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Phenyltrifluorosilane in Organoelemental and Organic Synthesis

M. G. Voronkov[a], O. M. Trofimova[a], E. A. Grebneva[a], N. F. Chernov[b], and K. A. Abzaeva[a]

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

[b] *East-Siberian State Academy of Education, Irkutsk, Russia*

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Abstract—Ways of phenyltrifluorosilane application in organoelementalal and organic synthesis are summarized and systematized for the first time. The methods of its synthesis, physicochemical properties, and reactivity are considered. Special attention is paid to the original experimental results obtained by the authors.

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INTRODUCTION

Unlike its closest analog phenyltrichlorosilane, a large-scale product, which found wide application in industry and research laboratories, phenyltrifluorosilane $C_6H_5SiF_3$ for a long time did not attract much attention of researchers and technologists. Specific reactivity of the C–Si bond in $PhSiF_3$ with respect to nucleophilic and electrophilic reagents, high tendency to complex formation and selectivity of cleavage of the Si–F bond are of great synthetic and theoretical interest. Due to all these specific features, phenyltrifluorosilane turned out to be an original and effective reagent and synthon in organoelemental and organic synthesis.

Phenyltrifluorosilane, the methods of its synthesis and some properties were fragmentarily mentioned in monograph [1] and reviews [2, 3].

Reactions of $PhSiF_3$, which favor its application in preparative organoelemental and organic chemistry, may be divided in three groups:

(1) reactions proceeding with retention of the C–Si and Si–F bonds, that is, with retention of the aromatic ring and SiF_3 group (processes with participation of the aromatic ring and reactions of complex formation);

(2) reactions proceeding with the rupture of the Si–F bond;

(3) reactions proceeding with the rupture of the C–Si bond.

1. Methods of Synthesis

Phenyltrifluorosilane was first synthesized in 1944 by the famous British chemist Emeleus, the founder of the chemistry of polyfluorinated organoelemental compounds, by the reaction of phenyltrichlorosilane with zinc fluoride [4].

$$2PhSiCl_3 + 3ZnF_2 \rightarrow 2PhSiF_3 + 3ZnCl_2.$$

Later on, the most popular method of $PhSiF_3$ synthesis became the Swarts reaction: The replacement of the chlorine atoms in phenyltrichlorosilane by fluorine by heating with antimony trifluoride [5].

$$PhSiCl_3 + SbF_3 \rightarrow PhSiF_3 + SbCl_3.$$

Since SbF_3 is moderately active fluorinating reagent, it is activated by addition of small amounts of $SbCl_5$ (the effectiveness of SbF_3 is increased with the growing amount of $SbCl_5$) [6, 7].

Phenyltrifluorosilane is also readily formed in 61% yield by the reaction of SbF_3 with phenyldichlorosilane [8]. This reaction proceeds with the formation of antimony metal and hydrogen and is similar to fluorination of $HSiCl_3$ with SbF_3 [9].

$$6PhSiCl_2H + 6SbF_3 \rightarrow 6PhSiF_3 + 2Sb + 4SbCl_3 + 3H_2.$$

Darmrauer suggested to replace the highly toxic antimony trifluoride in the synthesis of $PhSiF_3$ from $PhSiCl_3$ by another cheaper and less toxic fluorinating agent, sodium hexafluorosilicate Na_2SiF_6 [10]. The yield of $PhSiF_3$ in this reaction is 65%.

$$2PhSiCl_3 + 3Na_2SiF_6 \rightarrow 2PhSiF_3 + 6NaCl + 3SiF_4.$$

For conversion of $PhSiCl_3$ into $PhSiF_3$ metal fluorides (LiF, CaF_2) are also used, which are not proper fluorinating agents [11]. Their use is based on the elimination of the hydrogen fluoride at the action of concn. HCl in the *n*-butanol solution. Here the yield of $PhSiF_3$ reaches 70 and 90%, respectively.

$$PhSiCl_3 + 3/n\ M_nF_n \rightarrow PhSiF_3 + 3/n\ M_nCl_n,$$
$$M = Li\ (n = 1),\ Ca\ (n = 2).$$

Unexpectedly, in the reaction of phenyltrichlorosilane with potassium or ammonium hydrogen fluoride the yield of $PhSiF_3$ turned out to be very low, the major product of the reaction being benzene formed due to the C–Si bond cleavage [12].

$$PhSiCl_3 + 2MHF_2 \rightarrow [PhSiF_3] \rightarrow PhH + SiF_4 + 2MCl + HCl,$$
$$M = K,\ NH_4.$$

Apparently, $PhSiF_3$ is the intermediate in the reaction where the C–Si bond is broken by the eliminated HF. This reaction is the first example of the rupture of the C–Si bond in $PhSiF_3$ by the action of HF. Note that no rupture of the Ph–Si occurs in the reaction of KHF_2 with $MePhSiCl_2$, the yield of $MePhSiF_2$ being 80%.

For the preparation of $PhSiF_3$, a low-temperature reaction of $PhSiCl_3$ with anhydrous HF or concn. hydrofluoric acid was also used. No C–Si bond splitting occurs under these condition and the yield of $PhSiF_3$ amounts to 70–85% [13–16].

$$PhSiCl_3 + 3HF \rightarrow PhSiF_3 + 3HCl.$$

The C–Si bond in $PhSiCl_3$ is stable to the action of HF also at room temperature [13, 17].

In contrast to that, gaseous HF, HCl, HBr at low temperature in the absence of solvent and catalyst split the C–Si bond in phenylsilane [18].

$$PhSiH_3 + HX \rightarrow PhH + XSiH_3.$$
$$X = F,\ Cl,\ Br.$$

Unlike that in the cold in the presence of copper dichloride or oxide the reaction of HF with $PhSiH_3$ proceeds with simultaneous rupture of three Si–H bonds [18].

$$PhSiH_3 + 3HF \xrightarrow{CuCl_2\ (CuO)} PhSiF_3 + 3H_2.$$

Similarly, the reaction of HF with phenyltribromosilane also results in $PhSiF_3$. No rupture of the C–Si bond is observed [18]. The reaction of 40% aqueous HF with $PhSiH_2Cl$ also gives mainly $PhSiF_3$ [19].

$$PhSiBr_3 + 3HF \xrightarrow{20°C} PhSiF_3 + 3HBr.$$

An “exotic” method for preparation of $PhSiF_3$ was described based on the reaction of phenyltrichlorosilane with the complex of hexafluoroacetone and potassium fluoride [20]. This is not surprising since hexafluoroacetone is an ionizing agent. Pittman and Sharp suggest that anion $(F_3C)_2C(F)O^-$ is an intermediate in this reaction, which, however, seems doubtful.

$$PhSiCl_3 + 3(F_3C)_2C{=}O{\cdot}KF$$
$$\rightarrow PhSiF_3 + 3(F_3C)_2C{=}O + 3KCl.$$

Phenyltrifluorosilane can be also synthesized by the reaction of phenyltriethoxysilane with potassium hydrogen fluoride [21]. However, preliminary preparation of $PhSi(OEt)_3$ by the reaction of $Si(OR)_4$ with PhMgX (X = Cl, Br) is unprofitable.

$$PhSi(OEt)_3 + 3KHF_2 \rightarrow PhSiF_3 + 3KF + 3HOEt.$$

The reaction of phenyltrialkoxysilanes with boron trifluoride etherate also affords phenyltrifluorosilane in 60–65% yield [22]. However, both this or the previous method cannot be considered as convenient for preparation of phenyltrifluorosilane since, as the source of $PhSi(OAlk)_3$, $PhSiCl_3$ is used, which is easily transformed into $PhSiF_3$ by the alternative aforementioned procedures.

$$PhSi(OR)_3 + F_3B{\cdot}OEt_2 \rightarrow PhSiF_3 + B(OR)_3 + Et_2O,$$
$$R = Me,\ Et.$$

Note that $PhSiF_3$ is formed by the reaction of sodium phenylpentafluorosilicate with methyldichlorosilane [23].

$$Na_2[PhSiF_5] + MeSiHCl_2$$
$$\rightarrow PhSiF_3 + MeSiHF_2 + 2NaCl.$$

Some other methods for preparation of $PhSiF_3$ are also known, but they have no practical value and can be used only in special cases. For example, the method of synthesis of $PhSiF_3$ by the reaction of phenylmagnesium halides with tetrafluorosilane has been patented [16].

$$SiF_4 + PhMgX \rightarrow PhSiF_3 + MgXF,$$
$$X = Cl,\ Br.$$

The above reactions are not only of synthetic interest but also reflect the reactivity of the C–Si and Si–X bonds in the derivatives of phenylsilane $PhSiX_3$ (X = F, Cl, Br, H, OR) with respect to various fluorinating agents.

2. Physicochemical Properties

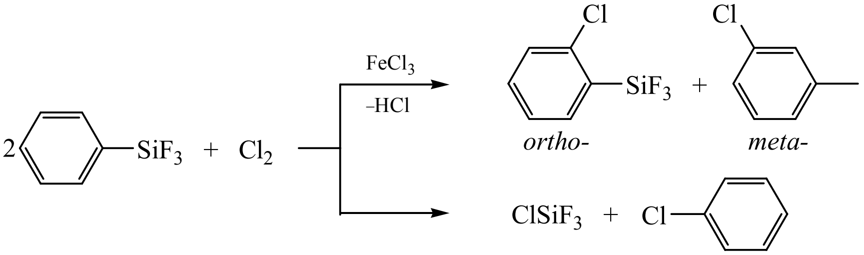
Phenyltrifluorosilane is a colorless easily hydrolyzed liquid with pungent odor due to eliminated HF, bp 101.8°C (750 mm Hg) [4], mp from –18 to –19°C [6], d_4^{20} 1.2169, n_D^{20} 1.4110 [5], μ 2.77 D [24], 2.72 D [25]. The structure of molecule $PhSiF_3$ was established by the gas electron diffraction method [26] and, in general, is similar to that of $PhSiCl_3$. The C–Si bond distance in molecule $PhSiF_3$ (1.822 Å) is the same as in $PhSiCl_3$ (1.820 Å) [27]. The Si–F bond distance in $PhSiF_3$ is equal to 1.57 Å, the angle FSiF is 105°, i.e., less than tetrahedral (in $PhSiCl_3$, ∠ClSiCl is 107°). In the ^{13}C NMR spectrum of phenyltrifluorosilane the chemical shift δ_C of the *ipso*-carbon atom (121.30 ppm) is smaller than that in the spectrum of phenyltrichlorosilane (131.55 ppm), which is indicative of a higher polarity of the C–Si bond in the molecule $PhSiF_3$ [28–31]. The bands at 940 and 850 cm^{-1} in the IR spectrum of $PhSiF_3$ belong to asymmetrical and symmetrical stretching vibrations of the Si–F bonds, respectively. Quantum-chemical calculations [32] have shown that the conjugation effect between the phenyl and trifluorosilyl groups in molecule $PhSiF_3$ is small. This is also proved by the UV spectrum of $PhSiF_3$ [33].

The most reactive in the molecule of $PhSiF_3$ are the C–Si and Si–F bonds. The mechanism of their splitting was calculated by the molecular orbital method, and the optimized geometries of the reagents and intermediates were found. The obtained data show that the rupture of the Si–F bond in $PhSiF_3$ proceeds via intermediates containing fluorine bridges Si···F···Si [34–36]. The C–Si bond is cleaved in the presence of anion F^- or the oxidizing agent with the formation of anions $[PhSiF_4]^-$ and $[PhSiF_5]^{2-}$ and their further oxidation into the anion-radical $[PhSiF_5]^{-\bullet}$. The latter is readily decomposed with the formation of anion $[SiF_5]^-$ and phenyl radical $Ph^\bullet$ (see Section 4.4.). The calculated mechanism of the rupture of the C–Si and Si–F bonds is consistent with the experimental data given below.

