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The reaction of chloroalkyl(vinyl)silanes with *N,N*-dichloro sulfonamides

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 419 346; e-mail: bagrat@irioch.irk.ru

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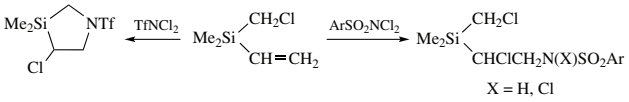
The reactions of *N*,*N*-dichloroarenesulfonamides with chloromethyl(dimethyl)vinylsilane or of *N*,*N*-dichlorotrifluoromethanesulfonamide with chloropropyl(dimethyl)vinylsilane give the NH- and NCl-containing products of chlorosulfonamidation of the double bonds. In contrast, *N*,*N*-(dichloro)trifluoromethanesulfonamide reacts with chloromethyl(dimethyl)vinylsilane to afford 4-chloro-3,3-dimethyl-1-[(trifluoroethyl)sulfonyl]-1,3-azasilolidine *via* intramolecular heterocyclization.



Keywords: chloroalkyl(dimethyl)vinylsilanes, *N*,*N*-dichloro sulfonamides, chloroamidation, heterocyclization, 1,3-azasilolidines.

Until recently, information about oxidative haloamidation of unsaturated silanes remained scarce. Free-radical addition of $TsNCl_2$ to vinyl- and allylsilanes proceeded with different regioselectivity leading to $Me_3SiCH(Cl)CH_2N(Cl)Ts$ and $Me_3SiCH_2C[N(Cl)Ts]CH_2Cl$, respectively,[1] in both cases the tosylamino residue having entered at the β-position with respect to silicon. The observed regioselectivity is specific for allylsilanes, whereas allyl ethers when treated with tosylamide and *N*-bromosuccinimide give the product of bromosulfonamidation with the tosylamino residue at the terminal carbon atom.[2] Probably, the first example of oxidative sulfonamidation of unsaturated silanes was the reaction of 3-silylated cyclohexa-1,4-dienes with chloramines in the presence of external oxidant K_2OsO_4.[3]

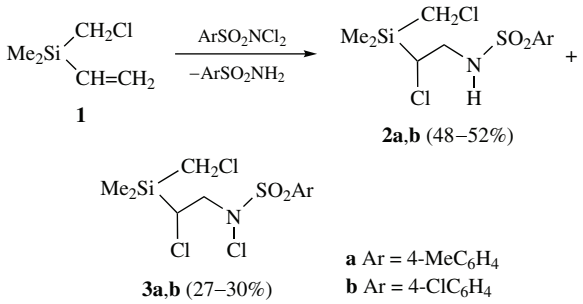
Recently, we reported on the sulfonamidation of vinylsilanes under oxidative conditions.[4] In the absence of external oxidant, *N*,*N*-dichlorotrifluoromethanesulfonamide (*N*,*N*-dichlorotriflamide, $TfNCl_2$) reacted with trimethyl(vinyl)silane and dimethyl(divinyl)silane to afford the products of chlorotriflamidation of one or two C=C bonds.[5] In the present work, we have studied the reactions of different *N*,*N*-dichloro sulfonamides with chloroalkyl(dimethyl)vinylsilanes, which can become a point of growth in these studies due to the presence of a reactive chloroalkyl group allowing the Si,N-heterocycles with sulfonamide moiety to be formed. Compounds containing in one molecule such a pharmacophoric motif and the silicon atom are of interest in terms of the so-called 'sila-pharmaca chemistry'.[6,7] Several allylsilanes, among other allylic systems, were shown to undergo Si–C bond splitting in the course of oxidative sulfonamidation in the presence of halogen-containing oxidants.[8] Note that our first trials to cyclize the products of chlorosulfonamidation into the corresponding aziridines failed.[5]

The reactions of twofold molar excess of chloromethyl(dimethyl)vinylsilane **1** with *N*,*N*-dichloroarenesulfonamides $ArSO_2NCl_2$ were carried out on cooling to –10 °C and subsequent warm-up to room temperature leading to the products of chlorosulfonamidation **2a**,**b** and their N-chlorinated analogues **3a**,**b** in the ~2:1 ratio (Scheme 1).† Obviously, the formation of NH-derivatives **2a**,**b** and arenesulfonamides $ArSO_2NH_2$ is caused by hydrolysis of sensitive N–Cl-containing species with air or solvent moisture.

In contrast, the reaction of *N*,*N*-dichlorotriflamide with vinylsilane **1** under the same conditions gives 4-chloro-3,3-dimethyl-1-trifluoromethylsulfonyl-1,3-azasilolidine **4** as the only product formed in 75% yield (Scheme 2).

