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# Reaction of *N*-Methyl-*N*,*N*-bis(silatranylmethyl)amine with Trichlorosilane

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**Abstract**—*N*,*N*-Bis(silatranylmethyl)methylamine reacts with trichlorosilane to form the amine hydrochloride and perchloropolysilane, the product of polymerization of dichlorosilylene. In the presence of 1,3-butadiene the main products of the reaction are the amine hydrochloride and 1,1-dichlorosilacyclopentene-3, the product of 1,4-addition of dichlorosilylene to 1,3-butadiene.

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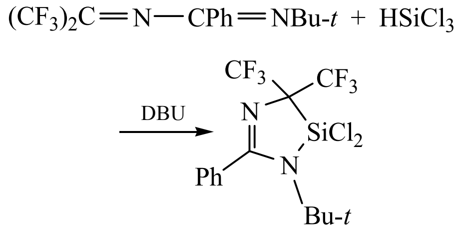
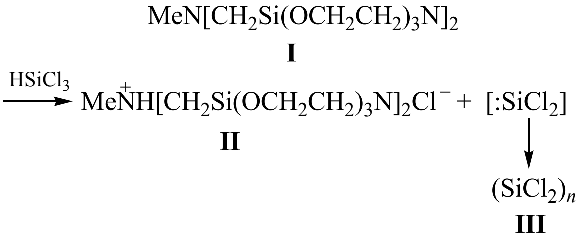
The reactivity of amines is drastically changed by introduction of an organosilicon substituent to the α-position of the amino group. Unlike their organic analogs, organosilicon amines readily reduce metal cations [1] and react with polychloromethanes $CH_nCl_{4-n}$ ($n$ = 0, 2) [2–4]. Recently we have found that the reaction of chloroform with *N*,*N*-bis(silatranylmethyl) methylamine proceeds as a typical haloform reaction with the formation of the amine hydrochloride and dichlorocarbene.[1] How the silicon analog of chloroform, trichlorosilane $HSiCl_3$, will react with α-silylamines? The reactions of reductive trichlorosilylation with the binary system trichlorosilane–tertiary amine $HSiCl_3$–$R_3N$ are known in organic and organoelement chemistry [5–8]. The key intermediate of these reactions, according to the NMR spectroscopy data, is a latent trichlorosilyl anion [9]:

$$HSiCl_3 + R_3N \rightarrow [R_3{}^{+}NH]SiCl_3^{-}.$$

The reaction of 1,3- or 1,4-diazabutadiene derivatives with trichlorosilane in the presence of such a strong base as 1,8-diazabicyclo[5.4.0]undec-7-ene leads to the formation of the products of cycloaddition: the five-membered Si-containing heterocycles [10, 11], which is indicative of the formation of dichlorosilylene in this reaction:



In the present work we have studied the reaction of *N*,*N*-bis(silatranylmethyl)methylamine (**I**) with trichlorosilane $HSiCl_3$. Mixing of compound **I** and $HSiCl_3$ in benzene causes an immediate vigorous exothermic reaction and formation of a precipitate. The precipitate represents a mixture of *N*,*N*-bis(silatranylmethyl)methylamine hydrochloride (**II**) and, apparently, perchloropolysilane $(SiCl_2)_n$ (**III**):



$$\underset{\textbf{I}}{MeN[CH_2Si(OCH_2CH_2)_3N]_2} \xrightarrow{HSiCl_3} \underset{\textbf{II}}{Me\overset{+}{N}H[CH_2Si(OCH_2CH_2)_3N]_2Cl^-} + [:SiCl_2] \downarrow \underset{\textbf{III}}{(SiCl_2)_n}$$

Salt **II** was isolated in almost quantitative yield and identified by spectral methods. Perchloropolysilane $(SiCl_2)_n$ was first synthesized by sublimation of octachlorocyclotetrasilane [12–14] and the authors mentioned that the compound is extremely sensitive to

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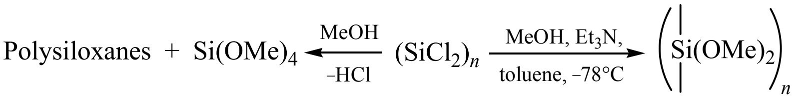
[1] Reaction of *N*,*N*-bis(silatranylmethyl)methylamine with chloroform will be published elsewhere.

moisture. Perchloropolysilane $(SiCl_2)_n$ isolated from the reaction performed by us represents a white solid with light yellow tint, practically insoluble in organic solvents. Compound **III** is very easily hydrolyzed by air moisture and vigorously reacts with methanol; the main products of this exothermic reaction are hydrogen chloride and tetramethoxysilane; nonidentified polysiloxanes amount to ca. 10%.