3. Chemical Properties

3.1. Reactions with participation of the aromatic ring. The reactions of electrophilic and radical substitution (chlorination, bromination, etc.) in the aromatic ring in $PhSiF_3$ and $PhSiCl_3$ are substantially different due to much larger electronegativity of the SiF_3 group compared with $SiCl_3$ [1, 5, 7, 37, 38]. This can be seen from the electronegativities by Pauling (χ): SiF_3 3.35, 3.49 [39], 3.14 [40] and $SiCl_3$ 2.78 [39], 2.66 [40], and by Mulliken: SiF_3 10.58 and $SiCl_3$ 8.88 [39]. The inductive and resonance constants of the SiF_3 group, which determine its influence on the course of the reaction of electrophilic substitution in the benzene ring have the following values: σ_I 0.42 [8, 41], 0.43 [31], 0.45 [41, 42]; σ* 2.62 [41]; σ_m^0 0.54, σ_p^0 0.66 [41]; ι 1.98 [43]. For the $SiCl_3$ group they equal, respectively: σ_I 0.21 [31], 0.39 [8]; σ* 1.77 [44]; σ_m^0 0.48, σ_p^0 0.56 [41]; ι 1.86 [43].

Electrophilic chlorination of $PhSiF_3$ in the presence of $FeCl_3$ affords the mixture of the *ortho*- and *meta*-chlorophenyltrifluorosilanes in the ratio of 18:82 [Eq. (1a)] [1, 5].



(1a)

(1b)

Under similar conditions, chlorination of $PhSiCl_3$ gives the mixture of the *ortho*-, *meta*-, and *para*-isomers in the ratio of 24:74:2 [5]. Thus, the SiF_3 group is a stronger *meta*-orientant and a weaker *ortho*-orientant than $SiCl_3$.

In the chlorination of $PhSiF_3$ the yield of the *meta*-isomer is by 58% higher, and of the *ortho*-isomer by 33% lower than in the case of $PhSiMe_3$, due to the larger electronegativity of the SiF_3 group [7, 38]. Therefore, the SiF_3 group is a strong *meta*-orientant, unlike the *ortho*- and *para*-orientant $SiMe_3$. An important difference in $PhSiX_3$ (X = F, Cl) at the chlorination or bromination in the presence of $FeCl_3$ is the splitting of the C–Si bond of $PhSiF_3$. The C–Si bond splitting of $PhSiX_3$ is also favored by lower steric hindrances originating from X = F, than from X = Cl. The C–Si bond rupture in $PhSiF_3$ at the halogenation is most probably due to the action of hydrogen halide HX (X = Cl, Br) eliminated as a result of aromatic substitution. The reaction of halogenation of $PhSiF_3$ can be recommended for the synthesis of relatively difficultly accessible 1,3-dihalobenzenes.

Electrophilic chlorination of $PhSiF_3$ in the presence of $FeCl_3$ or iodine that was converted during the reaction into ICl was studied in detail [7]. It was found that the ratio of the *ortho*-, *meta-,* and *para*-isomers of the formed monochlorinated product $ClC_6H_4SiF_3$ depended on the nature of the catalyst. When using iodine (or, more correctly, ICl) the yield of the *ortho*-isomer is sharply increased to 41.9%, while with $FeCl_3$ it is only 26.6%. In the formed mixture of the *ortho*-, *meta*-, and *para*-isomers of $ClC_6H_4SiF_3$ the ratio of the fraction of the *meta*-isomer to the total fraction of the *ortho*- and *para*-isomers is twice larger for catalysis with $FeCl_3$ (2.55), than with ICl [Eq. (1b)]. It is presumable that the electrophilicity and a larger volume of the iodine molecule or its chlorides hinder its nucleophilic attack on the silicon atom in the trifluorosilyl group.

The *meta*-orienting effect of the trifluorosilyl group is clearly seen at the bromination of $PhSiF_3$ in the presence of iron (*o:m:p* = 30:67:3) [45]. Note that the iodine-catalyzed *ortho*-substitution in $PhSiF_3$ is preferable (*o:m:p* = 68:25:7) compared to $PhSiCl_3$ (*o:m:p* = 17:19:64) or $PhSiMe_3$ (*o:m:p* = 21.5:26.7:51.8). The yield of the *ortho*-isomer of $BrC_6H_4SiF_3$ is 2.7 times (68%) larger than that of the *meta*-isomer (25%). The isomeric composition of the products of bromination $BrC_6H_4SiF_3$ is also affected by the intermediate formation of a stable charge-transfer complex between the brominating agent and, apparently, the catalyst with the aromatic ring of $PhSiF_3$.

The photochemical chlorination of $PhSiF_3$, as well as of $PhSiCl_3$, proceeds by the free-radical mechanism and results in the addition of chlorine to the aromatic ring with the formation of hexachlorocyclohexyltrifluorosilane with somewhat higher yield (48%), than that of hexachlorocyclohexyltrichlorosilane (40%) [46].

$$C_6H_5SiF_3 + 3Cl_2 \xrightarrow{h\nu} C_6H_5Cl_6SiF_3.$$

3.2. Complex formation. The electrophilicity of the silicon atom in the molecule $PhSiF_3$ is enhanced, due to high electronegativity of the three attached fluorine atoms and their small covalent radius (1.35 Å), so it easily adds anion F^-. However, with other nucleophiles $PhSiF_3$ reacts more reluctantly than $PhSiCl_3$.

With alkali and ammonia fluorides, phenyltrifluorosilane forms complexes containing the double charged anion of pentafluorosiliconium [47–50].

$$RSiF_3 + 2MF \rightarrow M_2^+[RSiF_5]^{-2},$$
$$R = Ph\ (Me, Et, Pr, HC{=}CH_2, FC{=}CF_2);\ M = Na, K, NH_4.$$

The reaction of $PhSiF_3$ with ammonium pentafluoroantimonate in aqueous medium proceeds with the formation of ammonium pentafluorosilicate [Eq. (2)] [51]. However, in the presence of ammonium fluoride, reaction (2) proceeds with the rupture of the C–Si bond and the formation of diphenylfluorostibine [Eq. (3)] [51, 52]. With hydrofluoric acid, $PhSiF_3$ forms a complex compound $H_2[PhSiF_5]$ [51].

$$PhSiF_3 + (NH_4)_2SbF_5 \xrightarrow{H_2O} (NH_4)_2[PhSiF_5] + SbF_3, \quad (2)$$

$$2PhSiF_3 + (NH_4)_2SbF_5 + 2NH_4F \xrightarrow{H_2O} Ph_2SbF + 2(NH_4)_2SiF_6. \quad (3)$$

From the reaction of $PhSiF_3$ with tetraethylammonium fluoride in acetonitrile the complex containing monocharged phenyltetrafluorosiliconium anion [Eq. (4)] was isolated [53]. Complexes of $PhSiF_3$ containing the phenyltetrafluorosiliconium anion have found preparative application as fluorinating agents or reagents for the synthesis of other organoelemental compounds.

$$PhSiF_3 + Et_4N^+F^- \xrightarrow{MeCN} Et_4N^+[PhSiF_4]^-. \quad (4)$$

It should be noted that phenyltrifluorosilane is capable of the formation of complex compounds with much weaker nucleophiles than fluoride anion. For example, with DMF $PhSiF_3$ forms a complex of the 1:6 composition stable up to 185°C [54].

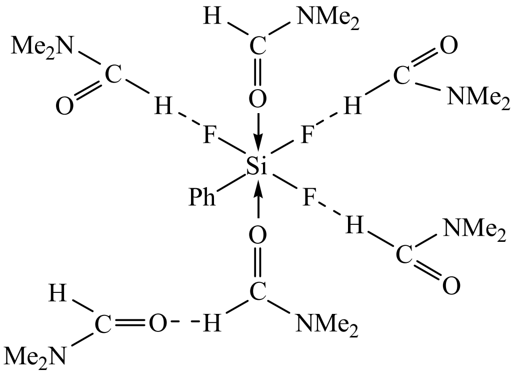
In the IR spectrum of this complex, the absorption band of the carbonyl group C=O is shifted to long-wave region as compared to its position in pure DMF, which is indicative of the formation of the coordination bond O→Si. The presence of an intense absorption band at 1080–1090 cm^{-1}, also belonging to the Si←O=C bond, is an additional indication of the structure of the complex. The spectrum also contains a band at 1710 cm^{-1}, which is indicative of the presence of a hydrogen bond between DMF and $PhSiF_3$.

In contrast, the reaction of $PhSiF_3$ with DMSO over 2–3 days at room temperature leads to a stable complex $2(Me_2SO)\cdot SiF_4$ [55, 56]. Also, diphenyldifluorosilane, diphenyl, and ~3% of benzene were identified in the reaction mixture pointing to the cleavage of the C–Si bond in $PhSiF_3$.

$$2PhSiF_3 + 2Me_2SO \rightarrow 2[(Me_2SO)\cdot PhSiF_3] \rightarrow 2Ph^{\cdot} + Si_2F_6,$$

$$Si_2F_6 \rightarrow SiF_4 + F_2Si\!:,$$

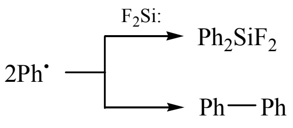
$$2Me_2SO + SiF_4 \rightarrow 2(Me_2SO)\cdot SiF_4.$$



Benzene is formed apparently via abstraction of the hydrogen atom from DMSO by the phenyl radical. This route of formation of benzene and diphenyl is proved by the early quantum-chemical calculations [34–36].

$$Ph^{\cdot} + MeS(O)Me \rightarrow PhH + {}^{\cdot}CH_2S(O)Me.$$

The complex of $PhSiF_3$ with DMSO formed in the first stage undergoes the degradation generating the phenyl radical and hexafluorodisilane. The latter, in turn, is decomposed into SiF_4 and difluorosilylene. The reac-tion of difluorosilylene with phenyl radical results in diphenyldifluorosilane. Biphenyl arises from recombination of the phenyl radicals. Apart from the aforementioned silicon compounds, the products of transformation of DMSO, methyl(fluoromethyl) sulfoxide and *S,S′*-dioxy(dimethyl) disulfide MeS(O)S(O)Me were also identified.



Under the same conditions, phenyltrifluorosilane reacts with DMF to give complex $2(Me_2NCHO)\cdot SiF_4$ and Ph_2SiF_2 [56]. Note that tertiary amines (Et_3N, pyridine) and acetonitrile do not form complexes with $PhSiF_3$ [56].

3.3. Reaction with splitting of the Si–F bond. Unlike many organic and inorganic silicon halides, isostructural fluoroderivatives are rather stable to the reactions of hydrolysis and alcoholysis. As compared to phenyltrichlorosilane, the reactions of hydrolysis and alcoholysis of $PhSiF_3$ proceed more reluctantly and often reversibly. On the curve of potentiometric titration of $PhSiF_3$ with 0.1 N solution of EtONa in DMF three jumps of potential are observed corresponding to the stepwise substitution of the three fluorine atoms by the ethoxy group [57]. On the contrary, at the titration of $PhSiCl_3$ under similar conditions only one jump of potential is observed corresponding to the substitution of all three chlorine atoms [58]. Strong protolytic stability of the Si–F bond in $PhSiF_3$ is not only due to the high electronegativity of the fluorine atom and the large energy of the Si–F bond, but also due to its low polarizability as compared to that of the Si–Cl bond. The decrease in the polarity of the Si–F bond in $PhSiF_3$ is ascribed to the d_π–p_π-conjugation between the benzene ring and the silicon atom, which competes with the similar conjugation between the Si and F atoms [58]. In spite of the maximum strength of the Si–F bond (561.46 kJ mol^{-1}) among all bonds formed by silicon, all three fluorine atoms in the molecule $PhSiF_3$ and its *meta*- and *para*-derivatives could be replaced by bromine by the reaction with BBr_3 at 250°C (yield of $ArSiBr_3$ is 80–90%) [8].

