

1-Halosilatranes

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Abstract

The electronic structure of 1-halosilatranes is discussed. Some new preparative methods based on hetero- and homo-lytic reactions of the silatrane and the Si- and C-substituted silatranes with halogenating reagents are described and also synthetic routes to 1-halosilatranes from certain organotrialkoxy- and organotrichlorosilanes. The electrophilic reactions of 1-iodosilatrane with ethers and esters, carbonyl compounds, alkoxy silanes and siloxanes, terminal alkynes and organomercurials have been studied.

Introduction

Of the Si-substituted silatranes [1], the 1-halosilatranes $\overline{\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ (X = halogen) are of special interest because of their structure and reactivity. In particular they have the shortest transannular coordinative Si ← N bond. Their physical properties differ from those of the other silatranes studied, and the reactivity of the Si–X bond, that is lower for X = F, Cl becomes extremely high when X = I. The first 1-halosilatranes were prepared 18 years ago [2–4], the attention of scientists was then mainly focussed on the physical properties of some of these compounds. 1-Iodosilatrane has practically not been characterized. Some of the described methods for preparing 1-halosilatranes leave much to be desired.

Here we summarize the results of investigations that have covered the methods of preparation, the structure and some chemical conversions of 1-halosilatranes and especially those carried out by us of which the reports were previously published in Russian, usually as short communications or as letters to the editor.

Structure and physical properties

The 1-halosilatranes (Table 1) are high-melting, crystalline substances that sublime without melting or decomposition at temperatures above 180°C. They are

Table 1

1-Halosilatrane $\text{XSi}(\text{OCHMeCH}_2)_n(\text{OCH}_2\text{CH}_2)_{3-n}\text{N}$

Compound	X		M.p. (°C) (recrystallization solvent)	Yield (%) (Scheme of preparation)
I	F ^a	0	subl. 330 (methanol)	74 (1)
				31 (2)
				55 (3)
				80 (12)
II	F	1	subl. 200	84 (12)
III	F ^b	3	237–238 (CHCl ₃ + CH ₃ OH)	77 (12)
IV	F ^c	1	196–199 (CHCl ₃)	55 (3)
V	Cl ^d	0	decomp. 200 (CH ₂ Cl ₂)	83 (4)
				60 (5)
				70 (8)
				97 (9)
				93 (11)
VI	Cl	1	293–294 (CHCl ₃)	64 (6)
VII	Cl	2	280.5–281.5	53.7 (6)
VIII	Cl ^e	3	265–266 (CHCl ₃ + CH ₃ OH)	50.7 (6)
IX	Br ^f	0	subl. 180 (CHCl ₃)	65 (4) 90 (11)
X	I	0	subl. 100	100 (10) 98.6 (11)

^a Sublimes at 200 °C [4]. ^b M.p. 212–214 and 217–220 °C for different mixtures of diastereomers [3].
^c $\text{FSi}[\text{OC}(\text{CF}_3)\text{CH}_2]_2\text{N}$. ^d Decomposes at 200 °C [2,4]. ^e M.p. 305–306 °C, for diastereomer ratios other than the statistical one [3]. ^f Decomposes at 200 °C [3].

soluble in polar solvents and insoluble in non-polar organic solvents [1–5]. The solubility of these compounds increases with increase in halogen atomic number of the halogen, and with the accumulation of methyl groups in the 3-, 7-, 10-silatrane ring positions.

The molecular structure of 1-fluorosilatrane (I) and 1-chlorosilatrane (V) has been confirmed by X-ray diffraction studies [6,7]. The silicon atom is in near-perfect trigonal bipyramidal coordination with the N and X atoms occupying axial positions. The length of the transannular coordinative Si ← N bond in silatrane (I) and (V) is 2.042 and 2.023 Å, respectively. This is the shortest distance, between Si and N atoms, to be found in silatrane. In contrast, the Si–F and Si–Cl bonds in these molecules are somewhat longer; 1.622 and 2.12 Å, respectively. In XSiH_3 , however, the Si–F bond length is 1.595 Å (X = F) [8] and that of Si–Cl is 2.048 Å (X = Cl) [9]. At the same time, the interatomic Si...F distance in 1-fluorosilatrane (I) is practically coincident with the axial Si–F bond length in another pentacoordinate silicon compound, (2-chlorobenzoyloxymethyl)trifluorosilane (1.620 Å [10]). However, this distance is shorter than that in hexacoordinate silicon compounds (1.71 Å in the anion $[\text{SiF}_6]^{2-}$ [11]). The Si–O–C angles in molecules I and V (120–120.7°) are slightly smaller than in other silatrane (~122°). The NC_3 fragment in crystal I is disordered probably due to increasing steric hindrance in the silatrane ring as the

Table 2

XPS data for 1-halosilatrane $\overline{\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ [13]

Substituent X	Binding energy (eV)				Binding energy of the substituents X	Si ← N bond order
	N_{1s}	Si_{2p}	O_{1s}			
F	402.8	105.4	534.1	F_{1s}	687.6	0.5598
	400.4 [12]	102.8 [12]				
Cl	402.5	105.0	534.0	$\text{Cl}_{2p\ 3/2}$	201.2	0.5430
	400.7 [12]	103.0 [12]				
Br	402.2	104.5	533.9	$\text{Br}_{3d\ 5/1}$	71.4	0.5370
	399.9 [12]	102.4 [12]				
I	402.0	104.1	534.0	$\text{I}_{3d\ 5/2}$	621.3	0.5317

Si and N atoms are brought closer together, so approaching an ideal trigonal-bipyramidal configuration.

From X-ray PES data and on the basis of the correlation between the Si_{2p} and N_{1s} bonding energy in silatrane it is suggested that as silicon becomes more positive, so does nitrogen [12]. The positive charge distribution over the Si and N atoms due to inductive effects in the axial X–Si–N bond system may be represented as the canonical resonance structure $\text{X}^-[\text{Si}-\text{N}]^+$ [12]. However, the smaller chemical shift value for 1-fluorosilatrane compared with that for 1-chlorosilatrane (Table 2) is not consistent with the electronegativities of these atoms. This is probably because of the difference in the relaxation energy with X = F or because of π -interaction of the latter atom with the silicon atom [12].

However, the XPS data [13] have shown that the bonding energies, E– Si_{2p} and E– N_{1s} in 1-halosilatrane $\overline{\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ decrease monotonously on going from X = F to X = I (Table 2). Linear correlations have been observed between the atomic charges (calculated by use of the expanded EHMO method) and the observed N_{1s} and Si_{2p} bonding energies, and between these bonding energies and donor–acceptor Si ← N bond order. The strength of the transannular Si ← N bond evaluated from bond orders is half that of the Si–O bond. In our opinion, this value is too high.

The higher positive charge on the silicon atom in silatrane compared with the corresponding Si–substituted triethoxysilane $\overline{\text{XSi}(\text{OCH}_2\text{CH}_2)_3}$ is indicated by a larger shift of the Si– K_α line in the X-ray fluorescence spectra of the silatrane [14]. Exceptions to this are the silicon atoms in chlorotriethoxysilane and 3,7-dimethyl-1-chlorosilatrane, which have calculated values resembling those of the Si-substituted triethoxysilane.

