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S I L A T R A N E S

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Introduction

For many years there was a prevailing conviction in science that silicon compounds are biologically inert and useless for medicinal purposes. This conviction was caused by the fact that among organic derivatives of this element there had been found no compounds displaying any physiological effect which could be attributed to the presence of the silicon atom. Moreover, organosilicon polymers, the silicones, were believed to be so inert and harmless to the human organism that they were used widely in implantation surgery[1].

The discovery of the specific biological activity of 1-arylsilatranes made in 1963[2] provoked extensive studies of this new (at this time) class of substances, and a search for other types of biologically active organosilicon compounds. Later on these investigations led to the birth of the problem "Silicon and Life" and a new branch of silicon chemistry - "Bio-organosilicon Chemistry"[1*]. In 1963 also a new term "silatranes" was coined[2,5] which is widely accepted now and included in the international chemical nomenclature.

The particular structure and the unusual chemical properties of silatranes have also attracted the attention of many scientists and, as a result, they have been studied in detail by almost all physical methods.

The biological activity of silatranes also has been studied in detail[1,4,4a]. It has been established that a number of non-toxic silatranes effectively stimulate protein biosynthesis in nucleic acids. Also, some silatranes which display neurotropic, anti-sclerotic, insect-repellent and other type of biological activity have been found.

During the latest years silatranes are being produced as reagents in the United States and in pilot scale in the USSR[7].

Silatranes, 5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3]-unde-

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* At present silicon is officially recognized as a vital essential element. A special Nobel Symposium, Stockholm, 1977 was devoted to the problem of biochemistry of silicon and biological activity of compounds of this element [3,4,4a].

canes, are cyclic organosilicon ethers of tris(2-oxyalkyl)-amines and their derivatives. Their heterocyclic skeleton has structure I (Fig.1)

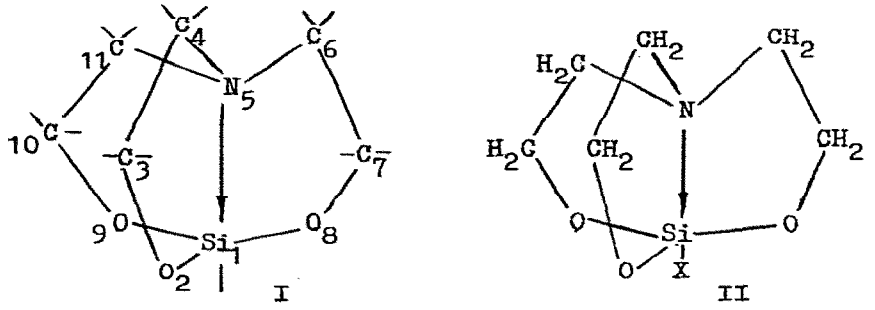


Fig. 1

In the above cited numeration of the silatrane skeleton atoms the silicon atom is in position 1. This system is most convenient as the majority of silatranes studied are Si-substituted, in other words, they have the substituent in position 1. Silatrane itself, the simplest compound of this class, has structure II where X = H (Fig.1).

However, there is another numeration system[6,9] according to which the tertiary nitrogen atom is in position 1 and the silicon atom has position 5.

At present some silatrane analogs are also known. These are substituted 2-carbasilatranes (III), 2,8,9-triazasilatranes (IV), 2,8,9-trithiasilatranes (V) and, finally, homosilatranes (VI) also considered in this review (Fig.2).

The first silatranes (II with X = C_6H_5 and C_2H_5O) were patented by Finestone in 1960 and even at that time the existence of the Si←N transannular coordinate bond in the silatrane molecule was suggested.

In 1961, in a letter to editor, Frye, Vogel and Hall[9] reported melting points for a number of new 1-substituted silatranes II (X = H, CH_3, n-$C_{18}H_{37}$, $C_6H_5(CH_3)CH$, CH_2=CH, $C_{10}H_{19}O$ (menthoxy) and for 1,3-dimethyl- and 3-methyl-1-phenylsilatranes as well. They also gave more exact melting points for 1-ethoxy- and 1-phenylsilatranes (100-102° and 208-209°, respectively) and reported some data which supported the intramolecular transannular Si—N bond in silatranes.

Since 1964 (2,5) a series of more than 50 papers by Voronkov and co-authors has begun to be published. These investigations have dealt with the structure, methods of preparation, and the chemical, physical and biological pro-

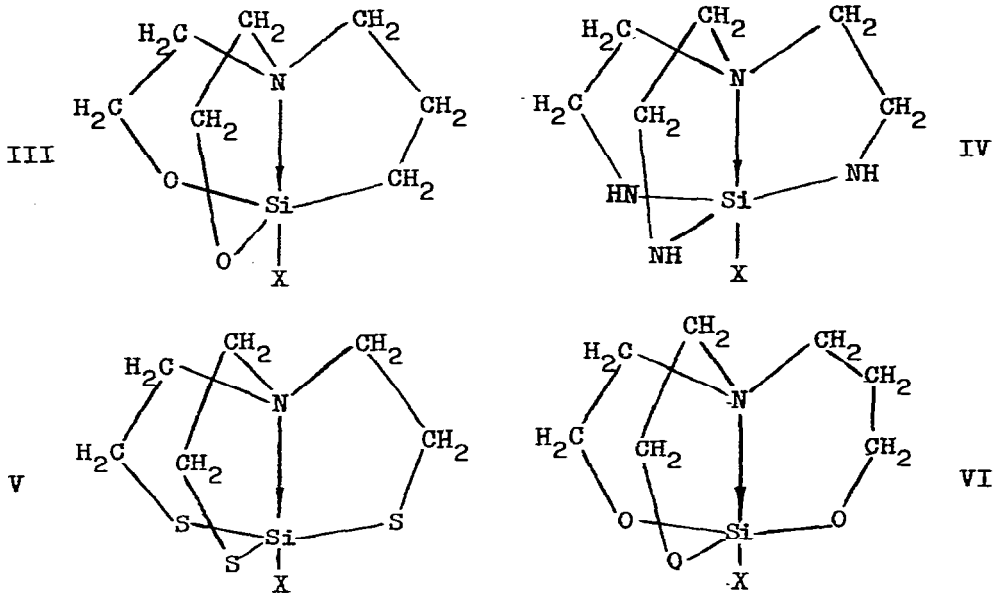


Fig. 2

perties of silatranes and their analogs.

It is now recognized that some of these compounds are very promising for application in agriculture, medicine and some branches of industry. The aim of this review is to summarize all the numerous data on physics and chemistry of silatranes.

The previously published reviews devoted to silatranes (3,4,10-26) are not up-to-date and cannot give an exhaustive consideration of all the data available in the literature.

Chapter I. Methods of Preparation

1.1. Transesterification of Si-Substituted Trialkoxysilanes.

Silatranes were first prepared by the American chemist A.B. Finestone (8) by azeotropic distillation of triethanolamine and organyltrialkoxysilanes with benzene:

$$XSi(OC_2H_5)_3 + (HOCH_2CH_2)_3N \longrightarrow XSi(OCH_2CH_2)_3N + 3C_2H_5OH \quad (1)$$

$X = C_2H_5O$, C_6H_5

The author failed to isolate pure 1-ethoxysilatrane judging from the low melting point reported (35-37°C). The same method for the synthesis of silatrane was used in 1961 by Frye, Vogel and Hall (9).

Among earlier works dealing with the synthesis of silatranes by the transesterification method only Samour's patent describes in detail the preparation conditions and properties of some new and a number of already known silatranes (27).

Thus, for example, C-methyl-substituted (in the atrane cycle) 1-vinyl- and 1-ethoxysilatranes are described. Samour was the first to propose the use of iron chlorides as catalysts in reaction (1). Later Finestone described mainly monocyclic silatrane analogs of type $X_2Si(OCHRCH_2)_2NR'$ where X = CH_3, C_6H_5, C_2H_5O; R = H, CH_3; R' = H, CH_3, C_2H_4OH having, as it was assigned, a coordination-bonded structure (28).

In their well-known handbook, V. Bažant a.o.(29) reported some unpublished data by Graham and Thompson who synthesized silatranes II where X = C_5H_{11}, CH_2=CH-CH_2 and 3,7,10-trimethyl-substituted 1-vinyl- and 1-ethoxysilatranes.

Voronkov and Zelchan (30,31) used the transesterification of lower tetraalkoxysilanes by an equimolar mixture of triethanolamine and higher alcohol for the synthesis of higher 1-alkoxysilatranes:

$$Si(OR)_4 + (HOCH_2CH_2)_3N + R'OH \longrightarrow R'OSi(OCH_2CH_2)_3N + 4ROH \quad (2)$$

R = CH_3, C_2H_5; R' = alkyl, cycloalkyl

Alkali hydroxides were used as catalysts. Some 1-alkoxysilatranes [R' = $(CH_3)_2CH$, $(CH_3)_3C$] do not form in the absence of a base catalyst. The synthesis is carried out by heating a mixture of the lower tetraalkoxysilane, triethanolamine and an alkohol-catalyst solution in an inert solvent until distillation of the lower alcohol formed is complete. In this case, unlike the method proposed by Finestone (8,28) and Samour (27), it is not necessary to prepare the corresponding alkoxytrimethoxy- or alkoxytriethoxysilanes separately, prior to the cyclization reaction.

The method developed by Voronkov and Zelchan (30,31) for preparation of alkoxysilatranes was extended to 1-aroxysilatranes (32). The same method was used to prepare 1-(4'-carbalkoxyphenoxy)silatranes:

4-$ROCOC_6H_4OSi(OCH_2CH_2)_3N$ where R = CH_3, C_2H_5, n-C_3H_7 (33)

An attempt to use this method for preparing 1-(4'-aminophenoxy)silatrane and 1-(2',4',6'-trinitrophenoxy)silatrane was not successful (32).

Transesterification of lower tetraalkoxysilanes with a mixture of triethanolamine and a monocarboxylic acid, which proceeds according to scheme (2), where R = CH_3CO and C_6H_5CO, was used for the synthesis of the corresponding 1-acyloxysilatranes (34). However, the synthetic possibilities of this method are rather limited.

A modification of (1) is the direct reaction of an alkylene oxide, 2-aminophenol and the corresponding organyltrialkoxysilane (15)

$$C_6H_5Si(OC_2H_5)_3 + 2CHR\text{-}CH_2\ (\text{O}) + 2\text{-}HOC_6H_4NH_2 \longrightarrow$$

$$C_6H_5Si(OCHRCH_2)_2(OC_6H_4)N + 3C_2H_5OH \qquad (3)$$

where R = alkyl, aryl

However, scheme (1) was found more favorable for the preparation of Si-substituted 3,7-dimethyl-10,11-benzosilatranes of the type $XSi[OCH(CH_3)CH_2]_2(OC_6H_4)N$ where X = CH_3, $ClCH_2$, CH_3CHCl, Cl_2CH, $Cl(CH_2)_3$ (34).

Transesterification of aminoalkyltrialkoxysilanes, $R_2N(CH_2)_nSi(OR')_3$, where R_2 = H_2, $(C_2H_5)_2$, $(CH_2)_4$, $(CH_2)_5$; R' = CH_3, C_2H_5; n = 1,3 by triethanolamine made possible the synthesis of the corresponding 1-aminoalkylsilatranes and their N-substitutes (27,35,36).

1-(Diethylaminomethyl)silatrane was obtained by heating of an equimolar mixture of triethanolamine and (diethylaminomethyl)triethoxysilane without solvent or catalyst. 1-(Piperidinomethyl)silatrane was obtained in chloroform solution. 1-(3'-Diethylamino-, 1-(3'-pyrrolidino- and 1-(3'-piperidinopropyl)silatranes, as well as 1-(pyrrolidinomethyl)silatrane, were isolated as thick oils and described only as the methiodide derivatives (35).

1-(3'-Perfluoroacyloxyaminopropyl)silatranes of the type $CF_3(CF_2)_nC(O)NH(CH_2)_3Si(OCH_2CH_2)_3N$, where n = 0-20, were prepared by transesterification of 3-(perfluoroacylaminopropyl)-trialkoxysilanes with triethanolamine in xylene in the presence of KOH (37).

Water-soluble N-pyrrolidino-, N-piperidino- and N-perhydroazepinoalkylsilatranes, $\overline{CH_2(CH_2)_mN}(CH_2)_nSi(OCH_2CH_2)_3N$, where m = 3,4,5; n = 1,3, were obtained in 66-70% yields (38).

A large amount of different carbofunctional derivatives of 1-alkylsilatranes of the type $X(CH_2)_mSi(OCHR'CH_2)_n(OCH_2CH_2)_{3-n}N$ where X = halogen, F_3C, RO, RCOO, $ROCH_2COO$, HS, RS, NCS,

$(RO)_2P(O)$, etc.; R = a hydrocarbon group; R' = CH_3, CF_3; n = 0-3, were synthesized by scheme (1) (39).

The first haloalkylsilatranes, 1-chloroalkylsilatranes, were prepared by the interaction of (chloroalkyl)trialkoxysilanes with the corresponding tris(2-oxyalkyl)amines in an o-dichlorobenzene solution (in 50-55% yield)(40) or without solvent (in 60-94% yield) in the presence of KOH as a base catalyst (41). 1-Chlorovinylsilatranes were formed from the corresponding chlorovinyltrialkoxysilanes in higher yields (85-93%) (42). An attempt to obtain 1-(trichloromethyl)silatrane was unsuccessful due to the Si-C bond cleavage:

$$3Cl_3CSi(OC_2H_5)_3 + 4(HOCH_2CH_2)_3N \rightarrow 3CHCl_3 + N[CH_2CH_2OSi(OCH_2CH_2)_3N]_3 + 9C_2H_5OH \quad (4)$$

However, 1-(dichloromethyl)silatranes were easy to prepare in 81-93% yields using scheme (1) (43).

1-Iodoalkyl- (44,45) and 1-bromoalkylsilatranes (46) can be obtained in o-xylene using the same method (5,8,27), but the yield of these and other difficultly accessible carbofunctional 1-alkylsilatranes did not exceed 30-50%.

All the earlier described syntheses of silatranes were carried out by a prolonged heating (for 2-20 hours) at high temperatures (100-200°C) with or without solvent and catalyst. The reaction equilibrium (scheme 1) shifted to the right due to removal of the alcohol formed from the reaction mixture.

