ISSN 1070-3632, Russian Journal of General Chemistry, 2016, Vol. 86, No. 11, pp. 2555–2557. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © N.F. Lazareva, I.M. Lazarev, 2016, published in Zhurnal Obshchei Khimii, 2016, Vol. 86, No. 11, pp. 1915–1918.

LETTERS TO THE EDITOR

Si–C Bond Cleavage in *N*-[(Trimethoxysilyl)methyl)]amine by Methanol

N. F. Lazareva* and I. M. Lazarev

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
**e-mail: nataly_lazareva@irioch.irk.ru*

Received June 23, 2016

Keywords: *N*-[(trimethoxysilyl)methyl]amine, tetramethoxysilane, Si–C bond splitting

DOI: 10.1134/S1070363216110256

The chemistry of *N*-(silylmethyl)amines RR^1R^2Si-$CH_2NR^3R^4$ having the silyl group in the α-position is one of most actual and rapidly developing areas of organoelemental chemistry [1, 2]. A steady interest to these compounds is due to combination in the geminal fragment N–CH_2–Si the basic (N atom) and acidic (Si atom) centers and, as a consequence, specific physicochemical properties [3, 4]. The chemistry of *N*-(triorganylsilyl)amines is well studied and its particular aspects have found application in synthetic organic chemistry [5–7]. Although the primary *N*-[(triethoxysilyl)methyl]amine $NH_2CH_2Si(OEt)_3$ was first synthesized in the 70s of the last century by heating a mixture of ammonia and chloromethyltriethoxysilane [8], its chemical properties are so far poorly studied. Apparently, this is due to both difficulties of its preparation (necessity of operating under high pressure) and a high hydrolytic instability.

The method of synthesis of amines $NH_2CH_2SiRMe_n$-$(OAlk)_{3-n}$ (Alk = Me, Et; *i*-Pr; *n* = 0–2) based on the reaction of ammonia with chloromethylsilanes $ClCH_2$-$Si(R)Me_n(OAlk)_{3-n}$ with addition of an alcohol to the reaction mixture (the ratio alcohol : silane 1 : 1 or 1 : 2) seemed very attractive [9]. The authors carried out the reaction at elevated temperatures and pressure, the target products were isolated by distillation in 43–58% yield; for the increase of the yield, the iodine-containing catalysts were used.

The goal of the present work was the modification of the above procedure in order to use it under normal pressure. We have studied the reaction of chloromethyltrimethoxysilane $ClCH_2Si(OMe)_3$ **1** with ammonia in methanol solution at normal pressure and room temperature (Scheme 1, table). The ratio silane/ammonia was varied from 1 : 3 to 1 : 10, the reaction was performed either without catalyst or in the presence of KI or $Bu_4N^+I^-$. The completion of the reaction was indicated by the disappearance of the $ClCH_2Si$ group signal in the ^1H NMR spectrum. It turned out that when using methanol as a solvent the mixture of *N*-[(trimethoxysilyl)methyl]amine **2** and tetramethoxysilane **3** is formed. In the ^1H NMR spectra of the reaction products after distillation the signals are observed of compound **2** [2.29 (CH_2), 3.56 ppm (OMe)] and a singlet at 3.62 ppm, belonging to compound **3**. The ^{29}Si NMR spectrum also contained two signals belonging to compounds **2** and **3** (–47.8 and –79.9 ppm respectively). The major product of the reaction is silane **3** irrespective of the ratio of the reagents and the presence of catalyst. We failed to separate the mixture of compounds **2** and **3**. In the absence of methanol the reaction of silane **1** with ammonia gives amine **2** in 39% yield.

The formation of $(MeO)_4Si$ can be the result of different reactions, such as a rearrangement of amine **2** to aminosilane $MeNHSi(OMe)_3$ and the alcoholysis of the latter (*a*), participation of the solvent in the process

Scheme 1.

$$ClCH_3Si(OMe)_3 + NH_3 \xrightarrow{\text{cat., } NH_3} H_2NCH_2Si(OMe)_3 + (MeO)_4Si$$

Reaction conditions and ratio of the reaction products

1 : NH_3 molar ratio	Catalyst (0.05 g)	Reaction time, h	**2** : **3**^{a}
1 : 3	–	48	12 : 88
1 : 5	–	48	10 : 90
1 : 10	–	48	10 : 90
1 : 3	KI	48	12 : 88
1 : 10	KI	36	10 : 90
1 : 3	$Bu_4N^+I^-$	48	5 : 95
1 : 10	$Bu_4N^+I^-$	36	0 : 100

[a] From integral intensities of the MeO groups in ^{1}H NMR spectra.

of nucleophilic substitution as a reagent (*b*) and the cleavage of the Si–C bond of the formed α-aminosilane with alcohol (*c*).