The effect of the halogen atom in the 1-halosilatrane on the degree of transannular interaction Si ← N has been determined from their ^1H , ^{13}C , ^{15}N , ^{19}F and ^{29}Si NMR spectra [7,15–24] (Table 3).

A decrease in the ^{15}N screening constants of 1-halosilatrane $\overline{\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ (X = F, Cl, Br) (I, V, IX) with increasing atomic number of X was revealed by heteronuclear ^1H INDOR (Table 3). This reflects the increasing degree to which the electron density is transferred from N to Si with strengthening (shortening) of the Si ← N bond upon sequential transition from 1-fluoro to 1-iodo derivative [18]. This is in line with X–Si bond polarizability and its lower order, rather than with the electronegativity of substituent X common to most silatrane [1].

Table 3

Chemical shifts in the ^1H , ^{15}N , ^{19}F and ^{29}Si NMR spectra of 1-halosilatrane, $\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$

X	δ (ppm)			
	OCH_2	CH_2N	^{15}N	^{29}Si
F ^a	3.19 (CHCl_3) [15,19]	2.95 (CHCl_3) [15,19]	-349.3 [17] (CHCl_3) -348.4 [17] (DMSO)	$^1J(\text{Si-F})$ 131.2 Hz [19] -100.5 [21] (CH_2Cl_2) -100.6 [17] (DMSO) -101.5 [21] (cryst.)
Cl ^b	3.91 (CH_2Cl_2) 3.97 [15,22] (CHCl_3)	2.97 (CH_2Cl_2) 3.01 [15,22] (CHCl_3)	-348.8 (CHCl_3) -347.8 [16,17] (DMSO)	-86.4 (CH_2Cl_2)
Br	3.94 (CH_2Cl_2) 4.01 (CHCl_3) [15,22]	3.01 (CH_2Cl_2) 3.04 (CHCl_3) [15,22]	-348.0 [25]	-88.8 (CH_2Cl_2)
I	3.97 (CH_2Cl_2)	3.05 (CH_2Cl_2)	-346.9 [25]	-98.6 (CH_2Cl_2)

^a $\delta(^{19}\text{F})$ chemical shift in the ^{19}F NMR spectra of $\text{FSi}(\text{OCHRCH}_2)_3\text{N}$ ($\text{R} = \text{H}$) is 142.8 ppm (relative to CFCl_3); $\delta(^{29}\text{Si})$ ($\text{R} = \text{CH}_3$, a symmetric diastereomer) is 101.1 ppm (in CHCl_3) [19]. ^b $^1J(^{15}\text{N-Si})$: 1.54 (CDCl_3), 2.57 Hz ($\text{DMSO-}d_6$); $^1J(^{15}\text{N-}^{13}\text{C})$: 6.86 (CDCl_3) and 6.68 Hz ($\text{DMSO-}d_6$) [20].

The dependence of ^{15}N NMR chemical shifts (δ) on $\text{Si} \leftarrow \text{N}$ bond length ($l(\text{Si} \leftarrow \text{N})$) in 1-substituted silatrane in the solid, solution and vapour state can be expressed by the equation [18]: $l(\text{Si} \leftarrow \text{N}) = -4.30 - (1.82 \pm 0.08) \times 10^{-2} \delta(\text{N})$. Use of this equation $l(\text{Si} \leftarrow \text{N})$ values for $\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$ in CH_2Cl_2 solution were evaluated as 2.06, 2.05, 2.03 and 2.01 Å for $\text{X} = \text{F}$, Cl , Br and I , respectively [25].

In the IR spectra of halosilatrane $\text{XSi}(\text{OCHRCH}_2)_n(\text{OCH}_2\text{CH}_2)_{3-n}\text{N}$ with $n = 0$ (I, V and IX) [6,26–28] an absorption band (most intense when $\text{X} = \text{Cl}$) is present in the region 584–595 cm^{-1} . The spectra of C-substituted 1-halosilatrane with $n = 1-3$ (II–IV, VI–VIII) show two absorption bands that are least intense when $\text{X} = \text{F}$ in the region 510–595 cm^{-1} . This is consistent with the assignment of the vibrations in this region to the silatrane ring pulsing vibrations [26].

The stretching absorptions $\nu(\text{Si-X})$ in the spectra of 1-halosilatrane are shifted to lower frequency compared with the corresponding Si-substituted triethoxysilane [3,26]. The Si–F frequencies in the spectra of 1-fluorosilatrane (I and III) are observed as intense bands at 750–785 cm^{-1} [3,6]. A band at 800 cm^{-1} is also assigned to the Si–F mode [3]. However, this assignment is not satisfactory since $\nu_{\text{as}}(\text{Si-O})$ intense vibrations in the 790–810 cm^{-1} region are also observed in the IR spectra of many silatrane [26].

In the IR spectrum of 1-chloro-3,7,10-trimethylsilatrane (VIII) the Si–Cl absorption band was found at 392 cm^{-1} . The stretching vibrations of $\nu(\text{Si-Br})$ appear at 360 cm^{-1} in the spectrum of 1-bromo-3,7,10-trimethylsilatrane [3].

In the mass spectra of 1-halosilatrane the intensity of the molecular ion peak, and the portion of ions containing the Si–X bond decrease in the following order for various X : $\text{F} > \text{Cl} > \text{Br}$ [27,29].

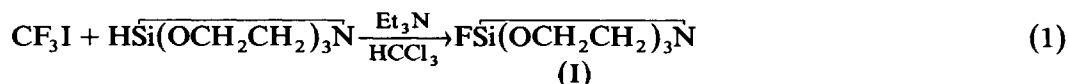
Methods and preparation

The first methods for preparing 1-halosilatrane were based on the reaction of silatrane * with the corresponding halogen X_2 ($X = Cl, Br, I$) in chloroform [2,3] and later in toluene [27]. Hydrogen halides HX ($X = Cl, Br$) or halosuccinimides turned out to be more suitable silatrane-halogenating agents [3]. 1-Halosilatrane were also prepared by reaction of 1-ethoxysilatrane with HF in an aqueous-alkaline medium [3] and with the halo anhydrides of sulfuric or phosphorus oxyacids [4]. The synthesis was reported recently of 1-chlorosilatrane from silicon tetrachloride and tris(2-trimethylsiloxyethyl)amine [20].

The reaction of 1-organosilatrane with halides of mercury [30,31] and of other heavy metals [30], seems to involve the reduction of benzene chloride and benzoyl chloride with silatrane [32], to give the corresponding 1-halosilatrane, although the latter have not been isolated. Some novel procedures developed by us to make 1-halosilatrane are described below.

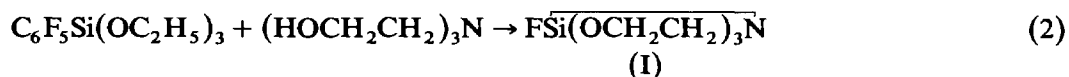
Ionic reaction

Reaction of silatrane with iodotrifluoromethane in the presence of triethylamine in chloroform solution at $80^\circ C$ gives 1-fluorosilatrane (I) in 74% yield (eq. 1).