Recently, a simple and convenient method for preparing silatranes and their carbofunctional derivatives has been proposed. According to this method, the shift of the reaction equilibrium to the right is achieved by removal of the silatrane itself and not of the alcohol formed (39). Moreover, the process is often carried out in alcohol medium. The reaction can occur in other low boiling organic solvents such as methanol, acetone, chloroform, dioxane, or n-hexane. In the case of C-methylsubstituted silatranes it is better not to use a solvent. The use of an alkoxide or hydroxide as a catalyst is not necessary. However, it facilitates the process and increases the main product yield. This method was used for preparing many difficultly accessible carbofunctional derivatives of 1-organylsilatranes (39-47). C-methylsubstituted 1-haloalkylsilatranes can be obtained in high yields under more drastic conditions, i.e., without solvent

and at higher temperatures (80-120°C).

The synthesis of 2-haloethylsilatranes failed even under mild conditions because on reaction with triethanolamine, (2-haloethyl)trialkoxysilanes undergo elimination to form ethylene, triethanolamine hydrohalide and tris(1-silatranoxyethyl)amine (43).

$$3XCH_2CH_2Si(OR)_3 + 7(HOCH_2CH_2)_3N \rightarrow 3CH_2{=}CH_2 + 3(HOCH_2CH_2)_3N\cdot HX + N[CH_2CH_2OSi(OCH_2CH_2)_3N]_3 \quad (5)$$

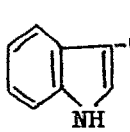
where X = Cl, Br; R = CH_3, C_2H_5

3'-Fluorosubstituted 1-(propyl)silatranes are formed in high yield according to scheme (1) (47).

A method of preparation of carbofunctional 1-methylsilatranes of the type $XCH_2Si(OCHRCH_2)_3N$ (X = halogen, HO, RO, RCOO, HSO_3, HS, NC, F_3C, R'R"N, NCS, R'NHCOO, $(RO)_2P(O)$, $R'SO_2NH$ where R = H, CH_3; R' = alkyl, aryl or alkenyl) according to scheme (I) has been patented (46,49). However, neither the synthesis of most of these compounds, nor their physical constants were reported (49). Moreover, it is doubtful that derivatives with X = F, HO, HSO_3, F_3C, $R'SO_2NH$, etc. could be obtained as organyltrichlorosilanes, XCH_2SiCl_3, and organyltrialkoxysilanes, $XCH_2Si(OR)_3$, required as starting materials are not accessible so far. Halomethyltrichloro- and trialkoxysilanes with X = Br, I (44,50), aroxymethyl- (51), aroyloxymethyl- (52) and organylthiomethyltrialkoxysilanes (53) have been described only recently. No 1-fluoromethylsilatranes, $FCH_2Si(OCHRCH_2)_3N$ with R = H, CH_3, CF_3 have been prepared as the initial fluoromethyltrihalo- or trialkoxysilanes are not available (54).

1-(O,O-Dialkylphosphonoalkyl)-, 1-thiocyanatoalkyl-, 1-(aroxymethyl)-, and 1-(aroyloxymethyl)silatranes (55-59) have been described recently.

The above method made it possible to obtain silatrane derivatives of synthetic phytohormones (ezo-substitutes of phenoxyacetic acids) of type $XC_6H_4OCH_2COO(CH_2)_nSi(OCH_2CH_2)_3N$ where X = H, halogen, CH_3, CH_3O; n = 1,3 and heteroauxine (3-indolylacetic acid)



$-CH_2COOCH_2Si(OCHRCH_2)_3N$

where R = H, CH_3 (39, 60-63).

According to scheme (1) 1-acryloxyalkyl- and 1-methacryloxyalkylsilatranes of the type $CH_2=C(R)COO(CH_2)_nSi(OCH_2CH_2)_3N$ where R = H, CH_3; n = 1-4 also were obtained (48,49).

Transesterification of Si-substituted trialkoxysilanes was used to prepare different types of sulfur-containing silatranes. Thus, for example, the synthesis of 1-mercaptoalkylsilatranes (39,64,65) and 1-(organylthioalky)silatranes (39, 66) of the series $RS(CH_2)_nSi(OCH_2CH_2)_m[OCH(CH_3)CH_2]_{3-m}N$ where R = H, alkyl, alkenyl, aryl, aralkyl, alkaryl; n = 1,3; m = 0-3, have been described. They are readily prepared according to scheme (1) without solvent and with a 5-10% methanol solution of sodium methoxide as a catalyst.

The synthesis of β-(oxyethylthiomethyl)trialkoxysilanes from sodium β-oxyethylmercaptide and (chloromethyl)trialkoxysilanes afforded the corresponding silacyclohexanes resulting from intramolecular transesterification:

$$ClCH_2Si(OR)_3 + HOCH_2CH_2SNa \longrightarrow (RO)_2Si\begin{array}{l}CH_2-S\\ \\O-CH_2\end{array}CH_2 + ROH \qquad (6)$$

These were converted into 1-(2'-oxyethylthiomethyl)silatrane, $HOCH_2CH_2SCH_2Si(OCH_2CH_2)_3N$, by transesterification with triethanolamine (67).

1-(2'-Thienyl)silatrane and its 5-substituted derivatives of the type $(5\text{-}XC_4H_2S)Si(OCH_2CH_2)_3N$, where X = H, alkyl, halogen, CN, were synthesized in high yield (75-90%) according to scheme (1) in an xylene solution and without catalyst (68).

A series of organylsilatranes which are C-trifluoromethyl-substituted in the atrane group was prepared by transesterification of the corresponding organyltrialkoxysilanes with tris-(2-oxyalkyl)amines having one, two or three trifluoromethyl groups (60,61,70).

$$XSi(OR)_3 + (HOCH_2CH_2)_nN[CH_2CH(CF_3)OH]_{3-n} \downarrow$$
$$XSi(OCH_2CH_2)_n[OCH(CF_3)CH_2]_{3-n}N + 3ROH \qquad (7)$$

X = CH_3, C_6H_5, $ClCH_2$, CH_3CHCl, $Cl(CH_2)_3$, $CF_3(CH_2)_2$;
R = CH_3, C_2H_5

The reaction was carried out without solvent in the presence of a 10% methanol solution of sodium methoxide. 2-Trifluoromethyl-2-oxyalkylamines in turn were synthesized from the 1,1,1-trifluoro-2,3-epoxypropane with ammonia, mono- or di-

ethanolamine in chloroform or aqueous medium.

Transesterification of hexaethoxydisiloxane by triisopropanolamine was used to prepare 3,7,10,3,7,10-hexamethyldisilatranoxane in 59% yield (15,71):

$$(C_2H_5O)_3SiOSi(OC_2H_5)_3 + 2[HOCH(CH_3)CH_2]_3N \xrightarrow{KOH,\ 240^\circ} N[CH_2CH(CH_3)O]_3SiOSi[OCH(CH_3)CH_2]_3N + 6C_2H_5OH \quad (8)$$

An attempt to prepare this compound without the base catalyst was unsuccessful.

Polydimethylsiloxanes blocked by silatrane groups of the type $N(CH_2CHRO)_3SiO[Si(CH_3)_2O]_nSi(OCHRCH_2)_3N$ and $N[(CH_2CHRO)(CH_2CHR'O)_2]SiO[Si(CH_3)_2O]_nSi[(OCHRCH_2)(OCHR'CH_2)_2]N$ where R = H, CH_3; R' = H, alkyl, alkenyl, cycloalkyl, aryl; n = 10 000 were obtained by transesterification of the corresponding α,ω-bis(trialkoxysilyl)polydimethylsiloxanes by tris(2-oxyethyl)amines (71).

Transesterification of tetraethoxysilane with an excess of triethanolamine gave tris(2-silatranyl-1-oxyethyl)amine (15):

$$3(C_2H_5O)_4Si + 4(HOCH_2CH_2)_3N \rightarrow N[CH_2CH_2OSi(OCH_2CH_2)_3N]_3 \quad (9)$$

Disilatranyl-1-oxyalkenes of the type $N(CH_2CH_2O)_3SiOROSi(OCH_2CH_2)_3N$ where R = $-(CH_2)_n-$, $-CH(CH_3)CH_2-$, $-CH_2CH_2OCH_2CH_2-$, n = 2-6, were obtained according to the general scheme (2) from tetraethoxysilane, triethanolamine and the corresponding alkanediol (72).

The reaction of bis(trialkoxysilylalkyl)sulfides with triethanolamine according to scheme (1) in the presence of an alkali alkoxide yielded bis(silatranylalkyl)sulfides of the type $N(CH_2CH_2O)_3Si(CH_2)_nS(CH_2)_nSi(OCH_2CH_2)_3N$ where n = 1,3(73).

The reaction of 1,2,3,4-diepoxybutane with diethanolamine and the corresponding triethoxysilane derivatives gave 1,1-disubstituted 3,3-disilatranyls (to 60% yield) (15).

$$\begin{array}{l} XSi(OCH_2CH_2)_2(OCHCH_2)N \\ \qquad\qquad\qquad\quad | \\ XSi(OCH_2CH_2)_2(OCHCH_2)N \end{array} \qquad X = C_2H_5O,\ C_6H_5$$

The first 1-substituted silatrane-3-ones were obtained by transesterification of trialkoxysilanes with N-bis(2-oxyethyl)-aminoacetic acid (74,75).

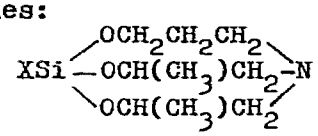
$XSi(OR)_3 + (HOCH_2CH_2)_2NCH_2COOH \rightarrow XSi(OCH_2CH_2)_2(OCOCH_2)N$ (10)

X = CH_3, C_2H_5, n-C_4H_9, CH_2=CH, C_6H_5, $C_6H_5CH_2$, 4-$ClC_6H_4CH_2$, 4-$CF_3C_6H_4$, 3-ClC_6H_4, 4-FC_6H_4.

The reactions were carried out in a 1:3 mixture of benzene and dimethylformamide. The yields are 30-75%. It was not possible to prepare 1-substituted silatrane-3,7,10-triones from aminotriacetic acid by this method.

The first attempts to synthesize silatranes with an enlarged atrane cycle by transesterification of phenyltrimethoxysilane with tris(3-oxypropyl)amine or bis(2-oxyethyl)-3-oxypropylamine were not successful (15). This led to the conclusion that the formation of a silatrane or a similar system involved strigent structural requirements that having only two carbons between the oxygen and nitrogen sites was an important determining factor.

However, in 1976, transesterification of organyltrialkoxysilanes with 3-oxypropyl-bis(2-oxypropyl)amine allowed the synthesis in 70-90% yield of the corresponding 1-organylhomosilatranes, i.e., 1-substituted 2,8,9-trioxa-5-aza-1-silabicyclo [4.3.3] dodecanes:



X = CH_3, CH_2=CH, C_6H_5, 3-ClC_6H_4, 4-BrC_6H_4, CH_3O, C_2H_5O, C_6H_5O, 2-$C_{10}H_7O$ (76,77).

The reaction was carried out in xylene in the presence of KOH. 1-Aroxyhomosilatranes (X = C_6H_5O, 2-$C_{10}H_7O$) were prepared by transesterification of 1-alkoxyhomosilatranes (X = CH_3O, C_2H_5O) with phenol or naphthol or according to scheme (2) from tetraethoxysilane, phenol or naphthol and 3-oxypropyl-bis-2-oxypropyl)amine. In both cases, the yield of the main product amounted to 80%. However, the latter method is more favorable as the reaction proceeds at a higher rate (77).

1.2. Methods of Preparation from Other Compounds of Type $RSiX_3$

An analog of transesterification of Si-substituted trialkoxysilanes with tris(2-oxyalkyl)amines is the reaction of organyltriacetoxysilanes with tris(2-oxyphenyl)amine which leads to the formation of 1-organyl-3,4,6,7,10,11-tribenzosilatranes (78,79).

$$XSi(OCOCH_3)_3 + (2\text{-}HOC_6H_4)_3N \longrightarrow XSi(OC_6H_4)_3N + 3CH_3COOH \quad (11)$$

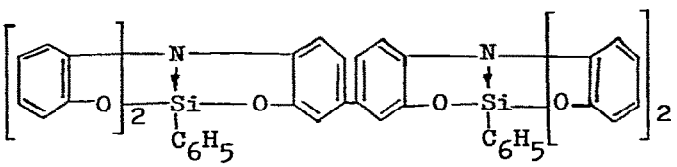
$X = CH_3$, $CH_2{=}CH$, C_6H_5

In this way, it was not possible to prepare the tribenzosilatrane itself from triacetoxysilane because the former reacts readily with the liberated acetic acid. That is why the reaction product is 1-acetoxytribenzosilatrane($X = OCOCH_3$). Similarly, the reaction of tris(2-oxyphenyl)amine with trimethoxy- or trichlorosilane forms the corresponding Si-substituted derivatives instead of tribenzosilatrane (79) :

$$HSiX_3 + (2\text{-}HOC_6H_4)_3N \longrightarrow XSi(OC_6H_4)_3N + 2HX + H_2 \quad (12)$$

$X = Cl$, OCH_3, $OCOCH_3$

Transesterification of phenylacetoxysilane with the corresponding polyatomic aminophenol gave bis(1-phenyltribenzosilatranyl) of the type



1-Organyltribenzosilatranes can be prepared from the corresponding organylchlorosilanes:

$$XSiCl_3 + (2\text{-}HOC_6H_4)_3N \longrightarrow XSi(OC_6H_4)_3N + 3HCl \quad (13)$$

In this case, however, the reaction proceeds slower than reaction (11). 1-Chlorotribenzosilatrane (X = Cl) forms from $HSiCl_3$ or $SiCl_4$ according to eq. (13).

1-Methylsilatrane was synthesized by the reaction of methyltris(diethylamino)silane with triethanolamine (80):

$$CH_3Si[N(C_2H_5)_2]_3 + (HOCH_2CH_2)_3N \longrightarrow CH_3Si(OCH_2CH_2)_3N + 3(C_2H_5)_2NH \quad (14)$$

The same method was used to prepare monocyclic analogs of silatranes of the type $(CH_3)_2Si(OCH_2CH_2)_2NR$, previously described by Finestone (8). The reaction was carried out by heating the reactant mixture until the diethylamine was completely distilled out of the system.

