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Mendeleev Commun., 2020, **30**, 117–118

Mendeleev Communications

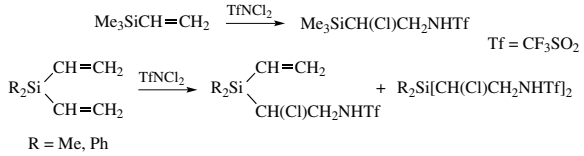
Chlorotriflamidation of vinylsilanes with *N,N*-dichlorotriflamide

Irina V. Ushakova and Bagrat A. Shainyan*

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation. Fax: +7 3952 41 9346; e-mail: bagrat@irioch.ik.ru

DOI: 10.1016/j.mencom.2020.01.039

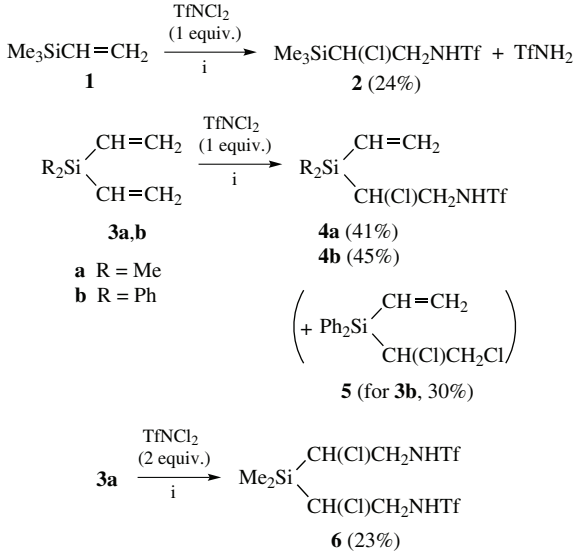
The reaction of *N,N*-dichlorotriflamide with vinylsilanes affords the products of chlorotriflamidation of the double bonds.



Keywords: *N,N*-dichlorotriflamide, vinylsilanes, divinylsilanes, chloroamidation, triflamides.

The haloamination of non-activated and activated alkenes with dihalogenosulfonamides RSO_2NX_2 (X = Cl, Br) represents a convenient route to polyfunctional adducts containing β-positioned amino group and mobile halogen atom suitable for further functionalization.[1–5] In contrast, reactions between *N,N*-dihalosulfonamides and vinylsilanes have been reported only once for the case of dichloramine T with vinyl- and allyltrimethylsilanes affording regioselectively the adducts bearing sulfonamide group at the terminal carbon atom, these products having been dehydrochlorinated to 1-tosyl-2-(trimethylsilyl)-aziridine.[6]

Of special interest among *N,N*-dihalosulfonamides is *N,N*-dichlorotriflamide $CF_3SO_2NCl_2$ ($TfNCl_2$) since strong electron-withdrawing properties of triflyl group should promote electrophilic chlorination reactions. Until our very recent studies,[7,8] no examples of oxidative triflamidation of vinyl silanes were known. *N,N*-Dichlorotriflamide was synthesized as early as in 1974,[9] however its chemistry is still scarce being investigated mainly in reactions with polyhaloethylenes.[10–14]



Scheme 1 *Reagents and conditions*: i, CCl_4, –10 °C, then 22 °C.

With that in mind, we report here the results of the reactions of *N,N*-dichlorotriflamide with some representative vinylsilanes. All reactions were carried out with gradual increase in the temperature from –10 °C to room temperature and were monitored by ^{1}H NMR spectroscopy. Since $TfNCl_2$ is hydrolytically unstable, its 1 : 10 v/v solution of freshly prepared reagent in dry CCl_4 was used.

The reaction of $TfNCl_2$ with trimethylvinylsilane **1** (1 : 1 molar ratio) leads to the product of chlorotriflamidation (**2**) (Scheme 1).[†] The side formation of triflamide $TfNH_2$ in the reaction is apparently due to partial hydrolysis of the starting $TfNCl_2$ with residual water.

