ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 7, pp. 1311–1312. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © E.N. Suslova, B.A. Shainyan, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 7, pp. 1214–1215.

LETTERS TO THE EDITOR

N-(Trimethylsilylmethyl)trifluoromethanesulfonamide

E. N. Suslova and B. A. Shainyan

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

Received February 13, 2012

DOI: 10.1134/S1070363212070237

Recently we have synthesized the first representative of the *N*-trifluoromethylsulfonyl-substituted five-membered Si,N-heterocycles, 3,3-dimethyl-1-(trifluoromethylsulfonyl)-1,3-azasilolidine, by the reaction of 2-bromoethyl(chloromethyl)dimethylsilane with trifluoromethanesulfonamide (triflamide) [1]. The side formation of the siloxane $(ClCH_2SiMe_2)_2O$ [1], as well as the inertness of the $SiCH_2Cl$ group of 2-chloroethyl(chloromethyl)dimethylsilane $ClCH_2SiMe_2CH_2CH_2Cl$ to hydrolysis [2] suggested a conclusion that first the halogen atom at the β- rather than the α-position to the silicon atom is replaced. In this connection it was interesting to clarify the possibility of substitution of the chlorine atom in chloromethylsilanes R_3SiCH_2Cl by a weak nucleophile like triflamide. Earlier it was shown that such a substitution occurs in a moderate yield in chloromethylsiloxane $(Me_2SiCH_2Cl)_2O$ where the C–Cl bond was more active than in silanes [3].

We have studied the reaction of triflamide with (chloromethyl)trimethylsilane and shown that in the presence of excess triethylamine upon heating to 80–90°C for 6–7 h *N*-trimethylsilylmethyl)trifluoromethanesulfonamide (**I**) is formed in 70% yield.

$$Me_3SiCH_2Cl + H_2NSO_2CF_3 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} \underset{\mathbf{I}}{F_3SO_2NHCH_2SiMe_3}.$$

The conversion of the starting silane amounts to 94%, no side products were detected. No reaction occurs at room temperature or in the absence of triethylamine as the acceptor of the evolved hydrogen chloride.

Performing the reaction at reflux in tetrahydrofurane or methanol with the same ratio of the reagents drastically slows down the process: from the ^1H NMR spectroscopy data, the conversion after 7 h was as low as 18–24%.

The closest analogs of the above transformation are the reactions of trialkyl(chloromethyl)silanes with sodium salt of *N*-ethylamide of ethylsulfonic acid upon protracted reflux (up to 70 h) in xylene [4] and of the silanes of the general formula $R_n(OR')_mSiCH_2Cl$ with the salts of arenesulfonamides $ArSO_2N(R'')K$ in dry DMF at high temperature (150°C) with the formation of the products of general formula $ArSO_2N(R'')CH_2SiR_n(OR')_m$ [5].

No reaction occurs between (chloromethyl)trimethylsilane and sodium salt of triflamide CF_3SO_2NHNa: after 6–7 h reflux in tetrahydrofurane or methanol the starting silane is practically completely recovered.

The acidity of compound **I** in methanol measured by the method of potentiometric titration was 12.84. Due to the electron donor effect of the trimethylsilyl group, compound **I** possesses the lowest acidity among the N-substituted triflamides we have studied [6].

The structure of product **I** was proved by the methods of ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopy, mass spectrometry, and elemental analysis. Note that the only significant peak (100%) is the one with *m*/*z* 73 $[Me_3Si]$, which is indicative of the fragmentation of compound **I** at the Si–CH_2 bond with localization of the positive charge on the Me_3Si fragment and the negative charge, on the triflamide fragment.

***N*-(Trimethylsilylmethyl)trifluoromethanesulfonamide (I).** To a mixture of 1.475 g of (chloromethyl) trimethylsilane and 2.366 g of trifluoromethanesulfonamide, 2.432 g of triethylamine was added dropwise at room temperature in the course of 15 min, the reaction mixture was stirred for 7 h at reflux (88°C). To the obtained suspension hexane was added, the organic layer was separated, to the precipitate water was

added, the formed organic layer was combined with the hexane fraction and dried over Na_2SO_4. After removal of the solvents at atmospheric pressure, 2.48 g of the residue was obtained containing, according to ^{1}H NMR, 80% of the target product and triethylamine that corresponds to the yield of the crude product of 70%. The analytically pure sample was obtained by column chromatography of this residue on silica gel (ICN), eluent hexane–ether from 9:1 to 1:1, R_f 0.70. Yield 1.2 g (42%), white crystals, mp 45–46°C. IR spectrum, ν, cm^{-1}: 3300 (NH), 2918 (CH_2), 1426 ($SiCH_2$), 1361 (SO_2), 1257 ($SiCH_3$), 1229, 1194 (CF_3), 1147 (SO_2), 1053 (SN), 854 (CS), 604 (CF_3), 462 (SO_2). ^{1}H NMR spectrum, δ, ppm: 0.15 s (9H, $SiMe_3$), 2.76 s (2H, CH_2N), 4.41 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: –3.27 (SiMe), 33.85 (CH_2N), 120.00 q (CF_3, J 320 Hz). ^{19}F NMR spectrum: δ_F –75.83 ppm. ^{29}Si NMR spectrum: δ_{Si} 2.31 ppm. Found, %: C 25.66; H 5.03; F 23.74; N 5.94; S 13.77. $C_5H_{12}F_3NO_2SSi$. Calculated, %: C 25.53; H 5.11; F 24.25; N 5.95; S 13.61.

Melting point was determined on a Micro-Hot-Stage PolyTherm A instrument. IR spectrum was taken on a Bruker Vertex 70 spectrometer in KBr. ^{1}H, ^{13}C, ^{19}F, ^{29}Si NMR spectra were recorded from $CDCl_3$ solutions on a Bruker DPX 400 instrument (400, 100, 376 and 79.5 MHz, respectively), chemical shifts measured relative to TMS (^{1}H, ^{13}C, ^{29}Si) or CCl_3F (^{19}F). Electron impact mass spectrum (70 eV) was obtained on a GCMS-QP5050A Shimadzu chromatomass spectrometer (quadruple mass analyzer, capillary column, liquid phase SPB-5). The pK_a value was measured by the method of potentiometric titration in methanol using 0.1 N solution of NaOH in methanol as titrant.

ACKNOWLEDGMENTS

This work was performed with the financial support from the Russian Foundation for Basic Research (grant no. 10-03-00110).

REFERENCES

1. Suslova, E.N. and Shainyan, B.A., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 8, p. 1735.
2. Bratt, S. and Jarvie, A.W.P., *J. Organomet. Chem*., 1995, vol. 489, nos. 1–2, p. C26.
3. Suslova, E.N. and Shainyan, B.A., *Russ. J. Gen. Chem*., 2010, vol. 80, no. 10, p. 2059.
4. Maslii, L.K. and Razbegaeva, T.P., *Zh. Obshch. Khim*., 1967, vol. 37, no. 1, p. 250.
5. Cermak, J. and Horacek, J., Author's Certificate no. 223439, *Ref. Zh. Khim*., 16N156P 1987.
6. Sterkhova, I.V., Meshcheryakov, V.I., Chipanina, N.N.. Kukhareva, V.A., Aksamentova, T.N., Turchaninov, V.K., and Shainyan, B.A., *Russ. J. Gen. Chem*., 2006, vol. 76, no. 4, p. 583.