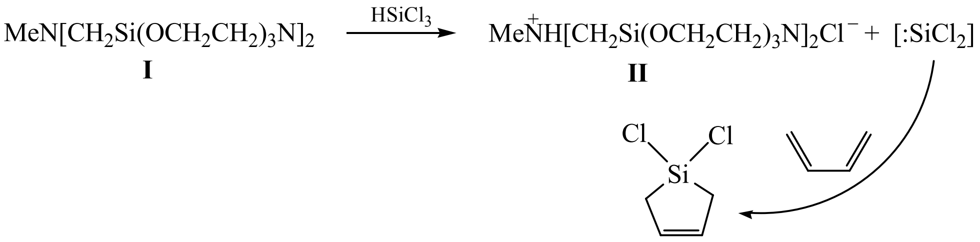


$$\text{Polysiloxanes} + Si(OMe)_4 \xleftarrow[-HCl]{MeOH} (SiCl_2)_n \xrightarrow[\text{toluene, }-78°C]{MeOH,\ Et_3N,} (-Si(OMe)_2-)_n$$

**IV**

The reaction of suspension of perchloropolysilane with methanol in toluene at –78°C in the presence of triethylamine proceeds in a different way. The spectral characteristics of the isolated reaction products and those of poly(dialkoxy)silylenes [12, 15] are similar (see the table), which is indicative of formation of poly(dimethoxy)silylene **IV** under these conditions. The minor products of the reaction were not identified. Apparently, they are polysiloxanes formed by partial hydrolysis of polysilanes **III, IV**. Similar results were obtained in the reaction of compound **III** with *n*-butanol (see the table).

1,3-Butadiene and its analogs were successfully used to trap silylenes (16 and references therein). It turned out that the main products of the reaction of amine **I** with trichlorosilane in the presence of 1,3-butadiene are its hydrochloride **II** and the product of 1,4-addition of dichlorosilylene to 1,3-butadiene, 1,1-dichlorosilacyclopentene-3 (**V**):



$$MeN[CH_2Si(OCH_2CH_2)_3N]_2 \xrightarrow{HSiCl_3} Me\overset{+}{N}H[CH_2Si(OCH_2CH_2)_3N]_2Cl^- + [:SiCl_2]$$

**I** **II**

**V**

The spectral characteristics of compound **V** are identical to those in [16, 17]. This result is an indirect evidence for the formation of dichlorosilylene in the reaction of *N*,*N*-bis(silatranylmethyl)methylamine **I** with trichlorosilane; in the absence of traps, dichlorosilylene undergo polymerization to perchloropolysilane **III**.

Spectral characteristics of poly(alkoxysilylenes) $[-Si(OR)_2-)_n$

| R | UV, $\lambda_{max}$, nm | NMR spectrum, δ, ppm | | | References |
|---|---|---|---|---|---|
| | | $^1H$ | $^{13}C$ | $^{29}Si$ | |
| Me | 318 | 3.72 | 64.8 | –9.7 | This work |
| Et | 337 | 1.2, 3.9 | 18.41, 60.96 | –10.4 | [15] |
| Pr | 336 | 0.9, 1.6, 3.8 | 10.32, 25.83, 67.14 | –9.3 | [15] |
| *i*-Pr | 288 | 1.40, 4.76 | 26.12, 70.93 | –11.2 | [12] |
| *n*-Bu | 340 | 0.9, 1.4, 1.5, 3.8 | 13.88, 18.92, 34.89, 65.15 | –9.1 | [15] |
| *n*-Bu | 328 | 0.87, 1.36, 1.53, 3.76 | 13.46, 18.34, 35.12, 64.75 | –9.8 | This work |

## EXPERIMENTAL

NMR spectra were registered on a Bruker DPX 400 spectrometer ($^1$H, 400.1 MHz; $^{13}$C, 100.6 MHz; $^{29}$Si, 79.5 MHz) for 10–20% solutions in $CDCl_3$ using TMS as an internal standard. UV absorption spectra were taken on a Specord UV Vis spectrophotometer at 200–450 nm. All reactions were carried out in thoroughly dried argon and dry solvents [18]. *N*,*N*-Bis(silatranylmethyl)methylamine was synthesized by the procedure described in ref. [19].

**Reaction of amine I with trichlorosilane.** To a suspension of 0.16 g (0.4 mmol) of amine **I** in 25 ml of dry benzene the equimolar amount (0.55 g) of $HSiCl_3$ in 35 ml of dry benzene was slowly added dropwise at vigorous stirring, not allowing the temperature of the reaction mixture to rise above 25°C. A white precipitate was instantly formed. The reaction mixture was stirred for 2 h, the precipitate filtered off, dried under vacuum. Compound **II** was extracted from the mixture with methylene chloride, yield 0.17 g (98%), the spectral characteristics are identical to those reported in the literature [3]. Insoluble residue of $(SiCl_2)_n$ **III** was washed with dry pentane, dried under vacuum to give 0.36 g of solid white, with light yellow tint, compound. Found, %: Si, 27.11; Cl, 72.68. $(SiCl_2)_n$. Calculated, %: Si, 28.37; Cl, 71.63.