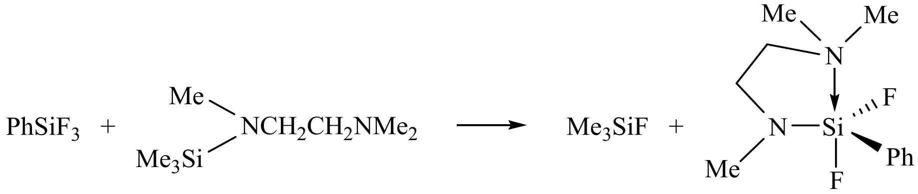
$$XC_6H_4SiF_3 + BBr_3 \rightarrow XC_6H_4SiBr_3 + BF_3$$
$$X = H,\ 3\text{-}F,\ 4\text{-}F.$$

$PhSiF_3$ is known to react with *N,N′*-trimethyl-(*N*-trimethylsilyl)ethylenediamine with evolution of trimethylfluorosilane and the formation of 1-phenyl-1,1-difluoro-2,5,5-trimethyl-2,5-diaza(sila)-λ^5-cyclo-pentane containing the pentacoordinate silicon atom and the donor-acceptor bond N→Si (yield 97%) [59].

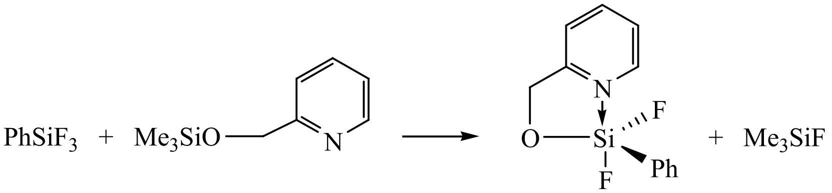
Similarly proceeds the reaction of $PhSiF_3$ with 2-(trimethylsiloxy)ethylamine and its *N*-methylated derivative also leading to the intracomplex heterocyclic compound having the pentacoordinate silicon atom and the coordinate bond N→Si, 1-phenyl-1,1-difluoro(2-aminoethoxy)silane (yield 81–99%) [59].

Finally, the reaction of $PhSiF_3$ with 2-(trimethylsiloxymethyl)pyridine at 80°C proceeds very slowly (70 h) with the formation of the intracomplex organosilicon derivative of pyridine in 98% yield [59].

The presence of the pentacoordinate silicon atom in the products of the three later reactions was proved by



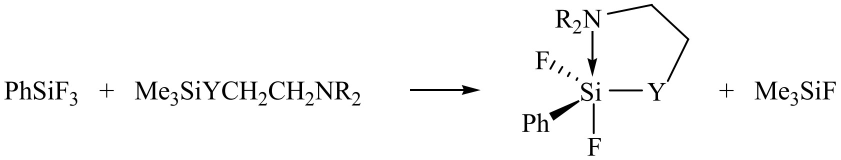
R = H, Me.



the method of low-temperature ^{19}F NMR spectroscopy. The hypervalent silicon atom is located in the center of the trigonal bipyramid, in whose axial positions the fluorine and nitrogen atoms are located.

These experiments have first shown that intra-complex heterocycles can be prepared from $PhSiF_3$ by general scheme (5).

It was found later that the reaction of $PhSiF_3$ with 8-(trimethylsiloxy)- or 8-(trimethylsilylthio) quinoline proceeds as transsilylation with the elimination of Me_3SiF and the formation of the (N→Si) 8-(phenyl-difluorosiloxy)- or (N→Si) 8-(phenyl-difluorosilylthio)-quinoline in 62 and 75% yield, respectively [60].



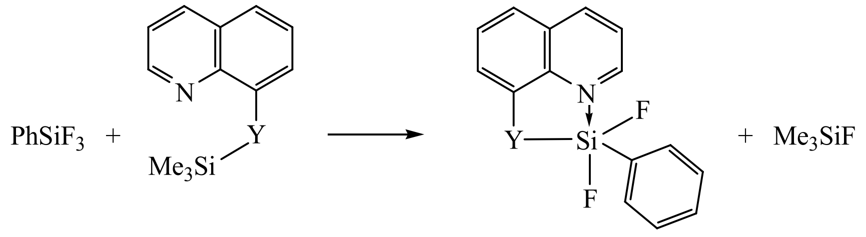
(5)

Y = NMe, O; $R_2 = H_2$, HMe, Me_2.

The presence of the N→Si intramolecular coordination in the product of reaction (6) (Y = S) is proved by an upfield displacement of the ^{29}Si chemical shift in the NMR spectrum (–79.8 ppm) and by a decrease in the coupling constant ^{29}Si–^{19}F (264 Hz) with respect to the spectrum of the reference compound of tetracoordinate silicon Ph_2SiF_2 (–28.65 ppm, 292 Hz). The chemical shift in the ^{19}F NMR spectrum (–136.9 ppm) of the product corresponds to the fluorine resonance of compounds of the pentacoordinate silicon.

The reaction of $PhSiF_3$ with trimethyl(2-dimethylaminoethoxy)silane proceeds as transsilylation with the rupture of the Si–F bond and the formation of the intra-complex (N→Si) phenyldifluoro(2-dimethylamino-ethoxy)silane (yield 50%), in which the silicon atom, according to ^{19}F and ^{29}Si NMR spectroscopy, is pentacoordinate [61].

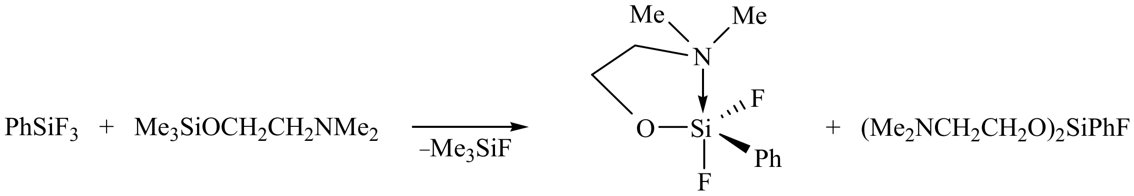
At the excess of trimethyl(2-dimethylaminoethoxy)silane, along with the main product, the (N→Si) phenylfluorobis(2-dimethylaminoethoxy)silane is formed (yield 45%), which contains the silicon atom in the formed coordination heterocycle. The ^{29}Si chemical shift in the spectra of compounds $F_2PhSiO\cdot CH_2CH_2NMe_2$ and $FPhSi(OCH_2CH_2NMe_2)_2$ is located



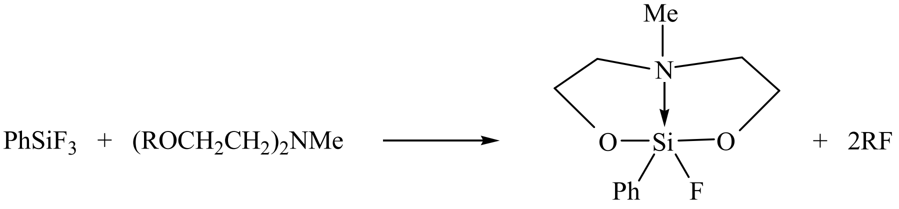
(6)

Y = O, S.

upfield relative to the structurally similar fluorides of tetrahedral silicon $F_2Si(OEt)Ph$ and $FSi(OEt)_2Ph$, respectively, and decreases with decreasing number of the Si–F bonds. The strength of the intramolecular coordination bond N→Si in these molecules decreases in the same order.



The reaction of $PhSiF_3$ with bis(2-hydroxyethyl) amine or *N*-methylbis(2-hydroxyethyl)amine and their trimethylsilyl derivatives proceeds with the rupture of two Si–F bonds with the formation of the intracomplex bicyclic (N→Si) 2-phenyl-2-fluoro-1,3-dioxa-6-aza-6-methyl-2-silacyclooctane (1-phenyl-1-fluoro-5-methyl-quasisilatrane) in 70–80% yield [62, 63].



R = H, Me_3Si.

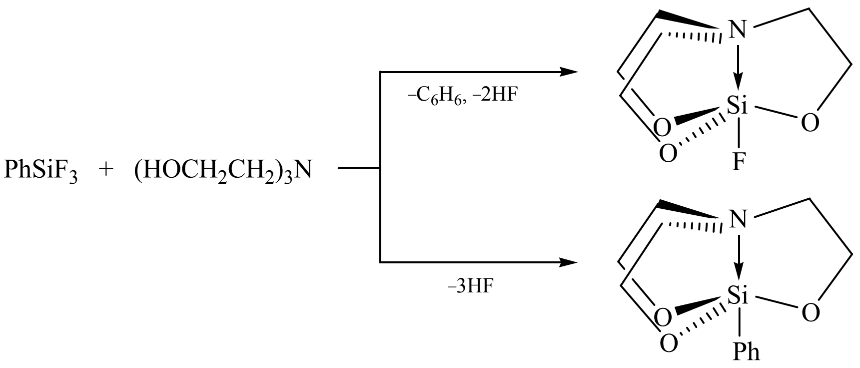
The coordination polyhedron of the silicon atom in the molecule $FPhSi(OCH_2CH_2)_2NMe$ is a distorted trigonal bipyramid ($\angle NSiF_a$ 172°), with the fluorine and nitrogen atoms in the axial positions, and with two endocyclic atoms O^1 and O^2 and the carbon atom C^5 of the exocyclic phenyl group in the three vertices of the equatorial plane of the bipyramid (Fig. 1) [64].

The length of the donor-acceptor bond N→Si (2.175 Å) in the molecule $FPhSi(OCH_2CH_2)_2NMe$ is substantially shorter than the sum of the van der Waals radii of the N and Si atoms, thus proving the coordination interaction between these heteroatoms. A smaller displacement of the silicon atom from the plane of the three surrounding oxygen atoms (ΔSi) in quasisilatrane $FPhSi(OCH_2CH_2)_2NMe$ (0.08 Å) as compared to that in $Ph_2Si(OCH_2CH_2)_2NMe$ (0.38 Å) [65] suggests an enhancement of coordination N→Si upon the replacement of one phenyl group at the silicon atom by a fluorine atom.

The reaction of diphenyldifluorosilane with *N*-methylbis(2-hydroxyethyl)amine or *N*-methylbis(2-trimethylsiloxyethyl)amine in the molar ratio of 1:1 proceeds in both cases with the cleavage of the two Si–F bonds and results in 1,1-diphenyl-5-methylquasisilatrane [(N→Si) 2,2-diphenyl-1,3-dioxa-6-aza-6-methyl-2-silacyclooctane] (yield 50–60%) containing the transannular donor–acceptor bond N→Si and a pentacoordinate silicon atom [62].

It is noteworthy that the replacement of one phenyl group by methyl in Ph_2SiF_2 changes the course of the reaction of $PhMeSiF_2$ with *N*-methylbis(2-hydroxyethyl)amine or its trimethylsilyl derivative (see Section 4.4), directing it to the splitting of the C–Si bond and elimination of C_6H_6 [62].