1-Organyl-2,8,9-triazasilatranes (81,82) and 1-phenyl-2,8,9-trithiasilatrane (82) were synthesized for the first time from organyltris(dialkylamino)silanes:

$$RSi[N(C_2H_5)_2]_3 + (H_2NCH_2CH_2)_3N \longrightarrow RSi(NHCH_2CH_2)_3N \quad (15)$$

R = H, CH_3, C_2H_5, $CH_2{=}CH$, C_6H_5, $ClCH_2$, $CF_3(CH_2)_2$

$$C_6H_5Si[N(C_2H_5)_2]_3 + (HSCH_2CH_2)_3N \longrightarrow C_6H_5Si(SCH_2CH_2)_3N \quad (16)$$

An original method for the synthesis of silatranes which, unfortunately, is described only in one example (R = 3-$O_2NC_6H_4$, 96% yield) involves the reaction of an organyltrifluorosilane with tris(2-trimethylsiloxyethyl)amine in aprotic solvent (15)

$$RSiF_3 + [(CH_3)_3SiOCH_2CH_2]_3N \longrightarrow RSi(OCH_2CH_2)_3N + 3(CH_3)_3SiF \quad (17)$$

1.3. Cleavage of Polyorganylsiloxanes

An original and convenient method of the synthesis of 1-organylsilatranes using agents more readily available than organyltrialkoxysilanes, such as polyorganylsilsesquioxanes, $(RSiO_{1.5})_n$, and polyorganylsiloxanols $RSiO_{1.5-m}(OH)_{2m}$, where m = 0-1.5, has been proposed by Voronkov and Zelchan (5,10,83,84) and later used by Frye (15).

$$1/n[RSiO_{1.5-m}(OH)_{2m}]_n + (HOCH_2CH_2)_3N \longrightarrow RSi(OCH_2CH_2)_3N + (1.5 + n)H_2O \quad (18)$$

KOH is used as a catalyst and the water formed is removed from the reaction mixture by continuous azeotropic distillation with a suitable inert solvent (xylene) (15,85). 1-Phenyl- and 1-(3'-nitrophenyl)silatranes were obtained in almost quantitative yield using this method, but without the catalyst (15,84).

It is possible to synthesize 1-organylsilatranes using polyorganylhydrosiloxanes, $(RSiHO)_n$:

$$1/n(RSiHO)_n + (HOCH_2CH_2)_3N \longrightarrow RSi(OCH_2CH_2)_3N + H_2O + H_2 \quad (19)$$

In this reaction, alcoholysis of the initial hydrosiloxane and cleavage of the siloxane bond occur. Silicic acid dissolves at 200-250°C in an excess of triethanolamine and reacts to form a mixture of mono-, di- and trisilatranyl ethers of the latter (15):

$$(3-n)SiO_2 + (4-n)(HOCH_2CH_2)_3N \downarrow$$

$$(HOCH_2CH_2)_nN[CH_2CH_2OSi(OCH_2CH_2)_3N]_{3-n} + 2(3-n)\ H_2O \quad (20)$$

An attempt to carry out a similar reaction with tris(2-oxypropyl)amine was unsuccessful (15).

1.4. The Synthesis from Boratranes

The reactivity of the Si-H bond in trichloro-, triacetoxy- and trialkoxysilanes does not permit the preparation of 1-hydrosilatrane and its derivatives or it affords very low yields. Thus, the reaction of tris(2-oxyphenyl)amine with compounds of type $HSiX_3$ gives only the corresponding Si-substituted silatranes, $XSi(OC_6H_4)_3N$ (X = Cl, $OCOCH_3$, OCH_3) (79).

An interesting method of preparing difficultly accessible 1-hydrosilatranes is the transesterification of trialkoxysilanes with the corresponding boratranes (85,86).

$$HSi(OR')_3 + B(OCHRCH_2)_3N \xrightarrow{Al(OR'')_3} HSi(OCHRCH_2)_3N \qquad (21)$$

R = H, CH_3; R' = CH_3, C_2H_5; R'' = alkyl

The synthesis is carried out by heating a mixture of boratrane with a 1.5 molar excess of trialkoxysilane in xylene at reflux in the presence of a catalytic quantity of an aluminium alkoxide. The 1-hydrosilatranes produced precipitate directly from solution or after removal of the solvent. The yields are 64-94%. Thus, it was possible to obtain silatrane itself and its C-substituted derivatives. These can be used subsequently in different transformations of the Si-H bond.

However, the attempted synthesis of the as yet unknown 1-(2'-haloethyl)silatranes according to scheme (21) was not successful (43).

1.5. Synthesis of 2-Carbasilatranes

2-Carbasilatranes were first prepared by Morehouse (87) in 1961 and later by other workers (88,90) in accordance with scheme (22):

$$R(C_2H_5O)_2SiCH_2CH_2CH_2NH_2 + R'CH\text{-}CH_2 \quad (22)$$

$$\downarrow$$

$$RSi(OCHR'CH_2)_2(CH_2CH_2CH_2)N + 2C_2H_5OH$$

R = CH_3, C_2H_5O, C_6H_5; R' = H, CH_3

2-Carbasilatranes are formed also in the reaction of organyl(3-chloropropyl)dialkoxysilanes with diethanolamine (89, 90) according to scheme (23):

$$R(C_2H_5O)_2SiCH_2CH_2CH_2Cl + (HOCH_2CH_2)_2NH \xrightarrow{-HCl} RSi(OCH_2CH_2)_2(CH_2CH_2CH_2)N + 2C_2H_5OH \quad (23)$$

The reaction is carried out in absolute ethanol in the presence of triethanolamine as an HCl acceptor.

In both cases, the yield of Si-substituted 2-carbasilatranes does not exceed 40-50%.

2. Synthesis from Silicon- and Carbofunctional Substituted Silatranes

2.1. Transformations of 1-Alkoxy- and 1-Oxysilatranes

It was not possible to prepare 1-oxysilatrane (silatranol-1) by hydrolysis of 1-alkoxysilatranes (15). This compound was synthesized by selective hydrolysis of tris-(2-silatranyl-1-oxyethyl)amine in chloroform (15):

$$N[CH_2CH_2OSi(OCH_2CH_2)_3N]_3 + 3H_2O \longrightarrow 3HOSi(OCH_2CH_2)_3N + (HOCH_2CH_2)_3N \quad (24)$$

The transesterification of lower 1-alkoxysilatranes by higher alcohols, glycols and glycerine was first patented by Samour (27):

$$nC_2H_5OSi(OCH_2CH_2)_3N + R(OH)_n \rightarrow N(CH_2CH_2O)_3SiOROSi(OCH_2CH_2)_3N + nC_2H_5OH \quad (25)$$

R = organo group of a higher alcohol, glycol, glycerine, (C_4-C_{20}); n = 1-3

In this case, the glycols may be condensed with tetraalkoxysilanes, $(RO)_4Si$, where R = alkyl, C_1-C_4, and introduced into the reaction with triethanolamine. A series of bis(1-silatranyloxy)alkanes was prepared in a similar way:

$N(CH_2CH_2O)_3SiOROSi(OCH_2CH_2)_3N$

R = $-(CH_2)_n-$, $-CH(CH_3)CH_2-$, $-CH_2CH_2OCH_2CH_2-$; n = 2-6 (72)

Transesterification of lower 1-alkoxyhomosilatranes of type $XSi[OCH(CH_3)CH_2]_2(OCH_2CH_2CH_2)N$, where X = CH_3O, C_2H_5O, by phenol or naphthol according to scheme (25) afforded the corresponding 1-aroxyhomosilatranes (77).

The reaction of 1-ethoxysilatrane with carboxylic acids was used to prepare 1-acyloxysilatranes (15):

$$C_2H_5OSi(OCH_2CH_2)_3N + RCOOH \xrightarrow{(CH_3CO)_2O} RCOOSi(OCH_2CH_2)_3N + C_2H_5OH \quad (26)$$

R = CH_3, C_6H_5

Transesterification of 1-ethoxysilatrane by triphenylsilanol leads to the formation of 1-(triphenylsiloxy)silatrane

$$C_2H_5OSi(OCH_2CH_2)_3N + (C_6H_5)_3SiOH \xrightarrow{(CH_3COO)_2Zn} (C_6H_5)_3SiOSi(OCH_2CH_2)_3N + C_2H_5OH \quad (27)$$

These reactions were carried out in o-dichlorobenzene at 150-200°C.

The action of concentrated hydrofluoric acid converts the ethoxy group in 1-ethoxysilatrane and its C-methyl-substituted derivatives to the 1-fluorosilatranes (15). No cleavage was observed.

$$C_2H_5OSi(OCHRCH_2)_3N + HF \longrightarrow FSi(OCHRCH_2)_3N + C_2H_5OH \quad (28)$$

R = H, CH_3

A convenient method of preparation of 1-halosilatranes is based on the reaction of 1-ethoxysilatrane with phosphorus and sulfur halides (91):

$$2C_2H_5OSi(OCH_2CH_2)_3N + M(O)X_2 \longrightarrow 2XSi(OCH_2CH_2)_3N + M(O)(OC_2H_5)_2 \quad (29)$$

M = S, X = Cl, Br; M = PCl, X = Cl; M = CH_3P, X = F

The synthesis is carried out at room temperature in DMF. The yield of 1-fluorosilatrane was 92%.

Starting from silatranol-1, 1-trimethylsiloxysilatrane could be prepared:

$$HOSi(OCH_2CH_2)_3N + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiOSi(OCH_2CH_2)_3N \quad (30)$$

and α,ω-bis(silatranyl-1-oxy)oligodimethylsiloxanes were prepared by a similar reaction:

$$2HOSi(OCH_2CH_2)_3N + Cl[(CH_3)_2SiO]_nSi(CH_3)_2Cl \downarrow$$
$$N(CH_2CH_2O)_3SiO[(CH_3)_2SiO]_nSi(CH_3)_2OSi(OCH_2CH_2)_3N + 2HCl \quad (31)$$

In both cases the reaction was carried out in chloroform in the presence of triethylamine as an HCl acceptor (15,71).

On reaction with acetyl chloride or acetic anhydride, silatranol-1 was converted into the unstable 1-acetoxysilatrane (15):

$$HOSi(OCH_2CH_2)_3N + CH_3COX \longrightarrow CH_3COOSi(OCH_2CH_2)_3N \quad (32)$$
$$X = Cl, OCOCH_3$$

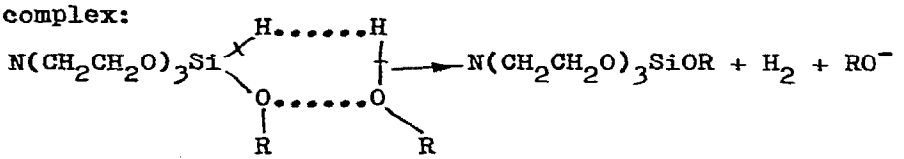
2.2. Reactions of 1-Hydrosilatranes

The reactivity of the Si-H bond in 1-hydrosilatranes provides the basis for the synthesis of various Si-substituted silatranes.

1-Hydrosilatrane reacts readily with alcohols and phenols in boiling xylene in the presence of sodium alkoxide or phenoxide to form the corresponding 1-organoxysilatranes (92):

$$HSi(OCH_2CH_2)_3N + ROH \xrightarrow{R\,O^-} ROSi(OCH_2CH_2)_3N + H_2 \quad (33)$$
$$R = CH_3,\ n\text{-}C_4H_9,\ i\text{-}C_4H_9,\ t\text{-}C_4H_9,\ C_6H_5,\ 4\text{-}CH_3C_6H_4,$$
$$4\text{-}(CH_3)_3CC_6H_4,\ 4\text{-}CH_3OC_6H_4,\ 4\text{-}ClC_6H_4,\ 4\text{-}O_2NC_6H_4,\ C_6F_5,\ \text{etc.}$$

In the presence of $ZnCl_2$ the reaction proceeds considerably more slowly and is not complete. Without catalysts or in the presence of H_2PtCl_6 the reaction does not occur at all. It is believed that the mechanism of the alkali-catalyzed reaction of alcohols with silatrane involves an intermediate complex:



In the case of 1-hydrosilatrane the nucleophilic attack at silicon is of the "flank" rather than the "backside" type.

The reaction of alkanediols with 1-hydrosilatrane was found to be a convenient method of synthesis of bis(1-silatranyloxy)alkanes (72,93). It was possible to isolate an ointment-like 1-(2'-oxyethoxy)silatrane, $HOCH_2CH_2OSi(OCH_2CH_2)_3N$,

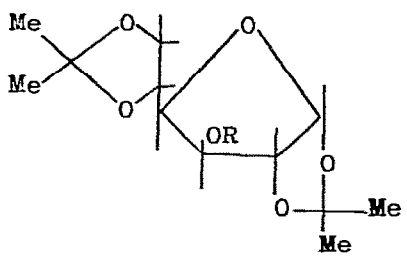
from the reaction products of 1-hydrosilatrane with an excess of ethylene glycol (72).

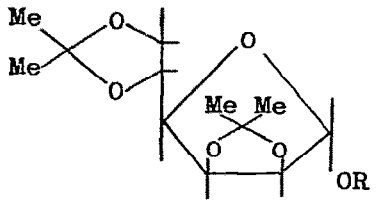
1-Hydrosilatrane undergoes the hydrocondensation reaction with carboxylic acids in the presence of $ZnCl_2$ (94):

$$HSi(OCH_2CH_2)_3N + RCOOH \xrightarrow{ZnCl_2} RCOOSi(OCH_2CH_2)_3N + H_2 \qquad (34)$$

R = CH_3, C_2H_5, C_6H_5, 3-C_5H_4N, 2-C_4H_3O

A reaction time of 2-3 hours is required, and the yields of 1-acyloxysilatranes are 40-80%. Dehydrocondensation of 1-hydrosilatrane with glucose and mannose yielded silatrane derivatives of carbohydrates of the following type(95,95a):





R = $Si(OCH_2CH_2)_3N$

1-Halosilatranes were first obtained in 71-81% yield by the reaction of silatrane with free halogens in chloroform in the presence of triethylamine as a hydrogen halide acceptor (96).

$$HSi(OCH_2CH_2)_3N + X_2 \longrightarrow XSi(OCH_2CH_2)_3N + HCl \qquad (35)$$

X = Cl, Br, I

3,7,10-Trimethylsilatrane may be converted into the corresponding chloro- and bromo derivatives by halogenation in the absence of an HX acceptor. The hydrogen halide formed is also involved into the reaction (15):

$$HSi[OCH(CH_3)CH_2]_3N + X_2 \longrightarrow XSi[OCH(CH_3)CH_2]_3N + HX \qquad (36)$$

$$HSi[CCH(CH_3)CH_2]_3N + HX \longrightarrow XSi[OCH(CH_3)CH_2]_3N + H_2 \qquad (37)$$

X = Cl, Br

The same compounds were obtained by the reaction of 3,7,10-trimethylsilatrane with the corresponding N-halosuccinimides (15):

$$HSi[OCH(CH_3)CH_2]_3N + (CH_2CO)_2NX \longrightarrow XSi[OCH(CH_3)CH_2]_3N + (CH_2CO)_2NH \quad (38)$$

X = Cl, Br

An attempt to obtain 3,7,10-trimethyl-1-iodosilatrane using reactions (37) and (38) was unsuccessful (15).