The reaction of $TfNCl_2$ with divinylsilanes **3a**,**b** was performed similarly as that with silane **1**. With the equimolar

[†] N-*[(2-Chloro-2-trimethylsilyl)ethyl]triflamide* **2**. To a solution of vinylsilane **1** (0.50 g, 4.6 mmol) in CCl_4 (10 ml), a solution of $TfNCl_2$ (1.00 g, 4.6 mmol) in CCl_4 (10 ml) was added dropwise, and the mixture was stirred at –10 °C for 1 h and then at room temperature for 4 h. The solvent was removed, the product was purified by column chromatography on silica (0.063–0.2 mm, eluent hexane–chloroform, 1 : 1). Yield 0.31 g (24%), colourless liquid. IR (ν/cm^{-1}): 3312, 2961, 2904, 1428, 1373, 1230, 1195, 1146, 1075, 974, 849. ^{1}H NMR ($CDCl_3$) δ: 0.15 (s, 3H, Me), 3.36 (m, 2H, $=CH_2$), 3.70 (m, H, CH), 5.57 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 3.73 (Me), 47.79 (CHCl), 50.61 (CH_2), 119.65 (q, CF_3, J_{CF} 320.2 Hz). ^{19}F NMR ($CDCl_3$) δ: –77.33. ^{29}Si NMR ($CDCl_3$) δ: –5.09. Found (%): C, 25.55; H, 4.83; Cl, 11.82; F, 20.67; N, 4.64; S, 12.04; Si, 8.79. Calc. for $C_6H_{13}ClF_3NO_2SSi$ (%): C, 25.40; H, 4.62; Cl, 12.49; F, 20.08; N, 4.94; S, 11.30; Si, 9.90.

N-*[1-Chloro-2-(triflamido)ethyl](dimethyl)vinylsilane* **4a**. To a solution of divinylsilane **3a** (0.56 g, 5 mmol) in CCl_4 (5 ml), a solution of $TfNCl_2$ (1.09 g, 5 mmol) in CCl_4 (10 ml) was added dropwise at stirring. The mixture was stirred at –10 °C for 5 h, the solvent was evaporated. The product was purified as above, the eluent was a hexane–chloroform (5 : 1) mixture. Yield 0.60 g (41%). Colourless liquid. IR (ν/cm^{-1}): 3313, 2959, 2879, 1428, 1375, 1230, 1197, 1146, 1076, 964, 840. ^{1}H NMR ($CDCl_3$) δ: 0.260 (s, 3H, SiMe), 0.267 (s, 3H, SiMe), 3.35–3.46 (m, 2H, CH_2N), 3.67–3.78 (m, 1H, CHCl), 5.51 (br. s, 1H, NH), 5.79–5.90 (m, 1H, CH=), 6.07–6.19 (m, 2H, $=CH_2$). ^{13}C NMR ($CDCl_3$) δ: –5.80 (SiMe), –5.18 (SiMe), 47.79 (CHCl), 49.94 (CH_2N), 133.60 ($=CH_2$), 135.84 (CH=), 119.62 (q, CF_3, J_{CF} 321.2 Hz). ^{19}F NMR ($CDCl_3$) δ: –77.27. ^{29}Si NMR ($CDCl_3$) δ: –3.93. Found (%): C, 29.57; H, 4.45; Cl, 11.58; F, 18.86; N, 4.20; S, 10.15; Si, 9.35. Calc. for $C_7H_{13}ClF_3NO_2SSi$ (%): C, 28.52; H, 4.10; Cl, 12.03; F, 19.27; N, 4.74; S, 10.84; Si, 9.50.

ratio of $TfNCl_2$ and silane **3a**, only the product of chlorotriflamidation of one double bond (**4a**) was formed (see Scheme 1). However, when the ratio $TfNCl_2$/**3a** was 2 : 1, self-heating from –10 to 10 °C took place. The reaction afforded, along with $TfNH_2$, the product of double chlorotriflamidation of both double bonds (**6**) (see Scheme 1). Compound **6** was formed as a mixture of two diastereomers in 11 : 9 ratio, which followed from the presence of two Si*C*H_3 signals in the ^{13}C NMR spectrum (proton signals of the two diastereomers overlap).†

