Silicon–carbon bond cleavage of organosilicon amines $Me_nN[CH_2Si(OCH_2CH_2)_3N]_{3-n}$ (n = 1, 2) by phenols

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Anomalously high basicity of organosilicon amines $Me_nN[CH_2Si(OCH_2CH_2)_3N]_{3-n}$ determines the ease of nucleophilic cleavage of the Si–C bond by phenols even at room temperature. The conversion of silatrane increases both with phenol acidity and basicity of the exocyclic nitrogen atom.

Introduction

It is known that the Si–C bond in the silatranes $RSi(OCH_2CH_2)_3N$ (R = Me, Ph, Vin) is easily cleaved by electrophiles such as bromosuccinimide, 3-chloroperbenzoic acid, bromine or iodine monochloride, and mercury salts.[1–4] The only example of nucleophilic cleavage of the Si–C bond is the reaction of 1-iodomethylsilatrane with *N*,*N*-dimethylaminoethanol.[5] However the cleavage of the Si–C bond by nucleophiles is observed in the case of acyclic $RSi(OR')_3$ and monocyclic $R_2Si(OCH_2CH_2)_2NR'$ silatrane analogs with tetracoordinated silicon atoms. For example, the intramolecular ring closure of 2,2-diorganyl-6-(hydroxyethyl)-1,3-dioxa-6-aza-2-silacyclooctanes in bicyclic silatranes proceeds *via* cleavage of a Si–C bond by a fragment $HOCH_2CH_2N$.[6–8]

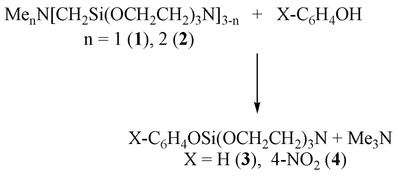
Recently in studies of hydrogen bonding of organosilicon amines, we found that *N*-methyl-*N*,*N*-bis(triethoxysilylmethyl)amine $MeN[CH_2Si(OEt)_3]_2$ reacts with phenol in a heptane solution. Transetherification of the ethoxy groups by phenol in the initial stage, following the cleavage of a Si–C bond, takes place and results in the formation of tetraphenoxysilane and trimethylamine.[9]

As was shown previously, phenol and 1-substituted organylsilatranes, $RCH_2Si(OCHR'CH_2)_3N$ (R = H, CH$_2$=CH, Cl, EtS; R′ = H, Me) form only one PhO–H ··· O–(Si) hydrogen bond both in non-polar and polar solvents without Si–C bond cleavage.[10] Phenol is coordinated by the nitrogen atom of 1-piperidinomethyl-3,7,10-trimethylsilatrane, $(CH_2)_5NCH_2Si(OCHMeCH_2)_3N$, in heptane solution this interaction being much stronger in comparison with triethylamine (K_{eq} 1100 and 52 dm^3 mol^{-1}, respectively).[11,12] The enhanced basicity of the piperidine nitrogen atom is due to the super electron-donor inductive effect of the silatranyl methyl group ($\sigma^* = -2.24$)[13–15] in comparison with other organosilicon groups CH_2SiR_3 (SiR_3 = $SiAlk_3$, $Si(OAlk)_3$, $\sigma^* \approx -0.6$). It is to be expected that the basicity of exocyclic nitrogen atoms in organosilicon amines $R_{3-n}N[CH_2Si(OCHRCH_2)_3N]_n$ increase with increasing n. Enhancement of the electron density on the exocyclic nitrogen is also confirmed by the considerable low frequency shift of the $CH_3(N)$ stretching vibration (2730 cm^{-1}) in the IR spectra of the methylbis(1-silatranylmethyl)amines, $MeN[CH_2Si(OCHRCH_2)_3N]_2$ (R = H, Me) as compared to methylalkylamines (2780–2830 cm^{-1}).[16] When we tried to involve $MeN[CH_2Si(OCHRCH_2)_3N]_2$ in intermolecular hydrogen bonding with phenol, a white precipitate was formed immediately when the phenol and $MeN[CH_2Si(OCHMeCH_2)_3N]_2$ were mixed in equimolar ratio in heptane solution. The IR spectrum of the isolated product (**A**) shows absorption bands of 3,7,10-trimethylsilatranyl and phenyl groups and the appearance of new bands at 2490 and 2590 cm^{-1} which can be assigned to the ammonium cation N$^+$–H.[17] It could be assumed that there is some interaction between phenol and silatrane $MeN[CH_2Si(OCHMeCH_2)_3N]_2$.