2.3. Reactions of 1-Halo- and 1-Haloalkylsilatranes

The use of 1-halosilatranes for the preparation of Si-derivatives has been described in only one example thus far, i.e., the conversion of 1-chlorotribenzosilatrane into the 1-phenoxyderivative (79):

$$ClSi(OC_6H_4)_3N + C_6H_5OH \longrightarrow C_6H_5OSi(OC_6H_4)_3N + HCl \quad (39)$$

1-Haloalkylsilatranes have a reactive halogen atom that should allow the preparation of various exocarbofunctional derivatives of 1-alkylsilatranes.

A convenient method for the synthesis of 1-(organylthioalkyl)silatranes in 60-85% yield is the reaction of 1-(haloalkyl)silatranes with alkali mercaptides or alkali salts of thiolcarboxylic acids

$$X(CH_2)_nSi(OCHR'CH_2)_3N + RSM \longrightarrow RS(CH_2)_nSi(OCHR'CH_2)_3N \quad (40)$$

R = C_2H_5, $C_6H_5CH_2$, $CH_3C(O)$, $C_4H_4ON_2$, NC

R' = H, CH_3; M = K, Na; X = Cl, Br, I; n = 1,3

Xylene, dimethylformamide or mixtures of these solvents may be used as the reaction medium (61,97).

The use of potassium thiocyanate in reaction (40) permits the preparation of 1-(thiocyanatoalkyl)silatranes.

1-(Silatranylalkyl)dialkylphosphonates were prepared by the Arbuzov reaction of 1-(haloalkyl)silatranes with trialkyl phosphites (55,98,99).

$$X(CH_2)_nSi(OCHR'CH_2)_3N + (RO)_3P \rightarrow (RO)_2P(O)(CH_2)_nSi(OCHR'CH_2)_3N + RX \quad (41)$$

R = CH_3, C_2H_5, i-C_3H_7; X = Cl, Br, I; R' = H, CH_3; n = 1,3

This reaction proceeds smoothly upon heating 1-(haloalkyl)-silatranes with an excess of trialkyl phosphite which acts as

a solvent at the same time. With X = I, the yields of the main products of the Arbuzov reaction are 95%.

The reaction of 1-halomethylsilatranes with triorganyl phosphines gave the corresponding phosphonium salts (100):

$$XCH_2Si(OCHR'CH_2)_3N + R_3P \longrightarrow [R_3\overset{+}{P}CH_2Si(OCHR'CH_2)_3N]X^- \qquad (42)$$

$R = C_2H_5$, C_3H_7, C_6H_5; X = Br, I; R' = H, CH_3

1-Chloromethylsilatranes do not react with tertiary phosphines. 1-Silatranylmethyltriorganylphophonium iodides also are formed in the absence of the solvents on melting the initial reactants ($R = C_6H_5$) or in alcohol medium ($R = C_2H_5$, C_3H_7).

It was not possible to replace the chlorine atom in 1-(chloroalkyl)silatranes by bromine by the reaction with NaBr, KBr, $AlBr_3$ and PBr_3 (46).

2.4. Additions to 1-Vinylsilatranes

The double bond in 1-vinylsilatranes is readily involved in free-radical addition processes and this permits the synthesis of a number of 2-substituted 1-ethylsilatranes of type $XCH_2CHYSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$.

The addition of perfluoroiodoalkanes to 1-vinylsilatranes gave the corresponding 1-(2'-perfluoroorganyl-1'-iodoethyl)-silatranes (101):

$$CH_2=CHSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N + R_FI \longrightarrow R_FCH_2CHISi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N \qquad (43)$$

$R_F = CF_3$, C_3F_7, C_6F_{13}; n = 0-3

The reactions were carried out in $CHCl_3$ or CCl_4 at room temperature with or without UV-radiation. The yields of the adducts were nearly quantitative.

The H_2PtCl_6-catalyzed hydrosilylation of 1-vinylsilatrane with methylfurylhydrosilanes afforded the corresponding adducts (102)

$$CH_2=CHSi(OCH_2CH_2)_3N + R_n(CH_3)_{3-n}SiH \xrightarrow{H_2PtCl_6} R_n(CH_3)_{3-n}SiCH_2CH_2Si(OCH_2CH_2)_3N \qquad (44)$$

R = 2-furyl, n = 1-3

The hydrosilane reactivity depends on the number of furyl groups. Thus, tri(2-furyl)silatrane reacted with 1-vinylsilatrane at room temperature whereas dimethyl(2-furyl)silane reacted only on heating. Hydrosilylation of 1-vinylsilatrane with oligomethylhydrosiloxanes having terminal trimethylsilyl groups in the presence of chloroplatinic acid afforded the corresponding oligomers having molecular weights of 1000 and 2000 (103).

Photochemical addition of organic and organosilicon compounds containing a thiol group to 1-vinylsilatranes resulted in 1-(2'-organylthioethyl)silatranes in 60-95% yield (60,61):

$$CH_2{=}CHSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N + RSH \xrightarrow{\downarrow} RSCH_2CH_2Si(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N \quad (45)$$

$R = C_2H_5$, $N(CH_2CH_2O)_3SiCH_2CH_2$, $(CH_3O)_3SiCH_2$, $(CH_3O)_3SiCH_2CH_2$, CH_3OCOCH_2; $n = 0-3$

The reactions proceed without any solvent. When the initial reactants were immiscible, chloroform or methanol can be used as a solvent.

It was impossible to obtain 1-(silatranylethyl)dialkyl phosphonates by scheme (41). However, they were prepared by photochemical addition of dialkyl phosphites to 1-vinylsilatranes (61):

$$CH_2{=}CHSi(OCHR'CH_2)_3N + (RO)_2PHO \xrightarrow{\downarrow h\nu} (RO)_2P(O)CH_2CH_2Si(OCHR'CH_2)_3N \quad (46)$$

$R = CH_3$, C_2H_5; $R' = H$, CH_3

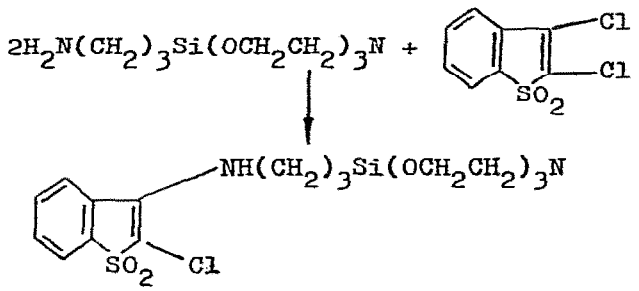
The process is performed by UV-radiation of the 1-vinylsilatrane with an excess of dialkyl phosphite at the boiling temperature of the latter. The reaction does not occur in the presence of peroxide.

Compared to 1-vinylsilatranes, C-substituted (in the atrane ring) 1-vinylsilatranes undergo different addition reactions (schemes 43-46) with facility.

2.5. Reactions of Aminoalkylsilatranes

Readily available 1-(3'-aminopropyl)silatrane was used for preparation of a number of its N-derivatives. In this

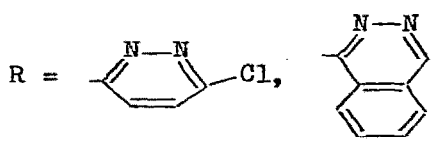
way, 1-(3'-benzoylaminopropyl)silatrane (35) and the product of condensation of the former with 2,3-dichlorobenzo b thiophene-1,1-dioxide were obtained (104):



$$+ N(CH_2CH_2O)_3Si(CH_2)_3NH_2 \cdot HCl \qquad (47)$$

The reaction of 1-(3'-aminopropyl)silatrane with 3,6-dichloropyridazine and 1-chlorophthalazine afforded the corresponding derivatives in 20-30% yield (35a):

$$H_2N(CH_2)_3Si(OCH_2CH_2)_3N + RCl \longrightarrow RNH(CH_2)_3Si(OCH_2CH_2)_3N \qquad (48)$$



The reaction of N,N-substituted 1-aminoalkylsilatranes with methyl iodide in toluene or ethanol gave crystalline methiodides (35).

Chapter II. Structure and Physical Properties

Silatranes are a unique class of heterocyclic pentacoordinate compounds. Their peculiar nature is due to the specificity of both the steric structure of the molecule and the electron-density distribution. All this influences spectroscopic and other physico-chemical properties of silatranes.

Some years ago all questions on the structure of silatranes seemed to be solved. However, more comprehensive and precise physico-chemical investigations carried out during the last few years have shown that the present ideas are only approximate and put forward a number of new theoretical problems which are not solved as yet.

It is not possible to overcome this situation using only a limited number of physical methods. The theory of silatrane

structure may be successfully developed by complex physico-chemical investigations. The results of such an approach are reported in this chapter.

1. Crystal and Molecular Structure

The crystal and molecular structure of silatranes has been studied by X-ray structural and conformation methods.

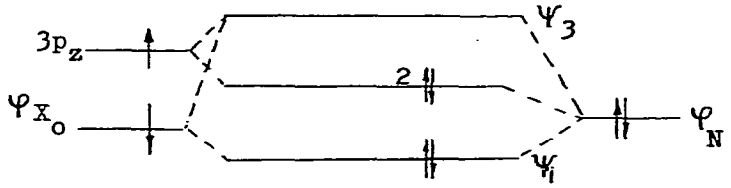
Crystallographic parameters and translational groups in the unit cells of 1-substituted silatranes have been determined, the cell volume and the number of molecules within each cell, as well as the X-ray density and packing coefficients of the crystal lattice, have been calculated (Table 1) (105-120, 120a). The unit cell of the silatrane crystal lattice usually contains four or eight close-packed molecules.

Valency angles and bond lengths, including the distance between the silicon and nitrogen, have been determined in molecules of the silatrane series (105-120, 120a) (Figs. 3-5, Table 2). This distance attracts special attention as it permits a better understanding of the degree of transannular interaction of the silicon and nitrogen atoms, hybridization of their valence orbitals and the influence of the substituents on the geometry of the silatrane skeleton.

In molecules of almost all silatranes which have been studied the Si—N distance is 2.0-2.4 Å. This is significantly shorter than the sum of van der Waals radii for the silicon and nitrogen atoms, 3.5 Å. This provides convincing evidence for the hypothesis proposed earlier on the existence of a transannular interaction between these atoms (8-10). Although a transannular interaction must take place, its nature is not yet clear. Until recently it was beyond doubt that this interaction was associated with a partial transfer of an unshared electron pair of the nitrogen atom to a vacant $3d_z^2$-orbital of the silicon atom which had sp^3d hybridization. However, the participation of 3d-orbitals of the silicon atom is not necessary to explain this interaction. There is an opinion (121, 122) that 3d-orbitals of the silicon atom are energetically less advantageous (as their energy exceeds by more than 10 eV that of the valence orbitals) and more diffuse than the 4s- and 4p-orbitals. Due to this fact, one should not neglect a possible participation of the silicon 4s- and 4p-orbitals in the Si—N bond formation.

The most adequate description of the electronic and steric

structure of silatranes is presented by the model of "hypervalence bonds"(123, 124) which allows one to explain some physical and chemical features of the silatranes*. According to this model, the silicon atom in the silatrane molecules uses three sp^2-hybridized orbitals for its bonding with three oxygen atoms. The interaction of this Si atom with the substituent and the N atom is effected by the formation of three-centered, three orbital hypervalence X-Si-N bond by a p_z-electron of the Si atom, a valence electron of the X substituent and a lone pair of the N atom. The coordination diagram of hypervalence bonding in silatrane molecules is given below



where φ_X, φ_N and $3p_z$ are atomic orbitals of the substituent, N and Si°, respectively; ψ_1, ψ_2 and ψ_3 are bonding, non-bonding and anti-bonding molecular orbitals, respectively. This model (123,124) suggests, first of all, that the influence of the σ-bound substituent X may be transfered only through the $3p_z$-orbital of the central Si atom.

The effect of Si←N bonding is defined by the following expression in the first order of the disturbance theory:

$$\Delta E_{Si \leftarrow N} \simeq \frac{\beta^2_{SiN}}{\left| \alpha_{Si^\circ} + \frac{\beta^2_{Si^\circ X^\circ}}{\alpha_{Si^\circ} - \alpha_{X^\circ}} - \alpha_{N^\circ} \right|}$$

where α and β are Coulomb and resonance integrals, respectively, the index "o" is related to the initial atomic levels and the $\frac{\beta^2_{Si^\circ X^\circ}}{\alpha_{Si^\circ} - \alpha_{X^\circ}}$ relation shows a decrease in the Si←N bonding due to X—Si interaction. If the electronegativity of the X substituent is nearly equal to or higher than that of

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* The idea of the existence of hypervalence bonds in molecules of elementoorganic compounds was developed by Musher (125). Nagy (114) was the first to use the term "hypervalency" for the explanation of the trans-influence of Si-substituents in silatranes. However, in this interpretation hypervalency was coincident with general ideas of sp^3-hybridization of the pentacoordinate Si-atom.