In the reaction of $PhSiF_3$ with tris(2-hydroxyethyl) amine, 1-fluoro- and 1-phenylsilatrane are formed in the molar ratio of 1:3 as a result of two parallel reactions of alcoholysis of the two Si–F bonds and protolysis of the C–Si bond, or alcoholysis of all three Si–F bonds [Eq. (7)] [62]. The reaction of $PhSiF_3$ with tris(2-trimethylsiloxyethyl)amine in hexane leads to the anticipated 1-phenylsilatrane in 86% yield [Eq. (8)].



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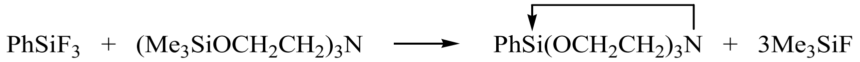


$$PhSiF_3 + (Me_3SiOCH_2CH_2)_3N \longrightarrow PhSi(OCH_2CH_2)_3N + 3Me_3SiF \quad (8)$$

In the reaction of $PhSiF_3$ with diethylene glycol or thiodiglycol, two Si–F are broken with the formation of 1-phenyl-1-fluoro-2,8-dioxa-5-chalcogenosilocanes, isostructural analogs of $PhFSi(OCH_2CH_2)_2NR$ [66].

$$PhSiF_3 + (HOCH_2CH_2)_2Y \xrightarrow[-2HF]{HCCl_3} PhFSi(OCH_2CH_2)_2Y,$$

$$Y = O, S.$$

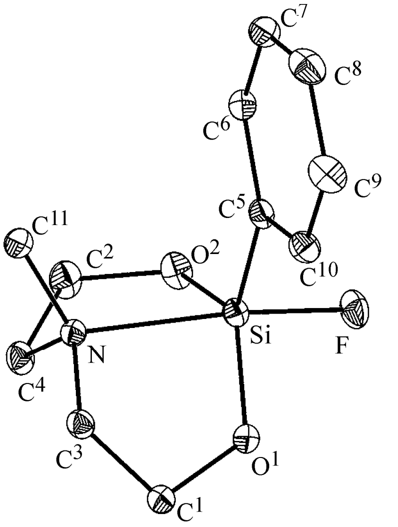
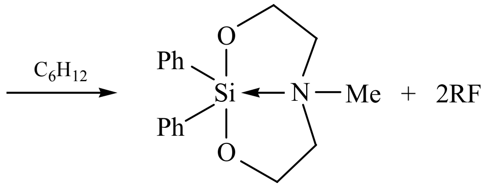


Fig. 1. Molecular structure of 1-fluoro-1-phenyl-5-methyl-quasisilatrane.

Using the methods of ^{19}F, ^{29}Si, and IR spectroscopy, as well as quantum chemistry at the DFT level of theory (B3LYP/6-311G**) it was found that a weak intramolecular coordination bond O→Si is realized in the molecule $PhFSi(OCH_2CH_2)_2Y$ (Y = O) [66]. NMR method also allowed to detect the formation of a dimer in which the silicon atoms of the two molecules are linked by the fluorine bridge Si···F···Si. For Y = S the interaction between the Si and S atoms in $PhFSi(OCH_2CH_2)_2S$ has the electrostatic nature.

$$Ph_2SiF_2 + (ROCH_2CH_2)_2NMe$$



R = H, Me_3Si.

$PhSiF_3$ (as well as Ph_2SiF_2) even at room temperature in the absence of catalyst splits the disiloxane group Si–O–Si of tetramethyldisiloxane [67]. Similarly, even at cooling (<20°C), $PhSiF_3$ splits the hexamethyl-disiloxane (HMDS) with the elimination of Me_3SiF and the formation of 1,1,1-trimethyl-3-phenyl-3,3-difluorodisiloxane [Eq. (9)] [68, 69]. The formed oligophenyldifluorodisiloxane is unstable and even at 20°C slowly disproportionates according to reaction (10) [70].

$$\mathrm{PhSiF_3 + (Me_2RSi)_2O \rightarrow PhF_2SiOSiRMe_2 + FSiRMe_2}, \quad (9)$$
$$\mathrm{R = H, Me.}$$

$$\mathrm{Me_3SiOSiF_2Ph \rightarrow (PhF_2Si)_2O + PhFSi(OSiMe_3)_2 + PhSiF_3 + PhSi(OSiMe_3)_3 + (Me_3SiOSiPhF)_2O + (Me_3Si)_2O + Me_3SiF.} \quad (10)$$

Unlike the reaction of $PhSiF_3$ with tetramethyl- and hexamethyldisiloxane, the reaction with 1,3-dimethyl-1,3-dichlorodisiloxane proceeds much slower and is followed by the processes of disproportionation and exchange of the Si–H and Si–Cl bonds for the Si–F bond [Eq. (11)] [67, 69].

$$\mathrm{PhSiF_3 + (MeClHSi)_2O \rightarrow PhF_2SiOSiMeClH + PhF_2SiOSiMeFH + (PhF_2SiO)_2SiMeH + PhFSi(OSiMeFH)OSiMeClH + PhFSi(OSiMeF_2)_2}. \quad (11)$$

The disproportionation of $PhSiF_3$ with $PhSiCl_3$ in the presence of aluminum halides AlX_3 (X = F, Cl, Br) leads to the mixed phenyl(chloro)fluorosilanes $PhSiCl_nF_{3-n}$ (n = 1, 2) [Eq. (12)], which split the Si–O bond of HMDS practically quantitatively within 1–14 h with the formation of trimethylchlorosilane and 1,1,1-trimethyl-3-phenyl-3,3-difluoro- or 1,1,1-trimethyl-3-phenyl-3-fluoro-3-chlorodisiloxanes [Eq. (13)] [71, 72]. The reaction of $PhSi(OSiMe_3)Cl_{n-1}F_{3-n}$ (n = 2) with excess HMDS results in 1,1,1,5,5,5-hexamethyl-3-phenyl-3-fluorodisiloxane [Eq. (14)].

$$\mathrm{PhSiF_3 + PhSiCl_3 \rightarrow PhSiClF_2 + PhSiCl_2F.} \quad (12)$$

$$\mathrm{PhSiCl_\mathit{n}F_{3-\mathit{n}} + (Me_3Si)_2O \rightarrow PhSi(OSiMe_3)Cl_{\mathit{n}-1}F_{3-\mathit{n}} + Me_3SiCl}, \quad (13)$$
$$n = 1, 2.$$

$$\mathrm{PhSi(OSiMe_3)ClF + (Me_3Si)_2O \rightarrow PhFSi(OSiMe_3)_2 + Me_3SiCl.} \quad (14)$$

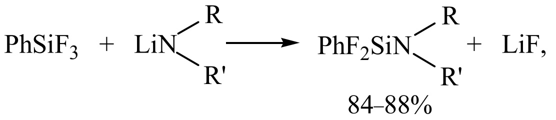
$PhSiF_3$ reacts unusually with vinyl butyl ether. The reaction proceeds at room temperature with the cleavage of the O–C_{sp}^{2} bond and the formation of phenyl(butoxy)difluorosilane and vinyl fluoride [Eq. (15)] [73]. In the earlier studied reactions of vinyl alkyl ethers no rupture of this bond was observed.

$$\mathrm{PhSiF_3 + CH_2{=}CHOBu \rightarrow PhSi(OBu)F_2 + CH_2{=}CHF.} \quad (15)$$

Phenyltrifluorosilane also easily (at 20°C) splits the Si–N–Si fragment of 1,1,3,3-tetramethyl- or hexamethyldisilazanes [Eq. (16)] [74, 75]. This reaction is a convenient route to organosilicon compounds with the F–Si–N group.

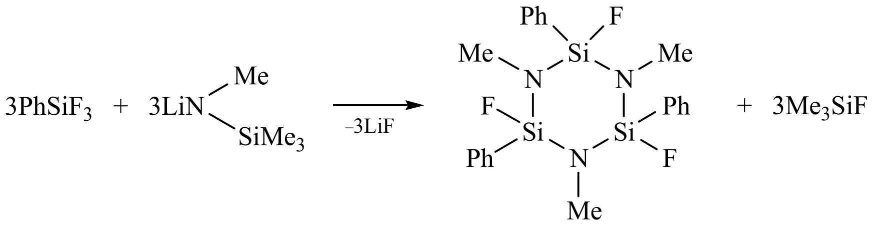
$$\mathrm{PhSiF_3 + (Me_2RSi)_2NH \rightarrow PhF_2SiNHSiMe_2R + Me_2RSiF}, \quad (16)$$
$$\mathrm{R = H, Me.}$$

Klingebiel et al. synthesized a huge number of organosilicon compounds having the F–Si–N fragment by the reaction of phenylfluorosilanes with N-lithiated nitrogen-containing organic compounds [76, 77]. Thus, $PhSiF_3$ reacts with N-lithium derivatives of amines (molar ratio 1:1) in petroleum ether [Eq. (17)].


$$\mathrm{PhSiF_3 + LiNRR' \longrightarrow PhF_2SiNRR' + LiF}, \quad (17)$$
84–88%

$\mathrm{R = R' = CHMe_2, SiMe_3; R = SiMe_3, R' = CHMe_2}$.

The reaction of $PhSiF_3$ with *N*-lithium(trimethylsilyl)methylamine proceeding with the elimination of Me_3SiF gives rise to six-membered 1,3,5-trimethyl-2,4,6-tri(fluorophenyl)cyclotrisilazane in 87% yield [Eq. (18)] [78]. *N*-Lithio-3-(trimethylsilyl)-2,2,4,4,6,6-hexamethyl-cyclotrisilazane reacts with $PhSiF_3$ with the formation of mono- and disubstituted trimethylsilyl(hexamethyl)cyclotrisilazanes [Eq. (19)] [78].



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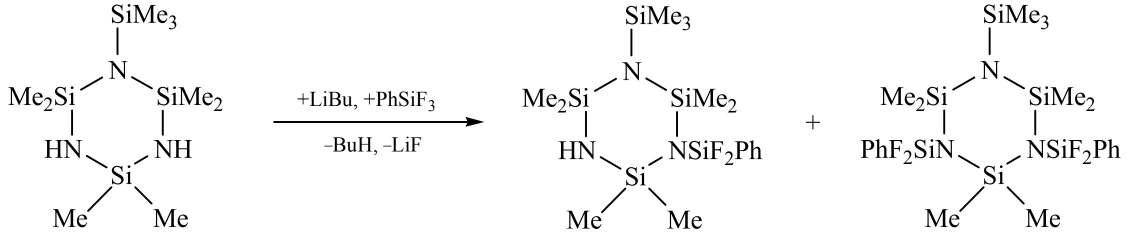

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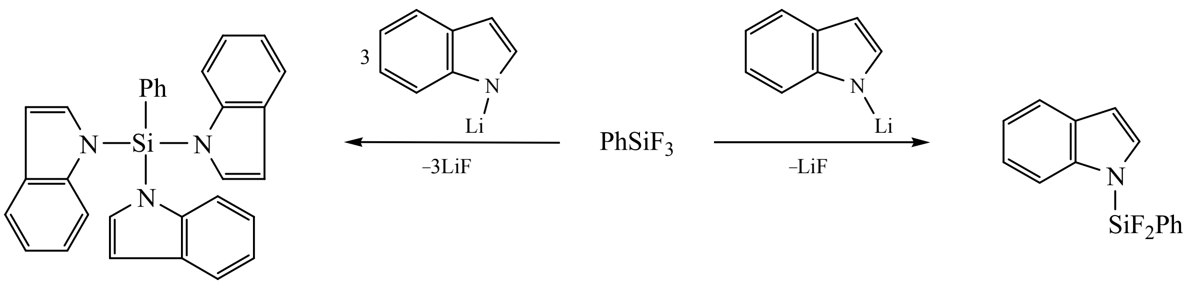

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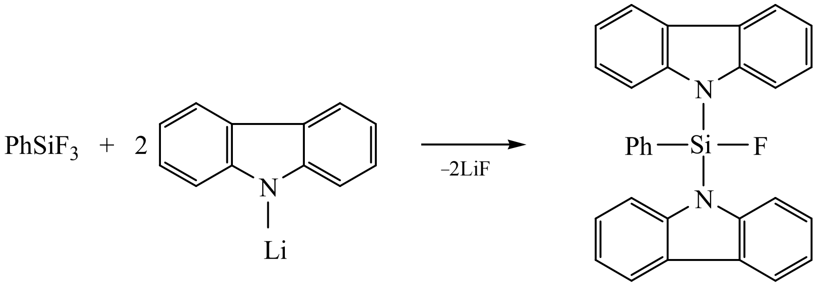
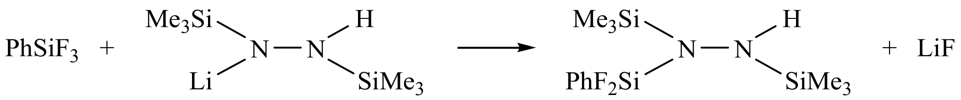


(21)

The reaction of $PhSiF_3$ with *N*-lithioindole affords difluorophenyl(*N*-indolyl)- and phenyltris(*N*-indolyl) silane in 90 and 84% yield, respectively [Eq. (20)] [79]. On the contrary, the reaction of $PhSiF_3$ with N-lithio-carbazole (molar ratio 1:2) in hexane–THF affords only phenylfluorobis(*N*-carbazolyl)silane in 67% yield [Eq. (21)] [80].