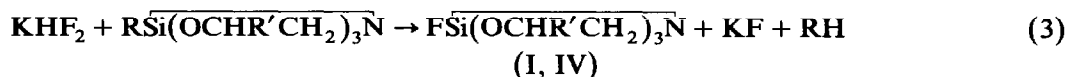


Reaction 1 is likely to involve initial formation of 1-trifluoromethylsilatrane which then decomposes to release difluorocarbene and to give I.

The KOH -catalyzed reaction of (pentafluorophenyl)triethoxysilane with triethanolamine also gives 1-fluorosilatrane (I) (in 31% yield) (eq. 2).



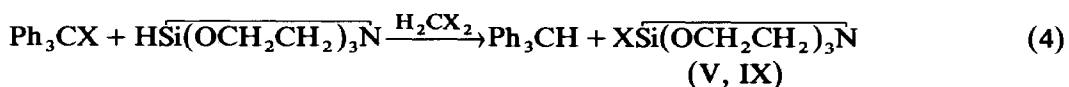
1-Fluorosilatrane, its ^{15}N -isotopomer, and 1-fluoro-3-trifluoromethylsilatrane (IV) were prepared by fusing 1-ethoxy- or 1-chloromethyl-silatrane with potassium difluoride at $200-240^\circ C$ in 55% yield (eq. 3).



($R = EtO$ and $ClCH_2$; $R' = H$ and CF_3)

Triorganosilanes $HSiR_3$ react rapidly with triphenylmethyl halides even at $20^\circ C$ in solvents that cause heterolytic dissociation of Ph_3CX [33,34].

We have studied the uncatalyzed reaction of silatrane with triphenylmethyl halides in the corresponding methylene halide [35] (eq. 4).



($X = Cl$ (V) and Br (IX))

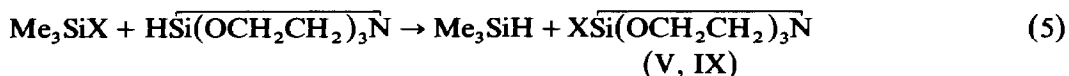
* $\overline{HSi(OCH_2CH_2)_3N}$

The rate of reaction 4 is appreciably higher when X is Br than when X is Cl. Thus, bromosilatane (IX) is formed in 70% yield at 20°C for 2.5 h, whereas 1-chlorosilatane (V) was formed at 24°C in 28% yield for the same reaction time. This is consistent with the higher degree of ionizability of triphenylmethyl bromide [33]. A much lower rate of the exchange reaction of triphenylmethyl halides with silatrane compared with that with triorganosilanes seems to be due to bulky groups that prevent side attack by the halotriphenylmethyl ion-pair $\text{Ph}_3\text{C}^+\text{X}^-$ on a silatrane bearing a pentacoordinate silicon atom with a nearly planar rigid $\text{Si}(\text{O})_3$ group.

In the reaction of silatrane with Ph_3CBr in methylene chloride, 1-bromosilatane (IX) was formed along with traces of 1-chlorosilatane (V). This indicates a possible secondary radical reaction of silatrane with CH_2Cl_2 , which is discussed below.

In the absence of catalysts the silatrane fails to react with trimethylchlorosilane or with trimethylbromosilane in CH_2Cl_2 or CH_2Br_2 , respectively, even upon prolonged heating (80 h) at 100°C. The known reaction of trialkylsilanes with alkylhalosilanes and the disproportionation of dialkylchlorosilanes are catalyzed by quaternary ammonium salts and amines [36–39].

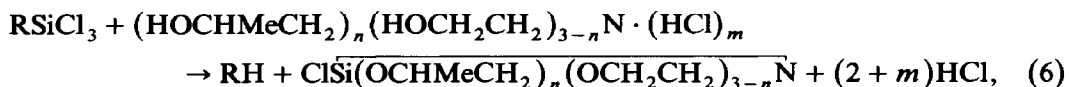
We have studied morpholine, quinoline, pyridine and *N*-cyanopiperidine as catalysts for the reaction of silatrane with trimethylhalosilanes (eq. 5).



(X = Cl, Br)

The highest turnover was achieved in the presence of quinoline because 1-chlorosilatane (V) was produced in 80% yield (Table 4). The conversion of the silatrane to (IX), in the presence of quinoline, upon treatment with trimethylbromosilane is low (31%).

The C-substituted 1-chlorosilatrane $\text{ClSi}(\overline{\text{OCHMeCH}_2})_2(\overline{\text{OCH}_2\text{CH}_2})_{3-n}\text{N}$ ($n = 1-3$, V–VII), are best prepared by reaction of tris(2-hydroxyalkyl)amines or their hydrochlorides with trichloromethyl-, vinyl- or phenyl-trichlorosilane involving the cleavage of the $\text{Si}-\text{C}_{sp^2}$ bond (eq. 6) [40].



(R = CCl_3 , $\text{CH}_2=\text{CH}$, C_6H_5 ; $n = 1$ (VI), $n = 2$ (VII), $n = 3$ (VII); $m = 0, 1$)

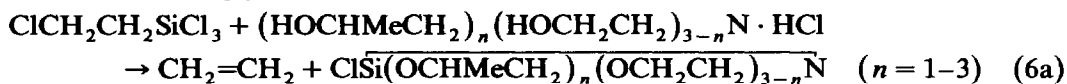
Table 4

The effect of some cyclic amines on the exchange reaction of silatrane with trimethylchlorosilane at 120°C

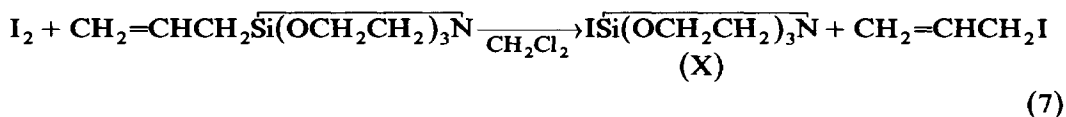
Amine	$\text{NCN}(\overline{\text{CH}_2})_4\text{CH}_2$			$\text{HN}(\overline{\text{CH}_2\text{CH}_2})_2\text{O}$	$\text{C}_5\text{H}_5\text{N}$	$\text{C}_9\text{H}_7\text{N}$	
Reaction time (h)	2	6	14	6	6	6	15
Yield of 1-chlorosilatane (%)	10	33	37	16	0 ^a	78	80

^a The same result was obtained for the reaction in the absence of initiator.

1-Chlorosilatrane (VI–VIII) can also be prepared by the reaction of the corresponding tris(2-hydroxyalkyl)amine hydrochlorides with (2-chloroethyl)trichlorosilane followed by β -elimination:

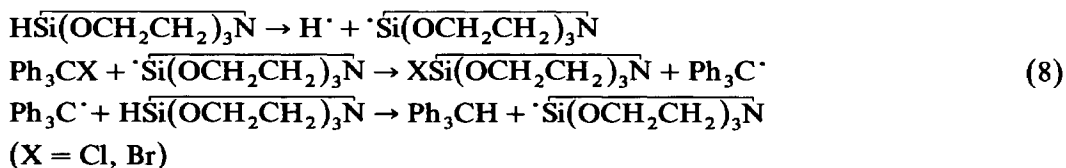


1-Allylsilatrane is split by iodine to give 1-iodosilatrane (X) (eq. 7).