Now we report our detailed study of the reaction of phenol and *p*-nitrophenol with *N*-methyl-*N*,*N*-bis(1-silatranylmethyl)amine $MeN[CH_2Si(OCH_2CH_2)_3N]_2$ **1** and *N*,*N*-dimethyl-(1-silatranylmethyl)amine $Me_2NCH_2Si(OCH_2CH_2)_3N$ **2**.

Results and discussion

We found that the compounds **1** and **2** react with phenol and 4-nitrophenol, and cleavage of the Si–C bond takes place, similarly to the previously investigated *N*-methyl-*N*,*N*-bis(triethoxysilylmethyl)amine $MeN[CH_2Si(OEt)_3]_2$:



$$\begin{array}{c} Me_nN[CH_2Si(OCH_2CH_2)_3N]_{3-n} + X\text{-}C_6H_4OH \\ n = 1\ (\mathbf{1}),\ 2\ (\mathbf{2}) \\ \downarrow \\ X\text{-}C_6H_4OSi(OCH_2CH_2)_3N + Me_3N \\ X = H\ (\mathbf{3}),\ 4\text{-}NO_2\ (\mathbf{4}) \end{array}$$

The IR, UV and ^{1}H NMR data of silatrane **3** are consistent with those of the compound prepared in accordance to ref. 18. Thus, in the IR spectra of the product **3** the group frequencies assigned to the silatranyl (585, 634, 782, 800, 920, 940, 1017, 1090, 1115 cm^{-1})[19] are retained, and the $CH_3(N)$ vibrations observed at 2700–2800 cm^{-1} (ref. 20) are absent. The assignment of the new bands at 500, 694, 767, 886, 1492, 1575, 1592, 3010, 3030, 3050, 3070 cm^{-1} to the C_6H_5 modes is quite clear. The ^{1}H NMR spectra of compound **3** in CD_3CN show the proton signals of the silatranyl group CH_2N (t, 2.93 ppm), CH_2O (t, 3.92 ppm) as well as those for the C_6H_5O group (m, 6.68 and m, 7.82 ppm). By treatment of silatranes **1** and **2** with *p*-nitrophenol the Si–C bond cleavage is also observed, with the formation of 1-(*p*-nitrophenoxy)silatrane **4**. The IR, UV and ^{1}H NMR spectral data are in good agreement with those for the compound prepared in accordance with ref. 18.

^{1}H NMR monitoring of the reaction, performed in CD_3CN solution at room temperature in a sealed NMR ampoule for 6 h, shows the presence in the reaction mixture of initial compounds **1** or **2**, phenol in use and generated 1-aroxysilatrane only. The conversion was determined by integration of the intensities of the CH_2N and CH_2O proton signals of the silatrane ring in the initial and the formed silatranes. The

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Table 1 Electronic absorption spectra of the ArOX in CH_3CN

Compound	λ_1 (ε)/nm	λ_2 (ε)/nm
$MeN[CH_2Si(OCH_2CH_2)_3N]_2$	≤ 210	
$PhOSi(OCH_2CH_2)_3N$	267 (1550), 273 (1900), 279 (1450)	222 (9100)
$PhOSi(OEt)_3$	262 (750), 267 (1000), 276 (800)	213 (6400)
$PhO^-(Et_4N)^+$	298 (800)	245 (12500)
PhOH	267 (1750), 273 (2300), 279 (1900)	216 (7900)
p-$NO_2C_6H_4OSi(OCH_2CH_2)_3N$	310 (6500)	
p-$NO_2C_6H_4OH$	308 (11900)	
$PhOH + MeN[CH_2Si(OCH_2CH_2)_3N]_2$[a]	267 273 279 299	216 244 sh

[a] Reaction mixture.

silatrane conversion increases both with phenol acidity and basicity of the exocyclic nitrogen atom. For example, the reactions of silatrane **1** with phenol or *p*-nitrophenol gave aroxysilatranes **3** or **4** in 13 and 32% yields, respectively. Conversions of the amine **2** and **1** by treatment with phenol are 6 and 13 %, respectively.