Table 1

Crystallographic Parameters of Silatranes, $XSi(OCH_2CH_2)_3N$

X	a, Å	b, Å	c, Å	β,°	V, Å^3	Z	ρ_o g/cm^3	ρ_c g/cm^3	Volume X, Å^3	Molec. volume Å^3	K,%	Refer.
CH_3	7.54	9.73	14.16	126.6	875.22	4	1.421	1.436	25.03	159.79	73.02	106
C_2H_5	9.33	16.45	6.65		1020.63	4	1.295	1.393	41.60	176.36	69.12	106
$(CH_3)_2CH$	9.52	17.12	6.85		1116.43	4	1.25	1.293	58.17	192.93	69.12	106
CH_2=CH	9.61	30.53	6.62		1942.26	8	1.378	1.378	37.58	172.34	70.99	106
$ClCH_2$	6.88	13.21	11.04		986.8	4	1.51					115
$Cl(CH_2)_3$	12.814	11.45	8.33			4	1.37					116
C_6H_5 (α-form)	13.09	18.37	10.02		2409.43	8	1.364	1.385	81.93	216.69	71.95	106
	13.22	18.52	10.05			8	1.353					108
C_6H_5 (β-form)	15.85	6.64	11.63		1226	4	1.351	1.361				113
C_6H_5 (γ-form)	8.47	12.95	11.12	90.8	1220	4	1.364	1.368				114
3-$O_2NC_6H_5$	10.10	11.01	12.96	111.3		4						110
C_6H_5O	13.64	3.41	10.83		1242.34	4	1.43	1.429	87.20	221.96	71.47	106
$[C_6H_5(CH_3)_2P]_2PtCl$	6.63	17.46	22.29	97.4		4						119
												120

Table 2

Silatranes, $XSi(OCH_2CH_2)_3N$

Parameters*		C_3- Group Parameters			ΔSi, Å	Refer.
Angle O-Si-O, deg.	N-C, Å	Angle C-N-C, deg.	C-C, Å	Angle N-C-C, deg.		
120	1.45	113	1.43	112	0.08	116a
118	1.47	114	1.54	105	0.21	120a
118	1.48	114	1.44	113	0.23	
119	1.50	114	1.53	106	0.15	115
119	1.42	113	1.43	112	0.17	115a
119	1.47	114	1.50	107	0.20	116
119	1.46	115	1.50	107	0.20	108
118	1.46	114	1.45	107	0.19	118
118	1.47	113	1.47	113	1.43	114
119	1.46	113	1.51	107	0.17	110
110	1.43	119	1.50	111	0.58	120
117	1.47	114	1.50	107	0.29	111
117 O-Si-C						219
116	1.47	114	1.50	108	0.28	117
119 O-Si-C						
119	1.44(C_4)		1.63 (C_3C_4)		0.17	118
	1.57 (C_6)		1.39 (C_6C_7)			
	1.89 (C_{12})		1.42 ($C_{11}C_{12}$)			

Structural Features of

X	Axial Parameters			Equatorial	
	Si—N, Å	Si-X, Å	Angle X-Si-N, deg.	Si-O, Å	Angle X-Si-O, deg.
Cl	2.02	2.15		1.65	
CH_3	2.17	1.87	179	1.67	93
C_2H_5**	2.21	1.88		1.66	
$ClCH_2$	2.12	1.91	180	1.67	96
$ClCH_2$[a]	2.12	1.88	178	1.64	96
$Cl(CH_2)_3$	2.18	1.88	180	1.66	
$C_6H_5(\alpha)$	2.19	1.88	178	1.66	97
$C_6H_5(\beta)$	2.15	1.91	177	1.65	97
$C_6H_5(\gamma)$	2.13	1.89	179	1.65	96
$3\text{-}O_2NC_6H_4$	2.12	1.91	180	1.66	96
$[C_6H_5(CH_3)_2P]_2Pt(Cl)$	2.89	2.29		1.65	108
CH_3[b]	2.34	1.87	177	1.66 1.90 Si-C	98 103 X-Si-C
CH_3O[b]	2.22	1.67	180	1.66 1.85 Si-C	
$ClCH_2$[c]	2.25	1.89		1.64	

* Average values

** After A.A. Kemme (217, 218)

[a] $ClCH_2Si(OCH_2CH_2)[OCH(CH_3)CH_2]_2N$

[b] 2-Carbasilatrane derivatives, $XSi(OCH_2CH_2)_2(CH_2CH_2CH_2)N$

[c] $ClCH_2Si(OCH_2CH_2)_2(OCH_2CH_2CH_2)N$

the Si atom, the Si←N interaction should decrease with increasing the X—Si bond strength. The X—Si bonds in silatranes are weaker, compared with normal covalent bonds of the terahedral silicon atom.

If the silicon atom has a less electronegative substituent ($|\alpha_X| \ll |\alpha_{Si}|$) the X—Si bond weakening should decrease the energy and, consequently, increase the Si←N bond length.

The Si←N bond energy is essentially dependent on the electronegativity of both the Si and N atoms. Thus, for example, a change in the character of C-C bond in the silatrane skeleton which leads to an increase of $|\alpha_N|$ should cause a decrease in the Si←N bond strength, other conditions being equal.

As the ionization potential of the central atom increases, the energy of the bonding orbital decreases and the hypervalence structure becomes less stable. This explains why the carbon analog of silatrane ("carbatrane") is so difficult to prepare and predicts an increase of the effect of X—M—N-bonding (M = Si) when the silicon atom in silatranes is replaced by germanium or tin atoms.

Despite its approximate character, the hypervalence bond model (123, 124) describes the electronic and steric structure of silatranes better than the wide-spread hypothesis of sp^3d-hybridization of the silicon atom. However, the nature of the transannular Si←N bond may be comprehensively understood only with further development of quantum chemistry.

The value of the Si atom displacement, Δ, from the equatorial plane of the trigonal bipyramid in the silatrane molecule toward the X substitutent is related to the interatomic Si←N distance by a simple dependence $\Delta = r_{Si \leftarrow N} - d$, where d is the distance between the N atom and the equatorial plane. For all silatranes studied this distance is approximately similar (d = 2.0 ± 0.05 Å) (112, 120a). Thus, the interatomic Si←N distance value is mainly determined by the silicon displacement out of the plane of the three oxygen atoms, i.e., by the Si atom hybridization.

The presence of an electron-withdrawing substituent at the silicon atom (Cl, 3-$O_2NC_6H_4$, $ClCH_2$) shortens the interatomic Si←N distance (Table 2). Insertion of a CH_2 group into the silatrane ring (3-homosilatranes) or replacement of the oxygen atom by this group (2-carbasilatranes) produces a more marked change in the heterocycle geometry and the inter-

atomic Si—N distance than the nature of the substituent at the silicon atom does. Thus, in the 1-methyl-2-carbasilatrane molecule the interatomic Si—N distance is longer by 0.10-0.30 Å than analogous bond for all 1-organylsilatranes studied.

In the 1-phenylsilatrane molecule (α-form) (108) (Fig.3, VII) the X-Si-O angle is smaller (97.1°) than in the 1-phenylbenzosilatrane molecule (100°) (109) (Fig. 3, VIII).

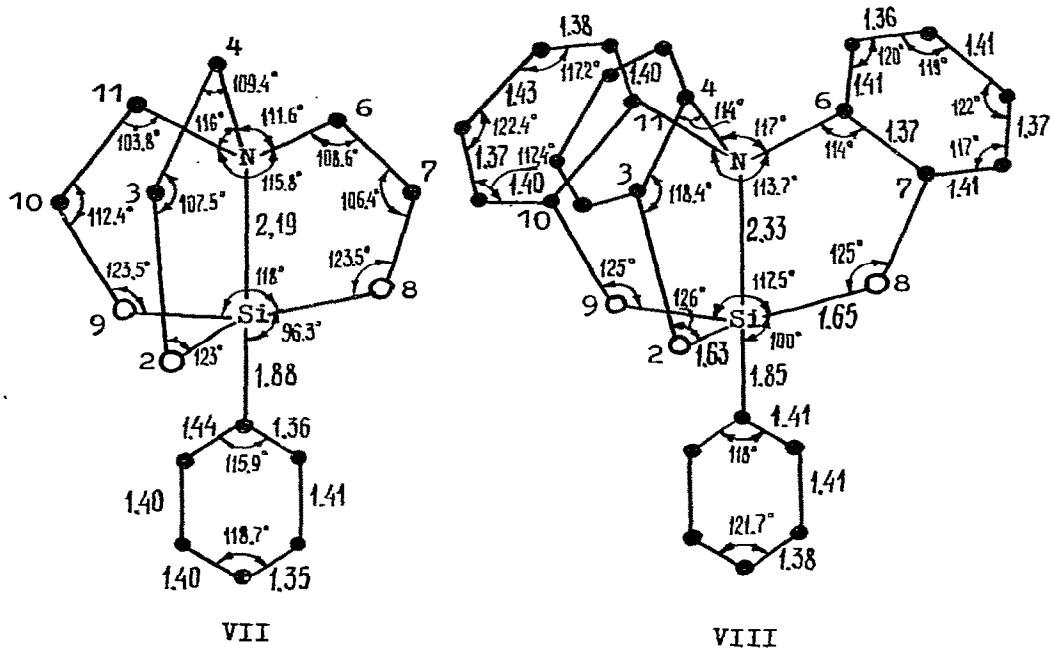


Fig. 3

When one of the oxygen atoms in the SiO_3 grouping is replaced by a more bulky CH_2 group, the X-Si-C angle, which is 103° in the 1-methyl-2-carbasilatrane molecule (111), becomes larger than two other X-Si-O angles which retain their normal value of 98° (Table 2).

The molecular structure thus defined has confirmed the previous suggestion that the atrane skeleton of silatranes is formed by three Si—N transannularly bonded five-membered heterocycles. The coordination polyhedron with the silicon atom in the center represents a distorted trigonal bipyramid.

The three five-centered heterocycles composing the silatrane skeleton have an envelope form with O, Si, N and C (3,7, 10) atoms lying in the same plane. The C (4,6,11) atoms which are in the α-position to the nitrogen atom form the corner of

this envelope (108-110,112-114,115a). 1-(Chloromethyl)homosilatrane which skeleton consists of two five-membered and one six-membered heterocycles displays a disordered structure of the five-membered heterocycles. The carbon atoms attached to the nitrogen atom are characterized by two peaks of electronic density which are 1.2 Å distant. The six-membered heterocycle has a planar structure (Fig. 5, XII).

The possible change in the silatrane cycle geometry (and, first of all, in interatomic Si←N and Si-X distances) due to non-valence interaction of the chlorine, silicon or oxygen atom attached to an alkyl substituent has been studied in the examples of 1-(chloromethyl)- (115) and 1-(3'-chloropropyl)-silatrane (116) (Fig. 4, IX,X, respectively). In molecule IX the axial bond forms a 90° angle with the equatorial plane of the bipyramid. The Si-C-Cl plane is almost co-planar with the N-Si-O(8) plane (the angle is 5.2°).

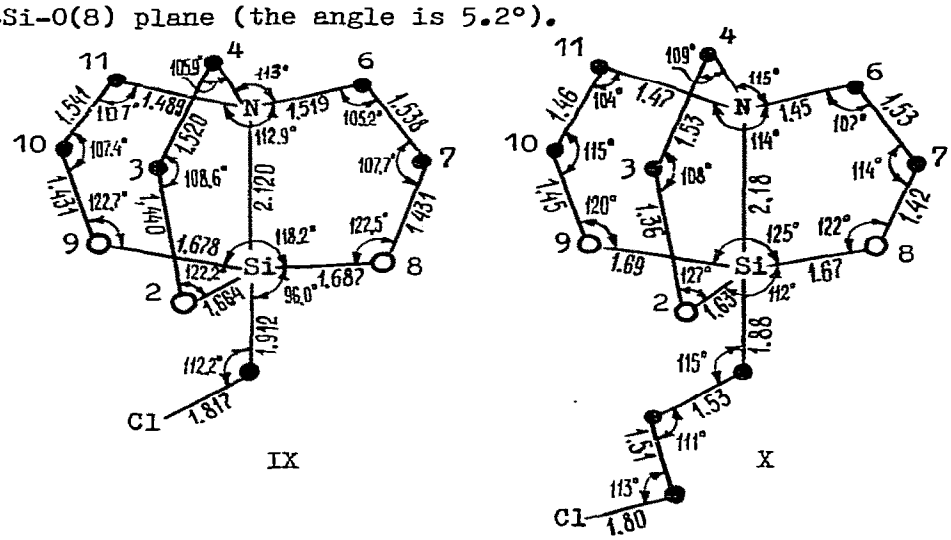


Fig. 4

Introduction of an electron-withdrawing substituent (chlorine atom) into the methyl group of 1-methylsilatrane does not affect the silatrane cycle geometry much. However, the Si←N bond shortens in this case by 0.06 Å thus amounting to 2.12 Å, the Si-C bond (1.912 Å) lengthening by 0.04 Å (Table 2). The intramolecular Si — Cl distance (3.1 Å) in 1-(chloromethyl)silatrane may indicate an interaction between the Cl and Si atoms ("α-effect").

In going from 1-chloromethylsilatrane to 3,7-dimethyl-1-chloromethylsilatrane the geometry of the Si coordination po-

lyhedron and the length of the Si—N bond hardly change (115a). In the 3,7-dimethyl-1-chloromethylsilatrane molecule (Table 2) only larger valence angles of the carbon atoms in the silatrane skeleton are observed: the N-C-C and C-C-O angles are 112° and 114°, respectively, those in 1-chloromethylsilatrane being 107° and 108°, respectively. Thus, the introduction of methyl groups into positions 3 and 7 of the silatrane cycle does not affect the degree of Si←N interaction considerably.

If the chlorine atom is separated from the silicon by more than one methylene group (116,117), the influence of the chlorine atom on the geometry of cyclic system is negligible as the inductive effect via the carbon chain diminishes quickly (Fig. 4). Unlike 1-chloromethylsilatrane, the interatomic Si←N distance and the Si-C bond length in 1-(3'-chloropropyl)silatrane are close to those in 1-ethylsilatrane, being 2.18 and 1.88 Å, respectively.