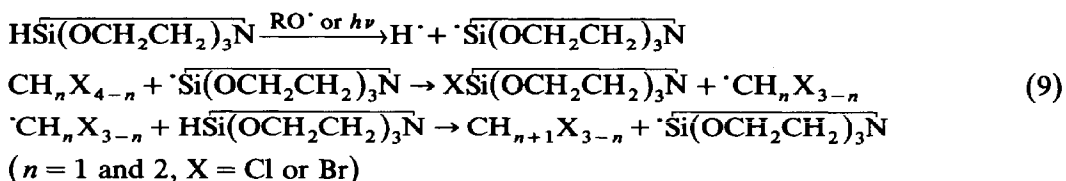


Homolytic reactions

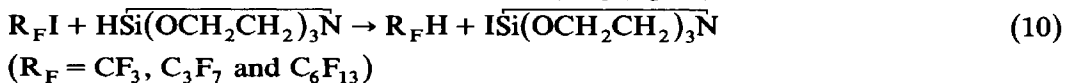
The first homolytic process used for the synthesis of 1-halosilatrane was the reaction of silatrane with triphenylmethylhalide in non-polar solvents [35]. The ESR spectrum of silatrane with tritylhalide in benzene shows a well-resolved isotropic signal of the trityl radical, which is not observed upon thermal generation from triphenylmethyl halide or triphenylmethane in the absence of silatrane. Hyperfine coupling constants ($\alpha_{\text{H}_o} = 2.53$, $\alpha_{\text{H}_m} = 1.11$ and $\alpha_{\text{H}_p} = 2.77$ G) are in full agreement with the spectrum of triphenylmethyl radical [41]. This is indicative of the fact that the reduction of triphenylmethyl halide with the silatrane seems to follow a homolytic mechanism:



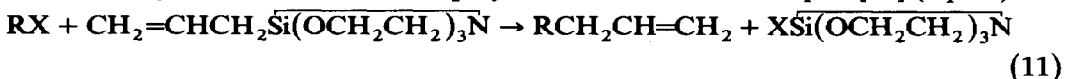
The reaction of silatrane with polyhalomethanes under peroxide or photochemical initiation provides a convenient route to 1-halosilatrane with $\text{X} = \text{Cl}, \text{Br}$ [35] (eq. 9).



Reaction of silatrane with iodoalkanes liberates much iodine and leads to resinification of the reaction mixture. With perfluoroalkyl iodides $\text{R}_\text{F}\text{I}$, however, silatrane smoothly forms 1-iodosilatrane (X) [5] (eq. 10).



The low solubility of silatrane in organic solvents restricts its use in the synthesis of 1-halosilatrane. Therefore, a preparative route to 1-halosilatrane, by the reaction of 1-allylsilatrane with alkane polyhalides has been developed [42] (eq. 11).



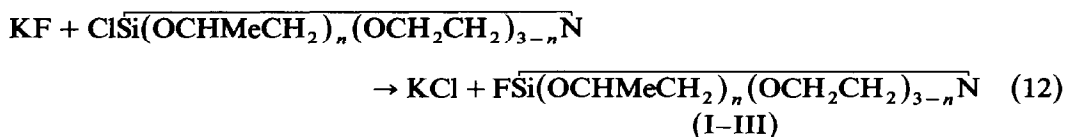
($\text{R} = \text{Cl}_3\text{C}, \text{CF}_3$ and C_3F_7 ; $\text{X} = \text{Cl}, \text{Br}, \text{I}$)

The corresponding 1-halosilatrane (V, IX and X) are formed in over 90% yield under the exposure of vacuum-treated reagent mixture to UV-irradiation for 1 h. To prepare 1-chlorosilatrane, the addition of about 5 mole% of a peroxide initiator is necessary. In the preparation of 1-chloro- (V) and 1-bromo-silatrane (IX), traces (~ 1%) of triethanolamine hydrohalide are formed as a by-product. When the reaction was carried out in the presence of lutidine-2,6 the yield of 1-halosilatrane (V, IX) was increased and thus their laborious purification could be avoided. The lutidine-2,6 hydrohalide impurity formed in this case is readily removed by sublimation in vacuo.

Reactivity

The reactions of 1-halosilatrane have not been studied much, until recently. Perhaps the only reported example of their conversion is the reaction of 1-chlorotribenzosilatrane with phenols to give the corresponding 1-aroxy derivatives [43].

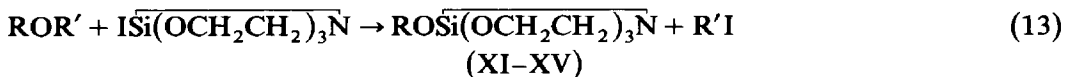
We have performed an exchange reaction of 1-chlorosilatrane (V, VI, VIII) with potassium fluoride in HMPA which gives the corresponding fluoro derivatives



($n = 0, 1$ and 3)

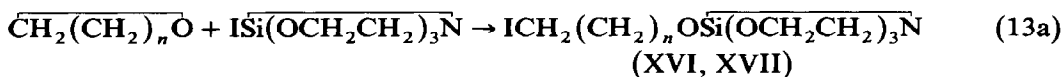
After the discovery of the cleavage reaction of the C-O-C and C-O-Si bonds with trialkyliodosilanes [44-47] and, in particular, with trimethyliodosilane, the latter has found wide use in organic and organosilicon synthesis [48-50].

From the NMR data the Si-I bond in 1-iodosilatrane is strongly polarized which suggests that this compound is an even more effective electrophile agent than trimethyliodosilane and should find use as a silatranyling and iodizing agent. The 1-iodosilatrane was shown to split quantitatively the C-O bonds in acyclic and cyclic ethers, alkoxy silanes and 1-alkoxy silatrane [51] (eq. 13, 13a).



(R, R' = Et(XI); R = Ph, R' = Me(XII); R = 3-ClC₆H₄, R' = Me(XIII);

R = Me₃Si, R' = Et(XIV); R = $\overline{\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}}$, R' = Et(XV))



($n = 1$ (XVI), $n = 3$ (XVII))

The C-O-C and Si-O-C groups are much more readily split by 1-iodosilatrane than by trimethyliodosilane. Thus, the reaction of 1-iodosilatrane with anisole at 20°C is complete after 3 h. However, cleavage with trimethyliodosilane at 130°C proceeds for 21 h [47]. Cleavage of tetrahydrofuran with 1-iodosilatrane at 20°C is

over after 15–20 min whereas a similar reaction with trimethyliodosilane is complete after 1 h at 60 °C [52].