The reaction of $PhSiF_3$ with 1-lithio-1,2-bis(trimethylsilyl)hydrazine (molar ratio 1:1) results in the corresponding phenyldifluorosilyl derivative of bis(trimethylsilyl)hydrazine in 80% yield [Eq. (22)] [81]. 1,1'-Bis(phenyldifluorosilyl)-2,2'-dimethylhydrazine was obtained by the reaction of $PhSiF_3$ with the mixture of *N*-phenyldifluorosilyl-*N,N′*-dimethylhydrazine and *N*-lithio-*N′,N′*-dimethylhydrazine (molar ratio 1:1:1) in 55% yield [Eq. (23)] [81]. With the Li-derivative of methylfluorenyl phenyltrifluorosilane affords a potential precursor, difluoro(phenyl)(methylfluoronyl)silane [Eq. (24)] in high yield (75%) [82].



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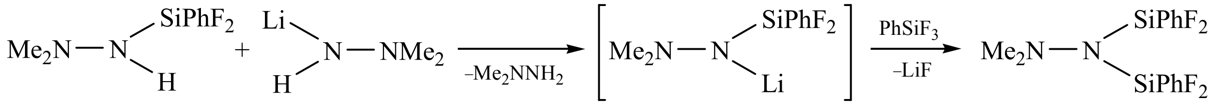

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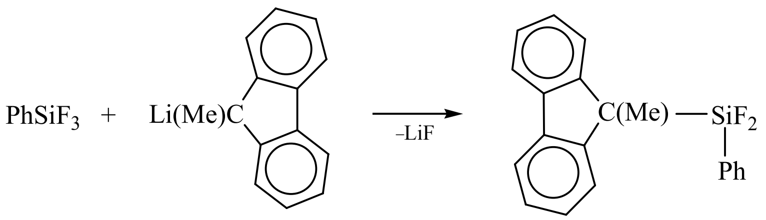
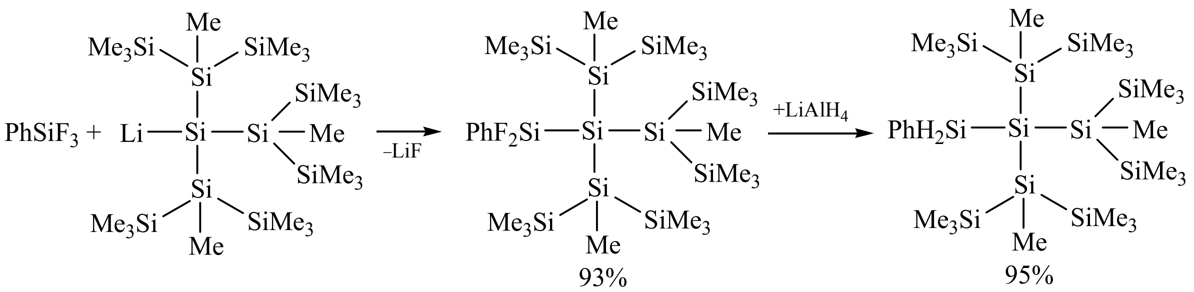


(24)

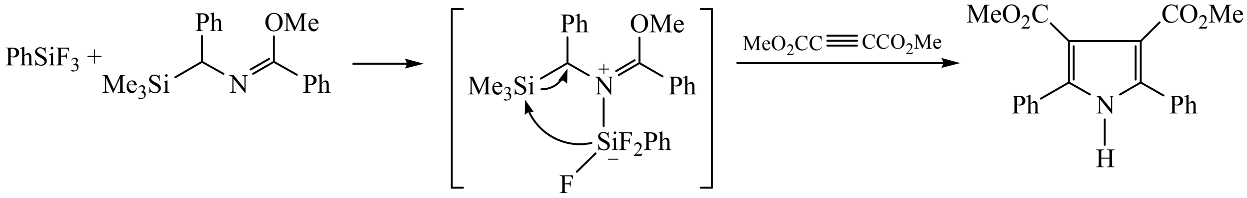
For the preparation of highly reactive organosilicon hydrides containing a bulky oligosilyl substituent X = $Si[Si(SiMe_3)_2Me]_3$ the reaction of phenyltrifluorosilane with lithiotris[bis(trimethylsilyl)methylsilyl]silane was used [83]. The reaction of the latter with $LiAlH_4$ results in the substitution of all fluorine atoms by hydrogen [Eq. (25)].

In the synthesis of 3,4-dimethoxycarbonyl-2,5-diphenylpyrrole, phenyltrifluorosilane plays a role of



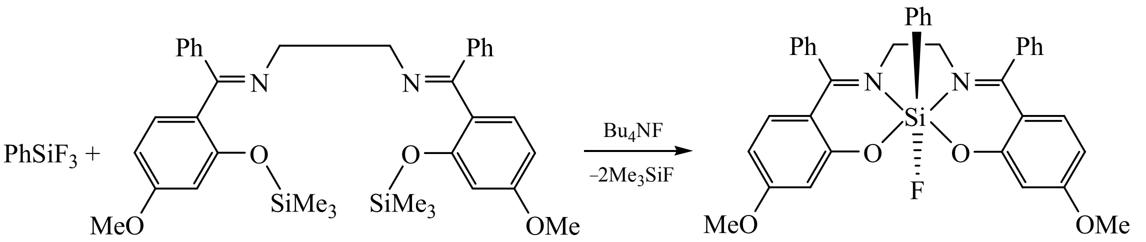
(25)

the quaternizing and desilylating agent [84]. This method is preferable since the reaction procedure is convenient and the reagents are cheaper as compared to the traditional methods [Eq. (26)].



(26)

In the presence of Bu_4NF, phenyltrifluorosilane enters in the reaction with the Schiff base to form a complex with the hexacoordinate silicon atom (yield 88%), containing in the *trans*-position the fluorine atom and the phenyl group in the coordination node ONNOSiFPh [Eq. (27)] [85].



(27)

3.4. Reactions with cleavage of the C–Si bond. The most interesting among chemical transformations of $PhSiF_3$ are the reactions proceeding with the splitting of the Ph–Si bond. Hydrogen halides are known to be capable of splitting the C–Si bond of arylsilanes $ArSiX_3$ (especially in the presence of $AlCl_3$) [86]. This process proceeds most easily for X = Me [Eq. (28)] [18].

$$PhSiMe_3 + HHlg \rightarrow PhH + HlgSiMe_3, \quad Hlg = Br, I. \qquad (28)$$

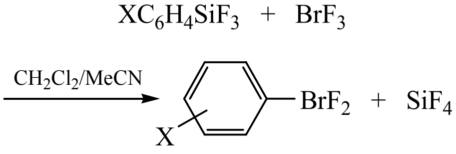
In the presence of three electronegative substituents (X = F, Cl) at the silicon in $PhSiX_3$ similar reactions proceed with difficulty. Thus, for example, at low temperatures (–40°C) hydrogen halides (HBr, HI) do not split the C–Si bond in $PhSiX_3$ (X = F, Cl) [18].

In the above reaction (1b) the C–Si bond is split, but the yield of the formed chlorobenzene is as low as ~3% [7].

The rupture of the C–Si bond of $PhSiF_3$ was observed when trying to synthesize this compound by the reaction of phenyltrichlorosilane with potassium or ammonium hydrogen fluoride [12]. However, the yield of $PhSiF_3$ was very low and the main products of the reaction were C_6H_6 and SiF_4.

Especially easily (–78°C) the C–Si bond of $PhSiF_3$ is cleaved in the reaction with bromine trifluoride in the mixture of methylene chloride and acetonitrile [87]. This reaction is a convenient method for preparation of arylbromodifluorides. In particular, 3- and 4-trifluoro-methylphenyltrifluorosilanes easily react with BrF_3 [Eq. (29)].

The reactions of splitting the C–Si bond of $PhSiF_3$ by metal salts, easily leading to their phenyl derivatives are of special interest in organoelemental synthesis. The reaction of phenyltrichlorosilane with



(29)

$X = 3\text{-}CF_3, 4\text{-}CF_3.$

concn. hydrogen fluoride and mercury dichloride in aqueous or alcoholic medium proceeds with the cleavage of the C–Si bond and the formation of phenylmercury chloride in up to 90% yield [Eq. (30)] [88]. The intermediate of this reaction was assumed to be phenyltrifluorosilane. However, the reaction of $PhSiF_3$ with $HgCl_2$ was not studied.

$$PhSiCl_3 + 6HF + HgCl_2 \xrightarrow{ROH} PhHgCl + H_2SiF_4, \quad (30)$$

$$R = H, Et.$$

However, later on it was found that the heating of $PhSiF_3$ with mercury diacetate [Eq. (31)] or oxide [Eq. (32)] in the absence of solvent in both cases resulted in diphenylmercury [88]. The yield of Ph_2Hg in reaction (32) is almost quantitative (99%). In acetic acid, reaction (33) is followed by the formation of mercury phenylacetate.

$$4PhSiF_3 + 2Hg(OCOMe)_2 \rightarrow 2Ph_2Hg + 3SiF_4 + Si(OCOMe)_4, \quad (31)$$

$$3nPhSiF_3 + nHgO \rightarrow nPh_2Hg + (PhFSiO)_n + 2nSiF_4, \quad (32)$$

$$4PhSiF_3 + 4Hg(OCOMe)_2 \xrightarrow{MeCOOH} 4PhHgOCOMe + 3SiF_4 + Si(OCOMe)_4. \quad (33)$$

Reactions of phenyltrifluorosilane [Eq. (34)] and its derivatives $XC_6H_4SiF_3$ [Eq. (35)] with mercury salts in aprotic media proceed already at room temperature with the cleavage of the Si–C bond and the formation of the arylmercury salts in practically quantitative yield (96–100%) [89, 90]. The $[XSiF_3]$ eliminated in the course of the reaction, apparently, undergoes disproportionation to SiX_4 and SiF_4. The rate of reaction (35) decreases with the increase of the σ_p-constant of the substituent X (Me < H < Cl < Br < NO_2). This method of synthesis of aromatic derivatives of mercury is the most simple and efficient among all described in the literature.