On mixing solutions of phenol with compound **1** or **2** in MeCN, in the absorption spectra, along with the π⟶π* absorption band of the free phenol and phenolate anion, there is a new band at 222 nm associated with 1-phenoxysilatrane **3** (Table 1, Fig. 1).

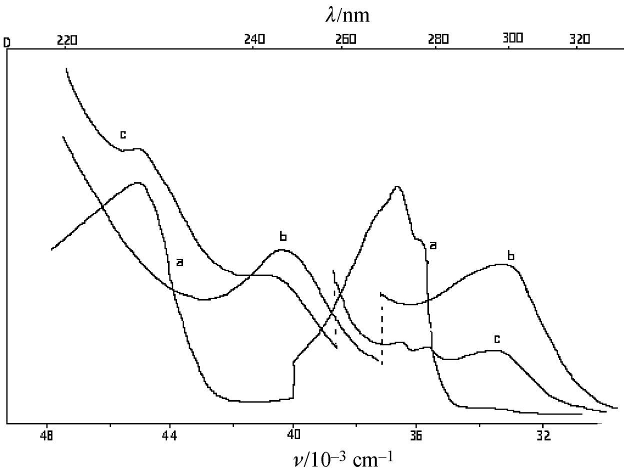


Fig. 1 UV absorption spectra of the phenoxysilatrane (a), tetraethylammonium phenolate anion (b) and mixture of phenol and **1** (c) in CH_3CN.

All these date made it apparent that the interaction of the phenol or *p*-nitrophenol with *N*-methyl-*N*,*N*-bis(1-silatranylmethyl)amine and 1-dimethyl(aminomethyl)silatrane resulted in Si–C bond cleavage and corresponding aroxysilatrane formation.

To gain some insight into the reaction mechanism we studied the interaction between silatranes **1** and **2** and phenols by means of UV spectroscopy. The electronic absorption spectrum of a 1 : 1 mixture of phenol and compound **1** in CH_3CN solution shows, as well as the absorption band of the free phenol at 216 and 267, 273 and 279 nm, the appearance of the new bands at 244 and 299 nm (Table 1, Fig. 1). The latter are coincident with the spectral characteristics of tetraethylammonium phenolate (245 and 298 nm). According to these data it seems most probable that a solvent-separated ion pair is formed in CH_3CN solution due to the following equilibrium (K_{eq} = 27 dm^3 mol^{-1}):[21]

$$PhOH + NMe[CH_2Si(OCHRCH_2)_3N]_2 \rightleftharpoons PhO^-(Solv)N^+HMe[CH_2Si(OCHRCH_2)_3N]_2$$

Only weak absorption in the 300 nm region is observed in the UV spectrum of the CH_3CN solution of a mixture of phenol with 10-fold excess of the base **2** (Fig. 2). These results indicate that compounds **1** are considerably stronger bases in comparison with trialkylamines and even with 1-*N*,*N*-dimethyl-(aminomethyl)silatrane **2**.