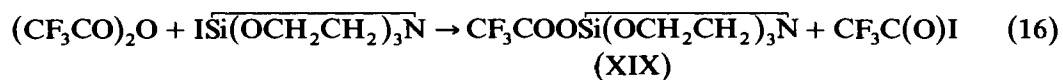
1-Iodosilatrane also splits the Si–O bond, but slightly more slowly than it does the C–O bond. Its reaction with hexamethyldisiloxane at 20 °C comes to an end after 4–5 h and gives 1-trimethylsiloxysilatrane (XIV) [51] (eq. 14).



The reaction of 1-iodosilatrane with ethylacetate affords the previously barely accessible 1-acetoxysilatrane (XVIII) (eq. 15).



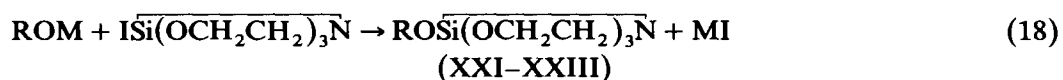
1-Trifluoroacetoxysilatrane (XIX) was obtained from the reaction of 1-iodosilatrane with trifluoroacetic anhydride (eq. 16).



1-Iodosilatrane readily adds to the acetaldehyde carbonyl group to form the novel 1-(α -iodoethoxy)silatrane (XX) (eq. 17).



The reaction of 1-iodosilatrane with alcohols and alkali metal alkoxides gives 1-alkoxysilatrane (eq. 18).

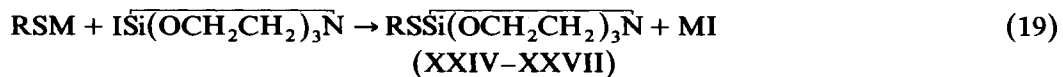


(R = Me, M = H, Na(XXI); R = Me₃C, M = H, K(XXII));

R = adamantyl, M = H (XXIII))

In contrast to this, reaction of trimethyliodosilane with alkanols forms the corresponding iodoalkane and trimethylsilanol [48].

The reaction of 1-iodosilatrane with thiols and alkali thiolates gave the novel 1-organothiosilatrane in high yield [53] (eq. 19).



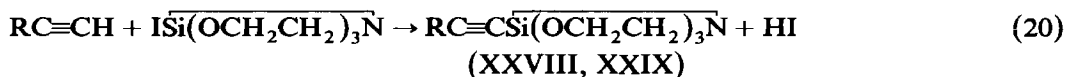
(R = Et, M = H, Na(XXIV); R = Me₃C, M = H(XXV); R = Ph, M = H(XXVI);

R = 4-MeC₆H₄, M = H(XXVII))

The reaction with RSH proceeds readily even without an HI acceptor.

The use of 1-iodosilatrane led to the development of some methods for introducing the hydrocarbon radical into the silatrane ring at the silicon atom. Thus, the

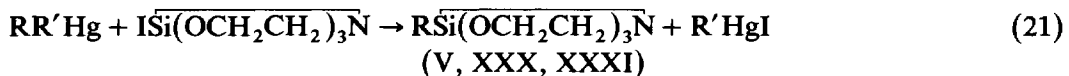
reaction of 1-iodosilatrane with mono-substituted acetylenes leads to 1-organoethynylsilatranes [54] (eq. 20).



(R = CH₂=CH (XXVIII); R = Ph (XXIX))

At room temperature only the mono-substituted acetylenes having an electron-withdrawing group at the triple bond are involved in the reaction 20.

1-Iodosilatrane readily reacts with diorganomercurials and ethylmercuriochloride to form the corresponding 1-organo-silatranes [55] (eq. 21).



(R, R' = Et (XXX); R, R' = Ph (XXXI); R = Cl (V), R' = Et)

The above reaction allowed the first of the spin-labeled silatranes, 1-(1-oxyl-2,2,6,6-tetramethyl-³Δ-dehydropiperidyl-4)silatrane (XXXII) to be obtained [56].

So, 1-iodosilatrane is a superelectrophilic reagent which shows an extremely high reactivity with respect to various classes of organic and organometallic compounds.

Experimental

¹H, ¹⁹F and ²⁹Si NMR spectra were recorded on a Tesla BS 487B spectrometer equipped with a special INDOR adapter and a Sigma accumulator. The spectra were measured relative to the internal standards: TMS for ¹H and ²⁹Si; CH₃¹⁵NO₂ for ¹⁵N; and CFC₃ for ¹⁹F. ESR spectra were recorded on a Thompson TMN-252 spectrometer. Electronic absorption spectra of Ph₃C cation were recorded on a Specord UV-Vis spectrophotometer. IR spectra were recorded in KBr pellets on a Zeiss UR-20 spectrometer. Mass spectra were run on a MX-1303 mass-spectrometer with a direct inlet system, at an ionization voltage 70 eV, and a MAT-212 chromatomass-spectrometer. A DMR-250 mercury tube was the UV source for the photochemical reactions with IR irradiation being absorbed by a water filter.

Silatrane was prepared by a published procedure [57] with magnesium propylate as a catalyst.

The initial 1-organo-silatranes were prepared by standard methods [1] and purified by sublimation in vacuo, or by recrystallization.

Other reactants and solvents were commercial products purified by appropriate procedures before use.

Methods for preparing 1-halosilatranes

1. *Reaction of silatrane with trifluoroiodomethane in the presence of Et₃N.* A solution of silatrane (1.1 g, 6.3 mmol), trifluoromethyl iodide (1.23 g, 6.3 mmol) and triethylamine (0.64 g, 6.3 mmol) in CHCl₃ (10 ml) was heated in a sealed tube for 3 h. The precipitate 1-fluorosilatrane (I) that formed was filtered off and dried. Yield 0.9 g (74%), subl.p. 330 °C. ¹H NMR spectrum (in CDCl₃, ppm): 3.91 (t, OCH₂), 2.95 (t, NCH₂).

2. *Reaction of pentafluorophenyltriethoxysilane with triethanolamine in the presence of KOH.* A mixture of $C_6F_5Si(OEt)_3$ (4.95 g, 15 mmol) and triethanolamine (2.24 g, 15 mmol) was heated in the presence of KOH (0.05 g). The EtOH formed was distilled off and the residue, a white flaky precipitate, insoluble in benzene and xylene, was extracted with hot chloroform. From the cooled filtrate white fibrous crystals (I) were obtained in 0.9 g (31%) yield. Found: C, 37.74; H, 6.51; F, 8.57; Si, 14.80. $C_6H_{12}FNO_3Si$ calcd.: C, 37.29; H, 6.26; F, 9.83; Si, 14.53%.

3. *Cleavage of 1-chloromethylsilatrane- ^{15}N and 1-ethoxy-3-trifluoromethylsilatrane with potassium bifluoride.* A mixture of 1-chloromethylsilatrane- ^{15}N (4.0 g, 17.8 mmol) and KHF_2 (1.4 g, 17.9 mmol) was heated in an argon flow at 220 °C until the melt solidified. The solid was ground, washed with cold chloroform and sublimed at 180 °C in vacuo (1 torr) to give 1-fluorosilatrane (I) in 1.9 g (55%) yield.