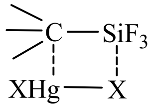
$$PhSiF_3 + HgX_2 \rightarrow PhHgX + [XSiF_3], \quad (34)$$

$$X = Cl, Br, I, CN, OCOMe,$$

$$4\text{-}XC_6H_4SiF_3 + Hg(OCOMe)_2 \rightarrow 4\text{-}XC_6H_4HgOCOMe, \quad (35)$$

$$X = Me, Cl, Br, O_2N.$$

The reaction of $PhSiF_3$ with mercury salts proceeds by the nucleophilic mechanism via an asynchronous four-centered cyclic transition state [90].



The first step is the nucleophilic attack at the silicon atom by the anion of the mercury salt, which leads to the pentacoordination of the silicon atom. As a result, the C–Si bond is strongly polarized due to the transfer of the electron density to the aromatic ring of $PhSiF_3$, thus increasing the positive charge on atom Si and the negative charge on atom C, which favors the interaction of the latter with cation $[HgX]^+$.

The replacement of even one fluorine atom in $PhSiF_3$ by an alkyl group makes reaction (34) more difficult (the yield of PhHgX becomes 10–15%). Unlike the reaction with $PhSiF_3$, the cleavage of the C–Si bond of $PhSiCl_3$ with mercury salts does not occur. With mercury acetate the reaction of substitution takes place, leading to the formation of $PhSi(OCOMe)_3$ in 85% yield [89].

Further study of the reaction of $PhSiF_3$ with HgO has proved the formation of diphenylmercury (yield 99%) and allowed to rationalize the mechanism of this reaction [89, 90].

$$PhSiF_3 + HgO \rightarrow [PhHg]^+[OSiF_3]^- \xrightarrow{PhSiF_3} Ph_2Hg + F_3SiOSiF_3, \quad (36)$$

The primary intermediate of reaction (36) is, apparently, the phenylmercury salt of oxytrifluorosiliconium, which further reacts with the second molecule of $PhSiF_3$.

The reaction of $PhSiF_3$ with antimony trifluoride in aqueous medium results in diphenylfluorostibine in 68% yield [Eq. (37)] [51]. Similarly proceeds the reaction of $PhSiF_3$ with SbF_3 and HF [Eq. (38)]. However, fluorostibine oxide is not formed. Therewith, the yield of Ph_2SbF was much lower (36%) [51].

$$2PhSiF_3 + 3SbF_3 + 2H_2O \rightarrow Ph_2SbF + 2H_2SiF_6 + 2FSbO, \quad (37)$$

$$2PhSiF_3 + SbF_3 + 4HF \rightarrow Ph_2SbF + 2H_2SiF_6, \quad (38)$$

The reaction of $PhSiF_3$ with ammonium pentafluoroantimonate, depending on the ratio of the reagents and conditions of the reaction leads either to phenylfluorostibine or triphenylstibine Ph_nSbF_{3-n} (n = 1–3) [51].

$$\mathrm{PhSiF_3 + (NH_4)_2SbF_5 \rightarrow Ph_{\mathit{n}}SbF_{3-\mathit{n}} + (NH_4)_2SiF_6}. \quad (39)$$

The main product of the reaction of $PhSiF_3$ with bismuth hydroxide, ammonium fluoride, and hydrofluoric acid in aqueous medium is triphenylbismuth (yield 50%) [51].

$$\begin{gathered}\mathrm{3PhSiF_3 + Bi(OH)_3 + 3HF + 6NH_4F} \\ \xrightarrow{\mathrm{H_2O}} \mathrm{Ph_3Bi + 3(NH_4)_2SiF_6 + 3H_2O}. \quad (40)\end{gathered}$$

The reaction of $PhSiF_3$ with triphenylfluoroplumbane in anhydrous system [HF+KF] or [$HF+NH_4F$] led to tetraphenyllead in 90% yield [Eq. (41)] [88]. The reaction of $PhSiF_3$ with lead tetraacetate [Eq. (42)] gave the same product in 71% yield [88]. In the mixture of 40% HF and 45% aqueous solution of NH_4F this reaction results in triphenylfluorolead in 75% yield [Eq. (43)] [91]. In the absence of ammonium fluoride the yield of triphenylfluorolead is even higher, 84% [Eq. (44)] [91, 92], and in the absence of hydrogen fluoride the yield of triphenylfluorolead is 74% [Eq. (45)].

$$\mathrm{PhSiF_3 + FPbPh_3 \rightarrow SiF_4 + Ph_4Pb}, \quad (41)$$

$$\begin{gathered}\mathrm{4PhSiF_3 + Pb(OCOMe)_4} \\ \mathrm{\rightarrow Ph_4Pb + 3SiF_4 + Si(OCOMe)_4}, \quad (42)\end{gathered}$$

$$\begin{gathered}\mathrm{3PhSiF_3 + Pb(OCOMe)_4 + 4HF + 6NH_4F} \\ \mathrm{\rightarrow Ph_3PbF + 3(NH_4)_2SiF_6 + 4MeCOOH}, \quad (43)\end{gathered}$$

$$\begin{gathered}\mathrm{3PhSiF_3 + Pb(OCOMe)_4 + 10HF} \\ \mathrm{\rightarrow Ph_3PbF + 3H_2SiF_6 + 4HOCOMe}, \quad (44)\end{gathered}$$

$$\begin{gathered}\mathrm{4PhSiF_3 + Pb(OCOMe)_4 + 12NH_4F} \\ \mathrm{\rightarrow Ph_4Pb + 4(NH_4)_2SiF_6 + 4MeCOONH_4}. \quad (45)\end{gathered}$$

The reactions of phenyltrifluorosilane with silver and copper salts, which include labile phenyl derivatives as intermediates, are especially interesting. The reaction of $PhSiF_3$ with silver carbonate at 70–100°C affords biphenyl and silver metal. The intermediate of this reaction is PhAg; carbon dioxide, tetrafluorosilane, and polyphenylfluorosiloxane are formed as side products [Eq. (46)] [88]. The reaction of $PhSiF_3$ with silver oxide also proceeds with intermediate formation of phenylsilver, which decomposes to silver and biphenyl [Eq. (47)] [88].

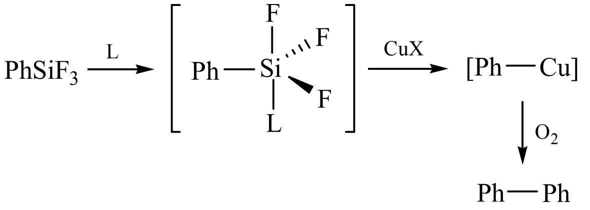
$$\begin{gathered}\mathrm{3\mathit{n}PhSiF_3 + \mathit{n}Ag_2CO_3} \\ \mathrm{\rightarrow \underset{\displaystyle 2Ag + Ph{-}Ph}{\underset{\downarrow}{2\mathit{n}[PhAg]}} + 2\mathit{n}SiF_4 + \mathit{n}CO_2 + (PhFSiO)_{\mathit{n}}}. \quad (46)\end{gathered}$$

$$\begin{gathered}\mathrm{3\mathit{n}PhSiF_3 + \mathit{n}Ag_2O} \\ \mathrm{\rightarrow \mathit{n}Ph{-}Ph + 2\mathit{n}Ag + 2\mathit{n}SiF_4 + (PhFSiO)_{\mathit{n}}}. \quad (47)\end{gathered}$$

The reaction of $PhSiF_3$ with basic copper carbonate leads to phenylcopper, which decomposes at the treatmenmt with water to benzene and copper oxide [Eq. (48)]. SiF_4, $(PhFSiO)_n$, and CO_2 are the side products of this reaction.

$$\begin{gathered}\mathrm{2PhSiF_3 + CuCO_3{\cdot}Cu(OH)_2 \rightarrow 2[PhCu]} \\ \xrightarrow{\mathrm{H_2O}} \mathrm{2PhH + Cu_2O}. \quad (48)\end{gathered}$$

Phenyltrifluorosilane in polar solvents (DMF, DMSO) at 60°C readily reacts with equimolar amount of copper chloride or cyanide with the formation of biphenyl in 79% yield [Eq. (49)] [93, 94]. The intermediate of this reaction is the complex of $PhSiF_3$ with the solvent (L), in which the Si atom is pentacoordinate. Its further reaction with copper salt leads to phenylcopper, which after oxidation with air oxygen forms biphenyl.



(49)

$L = Me_2SO$, $Me_2NC(O)H$; X = Cl, CN.

When using a palladium catalyst and KF in DMF, trimethylphenylsilane enters in the cross-coupling reaction with 4-iodoacetophenone. Therewith, due to the splitting of the Ph–Si bond, an asymmetric biaryl, 4-phenylacetophenone, is formed in 12% yield [Eq. (50)] [95]. The main product of the reaction is biphenyl (yield 61%). $PhSiF_3$ does not enter the similar reaction.

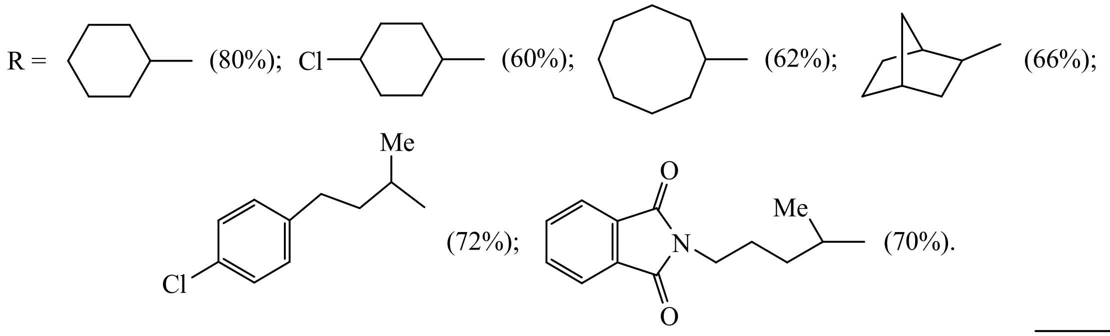
$$\begin{gathered}\mathrm{PhSiMe_3 + 4\text{-}I\text{-}C_6H_4COMe} \\ \xrightarrow[\mathrm{-Me_3SiI}]{\mathrm{(\eta^3\text{-}C_3H_5PdCl)_2}} \mathrm{4\text{-}PhC_6H_4COMe + Ph{-}Ph}\end{gathered} \quad (50)$$

Note that the Ph–Si bond in phenyl(hydrocarbyl)difluorosilane is easily cleaved with 4-iodoacetophenone leading to asymmetric biaryls in 68–87% yield.

$$\begin{gathered}\mathrm{PhSi(R)F_2 + 4\text{-}I\text{-}C_6H_4COMe} \\ \xrightarrow{\mathrm{(\eta^3\text{-}C_3H_5PdCl)_2,\ KF,\ DMF}} \mathrm{4\text{-}PhC_6H_4COMe + F_2RSiI}\end{gathered} \quad (51)$$

R = Me, Et, Pr, Ph.

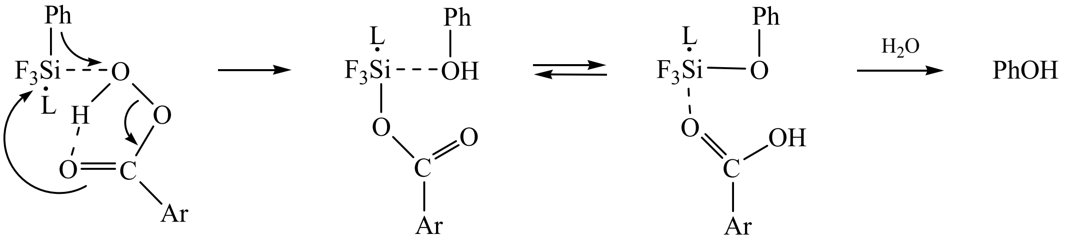
$$\mathrm{PhSiF_3 + BrR \longrightarrow PhR + [SiF_3Br]} \qquad (52)$$



Phenyltrifluorosilane in the presence of 4,7-diphenyl-1,10-phenanthroline, DMSO, and CsF enters the $NiBr_2$-catalyzed coupling reaction with primary bromides and iodides, as well as with inactivated secondary acyclic and cyclic bromides [Eq. (52)] [96].