In the 1-chloromethyl-3-homosilatrane molecule (Fig. 5, XII) the interatomic Si—N distance in considerably longer

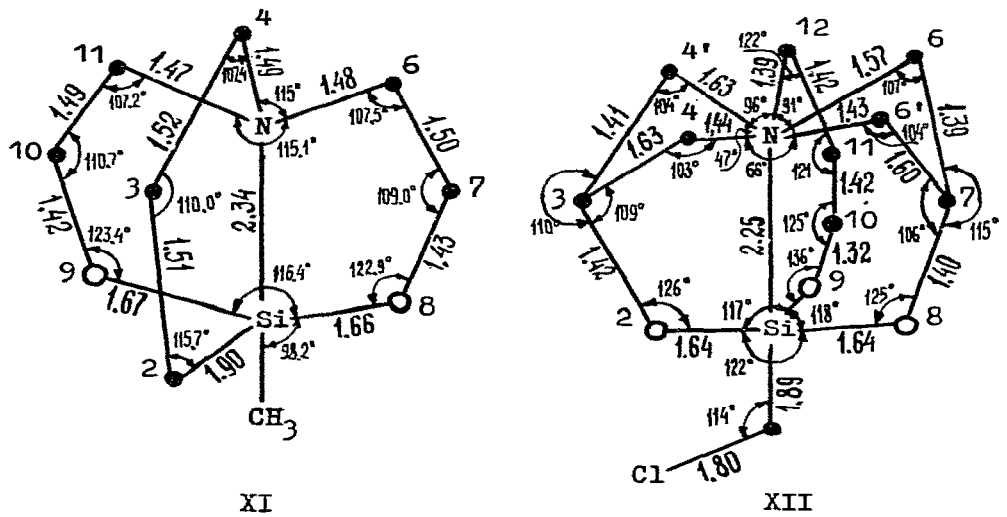
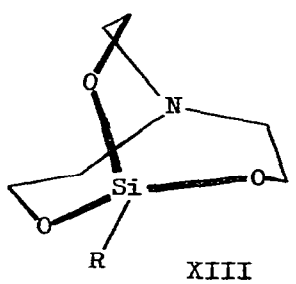


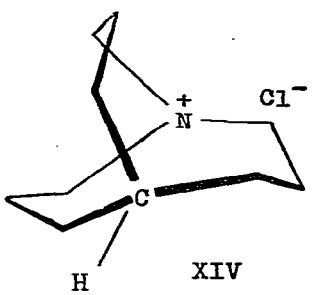
Fig. 5

(2.25 Å), whereas the Si atom is displaced out of the equatorial plane of the three oxygen atom by 0.17 Å. In this case, the lengthening of the Si←N distance results from a flattening in the NC_3 group, i.e., from nitrogen atom displacement by 0.11 Å toward the equatorial plane defined by C(4), C(6) and C(12) (118).

In 1-silatranyl-trans-bis[(dimethylphenyl)phosphino]-chloroplatinum, $Cl[C_6H_5(CH_3)_2P]_2PtSi(OCH_2CH_2)_3N$ (XIII), the interatomic Si←N distance is 2.89 Å, that is much longer than in normal silatranes (119,120). The NC_3 group has, in fact, a planar configuration and the $PtSiO_3$ group is tetrahedral. This seems to be caused by a strong +I-effect and a more bulky substituent at the silicon atom. The bond lengths and valence angle values in molecule XIII are listed in Table 2. The relationship $r_{Si\leftarrow N} - \Delta = d \simeq 2.0$ Å deduced for silatranes (112) is not observed ($\Delta = 0.53$ Å, $d = 2.36$ Å). This is due to the absence of a transannular Si←N interaction. The nitrogen atom, as compared to its normal position in silatranes, is displaced by 0.36 Å to the C(4)-C(6)-C(11) plane and only 0.07 Å distant. In the three Si-O-C-C-N half-rings, the β-carbon atoms lie out of the plane rather than the α-carbon atoms as in normal silatranes. Furthermore, the valence angle values in compound (XIII) are slightly greater than those in normal silatranes. This is partially associated with the fact that molecule (XIII) is a system composed of eight-membered, rather than five-membered rings. Thus, compound XIII is related, according to its structure, to 1-azobicyclo[3.3.3]undecane hydrochloride, XIV (126) (Fig. 6).



XIII



XIV

R = $[C_6H_5(CH_3)_2P]_2PtCl$

Fig. 6

However, a similar conformation of the simplest silatranes does not occur in the crystalline state as studied by X-ray diffraction. In these molecules it is the α- rather than the β-carbon atoms that lie out of the five-membered half-ring planes. This is likely to be due to the short interatomic Si—N distance. In fact, with the Si—N distance longer than 2.3 Å, the boat-chair conformation (Fig. 7, XV) typical for

bicyclo[3.3.3]undecane system (XVI and XVII) is realized in 2-carbasilatranes (126-129).

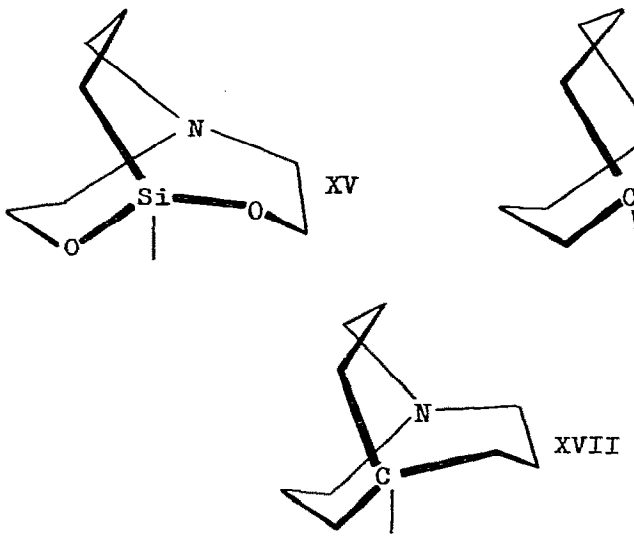


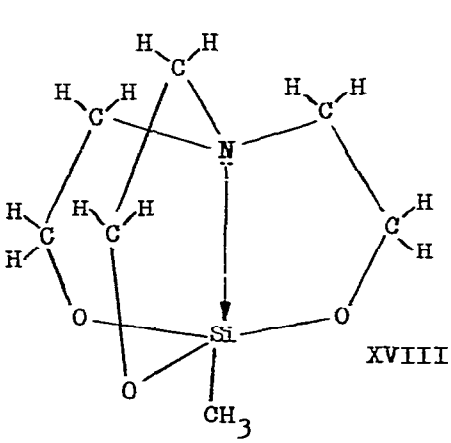
Fig. 7

Until recently many physico-chemical features of silatranes were explaned by the presence of the polar coordinate Si←N bond (5-19, 23-34) without considering some stereochemical factors, particularly, the existence of "Prelog strains" (134) in silatrane systems. These would cause the steric configuration of silatranes to resemble those of bicyclo[3.3.3]undecane systems, XVI and XVII (125-128) (Fig.7). Molecules of the compounds of this type have axial C_3-symmetry and may be considered as a system of three constituent eight-membered rings in the boat-chair conformation.

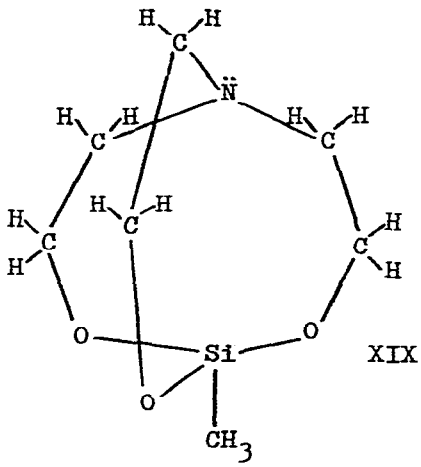
Dreiding's molecular models (135) of silatrane and related bicyclo[3.3.3]undecane systems show that the boat-boat conformation is not advantageous owing to intraannular repulsion of the circular hydrogen atoms. It might be suggested that the H-H repulsion interactions do not permit the silatrane molecules to occur in the exo-form. Thus, introduction of an additional CH_2-group into the silatrane skeleton produces strong Prelog strains in the enlarged half-ring, i.e., the N-C-C and C-C-C valence angles increase to 122° and the C-N, C-C and C-O bond lengths decrease (118) (Table 2). However, before quantitative calculations were carried out (130-133), the suggestion that conformational factors were of great importance in understanding the struc-

ture and some properties of silatranes (10,15,112) was not confirmed.

Calculations of the conformational energy (130, 131) of the endo- and exo-forms of the 1-methylsilatrane molecule (Fig. 8, XVIII and XIX) carried out by Westheimer's method have shown that a change in the type of silicon hybridization in XVIII from sp^3 to sp^3d is accompanied by a comformational energy gain equal to 11.4 kcal/mol (130).



XVIII



XIX

Fig. 8

The calculation for XVIII was done for a fixed Si—N distance of 2.19 Å. The energy barrier between the endo- and exo-forms does not exceed 1.6 kcal/mol. Without deformation of the valence angle and bonds, the endo- and exo-structures exist only within narrow limits of interatomic Si—N distance, 2.35-2.45 and 2.9-3.0 Å, respectively. According to the calculations, the exo-form of the 1-methylsilatrane molecule is unstable and should transform spontaneously to the stable endo-form (130). The conformational energy relations obtained for these forms have been used to confirm the previous conclusion that the nitrogen atom in silatranes can be involved only with difficulty in the intermolecular complexation interactions (130). However, the lack of necessary data does not allow one to consider the strain caused by the Si←N bond (131). Therefore, the conclusion that the formation of the transannular Si←N bond is accompanied by a decrease in the conformational energy of the endo-form has turned out to be erroneous.

Calculations undertaken with allowance for Si←N interaction have shown that the conformational energy of the real endo-form is higher by 1.4 kcal/mole than the minimum energy

of the exo-form. Thus, the more stable endo-structure of silatranes may be only explained by a considerable contribution from the energy of the transannular Si←N bond formation to the total energy of the molecule (131). At the same time, the conclusion (132) on the sufficient conformation energy gain (8.5 kcal/mole) when the silicon hybridization in the endo-form changes from tetrahedtral to trigonal-bipyramidal helds true.

The strain energy dependence on the interatomic Si—N distance has been studied for 1-methyl-2-carbasilatrane (132). The minimum conformational energy of its endo-form corresponds to an Si—N distance equal to 2.31 Å (19.4 kcal/mole) and 2.41 Å (32.4 kcal/mole) for the models with postulated Si atom coordination numbers of 5 and 4, respectively. The en endo-form is most stable with the Si—N distance equal to 3.10 Å and is least strained (1.8 kcal/mole). As the 1-methyl-2-carbasilatrane molecule exists only in the endo-form, it may be stable only when the energy of transannular interaction exceeds 17.6 kcal/mole.

The conformational calculations (130-132) describe well even fine details of the steric structure of silatranes. In particular, according to X-ray (112) and NMR studies, these have proven the non-planar structure of five-membered rings and a low inversion barrier. Moreover, they have shown that asynchroneous inversion of the three-fold cyclic skeleton of the 1-methyl-2-carbasilatrane molecule is energetically disadvantageous owing to a high barrier of the latter and a considerable increase (by 10 kcal/mole) in the strain energy of the asymmetric configuration.

The optimized data on the steric structure of silatranes (130,131) have been used for a quantum-chemical calculation (CNDO/2) of total energies of the silatrane molecule (133). The endo-form has turned out to be energetically more advantageous than the exo-form. The bond energies of the silatrane molecule do not change, in fact, in going from the endo- to the exo-form. The Si—N bond energy, however, does change. Its value for the endo-form is close to 25 kcal/mole, that for the exo-form is by one order of magnitude lower (1.6 kcal/mole). Thus, the conclusion (131,132) on the determining contribution of the Si—N interaction to stabilization of the endo-form is quantitatively confirmed. The quantum-chemical calculation (133) reveals also that the electronic density

"transfer" from the nitrogen atom is about 0.25ē for the endo-form of silatranes. Thus, the peculiar features of the silatrane structure are associated with Si←N interaction. The conformational effects, however, characteristic of bicyclo-[3.3.3]undecane systems are essentially affected by the Si←N hybridization character determined by the transannular interaction of the two atoms.

2. Physico-chemical Parameters

Most silatranes known are colorless, crystalline substances with high melting points (Tables 3-11). They usually show high thermal stability which enables them to be sublimated and distilled in vacuum without decomposition, sometimes at atmospheric pressure. Nearly all silatranes are readily soluble in chloroform and dimethylformamide. Most of them are almost insoluble in water, diethyl ether and n-hexane.

Table 3

1-Hydro- and 1-Halosilatranes, $XSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$

X	n	M.p.,°C	Ref.
H	3	256-258	85,86
		253-256	9,15
	2	207-208	85,86
	1	158-160	85,86
	0	115-116	85,86
		175-183	15
F	3	subl.	15
		>200	91
	0	212-214	15
Cl	3	>200 decomp.	91,96
	0	305-306	15
Br	3	>200 decomp.	91,96
	0	233-237	15
Cl*	-	>300	79

* 1-Chloro-3,4,6,7,10,11-tribenzosilatrane

Some silatranes are polymorphous. Thus, 1-methylsilatrane exists in two crystalline modifications (5,136). At normal temperature the β-modification having a melting point of 142° is stable. At 115.2° it converts into the α-modification with a melting point of 152.2°. Thus, 1-methylsilatrane has a double melting temperature. After crystallization from xylene it melts at 142-143° and at 151.5-152.5 after rapid cooling of the melt (5). On crystallization of 1-methylsilatrane in some solvents poorly-shaped crystals having a melting point of 141.7° (β^*-modification) are formed (136). The transition from the β-crystalline form to the α-modification is slow and occurs, according to thermographical data, within the 117-140° range. However, the β- and β^*-crystalline structures are identical and differ from that of α-modification of 1-methylsilatrane (136).

1-Phenylsilatrane may exist in three crystalline modifications, i.e., orthorhombic (α,β) and monoclinic (γ), with melting points of 210.3-211.3, 208 and 207°C, respectively (108,113,114). 3,7-Dimethyl-1-phenylsilatrane also has been isolated as two modifications, needles with a melting point of 90.4-91.4° and scaly crystals, m.p. 94.8-95.8°.