1-Fluoro-3-trifluoromethylsilatrane (IV). A mixture of 1-ethoxy-3-trifluoromethylsilatrane (0.3 g, 1.04 mmol) and KHF_2 (0.09 g, 1.15 mmol) was heated at 210 °C for 30 min. The residue was recrystallized from isopropanol. Yield of compound IV 0.17 g (62.2%), m.p. 196–199°. Found: C, 31.96; H, 4.05; N, 5.22; Si, 9.90. $C_7H_{11}F_4NO_3Si$ calcd.: C, 32.18; H, 4.24; N, 5.36; Si, 10.75%.

4. *Reaction of silatrane with triphenylmethyl halides in methylene halides.* 1-Chlorosilatrane (V). A solution of silatrane (0.23 g, 1.3 mmol) and triphenylmethyl chloride (0.36 g, 1.3 mmol) in 15 ml of CH_2Cl_2 was left to stand at 24 °C for 2.5 h. From 1H NMR data (integrated intensity ratio for NCH_2 groups of silatrane and 1-chlorosilatrane) the conversion of silatrane into 1-chlorosilatrane (V) was found to be 28%. The solution was sealed in an ampoule and heated to 140 °C for 2.5 h. The reaction mixture was evaporated to dryness in a water-bath and the residue was washed with hot heptane, pentane and dried. Yield of V 0.24 g (83%), decomp. temp. ≥ 200 °C. Found: C, 34.21; H, 5.98; Cl, 16.34; Si, 13.20. $C_6H_{12}ClNO_3Si$ calcd.: C, 34.36; H, 5.77; Cl, 16.91; Si, 13.39%.

1-Bromosilatrane (IX). A solution of silatrane (0.05 g, 0.28 mmol) and triphenylmethyl bromide (0.091 g, 0.28 mmol) in 5 ml of methylene bromide was kept at 20 °C for 2.5 h. From 1H NMR data the silatrane/1-bromosilatrane ratio of the reaction mixture was found to be 3/7, and UV spectroscopy of the solution indicated the presence of the triphenylmethyl cation [58]. Then 10 ml of heptane was added to the reaction mixture and the precipitate was filtered off, washed with pentane, and dried. Yield of IX 0.046 g (65%), decomp. ≥ 180 °C. Found: C, 27.82; H, 5.02; Br, 26.88; Si, 10.73. $C_6H_{12}BrNO_3Si$ calcd.: C, 28.36; H, 4.76; Br, 31.44; Si, 11.05%.

When the reaction is carried out in CH_2Cl_2 trace amounts of 1-chlorosilatrane (V) are present along with 1-bromosilatrane (IX), as shown by 1H NMR.

5. *Reaction of silatrane with trimethylhalosilanes.* The reaction of silatrane with trimethylchlorosilane in the presence of cyclic amines. A solution of silatrane (0.13 g, 0.74 mmol) and trimethylchlorosilane (0.086 g, 0.79 mmol) in 5 ml of CH_2Cl_2 was placed in 8 ampoules, and 15 mol.% of cyclic amine (*N*-cyanopiperidine, morpholine, pyridine or quinoline) was added to 7 of these; the ampoules were sealed and kept at 120 °C monitoring the reaction mixture with 1H NMR spectroscopy. The results obtained are presented in Table 4.

1-Chlorosilatrane (V). A solution of silatrane (3.5 g, 0.02 M), trimethylchlorosilane (4.4 g, 0.04 M) and quinoline (4 ml) was heated in a sealed ampoule at 120 °C for 6.5 h. The solvent was distilled off, and the white solid that remained

was washed with chloroform at 0°C, then recrystallized from methylene chloride. Yield of V 2.5 g (60%), decomp. temp. 200°C.

Reaction of silatrane with trimethylbromosilane. A solution of silatrane (0.70 g, 4 mmol) and trimethylbromosilane (0.64 g, 4 mmol) in CH₂Br₂ (20 ml) was heated in a sealed ampoule at 100°C for 5 h. ¹H NMR spectroscopy revealed that there was no reaction. To the solution was added 0.5 ml of quinoline and heating was continued for 14 h the degree of conversion was then found to be 31%.

6. *Reaction of tris(2-hydroxyalkyl)amine hydrochlorides with 2-chloroethyl-, trichloromethyl-, vinyl- and phenyltrichlorosilane.* 1-Chloro-3-methylsilatrane (VI). A mixture of (2-hydroxypropyl)bis(2-hydroxyethyl)amine hydrochloride (4.0 g, 0.02 M) with phenyltrichlorosilane (4.23 g, 0.02 M) was left to stand at 80°C until a homogeneous mass had formed (3 h), then kept for a further 2 h at 150°C under reduced pressure (12 Torr) until hydrogen chloride evolution ceased. The residue was recrystallized from a 1/2 mixture of chloroform ethanol. Yield of VI 3.1 g (64%), m.p. 293–294°C (with decomp.). Found: C, 37.98; H, 6.34; Cl, 16.00; Si, 12.41. C₇H₁₄ClNO₃Si calcd.: C, 37.58; H, 6.31; Cl, 15.85; Si, 12.55%.

1-Chloro-3,7-dimethylsilatrane (VII) A mixture of (2-hydroxyethyl)bis(2-hydroxypropyl)amine hydrochloride (4.27 g, 0.02 M) and vinyltrichlorosilane (3.22 g, 0.02 M) was left to stand for 3 h at 20°C, and for 30 min at 160°C. The residue was recrystallized from CHCl₃. Yield of VII 2.45 g (53.7%), m.p. 280.5–281.5°C. Found: C, 39.86; H, 6.65; Si, 11.90. C₈H₁₆ClNO₃Si calcd.: C, 40.41; H, 6.78; Si, 11.81%.

1-Chloro-3,7,10-trimethylsilatrane (VIII). (a) A mixture of tris(2-hydroxypropyl)amine hydrochloride (2.28 g, 0.01 M) and (trichloromethyl)trichlorosilane (2.53 g, 0.01 M) was left to stand at 30°C for 30 min, then heated at 130°C under reduced pressure (50 Torr) for 1.5 h. The residue was recrystallized from a CHCl₃/MeOH mixture (3/1). Yield of compound VIII 1.64 g (68%), m.p. 270–271.5°C. Found: C, 43.02; H, 7.18; Cl, 13.86; Si, 11.09. C₉H₁₈ClNO₃Si calcd.: C, 42.93; H, 7.21; Cl, 14.08; Si 11.15%. (b) A mixture of tris(2-hydroxypropyl)amine hydrochloride (2.28 g, 0.01 M) and (2-chloroethyl)trichlorosilane (2.0 g, 0.01 M) was left to stand at 20°C for 30 min, and at 140°C for another 30 min. After recrystallization of the reaction mixture from CHCl₃, 1.25 g (50%) of compound VIII, m.p. 268–271°C was obtained. Found: C, 42.89; H, 7.28; Cl, 13.76; Si, 11.14%.