The reaction of $TfNCl_2$ with silane **3b** proceeds in a somewhat different manner. With the ratio of reactants $TfNCl_2$/**3b** = 1 : 1, the product of monochlorotriflamidation (**4b**) (major) and the product of chlorination of one double bond (**5**) were formed (see Scheme 1). Note that dichloride similar to **5** was not detected in the reaction of $TfNCl_2$ with silanes **1** or **3a**. The second double bond of silane **3b** remains intact.

A probable reason for the formation of only the products of monoaddition, **4b** and **5**, is that the expected products of double addition may be too sterically crowded due to the presence of two phenyl groups at silicon atom. An attempt to involve the second double bond in the reaction by raising the $TfNCl_2$/**3b** ratio to 2 : 1 led only to the increase in the yield of dichloride **5**, while the second double bond in **5** did not participate in the reaction. Neither prolongation of the reaction nor raising the temperature to 50 °C gave the desired bis-adduct.

To evaluate the utility of the synthesized adducts, we treated compound **2** with potassium carbonate using the conditions described in our recent study,[8] in which the target aziridine was obtained in only 3% yield. However, even with twofold excess of K_2CO_3 in dichloroethane, only unreacted compound **2** was recovered and no aziridine was formed. A probable reason for the failed elimination of HCl from **2** (as well as of HBr)[8] can be a high NH acidity of TfNH moiety, resulting in the formation of the salt with strongly reduced negative charge on the nitrogen atom due to the electron-withdrawing effect of the triflyl group, thus decreasing the probability of substitution at the C–Hal bond in molecule **2** (see Scheme 1) or in its bromine analogue.[8]

To summarize, the hitherto unknown reactions of *N*,*N*-dichlorotriflamide with trimethylvinylsilane, dimethyl(divinyl) silane and diphenyl(divinyl)silane have been accomplished to afford mainly the promising products of chlorotriflamidation at one or two bonds.

This work was performed with the use of the analytical equipment of Baikal Center of Collective Use of the Siberian Branch of the Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.039.

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Received: 25th July 2019; Com. 19/5998

Bis[1-chloro-2-(triflamido)ethyl](dimethyl)silane **6**. The reaction was performed and treated as described above, with the use of $TfNCl_2$ (2.18 g, 0.01 mol) in CCl_4 (10 ml) and stirring at –10 °C for 8 h. Yield 1.10 g (23%), colourless liquid. IR (ν/cm^{-1}): 3306, 2931, 2859, 1431, 1374, 1230, 1197, 1144, 1075, 967, 845, 608. ^1H NMR ($CDCl_3$) δ: 0.380 (br. s) and 0.394 (s, 6H in total, SiMe), 3.52–3.61 (m, 2H, CH^{A}N), 3.63–3.70 (m, 2H, CHCl), 3.77–3.86 (m, 2H, CH^{B}N), 5.43 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: –7.27 (SiMe, major diastereomer), –6.88 (SiMe, minor diastereomer), 47.00 (CH_2), 47.23 (CHCl), 119.08 (q, CF_3, J_{CF} 296.5 Hz). ^{19}F NMR ($CDCl_3$) δ: –77.27. ^{29}Si NMR ($CDCl_3$) δ: –5.61. Found (%): C, 20.25; H, 2.88; Cl 14.30; F, 24.01; N, 6.01; S, 13.18; Si, 5.14. Calc. for $C_8H_{14}Cl_2F_6N_2O_4S_2Si$ (%): C, 20.05; H, 2.94; Cl, 14.79; F, 23.78; N, 5.84; S, 13.38; Si, 5.86.

The synthesis and spectral characteristics of compounds **3b**, **4b** and **5** are described in Online Supplementary Materials.