenyl protone) τ.

Transamination Reaction of Diaminosilane with *n*-Butylamine. A mixture of 6.5 g of *n*-butylamine and 13.1 g of diaminosilane was refluxed for 2.5 hr with stirring. The mixture was fractionally distilled under reduced pressure, giving 9.2 g (65.0%) of a pale yellow liquid, which solidified at room temperature; bp 192—193°C/0.5 mmHg, $n_{\rm D}^{20}$ 1.4217. Found: C, 54.45; H, 10.99; N, 3.73; Si, 11.86%. Calcd for $C_{32}H_{74}O_8N_2Si_3$: C, 54.97; H, 10.66; N, 4.01; Si, 11.86%. IR: 3350 (w, $\nu_{\rm NH}$) cm^{-1}. NMR: 9.12 (doublet, CH_3), 8.72 (Bu^t), 7.22 (quartet, CH_2) τ.

The Reaction of Tri-*t*-butoxysiloxytrichlorosilane with Ammonia. To a solution of 22.6 g of tri-*t*-butoxysiloxytrichlorosilane in 300 m*l* of dry ethyl ether, dry ammonia gas was introduced at −5 to −10°C for about 1 hr with agitation. After the absorption of ammonia had ceased, the mixture was stirred for 30 min at room temperature. After the above treatment had been repeated, ammonium hydrochloride was filtered out and the product washed with ehter. The evaporation of the solvent *in vacuo* gave a transparent, colorless, viscous liquid (14.3 g). This residue was submitted to analysis without further purification. Found: C, 44.47; H, 9.81; N, 8.36; Si, 17.30%, mol wt 1190, $n_{\rm D}^{20}$ 1.4270. Calcd for $(C_{12}H_{15}O_4N_2Si_2)_n$: C, 44.86; H, 9.39; N, 8.69; Si, 17.41%, mol wt 1289 (n=4).

This residue (7.9 g) was distilled *in vacuo* to give a transparent, highly viscous liquid (4.0 g); bp 220—222°C/0.5 mmHg, $n_{\rm D}^{20}$ 1.4250. Found: C, 44.58; H, 9.91; N, 7.68; Si, 17.30%, mol wt 1280. IR: 3450 and 3350 (doublet, m, $\nu_{\rm NH}$), 1530 (m, $\delta_{\rm NH_2}$), 1050 (vs, $\nu_{\rm Si-O-Si}$), 950 (s, $\nu_{\rm Si-N-Si}$) cm^{-1}.

After the distillation of the above product, 3.0 g of a white solid remained as a residue. The solid was further purified by the following procedure: to 50 m*l* of vigorously-stirred methanol, 3.0 g of the solid dissolved in 10 m*l* of benzene was added, drop by drop; then the precipitate was filtered and dried *in vacuo*, giving 2.6 g of a white powder, mp 240—243°C. Found: C, 43.02; H, 9.17; N, 6.07; Si, 19.90%. IR: 3450 and 3350 (w, $\nu_{\rm NH}$), 1050 (vs, $\nu_{\rm Si-O-Si}$), 950 (s, $\nu_{\rm Si-N-Si}$) cm^{-1}.

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