Some carbofunctional 1-alkylsilatrane derivatives containing fluorine, sulfur and phosphorus atoms are viscous liquids distilled easily in vacuum (Table 12). Among 2-carbasilatranes, $XSi(OCH_2CH_2)_2(CH_2CH_2CH_2)N$, there are some compounds which are liquids (X = C_2H_5, C_2H_5O) (Table 12). All liquid silatranes dissolve easily in water even in diethyl ether, heptane and carbon tetrachloride. The molecular refraction values for liquid silatranes are consistent with the data calculated from group increments within 0.1-1.0 ml/mole precision (Table 12).

$HSi(OCH_2CH_2)_3N$ and its C-methylsubstituted derivatives, $HSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$ (Table 3) are white, fibrous, crystalline compounds resembling glass cotton. They are soluble in polar organic solvents and water, in which they hydrolyze readily. 1-Halosilatranes (Table 3) have high melting points and are poorly soluble in polar solvents. Some of them show rather high solvolytic stability. Thus, 1-chloro- and 1-bromo-3,7,10-trimethylsilatranes may be recrystallized from alcohols with a negligeble loss (15).

Among colorless, crystalline 1-organosilatranes (Table 4),

Table 4

1-Organoxysilatranes, $ROSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$

R	n	M.p., °C	Refer.
H	3	205-210	15,71
CH_3	3	155-156	10,31
C_2H_5	3	102-103	10,31
		35-37	8,28
		100-102	9
	2	64-65	
	0	81.7-82.2	27
$n\text{-}C_3H_7$	3	79-80	10,31
$(CH_3)_2CH$	3	129.5-131	10,31
$n\text{-}C_4H_9$	3	113-113.5	10,30,31
$(CH_3)_2CHCH_2$	3	99-100	10,30,31
$(CH_3)_3C$	3	146.5-147.5	10,30,31
$CH_3CH_2(CH_3)CH$	3	131-132	10,30,31
$n\text{-}C_5H_{11}$	3	102.5-103.5	10,30,31
$(CH_3)_2CHCH_2CH_2$	3	134.5-136	10,30,31
$(CH_3)_3CCH_2$	3	178-180	10,30,31
$n\text{-}C_6H_{13}$	3	82-83	10,30,31
$CH_3(CH_2)_{13}$	3	80-81	
$HO(CH_2)_4$	3	108-110	72
$CH_3C(O)$	3	173-174	94
		172-175	
$CH_3CH_2C(O)$	3	190-192	94
C_6H_{11}	3	193.5-195.5	10,30,31
$C_6H_5CH_2$	3	190.5-192	10,30,31
C_6H_5	3	228-229.5	10,32
$2\text{-}CH_3C_6H_4$	3	218-219.5	10,32
$3\text{-}CH_3C_6H_4$	3	162.5-163.5	10,32
$4\text{-}CH_3C_6H_4$	3	188-189	10,32
$4\text{-}(CH_3)_3CC_6H_4$	3	252-253	10,32
$5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3$	3	217.5-218.5	10,32
C_6F_5	3	263-264	92
$4\text{-}ClC_6H_4$	3	166-167	10,32
$2,4,6\text{-}Cl_3C_6H_2$	3	230-230.5	10,32
$4\text{-}CH_3OC_6H_4$	3	183-184	92
$4\text{-}CH_3OOCC_6H_4$	3	178-180	33
$4\text{-}C_3H_7OOCC_6H_4$	3	141-145	33

Table 4 (continued)

$4\text{-}C_2H_5OOCC_6H_4$	3	162-164	33
$C_6H_5C(O)$	3	221-222.5 240	94 15
$2\text{-}O_2NC_6H_4$	3	233-234	10,32
$3\text{-}O_2NC_6H_4$	3	197.5-198.5	10,32
$4\text{-}O_2NC_6H_4$	3	182.5-184	10,32
$2\text{-}C_{10}H_7$	3	184.5-185.5	10,32
$C_{10}H_{19}$ (menthoxy)	3	152-154	9
$2\text{-}C_4H_3O$	3	245-246	75
C_5H_4N	3	171-173	94
$N_{1/3}CH_2CH_2O$*	3	260	15,43
$(CH_3)_2HSi$	3	98	15
$(CH_3)_3Si$	3	156	15
$CH_2{=}CH(CH_3)_2Si$	3	127	15
$C_6H_5(CH_3)HSi$	3	108	15
$(CH_3)_2C_6H_5Si$	3	83	15
$CH_3(C_6H_5)_2Si$	3	130	15
$(C_6H_5)_3Si$	3	256	15

* $N[CH_2CH_2OSi(OCH_2CH_2)_3N]_3$

only compounds with R = $O_2NC_6H_4$ have a yellow color. 1-Alkoxysilatranes are readily soluble in water and most organic solvents ($CHCl_3$, CCl_4, acetone, dioxane, benzene, ethyl acetate), but unsoluble ib cold petroleum ether. Only 1-methoxysilatrane and 1-n-tetradecoxysilatrane are soluble in the latter (31).

1-Aroxysilatranes are soluble only in chloroform, dimethylformamide and acetonitrile. In other solvents, including water, 1-aroxysilatranes are much less soluble than 1-alkoxysilatranes (32).

Unlike 1-organylsilatranes, 1-organoxy derivatives are decomposed comparatively fast by moisture of the air. 1-Acyloxysilatranes display the least hydrolytic stability (15,94).

1-Alkyl- and 1-arylsilatranes, $RSi(OCHR'CH_2)_3N$, are soluble in halogenated hydrocarbons, nitrobenzene, dimethylformamide and acetonitrile. The nature of the hydrocarbon substituent R influences physical properties of such silatranes. Thus, 1-methylsilatrane is practically insoluble in diethyl ether, in contrast to its nearest homologs (R = C_2H_5,

Table 5

1-Organylsilatranes, $XSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$

X	n	M.p., °C	Refer.
$CH_3(\alpha)$	3	151.5-152.5	5,10,83
		151-153	9,125
		152.2	9,125
$CH_3(\beta)$	3	123-125	9,125
		141.7	9,125
		142-143	5,10,83
		139.5-142	28
CH_3	2	95-97	9
	0	132-133	
C_2H_5	3	132-133.5	5,10,15,83
		134-135	27
	0	52.5-53.5	
$CH_3CH_2CH_2$	3	84	74,75
$(CH_3)_2CH$	3	106.5-107.5	5,10,83
CH_2CH_2CH	3	143-144	
$CH_2=CH$	3	165-166.2	5,10,83
		166.2-167.4	27
		163-165	9
	0	103.3-104.5	27
$CH\equiv C$	3	248-250	
$C_6H_5C\equiv C$	3	275	
$C_6H_5CH=CH$	3	238-240	
$C_6H_5CH_2CH_2$	3	107-108	
$C_6H_5CH_2$	3	256-257	176
$4\text{-}FC_6H_4CH_2$	2	225	176
$3\text{-}FC_6H_4CH_2$	3	210.5-211	176
$C_6H_5(CH_3)CH$	3	192-194	9
C_6H_5	0	133-134	10
		134-135	176
	1	86.5-89	5,10,83
	2	95-96	10
	3	203.6-204.2	8
		208-209	9
		210.3-211.3	5,10,83,84
		209-210	176
$4\text{-}ClC_6H_4$	3	233-235	
$3\text{-}ClC_6H_4$	3	203-203.5	205
$4\text{-}FC_6H_4$	3	195-196.5	175
$4\text{-}CH_3C_6H_4$	3	195-195.5	205
$3\text{-}CH_3C_6H_4$	3	148.5-149.5	
$2\text{-}CH_3C_6H_4$	3	162-164	

Table 5 (continued)

$4\text{-}CH_3OC_6H_4$	3	192-193	205
$4\text{-}ClCH_2C_6H_4$	3	191.3-192.3	
$4\text{-}FCH_2C_6H_4$	3	181.5-182.5	
$4\text{-}CF_3C_6H_4$	3	172-173	
$3\text{-}O_2NC_6H_4$	3	161-161.5	110,205
$(CH_3)_3SiCH{=}CH$	3	151	
$C_6H_5(CH_3)_2SiCH{=}CH$	3	119-120	
$CH_3[(CH_3)_2SiCH{=}CH]_2$	3	123-124	
$(CH_3)_3SiC{\equiv}C$	3	240	
$HC{\equiv}C(CH_3)_2SiCH{=}CH$	3	152	
1,3-diphenyl*	2	165	15
1,4-diphenyl**	2	270	15
$C_{18}H_{37}$	3	85-86	9
C_2H_5***	2	117	216
C_6H_5****	2	119	216
C_6H_5*****	2	108	216

*$C_6H_5Si(OCH_2CH_2)_2[OCH(C_6H_5)CH_2]N$
**$C_6H_5Si(OCH_2CH_2)_2[OCH_2CH(C_6H_5)]N$
***$C_2H_5Si(OCH_2CH_2)_2[OCH(CH_2Cl)CH_2]N$
****$C_6H_5Si(OCH_2CH_2)_2[OCH(CH_2Cl)CH_2]N$
*****$C_6H_5Si(OCH_2CH_2)_2[OCH(CH{=}CH_2)CH_2]N$
Here and in the following tables the data with no references are reported by the present authors

iso-C_3H_7). As a rule, 1-arylsilatranes are less soluble in most solvents than 1-alkylsilatranes. They both are rather stable to moisture and oxygen of the air. Noticeable hydrolytic decomposition of 1-methylsilatrane is observed only after 28 days (when kept in the open vessel).

The solubility of 1-(haloalkyl)silatranes, $X(CH_2)_nSi(OCHRCH_2)_3N$, where X = F, Cl, Br, I; R = H, CH_3, CF_3; $n \geq 1$ (Tables 6,7), in alcohols, aromatic and chlorinated hydrocarbons increases markedly with the number of methylene groups in the hydrocarbon group. Thus, 3,7,10-trimethyl- and 3,7,10-trifluoromethyl-1-(4'-chlorobutyl)-silatranes are readily soluble in water, benzene and even in n-hexane, whereas 1-chloromethylsilatrane is markedly soluble only in chloroform. Nearly all halomethylsilatranes have higher melting

Table 6

Exo-Halosubstituted 1-Alkylsilatranes, $XSi(OCH_2CH_2)_n\ OCH(CH_3)CH_2\ 3\text{-}n^N$

X	n	M.p., °C	Refer
$ClCH_2$	0	102-103	39,41,43
	1	22-123	41,43
	2	86-87	41,43
	3	215-217 222-223	39,40,43 36a
Cl_2CH	0	161-162	41,43
	1	144-145	43
	2	175-176	43
	3	266-267 265-268	39,43 36a
$BrCH_2$	3	200-201	39,46
Br_2CH	3	260	
ICH_2	0	95-96	
	1	73-75	39,44,45
	2	115-116	39,44,45
	3	190-191 187-188	39,44,45 36a
CH_3CHCl	0	79-80	43
	1	85-86	43
	2	92-93	43
	3	156-157	36a,39,43
$F(CH_2)_3$	0	60-61	47,70
		154/2*	
	3	71-72	47,70
$CF_3(CH_2)_2$	0	58-60	47,70
		136/1*	
	1	32-35	47,70
		150/4*	
	2	36-38	47,70
		122/1*	
	3	107-108	39,47,70
$Cl(CH_2)_3$	3	130-131 129-131	39,40 36a
$Cl(CH_2)_4$	0	73-74	41,43
$Br(CH_2)_3$	3	141-142	35,42
$I(CH_2)_3$	3	167-168 166-167	35,41 36a

Table 6 (continued)

CF_3CH_2CHI	3	119.5-120.5	
$C_3F_7CH_2CHI$	3	137-138.5	
$C_6F_{13}CH_2CHI$	3	135-136	
$CH_2=CCl$	3	170-171	42
$Cl_2C=CH$	3	110-112	42
ClCH=CH	3	142-143	42
ClCH=CCl	3	185-186	42

* B.p., °C/p, mm

points than the corresponding 1-(3'-halopropyl)-silatranes (Table 6). The melting point of halomethylsilatranes (n = 1) falls as the atomic number of the halogen increases (Cl>Br>I) and that of 1-(3'-halopropyl)silatranes (n = 3) rises in the same order (F<Cl<Br<I).

3'-Fluorosubstituted 1-propylsilatranes are soluble even in lower alcohols and diethyl ether, whereas 2-polyfluoroorganyl-1-iodoethylsilatranes are soluble only in chloroform, acetone, dimethylformamide.

Introduction of methyl- and trifluoromethyl groups into the silatrane skeleton considerable changes their physical properties (70,213). All C-methyl- and C-trifluoromethyl substituted silatranes have higher melting points and better solubility in halogenated and aromatic hydrocarbons than the corresponding unsubstituted compounds (Tables 3-8,12).

1-Mercaptoalkyl- (61), 1-acetylthioalkyl- (56) and 1-thienylsilatranes (64) have a specific unpleasant odor. They are hardly soluble in water, benzene, heptane, CCl_4. Triorganyl (silatranyl)phosphonium iodides are readily soluble in chloroform, alcohol, dimethylformamide.

1-Aroxyalkyl-, 1-organylthioalkyl- and 1-acyloxyalkylsilatranes are stable to air moisture, have higher melting points and are more difficult to dissolve in alcohols, aromatic hydrocarbons and heptane than 1-aroxy- and 1-acyloxysilatranes (Table 8).

3,10-Dimethyl-3,4-benzosilatranes, $XSi[OCH(CH_3)CH_2]_2(OC_6H_4)N$, have been obtained as transparent viscous oils which are easily distilled in vacuum (Table 9). After storage for months, most of them are converted into

low-melting, crystals which are readily soluble in organic solvents such as $CHCl_3$, alcohols, aromatic hydrocarbons, etc. Tribenzosilatranes have extremely high melting points (>250°) and some of them (with X = C_6H_5, CH_3COO) do not melt on heating to 300°C.

2-Carbasilatranes (Table 10) have lower melting points than the corresponding silatranes. Almost all of them are easily soluble in diethyl ether, pentane, hexane and water.

Table 7

Ezo-trifluoromethylsubstituted Silatranes, $XSi(OCH_2CH_2)_n[OCH(CF_3)CH_2]_{3-n}N$

X	n	M.p., °C	B.p., °C/p, mm	n_D^{20}
CH_3	0	108-109		
	1	79-80		
	2	93-94		
$ClCH_2$	0	119-120		
	2	120-121		
CH_3CHCl	1	163-164		
	2	118-119		
$Cl(CH_2)_4$	0		137-138/1	1.4133
$CF_3(CH_2)_2$	2	63-63.5	123/1	1.4218
C_6H_5	2	133-133.5		

1-Substituted 2,8,9-triazasilatranes (Table 10) are low-melting, colorless, crystalline compounds which are rather sensitive to moisture (81,82,137). They can be distilled in high vacuum and are soluble in most organic solvents (81).