This difference in reactivity is, apparently, due to higher NH-acidity of the intermediate triflamide derivative **A** (see Scheme 2) compared to arenesulfonamide analogues **2a**,**b** (see Scheme 1). No similar cyclization occurred in the reaction in Scheme 1 in the presence of 3-fold excess of K_2CO_3 or even of 10-fold excess of triethylamine as HCl scavengers.

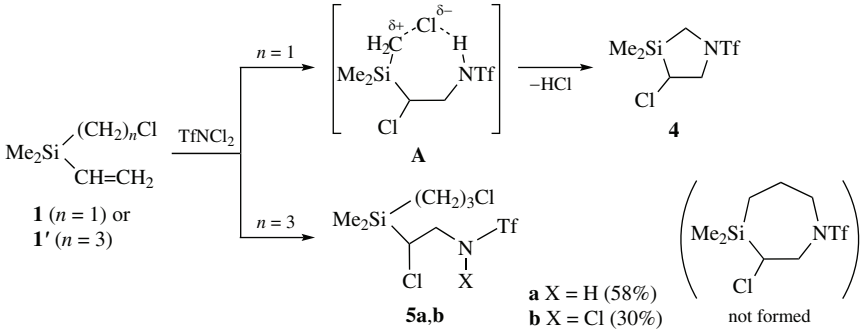
It was of interest to compare reactivities of silane **1** bearing $SiCH_2Cl$ group and its homologue, chloropropyl(dimethyl)vinylsilane **1′** with $Si(CH_2)_3Cl$ group, as this problem was not well



Scheme 1 *Reagents and conditions*: CCl_4, –10 → 20 °C, 2–3 h.

† *Reaction of vinylsilane **1** with* N,N-*dichloro*-p-*toluenesulfonamide*. To a solution of vinylsilane **1** (1.6 g, 12 mmol) in CCl_4 (15 ml) cooled to –10 °C, a solution of *N*,*N*-dichloro-*p*-toluenesulfonamide (1.4 g, 6 mmol) in CCl_4 (15 ml), prepared by the known procedure,[9] was added dropwise within 1 h. The reaction mixture was warmed to room temperature, and the reaction was complete in 1 h. The solvent was removed, the residue was separated on a silica gel column eluted with dichloromethane/hexane (2:1) to give products **2a** (1.06 g, 52%) and **3a** (0.67 g, 30%).

Other syntheses, in general, were performed similarly. For details and compound characterization, see Online Supplementary Materials.



Scheme 2 *Reagents and conditions*: CCl_4, –10→20 °C, 2–3 h.

clarified in the literature. Surprisingly, silane **1′** reacts with *N*,*N*-dichlorotriflamide in a different manner than silane **1** (see Scheme 2). No cyclization occurs; instead, the products of chlorotriflamidation, similar to those in Scheme 1, were obtained. The NH- and NCl-containing products **5a** and **5b** were isolated in 58 and 30% yields, respectively. If the cyclization reaction follows the S_N2 mechanism, the electron-donating effect of the silyl group would have much stronger retarding effect on cyclization of silane **1** than on silane **1′** having more remote C–Cl bond. The absence of cyclization products from silane **1′** may be indicative of a determining role of the NH···Cl bonding during cyclization, as the incipient α-carbocation in the case of silane **1** (see Scheme 2) is more stable than the incipient γ-carbocation in the case of silane **1′**. A conceivable possibility of the difference in stability of the rings in Scheme 2 seems unlikely because both five- and seven-membered Si,N-rings have been synthesized by Hg^{II}-induced cyclization of dimethyl(ω-phenylaminoalkyl)alkenylsilanes in comparable yields.[10]

In summary, carrying out the reactions between chloroalkyl(vinyl)silanes and *N*,*N*-dichloro sulfonamides revealed that their course is determined by two principal factors: the NH-acidity of sulfonamide and the length of the chloroalkyl chain. The reactions of *N*,*N*-dichloro derivatives of less acidic arenesulfonamides with dimethyl(chloromethyl)vinylsilane or of strongly acidic triflamide with dimethyl(chloropropyl)vinylsilane give the NH- and NCl-containing products of chlorosulfonamidation, whereas dichlorotriflamide with dimethyl(chloromethyl)vinylsilane affords the cyclic product of 1,3-azasilolidine type.

This work was performed using the equipment of the Baikal Analytical Center for Collective Use of SB RAS.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.11.035.

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