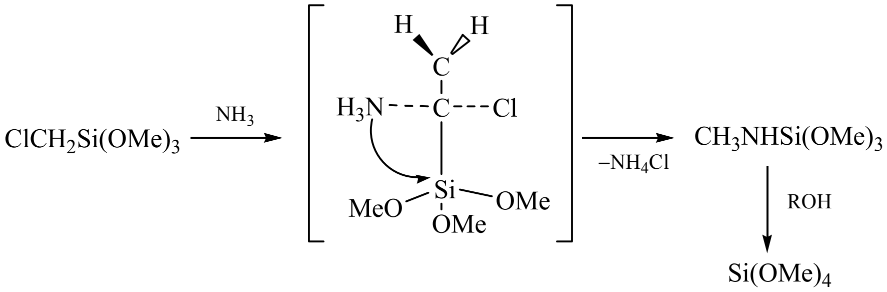
According to [10], amination of chloromethylalkoxysilanes is a typical reaction of bimolecular nucleophilic substitution S_N2. It can be assumed that tetramethoxysilane is formed by alcoholysis of *N*-silylamine generated as a result of migration of the nucleophile from the carbon atom to the silicon atom in the transition state (Scheme 2).

The examples of 1,2-migration of the silyl group are well known in the literature for α-functional silanes [11–16], but the isomerization of *N*-(silylmethyl)-amines (the aza-Brook rearrangement) to the corresponding alkylaminosilanes proceeds only in the presence of such a strong base as *n*-BuLi. There are no data in the literature on the thermal rearrangement except for a theoretical work [17]. Besides, realization of this mechanism would lead to the formation of the products of rearrangement in any reactions of amines with halomethylsilanes, which is not the case, so, the route *a* should be excluded from the consideration.

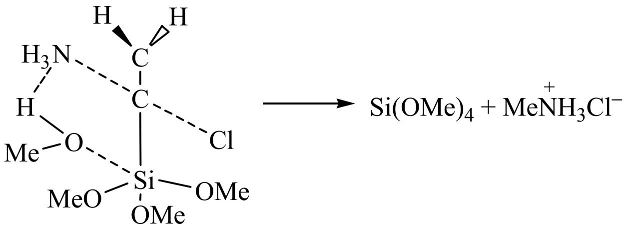
It is known that alcohols form hydrogen bonds with amines (see [18, 19] and references therein). So, it could be assumed that the reaction of chloromethyltrimethoxysilane with ammonia in methanol due to high basicity of the nitrogen atom in *N*-silylmethylated amines [20–26] occurs via the cyclic transition state with participation of the molecule of the solvent (Scheme 3). Its transformation can proceed with breaking of the Si–C bond and lead to the formation of tetramethoxysilane and methylamine hydrochloride.

It cannot be excluded as well that the Si–C bond suffers cleavage as a result of interaction with the second molecule of methanol with the H-complex. The examples of the solvent nucleophilic assistance to the Si–C bond splitting in radical-cations of *N*-silylmethylamines are described in the literature [27–29]. The driving force of the reaction could be the formation of a stronger Si–O bond (E_{diss} of the Si–O and Si–C bond is 530 and 360 kJ/mol [30]). However, according to the data of IR spectroscopy and elemental analysis, in the reaction only ammonium chloride is formed; therefore, the absence of methylamine hydrochloride in the products of the reaction is indicative of

Scheme 2.



Scheme 3.



the cleavage of the Si–C bond in the already formed compound **2**.

The obtained data prove that methanol cannot be used as a solvent for the synthesis of *N*-[(trimethoxysilyl)methyl]amine. Now under way is an investigation of the influence of the structure of the silane, solvent, and catalyst on the reaction of the Si–C bond cleavage using spectral and quantum-chemical methods, which would allow avoiding side reactions in the synthesis of compounds with the N–C–Si motif and elaborating new methods of protodesilylation.

EXPERIMENTAL

NMR spectra were registered on a Bruker DPX-400 spectrometer [400.1 (^{1}H), 79.5 MHz (^{29}Si)] in solutions in C_6D_6 using HMDS as an internal reference. All reactions were performed in an argon atmosphere. Methanol was dried as described in [31]. Liquid ammonia was evaporated, the gas flow passed through the traps with NaOH, ammonia was condensed, sodium metal was dissolved in it and it was recondensed to a dry trap.

Reaction of ammonia with (chloromethyl)trimethoxysilane in methanol. In 200 mL of dry methanol cooled to –50°C ammonia was dissolved and 3.4 g (0.02 mol) of (chloromethyl)trimethoxysilane was added. The reaction mixture was slowly heated to room temperature in a sealed vessel and kept for 36–48 h. Methanol was removed, to the residue pentane was added, the precipitate was filtered, washed with pentane, the filtrate was distilled. Fraction with bp 117–119°C was collected and analyzed.