7. *Iodine-cleavage of 1-allylsilatrane.* To a solution of 1-allylsilatrane (0.215 g, 1 mmol) in 5 ml of CH₂Cl₂ cooled to –60°C was added dropwise iodine (0.25 g, 2 mmol) in 25 ml of CH₂Cl₂ under dry nitrogen. The solution was left to stand at 20°C for 2 h and the volume of the solution was reduced to 11 ml by evacuation (12 Torr).

The ¹H NMR spectrum of the solution indicated that 15% of 1-iodosilatrane (δ, ppm: 3.96, t, OCH₂, 3.04, t, NCH₂) was present. A run repeated 48 h later showed only traces of 1-iodosilatrane.

8. *Reaction of silatrane with triphenylchloromethane in benzene.* A solution of silatrane (0.012 g, 0.069 mmol) and triphenylchloromethane (0.020 g, 0.072 mmol) in 200 ml of benzene was heated for 20 h at 60°C. The precipitate was washed with pentane and dried. Yield of 1-chlorosilatrane (V) 0.010 g (70%), decomp. 200°C.

The ESR spectrum of the triphenyl radical was recorded at 60°C several minutes after degassed benzene solutions of the reactants had been mixed.

9. *Reaction of silatrane with HCCl_3 and HCBBr_3 .* (a) A solution of silatrane (0.05 g, 0.285 mmol) and benzoyl peroxide (0.003 g, 5% mol) in 25 ml of CHCl_3 was heated for 10 h at 60°C . Then 15 ml of heptane was added, the precipitate that formed was filtered off, and dried in vacuo. Yield of 1-chlorosilatrane (V) 0.058 g (96.8%), decomp. 200°C . (b) A solution of silatrane (0.175 g, 1 mmol) and benzoyl peroxide (0.005 g) in 20 ml of bromoform was heated for 1 h at 60°C . The ^1H NMR spectrum of the solution shows the OCH_2 and NCH_2 group proton chemical shifts of only 1-bromosilatrane (IX). Reactions (a) and (b) are inhibited by trace amounts of hydroquinone.

10. *Reaction of silatrane with heptafluoriodopropane.* A solution of silatrane (0.24 g, 1.39 mmol) and heptafluoriodopropane (0.42 g, 1.40 mmol) in 10 ml of acetonitrile was degassed and exposed to UV-irradiation in a sealed ampoule for 30 min at 20°C . Acetonitrile and heptafluoropropane were evaporated off in vacuo to give 0.42 g (~100%) 1-iodosilatrane (X). The 1-iodosilatrane (X) was identified from its ^1H NMR spectrum/ in CH_2Cl_2 , δ , ppm: 3.97, t (OCH_2), 3.05, t (NCH_2)/ and by the presence of the ion $[M - \text{I}]^+ m/e$ 174.

11. *Reaction of 1-allylsilatrane with polyhalomethanes and perfluoroiodoalkanes.* (a) Reaction with CCl_4 . A vacuum-treated solution of 1-allylsilatrane (0.43 g, 2.0 mmol) and t-butyl peroxide (0.013 g, 5 mol%) in CCl_4 (16.0 g, 104 mmol) was exposed to UV-irradiation for an hour at 20°C . Volatile substances were evaporated off. The solid residue was recrystallized from chloroform and dried. Yield of 1-chlorosilane (I) 0.39 g (92.6%), decomp. 200°C . Found: C, 33.91; H, 5.69; Si, 13.35; Cl, 17.21. (b) Reaction with BrCCl_3 . 0.75 g (90%) of 1-bromosilatrane (IX) decomp. 200°C was obtained after irradiation with UV of a solution of 1-allylsilatrane (0.71 g, 3.3 mmol) and trichlorobromomethane (0.70 g, 3.5 mmol) in 10 ml of CH_2Cl_2 for 1 h, the volatile substances had been evaporated off, and the residue had been recrystallized from chloroform. Found: C, 29.01; H, 4.80; Br, 32.10; Si, 11.82. (c) Reaction with $\text{C}_3\text{F}_7\text{I}$. A vacuum-treated mixture of 1-allylsilatrane (0.71 g, 3.3 mmol) and heptafluoriodopropane (15 ml) was exposed to UV-irradiation for 30 min at 20°C . Volatiles were then evaporated off to give 1-iodosilatrane (X), yield 0.98 g (98.6%), decomp. $\geq 100^\circ\text{C}$ (in a sealed vacuumized tube).

Reactions of 1-halosilatrane

1. *Exchange reaction of 1-chlorosilatrane and its C-methylsubstituted silatrane with KF.* (a) A mixture of 1-chlorosilatrane (0.28 g, 1.33 mmol) and potassium fluoride (0.10 g, 1.71 mmol) in 15 ml of hexametapol (HMPA) was stirred for 14 h at 100°C . The reaction mixture was filtered, and HMPA was distilled off under vacuum (2 mmHg). The residue was recrystallized from isopropanol. Yield of 1-fluorosilatrane (I) 0.21 g (80%), subl. 300°C .

(b) A mixture of 1-chloro-3-methylsilatrane (0.99 g, 4.32 mmol) and potassium fluoride (0.32 g, 5.51 mmol) in 50 ml of HMPA was stirred for 14 h at 100°C . The filtrate was evaporated to dryness in vacuum and the residual solid was recrystallized from methanol. Yield of 1-fluoro-3-methylsilatrane (II) 0.77 g (84%), subl. 200°C . Found: C, 40.86; H, 7.42; F, 8.56; Si, 13.79. $\text{C}_7\text{H}_{14}\text{FNO}_3\text{Si}$ calcd.: C, 40.56; H, 6.81; F, 9.17; Si, 13.55%.

Table 5

Silatranylation reaction of organic and organoelement compounds with 1-iodosilatrane (IV) and physicochemical constants of the 1-organosilatranes obtained