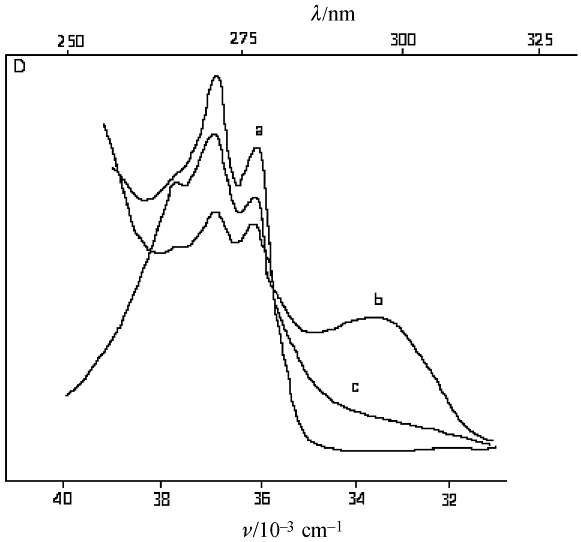


Fig. 2 Electronic absorption spectra of the phenol solutions [PhOH] = 4.1 × 10^{-3} mol dm^{-3} (a) in MeCN, in the presence of **1**, [**1**] = 1.1 × 10^{-2} mol dm^{-3} (b), in the presence of **2**, [**2**] = 4.4 × 10^{-2} mol dm^{-3} (c) (thickness 0.1 cm).

The electronic absorption spectra of *p*-nitrophenol and amine **2** in CH_3CN solution show, as well as the absorption maximum for free *p*-nitrophenol, a band at 426 nm arising from the solvent-separated ion pair formation similar to the complex 4-nitrophenol with trialkylamines.[19,20] The equilibrium constant for this compound is greater (1400 dm^3 mol^{-1}) than for trialkylamines (130–300 dm^3 mol^{-1}) (Table 2).[20]

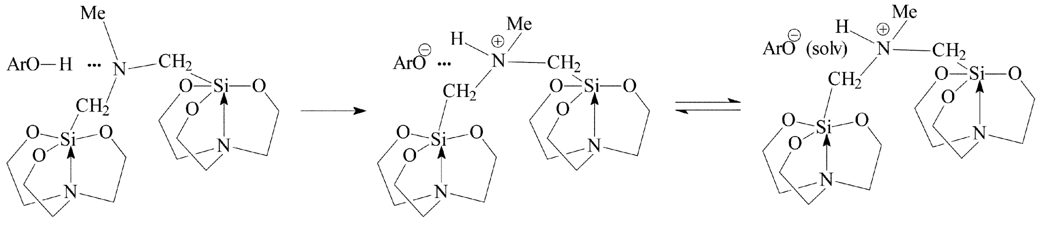
The absorption band of the π⟶π* transition of free 4-nitrophenol at 308 nm is not observed in the spectra of a 1 : 1.4 mixture of *p*-nitrophenol : methylbis(1-silatranylmethyl)amine **1** in CH_3CN. The formation of a solvent-separated ion pair is reflected by the appearance the band at 430 nm (Fig. 3). The further increase in amine concentration (2–7-fold) does not lead to enhancement of the absorption intensity of this band. These data demonstrate that there is essentially total proton transfer even at an equimolar ratio of *p*-nitrophenol and compound **1** resulting in a solvent-separated ion pair $ArO^-(Solv)N^+HMe[CH_2Si(OCH_2CH_2)_3N]_2$). The equilibrium constant of this interaction is too high (K_{eq} = 2700 dm^3 mol^{-1}) relative to the other hydrogen bonds of *p*-nitrophenol with trialkylamines. Such high basicity of the exocyclic nitrogen atom appears to be due to the strongest electron-donor effect of two silatranylmethyl groups.

Taking into account the exocyclic nitrogen atom basicity in the compounds $Me_nN[CH_2Si(OCH_2CH_2)_3N]_{3-n}$ (n = 1, 2), the Si–C bond cleavage can be described by the following scheme:

Table 2 Electronic absorption spectra (λ/nm, ε/dm^3 mol^{-1} cm^{-1}) and equilibrium constants (K_{eq}/dm^3 mol^{-1}) for the *p*-nitrophenol (ArOH) interaction with trialkylamines in acetonitrile

Amine	ArOH [λ (ε)]	ArO(Solv)N$^+$H$_3$ [λ (ε)]	K_{eq}
$MeN[CH_2Si(OCH_2CH_2)_3N]_2$	308 (12000)	430(37800)	2700[a]
$Me_2NCH_2Si(OCH_2CH_2)_3N$	308(12000)	426(35100)	1400[a]
Et_3N	308[b], 310[c]	426	270[b], 230[c]
Bu_3N	310	420	300[c]
Oct_3N	310	420	126[c]