Similar to the other aryltrifluorosilanes, $PhSiF_3$ is easily split with 3-chloroperbenzoic acid in DMF to form phenol in 77% yield [Eq. (53)] [97]. The following mechanism was suggested [Eq. (54)]. The process starts by the coordination of DMF with the silicon atom of $PhSiF_3$. Then, the intermediate containing the pentacoordinate silicon atom forms a complex with 3-chloroperbenzoic acid with a hexacoordinate silicon atom and a strongly polarized C–Si bond. The phenyl group in the complex migrates to the peroxide oxygen atom of 3-chloroperbenzoic acid. The subsequent hydrolysis of the rearrangement product leads to formation of phenol.

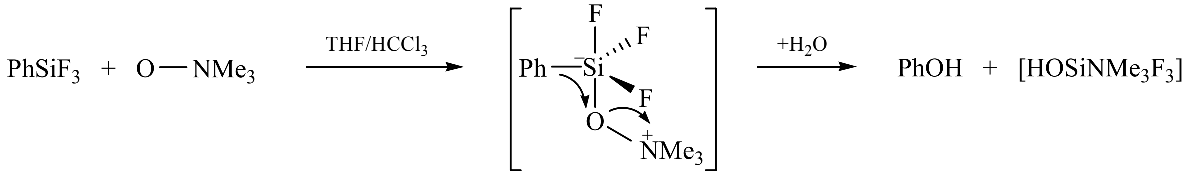
$$\mathrm{PhSiF_3 + 3\text{-}ClC_6H_4COOOH \xrightarrow{DMF} PhOH + [3\text{-}ClC_6H_4COOSiF_3]} \qquad (53)$$



(54)

L = $Me_2NC(O)H$.

Already at room temperature in the absence of catalyst phenyltrifluorosilane reacts with trimethylamine *N*-oxide to form phenol in 80% yield (after hydrolysis of the reaction mixture) [Eq. (55)] [98]. The intermediate of the reaction of oxidative cleavage of the C–Si bond is the 1:1 complex of the two reagents containing the pentacoordinate silicon atom where the phenyl group suffers the 1,2-migration from the Si to O atom. The process, apparently, proceeds via the formation of four-centered intermediate complex, which after decomposition and hydrolysis gives phenol. Under similar conditions $PhSiCl_3$ does not react with trimethylamine *N*-oxide, probably, because of lower electrophilicity of the silicon atom.



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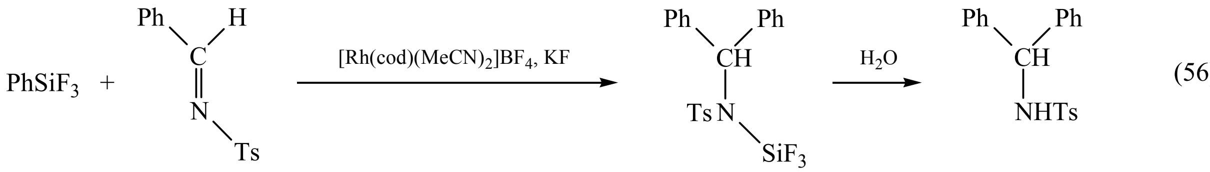


(56)

As distinct from $PhSiMe_3$ and $PhSiMe_2F$, $PhSiF_3$ reacts, though poorly, with *N*-tosylbenzylideneamine leading to the corresponding trifluorosilylamine, whose subsequent hydrolysis affords 2,2-diphenyl-*N*-sulfonyl-amine in 22% yield [Eq. (56)] [99].

Earlier, the alcoholysis of phenyltrifluorosilane was assumed to proceed only with the cleavage of the Si–F bonds [58]. However, it was shown recently [100] that the reflux of $PhSiF_3$ with aliphatic alcohols resulted in the rupture not only of the Si–F bond [Eq. (57)], but also of the C–Si bond [Eq. (58)]. The products of reaction (58) are benzene, alkoxyfluoro- and tetra-alkoxysilanes, and, in smaller amounts, phenyl(alkoxy)-fluorosilanes.

$$PhSiF_3 + HOR \longrightarrow PhSi(OR)_nF_{3-n} \qquad (57)$$

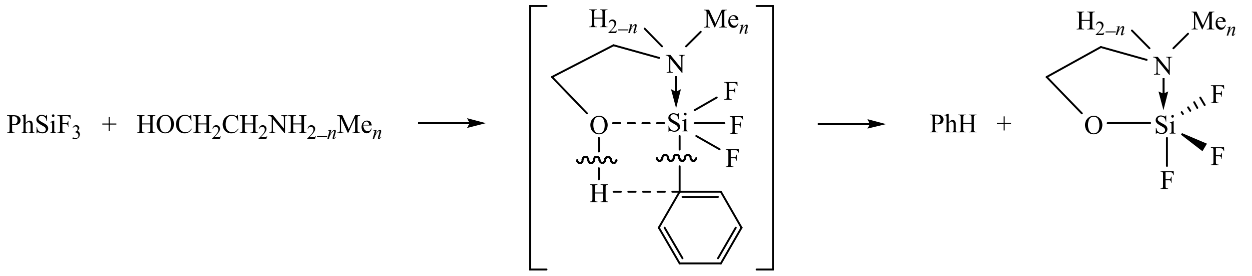
$$PhSiF_3 + HOR \longrightarrow PhH + (RO)_mSiF_{4-m} \qquad (58)$$

R = Me, Et, Bu, Oct; $n = 1, 3$; $m = 0–4$.

With higher alcohols (hexanol and octanol) the yield of the corresponding alkoxyfluorosilanes, the products of C–Si bond splitting in the $PhSiF_3$, is much higher. This is not only due to steric factors, but also because of the fact that higher alcohols ($R = C_6H_{13}$, C_8H_{17}) are stronger bases and weaker acids than lower alcohols (R = Me, Et), according to the Kamlet–Taft parameters [101]. Unexpectedly, the reaction turned out to be followed by the formation of a white powder-like precipitate insoluble in conventional solvents and corresponding to the empirical formula F_2SiO. With the increase in the length of the chain of the alkyl radical R from CH_3 to C_8H_{17} the yield of this inorganic polymer (fluorosil) increases to ~20% ($R = C_6H_{13}$) [102].

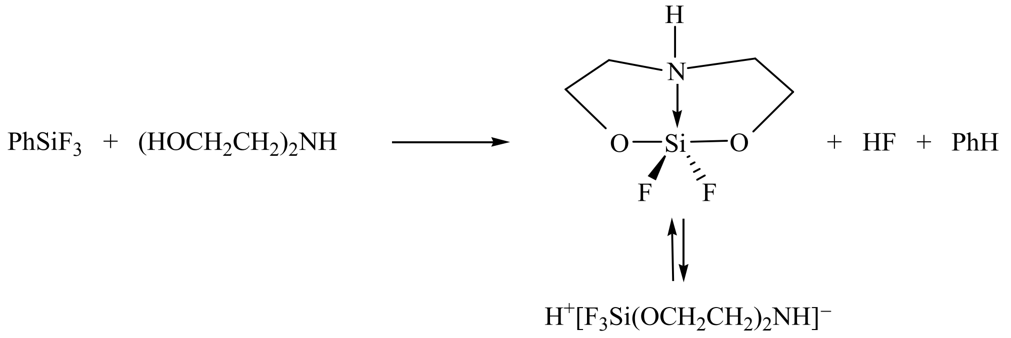
Investigation of the reaction of C–Si bond splitting in phenyltrifluorosilane has shown that the reaction of $PhSiF_3$ with 2-hydroxyethylamine, its mono- or di-*N*-methylderivatives proceeds with the splitting of the C–Si bond, the elimination of benzene, and the formation of trifluorohyposilatranes, (N→Si) trifluoro-(2-amino-ethoxy)-, trifluoro(2-methylaminoethoxy)- or trifluoro(2-dimethylaminoethoxy)silanes (yield 65–80%). All these intracomplex compounds have a pentacoordinate silicon atom and a short transannular donor-acceptor N→Si bond in the five-membered coordination cycle [61].

The process is assumed to begin with the coordination of the silicon atom of phenyltrifluorosilane to the nitrogen atom of 2-hydroxyethylamine with subsequent formation of the four-centered transition complex and is completed with the elimination of benzene and the formation of trifluorohyposilatranes containing the five-membered coordination cycle closed by the intramolecular donor–acceptor bond N→Si.

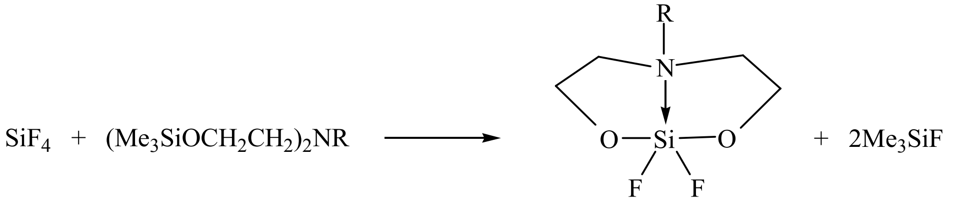


(59)

The reaction of $PhSiF_3$ with bis(2-hydroxyethyl)-amine also proceeds with the cleavage of the C–Si bond and leads to the bicyclic 1,1-difluoroquasi-silatrane containing the N→Si coordination bond and the pentacoordinate silicon atom [62]. Further reaction of $F_2Si(OCH_2CH_2)_2NH$ with the eliminated HF results in its hydrofluoride [Eq. (60)]. When passing gaseous SiF_4 into the solution of bis-(2-trimethylsiloxyethyl)-



(60)



(61)

R = H, Me.

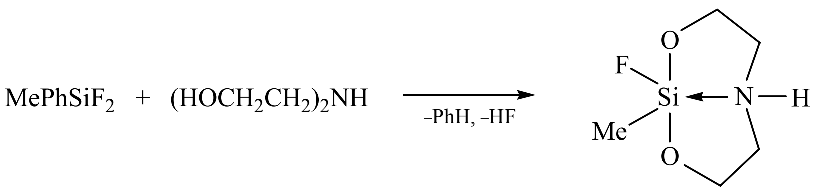
amine or its *N*-methyl derivative, 1,1-difluoroquasisilatrane is also formed [Eq. (61)] [103, 104].

The N→Si coordination bond in 1,1-difluoroquasisilatrane ($d_{\mathrm{N\to Si}}$ 1.981 Å, Fig. 2) is the shortest among the silatranes [105] and quasisilatranes [63, 64, 106, 107] so far studied by the XRD method. The only exception is the oxonium complex $\mathrm{BF_4^-}\cdot[\mathrm{Me_2OSi(OCH_2CH_2)_3N}]^+$ (1.965 Å) [108]. The deviation of the silicon atom ΔSi (0.11 Å) from the equatorial plane $\mathrm{O_1O_2F_2}$ of the bipyramid in this quasisilatrane is smaller than in silatranes (0.12–0.21 Å).