Reagent	Reaction time (h)	Product	Yield (%)	M.p. (°C) (recrystallization solvent)
$C_2H_5OC_2H_5$	0.25	$C_2H_5OSi(OC_2H_4)_3N$ (XI)	99	101–102 (heptane)
$C_6H_5OCH_3$	3.0	$C_6H_5OSi(OC_2H_4)_3N$ (XII)	99	228–229 228–229.5 [1]
$3-ClC_6H_4OCH_3$	3.0	$3-Cl-C_6H_4OSi(OC_2H_4)_3N$ (XIII)	95	158–159 156–157
$Me_3SiOC_2H_5$	5	$Me_3SiOSi(OC_2H_4)_3N$ (XIV)	70	($CHCl_3 + Et_2O$) 156 [1]
$(Me_3Si)_2O$	4	(XIV)	90	156
$N(C_2H_4O)_3SiOC_2H_5$	2	$[N(C_2H_4O)_3Si]_2O$ (XV)	97	124 ($CHCl_3 + Et_2O$)
CH_2CH_2O	0.3	$ICH_2CH_2OSi(OC_2H_4)_3N$ (XVI)	99	89–90
$MeCOOEt$		$MeCOOSi(OC_2H_4)_3N$ (XVIII)	60	173–174 173–174 [1]
$(CF_3CO)_2O$		$CF_3COOSi(OC_2H_4)_3N$ (XIX)	55	decomp. 180 °C
$MeCHO$		$CH_3CHIOSi(OC_2H_4)_3N$ (XX)	60	decomp. 110 °C
CH_3OH	1	$CH_3OSi(OC_2H_4)_3N$ (XXI)	90	155–156 155–156 [1]
CH_3ONa	0.5	XXI	95	155–156
Me_3COH	1.5	$Me_3COSi(OC_2H_4)_3N$ (XXII)	90	146–147.5 146.5–147.5 [1]
Me_3COK		XXII	95	146.5–147.5
$AdOH$	6	$AdOSi(OC_2H_4)_3N$ (XXIII)	90	150–151
$EtSH$	3	$EtSi(OC_2H_4)_3N$ (XXIV)	95	101
$EtSNa$	3	XXIV	95	101 (C_6H_6)
Me_3CSH	3	$Me_3CSSi(OC_2H_4)_3N$ (XXV)	82	54
$PhSH$	3	$PhSi(OC_2H_4)_3N$ (XXVI)	92	95
$4-MeC_6H_4SH$	3	$4-MeC_6H_4SSi(OC_2H_4)_3N$ (XXVII)	85	92
$CH_2=CHC\equiv CH$	6	$CH_2=CHC\equiv CSi(OC_2H_4)_3N$ (XXVIII)	90	
$PhC\equiv CH$	6	$PhC\equiv CSi(OC_2H_4)_3N$ (XXIX)	80	275
Et_2Hg	12	$EtSi(OC_2H_4)_3N$ (XXX)	80	134–135 134–135 [1]
$EtHgCl$	12	$ClSi(OC_2H_4)_3N$ (V)	95	decomp. 200 °C
Ph_2Hg	96	$PhSi(OC_2H_4)_3N$ (XXXI)	50	210–211 210.3–211.3 [1]

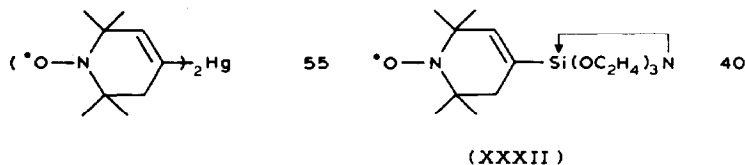


Table 6

 ^1H , ^{15}N and ^{29}Si NMR chemical shifts of the silatranes $\overline{\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ in CDCl_3 (δ , ppm)

R	$\delta(^1\text{H})$ (ppm)			$\delta(^{15}\text{N})$ (ppm)	$\delta(^{29}\text{Si})$ (ppm)
	OCH ₂	NCH ₂	R		
CH ₃	3.86	2.90		-352.7	-95.4
C ₂ H ₅ O(CH ₂ Cl ₂)	3.76	2.83		-353.2	-95.4
C ₂ H ₅ S	3.87	2.94	1.25 (CH ₃) 2.60 (CH ₂)		-76
Me ₃ CO	3.79	2.78		-356.3	-95.2
Me ₃ CS	3.86	2.83	1.36		
PhO	3.89	1.89		-350.4	-99.2
PhS	3.91	1.96	7.24		
3-ClC ₆ H ₄ O	3.93	2.96		-350.0	-99.8
4-CH ₃ C ₆ H ₄ S	3.88	2.92	2.28 7.08		
IC ₂ H ₄ O	3.85	2.89			-95.9
IC ₄ H ₈ O(CH ₂ Cl ₂)	3.77	2.84			-95.2
CH ₃ CHIO	3.82	2.83			
CH ₃ C(O)O	3.94	3.02			-99.7
CF ₃ C(O)O	4.01	3.09			
Me ₃ SiO	3.78	2.76		-354.5	-98.2
$\overline{\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{SiO}}$	3.81	2.75		-356.5	-99.5
I-AdO	3.80	2.79			-94.9
C ₆ H ₅ C=C	3.93	2.93			-94.7
CH ₂ =CHC=C	3.90	2.94			-94.9
C ₂ H ₅	3.78	2.80			-67.1
C ₆ H ₅	3.91	2.92			-80.2

(c) 1-Fluoro-3,7,10-trimethylsilatrane (III). A solution of 1-chloro-3,7,10-trimethylsilatrane (1.0 g, 4.0 mmol) in 50 ml of HMPA and anhydrous potassium fluoride (0.26 g, 5 mmol) was stirred for 10 h at 100°C. The filtrate was evaporated to dryness in vacuum and the residue was recrystallized from isopropanol. Yield of III 0.72 g (77.0%), m.p. 237–238°C. Found: C, 45.36; H, 7.76; F, 7.36; Si, 11.20. C₉H₁₈FNO₃Si calcd.: C, 45.93, H, 7.71; F, 8.07; Si, 11.93%.

2. *Silatranylation reactions.* Cleavage of ethers and esters, alkoxy silanes and siloxanes by 1-iodosilatrane (X) was performed by the general procedure given below.

A solution of 1-allylsilatrane (9.2 mmol), C₃F₇I (10–24 mmol) and the corresponding oxygen-containing reagent (9.2–18.4 mmol) in 20 ml of CH₂Cl₂ was vacuum-treated, irradiated with UV for 30 min, then stirred until the pinkish precipitate disappeared, and the volatile reaction products and the solvent were evaporated off. The silatrane (XI–XXII or XXIII) residue was recrystallized from CH₂Cl₂ or from some other suitable solvent.

The reagent used, the reaction time (at 20°C), the silatrane obtained, its yield, m.p., solvent of recrystallization (other than CH₂Cl₂) are presented in Table 5. ^1H and ^{29}Si NMR data are given in Table 6.

1-Ethylthiosilatrane (XXIV). A vacuum-treated solution of 1-allylsilatrane (0.54 g, 2.51 mmol) and heptafluoroiodopropane (2.08 g, 7.03 mmol) in 10 ml of CH₂Cl₂ was exposed to UV-irradiation for 30 min until a white precipitate formed. Onto the

1-iodosilatrane thus formed, was condensed in vacuum 0.31 g (5.0 mmol) of ethylmercaptane. The solution was stirred for 3 h at 30°C, volatile products were evaporated off, the solid residue was recrystallized from benzene to give 0.54 g (92%) of XXIV. The reactions with other sulfur-containing compounds, alkynes and organylmercurials were similarly carried out. The reaction conditions and characteristics of products XXIV–XXXII are presented in Tables 5 and 6.

Conclusion

Some new, effective methods (including radical reactions) have been developed for the synthesis of 1-halosilatranes which had been seldom prepared previously and had received very little attention. Of the Si-substituted silatranes, 1-halosilatranes have the shortest Si ← N intramolecular bond, which decreases on going from the F to the I derivative. This is consistent with the hypervalent bond model [59].

Characterized for the first time, 1-iodosilatrane is a good reagent for introducing a silatrane group into a wide range of organic and organoelement molecules. The most convenient route to this new synthon is by reaction of 1-allylsilatrane with perfluoroiodoalkanes. The silatranylation reactions of compounds that are stable to R_FI are best carried out in situ (reaction schemes 13–18). The interaction of 1-iodosilatrane with ethers or oxacyclanes is realized even in the nascent state.

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