[a] At 22 °C. [b] At 20 °C.[22] [c] At 26 °C.[23]



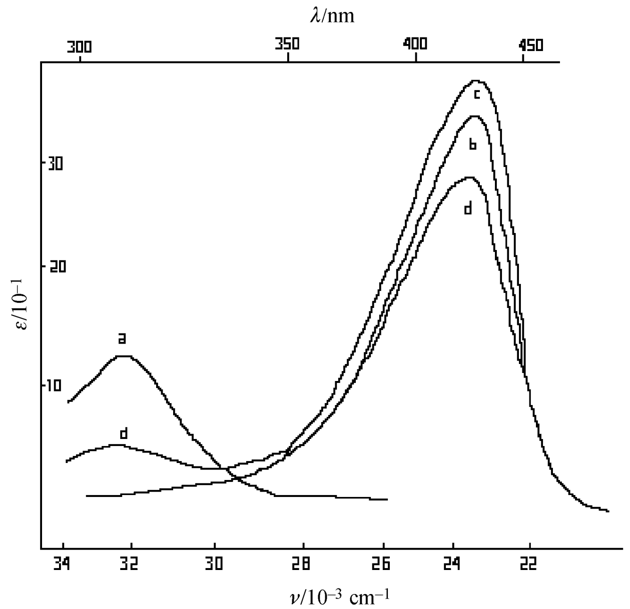


Fig. 3 Electronic absorption spectra of *p*-nitrophenol [p-$NO_2C_6H_4OH$] = 3.6 × 10^{-4} mol dm^{-3} in MeCN in the presence of varying quantities of **1** (a: [**1**] = 0; b: [**1**] = 5.1 × 10^{-4}; c: [**1**] = 1.0 × 10^{-3} mol dm^{-3}) and **2** (d: [**2**] = 1.1 × 10^{-3} mol dm^{-3} and [p-$NO_2C_6H_4OH$] = 5.0 × 10^{-4} mol dm^{-3}) (thickness 0.05 cm)

As shown above, proton transfer occurs in the complex of phenol with silatrane in CH_3CN to give the solvent-separated ion pair. $Me_nN^+H(CH_2)_{3-n}$ (n = 1, 2) groups are strongly electron-withdrawing (σ^* = 3.7–4.8)[24] whereas the $CH_2Si(OCHRCH_2)_3N$ fragment is a strong electron-donor[15] so there is strong polarization of the Si–C bond. As a result of the attack of the ArO$^-$ anion at silicon a zwitterionic intermediate (**A** or **A′**) is formed without donor–acceptor N⟶Si bonds.

It seems possible, that the intermediate can also exist as a zwitterionic hexacoordinate structure with an N⟶Si bond. Independently of the structure the resulting intermediate undergoes subsequent transformations with Si–C bond cleavage resulting in the formation of compounds (**B**) and (**C**). These transformations are thermodynamically advantageous because the Si–O bond is stronger than the Si–C bond (the dissociation energies are 530 and 360 kJ mol^{-1}, respectively).[25]

Conclusions

Thus, the anomalously high basicity of organosilicon amines $Me_nN[CH_2Si(OCH_2CH_2)_3N]_{3-n}$ determines the ease of nucleophilic cleavage of the Si–C bond by phenols even at room temperature.

Experimental

Electronic absorption spectra were measured on a SPECORD UV Vis. The solutions were prepared in a dry glove box. The equilibrium constants for the interaction of *p*-nitrophenol with compounds **1** and **2** in CH_3CN have been measured by using a previously described method[26] ([p-$NO_2C_6H_4OH$] = 3.7 × 10^{-4} mol dm^{-3}, [**1**] = 5.1–25.5 × 10^{-4} mol dm^{-3} and [p-$NO_2C_6H_4OH$] = 5 × 10^{-4} mol dm^{-3}, [**2**] = 1.1–3.2 × 10^{-3} mol dm^{-3}, thickness 0.05 cm). IR spectra were recorded on a SPECORD 75 IR spectrophotometer as KBr pellets or Nujol mulls. ^{1}H NMR spectra were recorded on a JEOL 90Q spectrometer. *N*-methylbis(1-silatranylmethyl)amine **1** and *N*,*N*-dimethyl(aminomethyl)silatrane **2** were synthesized as described earlier in ref. 16 and 27.