**Reaction of compound III with alcohols.** A suspension of perchloropolysilane (0.1 mmol) in dry toluene was mixed with equimolar amount of methanol at –78°C in the presence of triethylamine. The reaction mixture was kept at this temperature for 3 h, the formed precipitate of triethylamine hydro-chloride filtered off, solvent removed under vacuum, the residue kept under vacuum for 5 h at room temperature to afford poly(dimethoxy)silylene **IV** as a viscous, slightly opalescent oil. Poly(di-*n*-butoxy)-silylene was prepared similarly.

**Reaction of amine I with trichlorosilane in the presence of 1,3-butadiene.** The ampoule blown with dry argon was charged with amine **I** (3 mmol) and 3.5 mmol of 1,3-butadiene. The mixture was degassed, frozen, 3 mmol of trichlorosilane was added, the mixture was frozen in liquid nitrogen, the ampoule was evacuated and sealed. The reaction mixture was stirred for one day at room temperature, then heated at 140°C for 2 h, cooled, the ampoule was opened, added 15 ml of pentane and filtered off the precipitate. The spectral characteristics of the solid residue correspond to compound **II**. The filtrate was evaporated, the oily residue was analyzed. The NMR spectra contain the signals of 1,1-dichlorosilacyclopentene-3 **V** as the main pro-duct, at δ 1.87 ($CH_2$) and 6.02 (CH) ppm ($^1$H NMR), and 21.98 ($CH_2$) and 129.57 (CH) ppm ($^{13}$C NMR), as well as minor unidentified products.

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## REFERENCES

1. Lazareva, N.F., Vakul'skaya, T.I., Albanov, A.I., and Pestunovich, V.A., *Appl. Organometal. Chem.*, 2006, vol. 20, no. 10, p. 696.
2. Lazareva, N.F., Brodskaya, E.I., Belyaeva, V.V., and Voronkov, M.G., *Russ. J. Gen. Chem.*, 2000, vol. 70, no. 10, p. 1547.
3. Lazareva, N.F., Vakul'skaya, T.I., and Lazarev, I.M., *J. Phys. Org. Chem.*, 2009, vol. 22, no. 2, p. 144.
4. Lazareva, N.F., Lazarev, I.M., and Dianova, N.G., *Russ. Chem. Bull. Engl. Transl.*, 2008, no. 10, p. 2235.
5. Benkeser, R.A., *Acc. Chem. Res.*, 1971, vol. 4, no. 3, p. 94.
6. Du Mont, W.-W., Müller, L P., Müller, L., Vollbrecht, S., and Zanin, A.J., *J. Organomet. Chem.*, 1996, vol. 521, nos. 1–2, p. 417.
7. Benkeser, R.A. and Gad, J.M., *J. Am. Chem. Soc.,* 1970, vol. 92, no. 3, p. 720.
8. Benkeser, R.A. and Snyder, D. C., *J. Organomet. Chem.*, 1982, vol. 225, no. 1, p. 107.
9. Benkeser, R.A., Foley, K.M., Grutzner, J.B., and Smith, W.E., *J. Am. Chem. Soc.*, 1970, vol. 92, no. 3, p. 697.
10. Karsch, H.H., Schlüter, P.A., Bienlein, F., Herker, M., Witt, E., Sladek, A., and Heckel, M., *Z. Anorg. Allg. Chem.*, 1998, vol. 624, no. 2, p. 295.
11. Karsch, H.H., Bienlein, F., Sladek, A., Heckel, M., and Burgefi, K., *J. Am. Chem. Soc.*, 1995, vol. 117, no. 18, p. 5160.
12. Koe, J.R., Powell, D.R., Buffy, J.J., Hayase, S., and West, R., *Angew. Chem. Int. Ed.*, 1998, vol. 37, no. 10, p. 1441.
13. Hengge, E. and Kovar, D., *Z. Anorg. Allg. Chem.*, 1979, vol. 458, no. 1, p. 163.
14. Koe, J.R., Powell, D.R., Buffy, J.J., and West, R., *Polyhedron*, 1998, vol. 17, no. 10, p. 1791.
15. Koe, J.R., Motonaga, M., Fujiki, M., and West, R., *Macromolecules*, 2001, vol. 34, no. 4, p. 706.
16. Kang, S.-H., Han, J.S., Lee, M.E., Yoo, B.R., and Jung, I.N., *Organometallics*, 2003, vol. 22, no. 13, p. 2551.
17. Damrauer, R., Simon, R., Laporterie, A., Manue,l G., Park, Y.T., and Weber, W.P., *J. Organomet. Chem.*, 1990, vol. 391, no. 1, p. 7.
18. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
19. Lazareva, N.F., Brodskaya, E.I., Belyaeva, V.V., and Voronkov, M.G., *Russ. J. Gen. Chem.*, 2001, vol. 71, no. 5, p. 815.