Earlier $\mathrm{F_2Si(OCH_2CH_2)_2NMe}$ was prepared in a low yield by transetherification of diethoxydifluorosilane $\mathrm{F_2Si(OEt)_2}$ with bis-(2-hydroxyethyl)amine [109].

The reaction of methylphenyldifluorosilane with bis-(2-hydroxyethyl)amine proceeds with the cleavage of the Ph–Si and Si–F bonds and the formation of 1-methyl-1-fluoroquasisilatrane [62].

Reaction (62) is the first example of the protolytic cleavage of the Ph–Si bond of phenyl(hydrocarbyl) difluorosilanes. The coordination polyhedron of the silicon atom in the molecule of 1-methyl-1-fluoroquasisilatrane is a slightly distorted bipyramid. In its axial positions a highly electronegative fluorine atom and the NH group are located, and in the three vertices of the equatorial plane there are two endocyclic oxygen atoms and the $\mathrm{CH_3}$ group (Fig. 3) [106]. The axial angle NSiF is 171°. The length of the transannular donor-acceptor bond N→Si (2.058 Å) is nearly the same as in 1-fluorosilatrane (2.042 Å) [110].



(62)

The reaction of $\mathrm{PhSiF_3}$ with 8-hydroxy- or 8-mercaptoquinoline $\mathrm{NC_9H_6YH}$ (Y = O, S) proceeds with the rupture of the C–Si bond and the formation of intracomplex heterocyclic derivatives of pentacoordinate silicon (N→Si) 8-(trifluorosiloxy)- or 8-(trifluorosilyl-thio)quinoline in 71 and 54% yield, respectively, in which the $\mathrm{YC_9H_6N}$ fragment acts as a bidentate ligand [60].

In molecules $\mathrm{NC_9H_6YSiF_3}$ (Y = O, S), the silicon atom is linked with the O or S atom by a covalent bond Y–Si, whereas the donor-acceptor bond N→Si closes

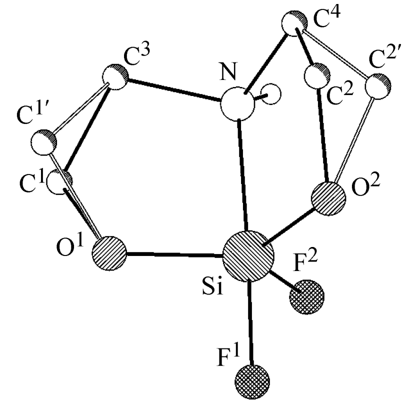


Fig. 2. Molecular structure of 1,1-difluoroquasisilatrane.

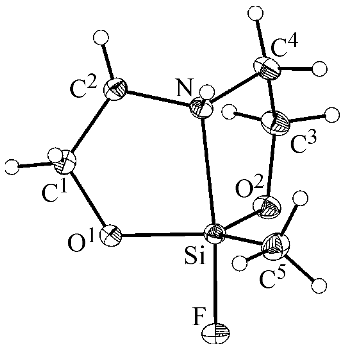
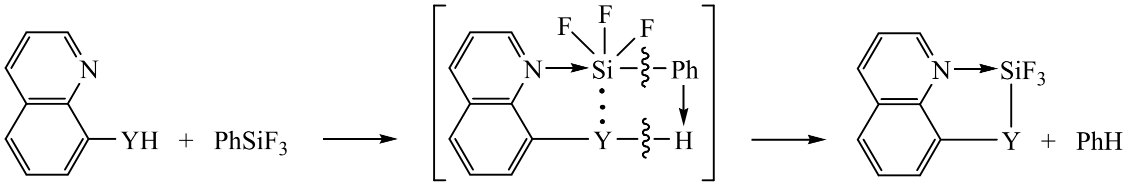


Fig. 3. Molecular structure of 1-methyl-1-fluoroquasisilatrane.

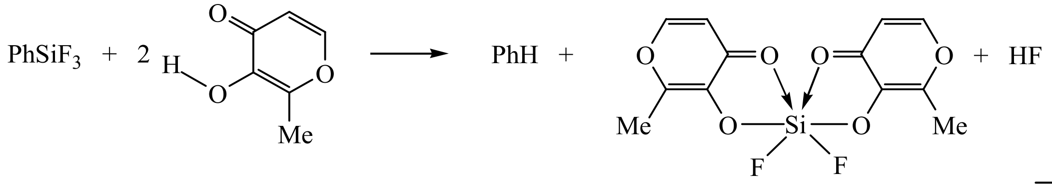
the five-membered coordination ring. This reaction is favored by an enhanced nucleophilicity of the nitrogen atom of the NC_9H_6YH fragment as compared to the O or S atom, resulting in formation of the intermediate.



(63)

Y = O, S.

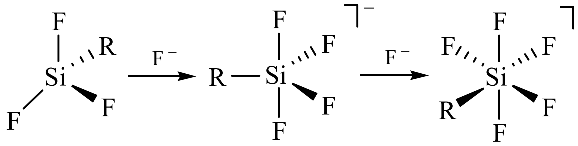
The reaction of $PhSiF_3$ with 3-hydroxy-2-methyl-4-pyrone (maltol), an available natural ligand possessing a complex of practically useful properties, proceeds with the rupture of the C–Si and Si–F bonds and the formation of the spirocyclic (C=O→Si←O'=C') bis(2-methyl-4-pyrono-3-oxy)difluoro-λ^6-siliconium in 71% yield [Eq. (64)] [111]. In the molecule of the latter (Fig. 4) the central hexacoordinate silicon atom binds the two five-membered coordination rings in one coordination node O_4SiF_2 with the *trans*-arrangement of the Si–F and C=O→Si bonds in the coordination polyhedron [112].



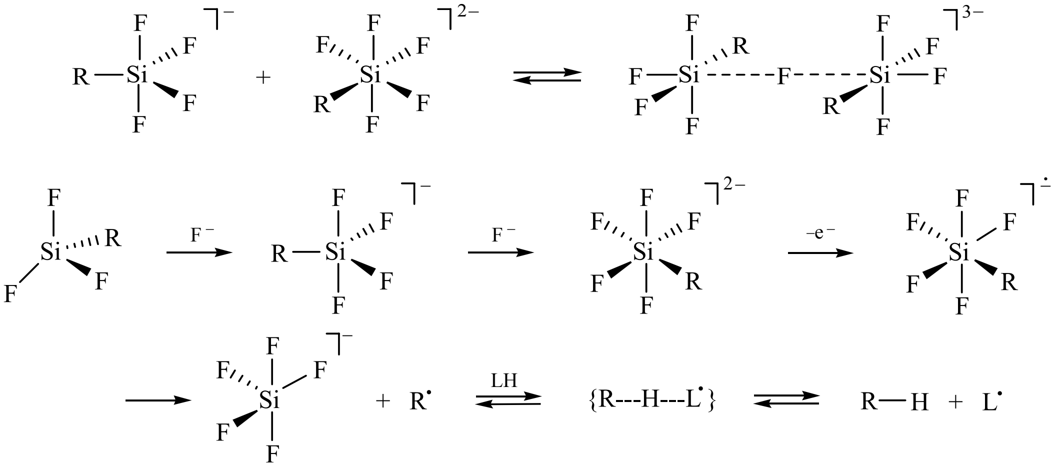
(64)

The coordination polyhedron of the silicon atom is a slightly distorted octahedron. The length of the axial bonds O→Si in the molecule is the same (1.868 Å) and it is by 0.10 Å longer than the equatorial bond O–Si. The lengths of the $Si–F^1$ and $Si–F^{1A}$ bonds are identical (1.651 Å).

The mechanism of the cleavage of the most reactive bonds C–Si and Si–F in the molecule $PhSiF_3$ was calculated using the method of molecular orbitals [36]. It was found that the cleavage of the Si–F bond in $PhSiF_3$ by $F^–$ anion proceeds via the intermediates containing fluorine bridges Si···F···Si [34–36]. This



R = F, Me, Ph.



anion is often present in the reaction medium in the form of HF formed by the reaction of $PhSiF_3$ with the air moisture or with water adsorbed on the surface of glass (which is completely eliminated only above 300°C). The reaction of $PhSiF_3$ with F^- anion proceeds with the formation of intermediates containing a penta- or hexacoordinate silicon atom [34–36]. This results in a slight (up to 10%) elongation of the Si–F bond. Such a weakening of this bond in the intermediates is insufficient for its rupture under mild temperature conditions.

Anions $[RSiF_4]^-$ and $[RSiF_5]^{2-}$ can be bound by the intermolecular fluoride bridge to form a triple-charged ion. The bridge bond Si–F in the latter is elongated to 20%, which favors its easy rupture into the starting anions.

The weakening of the C–Si bond and its rupture proceeds in another way. The C–Si bond in $PhSiF_3$ is cleaved in the presence of anion F^- and oxidizing agents with the formation of anions $[PhSiF_4]^-$ and $[PhSiF_5]^{2-}$, with subsequent oxidation into the anion-radical $[PhSiF_5]^{-\bullet}$, which undergoes fast decomposition to anion $[SiF_5]^-$ and phenyl radical $Ph^\bullet$. The phenyl radical further reacts with the protic solvent (LH) to form benzene.

According to calculations, the C–Si bond in the intermediates $[PhSiF_4]^-$ and $[PhSiF_5]^{2-}$ is only slightly elongated (by ~10%) that has a small effect and does not favor the splitting reaction. This bond is stretched more (70–90%) at the oxidation of the double charged anion $[PhSiF_5]^{2-}$ leading to the corresponding anion-radical $[PhSiF_5]^{-\bullet}$. The theoretically suggested mechanisms of the cleavage of the C–Si and Si–F bonds are consistent with the experimental data.

In conclusion, it should be stressed that the unusual reactivity of phenyltrifluorosilane is a keystone for new methods of synthesis of the earlier unknown types of the Si-fluorinated intracomplex organosilicon

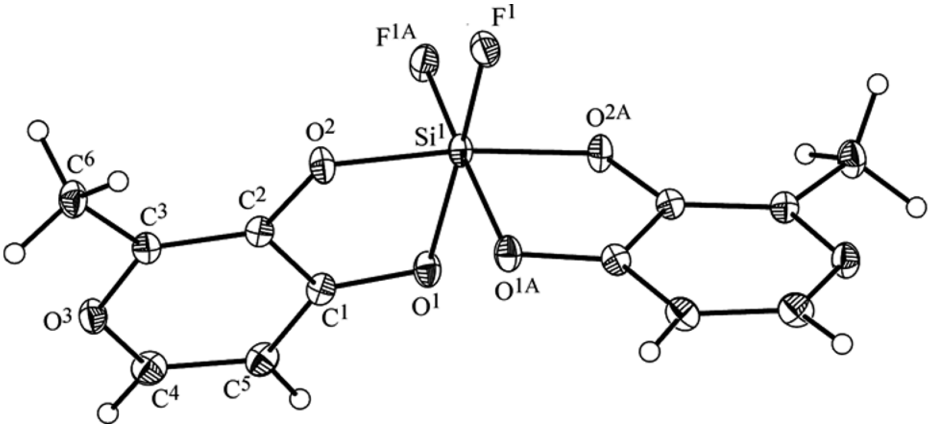


Fig. 4. Molecular structure of (C=O>Si←O'=C') bis(2-methyl-4-pyrono-3-oxy)difluoro-λ^6-siliconium.

compounds, in which the silicon atom is penta- or hexacoordinate. All the data presented in this review are indicative of the fact that phenyltrifluorosilane is a promising, uncommon, and efficient reagent. It is of no doubt that the use of phenyltrifluorosilane in organoelemental and organic synthesis will attract the attention of synthetic chemists. It will not only find a wide application in the laboratory practice but will also open new fields of application in organoelemental and organic synthesis.

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