Reaction of silatranes with phenols

A mixture of 0.001 M of silatrane (**1** or **2**) and the corresponding phenol (0.003 M for **1** or 0.002 M for **2**) was heated at 60–75 °C until trimethylamine flow stopped. Trimethylamine was bubbled in the trap containing benzene solution of HCl, and trimethylamine hydrochloride was isolated by recrystallization from benzene, mp 276–277 °C (lit. 277–278 °C).[28] 1-Phenoxysilatrane was isolated by recrystallization from a benzene–heptane mixture (yield: 88 and 83% for **1** and **2**, respectively). Found, %: C 54.08, H 6.83, N 5.43, Si 10.61. $C_{12}H_{17}NO_4Si$. Calc. %: C 53.91, H 6.41, N 5.24, Si 10.51. 1-(*p*-Nitrophenoxy)silatrane was purified by recrystallization from toluene (yield: 95 and 92 % for **1** and **2**, respectively). Found,%: C 45.95, H 45.01, N 9.03, Si 9.05. $C_{12}H_{16}N_2O_6Si$. Calc. %: C 46.14, H 45.16, N 8.97, Si 8.99.

Study of Si–C bond cleavage by ^{1}H NMR spectroscopy

0.00005 M of compound (**1** or **2**) was mixed with 0.00015 M (**1**) or 0.0001 M (**2**) of suitable phenol in 1 mL of previously dried CD_3CN. The reaction mixture was placed in an ampoule. Tetramethylsilane was used as the reference. ^{1}H NMR spectra were measured at room temperature (20–22 °C) at fixed intervals.

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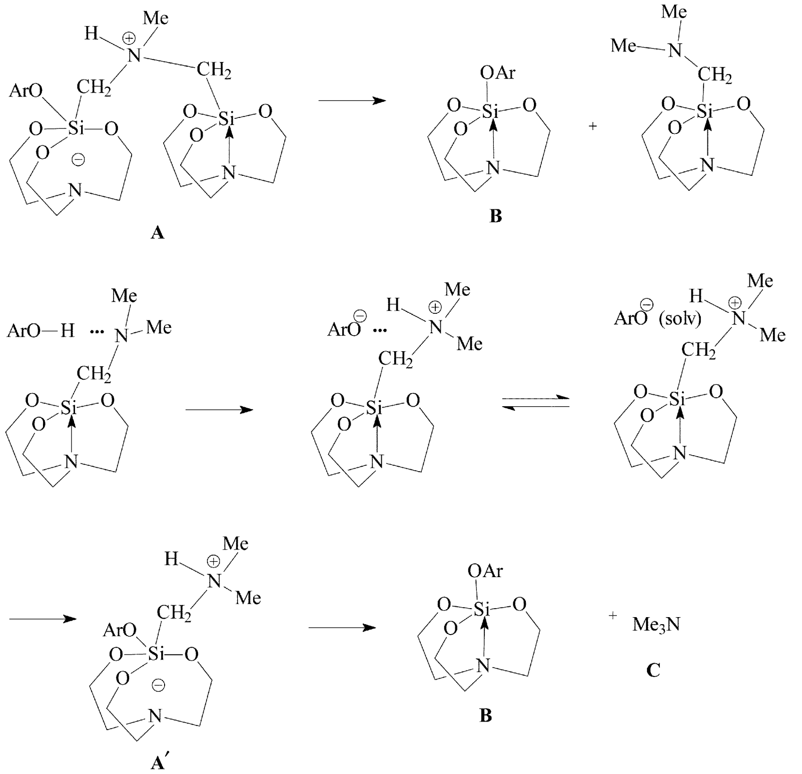

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