REFERENCES

1. Picard, J.-P., *Can. J. Chem.*, 2000, vol. 78, no. 11, p. 1363. doi 10.1139/v00-090
2. Picard, J.-P., *Adv. Organomet. Chem.*, 2005, vol. 52, p. 175. doi 10.1016/S0065-3055(04)52004-X
3. Lukevits, E.Ya. and Sturkovich, R.Ya., *Izv. Akad. Nauk Latv. SSR*, 1977, no. 9, p. 29.
4. Feshin, V.P., Romanenko, L.S., and Voronkov, M.G., *Russ. Chem. Rev.*, 1981, vol. 50, no. 3, p. 248 doi 10.1070/RC1981v050n03ABEH002589
5. Fleming, I., Barbero, A., and Walter, D., *Chem. Rev.*, 1997, vol. 97, no. 6, p. 2063. doi 10.1021/cr941074u
6. Fensterbank, L., Malacria, M., and Sieburth, S.McN., *Synthesis*, 1997, no. 8, p. 813. doi 10.1055/s-1997-1295
7. Oestreich, M., *Chem. Eur. J.*, 2006, vol. 12, no. 1, p. 30. doi 10.1002/chem.200500782
8. Fialova, V., Bažant, V., and Chvalovsky, V., *Coll. Czech. Chem. Comm.*, 1973, vol. 38, no. 12, p. 3837. doi 10.1135/cccc19733837
9. USSR Author's Certificate 395371, *Russ. Zh. Khim.*, 1974, no. 22, p. 119.
10. Shchegolev, A.E., Finogenov, Yu.S., Yakovlev, I.P., and Ivin, B.A., *Zh. Obshch. Khim.*, 1985, vol. 55, no. 5, p. 1084.
11. Moser, W.H., *Tetrahedron*, 2001, vol. 57, no. 11, p. 2065. doi 10.1016/S0040-4020(00)01089-9
12. Brook, A.G., *Acc. Chem. Res.*, 1974, vol. 7, no. 3, p. 77. doi 10.1021/ar50075a003
13. Duff, J.M. and Brook, A.G., *Can. J. Chem.*, 1977, vol. 55, no. 13, p. 2589. doi 10.1139/v77-358
14. Sieburth, S.McN., O'Hare, H.K., Xu, J., Chen, Y., and Liu, G., *Org. Lett.*, 2003, vol. 5, no. 11, p. 1859. doi 10.1021/ol034397y
15. Brook, A.G. and Duff, J.M., *J. Am. Chem. Soc.*, 1974, vol. 96, no. 14, p. 4692. doi 10.1021/ja00821a065
16. Honda, T. and Mori, M., *J. Org. Chem.*, 1996, vol. 61, no. 4, p. 1196. doi 10.1021/jo952116x
17. Yu, Y. and Feng, S., *J. Phys. Chem. A*, 2006, vol. 110, no. 45, p. 12463. doi 10.1021/jp065454i
18. *Molecular Interactions*, Ratajczak, H. and Orville-Thomas, W.J., Eds., Chichester: Wiley, 1980.
19. Popov, A.F. and Piskunova, Zh.P., *Problemy fiziko-orgnicheskoi khimii* (Problems of Physical Organic Chemistry), Kiev: Naukova Dumka, 1978, p. 3.
20. Noll, J.E., Daubert, B.F., and Speier, J.L., *J. Am. Chem. Soc.*, 1951, vol. 73, no. 8, p. 3871. doi 10.1021/ja01152a093
21. Voronkov, M.G., Kashik, T.V., Lukevits, E.Ya., Deriglazova, E.S., Pestunovich, A.E., and Moskovich, R.Ya., *Zh. Obshch. Khim.*, 1974, vol. 44, no. 4, p. 778.
22. Voronkov, M.G., Kashik, T.V., Lukevits, E.Ya., Deriglazova, E.S., and Pestunovich, A.E., *Zh. Obshch. Khim.*, 1975, vol. 45, no. 10, p. 2200.
23. Voronkov, M.G., Kashik, T.V., Deriglazova, E.S., Lukevits, E.Ya., Pestunovich, A.E., and Sturkovich, R.Ya., *Zh. Obshch. Khim.*, 1976, vol. 46, no. 7, p. 1522.
24. Zingler, G., Kelling, H., and Popowski, E., *Z. Anorg. Allg. Chem.*, 1981, vol. 476, p. 41. doi 10.1002/zaac.19814760506
25. Voronkov, M.G., Kashik, T.V., Deriglazova, E.S., Kositsyna, E.I., Pestunovich, A.E., and Lukevits, E.Ya., *Zh. Obshch. Khim.*, 1981, vol. 51, no. 2, p. 375.
26. Popowski, E., Zingler, G., and Kelling, H., *Z. Chem.*, 1974, vol. 14, no. 7, p. 289. doi 10.1002/zfch.19740140726
27. Gould, I.R., Godleski, S.A., Zielinski, P.A., and Farid, S., *Can. J. Chem.*, 2003, vol. 81, p. 777. doi 10.1139/v03-073
28. Zhang, X., Yeh, S.-R., Hong, S., Freccero, M., Albini, A., Falvey, D.E., and Mariano, P.S., *J. Am. Chem. Soc.,* 1994, vol. 116, p. 4211. doi 10.1021/ja00089a010
29. Dinnocenzo, J.P., Farid, S., Goodman, J.L., Gould, I.R., Mattes, S.L., and Todd, W.P., *J. Am. Chem. Soc.*, 1989, vol. 111, p. 8973. doi 10.1021/ja00206a061
30. Fleming, I., in *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon Press, 1979, vol. 6.
31. Jou, F.-Y. and Freeman, G.R., *J. Phys. Chem. A*, 1977, vol. 81, p. 909. doi 10.1021/j100524a021