3-Homosilatranes (Table 10) are monomers, as are other described types of silatranes. They can be distilled and sublimed in vacuum and dissolve readily in halogenated hydrocarbons, ethanol and xylene. Melting points of 3-homosilatranes are lower than those of the corresponding silatranes and close to those of the corresponding 1-substituted 3,7 - dimethylsilatranes.

In all the silatranes investigated the replacement of hydrogen atoms in the atrane ring by methyl groups reduces melting points and increases solubility.

Table 8

Exo-carbofunctional 1-Alkylsilatrane Derivatives, $X(CH_2)_mSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$

X	m	n	M.p., °C	
HS	1	3	134-134.5	64
	2	3	133-134	64
	2	2	162-163/1*	
	3	3	95-96	64
			70	65
NC	2	3	-	65
			190-191	39,36a
CH_3O	1	3	118-119	58
CH_3S	1	3	134-135	
NCS	1	3	197-198	97
			170-171	39,56
	3	3	96-97	56
C_2H_5S	1	3	166-168	66
	1	2	72-73	66,97,214
			183-185/1*	
	1	1	185-186/1.5*	
	1	0	78-79	66,97,214
			156-157/1*	
	2	3	81-82	66,214
	2	2	37	
			195-196/1.5*	
	2	0	34-35	66
			172-173/1.5*	
	3	3	68-69	39,97,124
C_3H_7S	1	3	149-150	66
	2	3	73-74	
C_4H_9S	1	3	83-84	66,214
	3	3	48-49	
$(CH_3)_2CHCH_2S$	1	3	126-127	66
$(CH_3)_3CS$	1	3	201-202	66,214
$CH_2=CHCH_2S$	1	3	165-166	66,214
C_6H_5O	1	3	167-168	39,58
	3	3	108-109	
$4\text{-}CH_3C_6H_4O$	1	3	206-207	
$2\text{-}CH_3C_6H_4O$	1	3	159-160	
$2\text{-}CH_3OC_6H_4O$	1	3	142-143	39,58
	3	3	95-96	39,58
$4\text{-}FC_6H_4O$	1	3	167-168	
$4\text{-}ClC_6H_4O$	1	3	150-151	

Table 8 (continued)

4-BrC_6H_4O	1	3	171-172	
4-IC_6H_4O	1	3	197-198	
1-$C_{10}H_7O$(1-naphthoxy)	1	3	62	66
C_6H_5S	1	3	245-246	39,66
	1	2	114-116	97
	2	3	110-111	
4-$CH_3C_6H_4S$	1	3	199-200	66
1-$C_{10}H_7S$	1	3	204-205	66
$C_6H_5CH_2S$	1	3	150-151	66
	1	2	116-117	66
	1	1	99-100	66
C_4H_4S(5-thienyl)	0	3	221-222	68,69
2-ClC_4H_3S	0	3	232.5-233.5	68,69
2-BrC_4H_3S	0	3	233-234	68,69
2-$CH_3C_4H_3S$	0	3	190-192	68,69
2-NCC_4H_3S	0	3	143-146	68,69
$HOCH_2CH_2S$	1	3	168-169	67
CH_3OOCCH_2S	1	3	115-116	
	2	2	50-51	
			225*	
	2	0	80-81	
$C_2H_5OOCCH_2S$	1	3	105-106	
$CH_3C(O)S$	1	3	210-211	39,97
	2	3	125-127	
	3	3	70-71	
CH_3COO	2	3	150-151	
$CH_2=CHCOO$	1	3	148-151	49
$CH_2=C(CH_3)COO$	3	3	54	65
C_6H_5COO	1	3	185-186	
4-$CH_3C_6H_4COO$	1	3	150-151	59
4-$CH_3OC_6H_4COO$	1	3	156-157	
2-$CH_3OC_6H_4COO$	1	3	165-168	
4-FC_6H_4COO	1	3	190	
4-ClC_6H_4COO	1	3	193-194	59
4-BrC_6H_4COO	1	3	174-175	59
4-$O_2NC_6H_4COO$	1	3	193	
2-$CH_3C_6H_4OCH_2COO$	1	3	147.5-149	
4-Cl-2-$CH_3C_6H_3OCH_2COO$	1	3	123-125	
4-$FC_6H_4OCH_2COO$	1	3	140-141	
2,4-$Cl_2C_6H_3OCH_2COO$	1	3	155-157	
3-$C_8H_6NCH_2COO$	1	3	197-199	decomp.

	3	3	147-149 decomp.	
	1	0	245-246	
H_2N	3	3	87.2-87.9	27
			84-87	36
			87.5-88.5	39
$(C_2H_5)_2N$	1	3	82-83	35
C_6H_5NH	1	3	194.5-197	49
$H_2N(CH_2)_2NH$	3	3	123-125	36
$\overbrace{CH_2CH_2N}$	2	3	177	216
$\overbrace{CH_2(CH_2)_2CH_2N}$	1	3	128-130	38
	3	3	101-103	38
$\overbrace{CH_2(CH_2)_3CH_2N}$	1	3	156-157	35,38
	3	3	119-120	35
$\overbrace{CH_2(CH_2)_4CH_2N}$	1	3	82-84	38
	3	3	91-92	38
C_6H_5CONH	3	3	178-179	35
$C_8H_4O_2ClSNH$	3	3	226-228	104
$2\text{-}CH_3C_6H_4O_2SNH$	1	3	144-145	49
$[CH_3(C_2H_5)_2N]I$**	1	3	218-220	35
	3	3	215-217	35
$[(CH_3)\overbrace{CH_2(CH_2)_2CH_2N}]I$**	1	3	217-218	35
$[(CH_3)\overbrace{CH_2(CH_2)_3CH_2N}]I$**	1	3	227-229	35
NNC(Cl)CHCHCNH	3	3	135	216
$CH_3CON(C_4H_9)$	1	3	136	216
CH_3CONH	3	3	142	216
$2\text{-}C_4H_3ON_2S$	1	3	265	97
$(CH_3O)_3SiCH_2S$	2	1	51-52	97
	2	0	58-60	97
$(C_2H_5O)_2P(O)$	1	3	72-73	39,55,98,99
	1	2	239-240/3*	
	1	0	200-201/1*	
	3	3	51-53	39,55,98,99
	3	0	184-186/0.12*	55,99
$[(CH_3)_2CHO]_2P(O)$	1	3	63-64	55,98
	3	3	10-11	98
			165-168/0.1*	
$[(C_2H_5)_3\overset{+}{P}]I^-$	1	3	167-168	100
$[(C_3H_7)_3\overset{+}{P}]I^-$	3	3	99-100	100
$[(C_6H_5)_3\overset{+}{P}]I^-$	1	3	36- 37	100
	1	0	181-182	100

* B.p., °C/p, mm

** Methiodides of siletranes having the nitrogen atom in the substituent

Table 9

1-Substituted 3,4-Benzo- and 3,4,6,7,10,11-Tribenzosilatranes, $XSi(OC_6H_4)_n(OCHRCH_2)_{3-n}N$

X	R	n	M.p., °C	B.p., °C/p, mm	Refer.
Cl		3	>300 subl.		79
CH_3	CH_3	1	63-64	128-131/2	
CH_3		3	289-290	-	79
CH_2=CH		3	273-275		79
CH_3O		3	280-283	-	79
$ClCH_2$	CH_3	1	71-73	178-179	34
Cl_2CH	CH_3	1	-	222-223/4	34
CH_3CHCl	CH_3	1	-	163-164/1.5	34
$ClCH_2(CH_2)_2$	CH_3	1	-	192-194/3	34
CH_3COO		3	>300 subl.		79
C_6H_5	H	1	145		15
C_6H_5		3	>300 subl.		78,79
4-$CH_3C_6H_4$		3	279-280		166
C_6H_5O		3	230-232		79

Table 10

Silatrane Analogs

X	R	M.p., °C	B.p., °C/p, mm	Refer.
		$XSi(OCHRCH_2)_2(CH_2CH_2CH_2)N$		
CH_3	R	57-58	106-107/5	89,90
		60-61	74-78/0.8	87
			94/0.3	45
C_2H_5	H	-	102/3	89,90
C_6H_5	H	61-61.5		89,90
C_2H_5O	H	52.5-54.5	133-135/2	89,90
		51-54	110-117/0.5	87
C_2H_5O	CH_3	-	120/2	89,90
			101-104/0.9	84
		$XSi(OCHRCH_2)(OCH_2CH_2CH_2)N$		
CH_3	H	101-102		138
CH_3	CH_3	115-116		76,77

Table 10 (continued)

$ClCH_2$	H	120		118,138
$CH_2=CH$	H	66-67		138
$CH_2=CH$	CH_3	47-48		76,77
C_6H_5	H	55		138
C_6H_5	CH_3	99-100		76,77
$3\text{-}ClC_6H_4$	H	65		138
$3\text{-}ClC_6H_4$	CH_3	60-61		76,77
$4\text{-}ClC_6H_4$	H	110-112		138
$4\text{-}ClC_6H_4$	CH_3	101		76,77
$4\text{-}BrC_6H_4$	H	132-134		138
$4\text{-}BrC_6H_4$	CH_3	92-93		76,77
CH_3O	H	83-85		138
CH_3O	CH_3	75		76,77
C_2H_5O	CH_3	37		76,77
C_6H_5O	CH_3	88		76,77
$2\text{-}C_{10}H_7O$	CH_3	139		76,77
		$XSi(OCH_2CH_2)_2(OCOCH_2)N$		
CH_3		197-202		75
C_2H_5		130-132		75
C_4H_9		135-136.5		75
$CH_2=CH$		121 decomp.		75
$C_6H_5CH_2$		213-215		75
$4\text{-}ClC_6H_4CH_2$		152-154		75
C_6H_5		137-138		75
$3\text{-}CH_3C_6H_4$		171-172		75
$3\text{-}CF_3C_6H_4$		135-137		75
$4\text{-}FC_6H_4$		185-186		75
$3\text{-}ClC_6H_4$		165-167		75
$4\text{-}ClC_6H_4$		202-203		75
		$XSi(NHCH_2CH_2)_3N$		
H		50-55	110/0.02	81
		51-55		137
CH_3		50-54	115/0.1	81
		57-60		137
C_2H_5		47-48		137
$CH_2=CH$		42-44	110/0.05	81
		44-45		137
C_6H_5		90-93	149/0.05	81,82,137

Distortion of the symmetry of the silatrane skeleton caused by the insertion of a methylene group (3-homosilatrane) or by the replacement of one of the oxygen atoms by a methylene group (2-carbasilatrane) affects the solubility and the physical state of the compound more strongly than the introduction of substituents such as CH_3, CF_3, into the skeleton or the condensation of the latter with the benzene ring.

Disilatranoxanes (Table 11) are thermally stable and can be distilled in vacuum. Bis(1-silatranyloxy)alkanes, $N(CH_2CH_2O)_3SiOROSi(OCH_2CH_2)_3N$, have high melting points (Table 11). They are soluble in water and hot dimethylformamide, from which they crystallize on cooling. Like bis-(1-silatranyloxy)polysiloxanes, these compounds show lower melting points and higher solubilities as the distance between two silatrane groups gets larger (Table 11).

Bis(1-phenyltribenzosilatrane), $[N(C_6H_4O)_2Si(C_6H_5)OC_6H_4-]_2$, sublimes without decomposition at 500°C.

The main physical constants of all known silatranes are shown in Tables 3-12.

3. Dipole Moments

The existence of the Si←N donor-acceptor bonding in silatranes was first confirmed by dipole moment measurements (10, 12, 137, 144). However, the data of previous investigations have been reviewed and critically analyzed (145-147,142,142a). Dipole moments, μ, of six silatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_3, $(CH_3)_2CH$, CH_2=CH, C_6H_5, C_2H_5O, C_6H_5O), were first measured in benzene solution at 25°C in 1965 (Table 13)(139)*. Tetrahedral values of C-N-C, Si-O-C and O-Si-O valence angles and moments of 0.37, 0.45, 1.54 and 0.74D for the C-H, C-N, Si-O and C-O bonds, respectively, were used in the calculations. The measured μ values for the silatranes studied (5.3-7.1D) exceed those calculated from the vector scheme for their exo-form (0.09-0.66D) (Fig.9, I). This exaltation of the dipole moments was attributed to the transannular Si←N bond (139).

The measured μ value for the silatrane skeleton was 5.2 ± 0.2D, its vector being directed from nitrogen to silicon. The

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* Total polarization was calculated using the Hedestrand method.

Table 11

Compounds Containing Two and Three Silatrane Groups

Compound	M.p., °C	Refer.
$[N(CH_2CH_2O)_3Si]_2O$	185-190	78
$\{N[CH_2CH(CH_3)O]_3Si\}_2O$	215/0.1*	15
$[N(C_6H_4O)_3Si]_2O$	450 subl.	79
$[N(CH_2CH_2O)_3SiOCH_2]_2$	>350 decomp.	72
$N(CH_2CH_2O)_3SiOCH_2$ $N(CH_2CH_2O)_3SiOCH(CH_3)$	264-267	72
$[N(CH_2CH_2O)_3SiOCH_2]_2CH_2$	290	72
$[N(CH_2CH_2O)_3SiOCH_2CH_2]_2$	243-247	72
$[N(CH_2CH_2O)_3SiOCH_2CH_2]_2CH_2$	255	72
$[N(CH_2CH_2O)_3SiO(CH_2)_3]_2$	208-210	72
$[N(CH_2CH_2O)_3SiOCH_2CH_2]_2O$	210	72
$[N(CH_2CH_2O)_3SiCH_2]_2S$	284-285	73
$\{N(CH_2CH_2O)_2[CH_2CH(CH_3)O]SiCH_2CH_2\}_2S$	204-205	
$N(CH_2CH_2O)_2[CH_2CH(CH_3)O]SiCH_2CH_2\backslash S$ $N(CH_2CH_2O)[CH_2CH(CH_3)O]_2SiCH_2CH_2/$	208-210	
$[N(CH_2CH_2O)_3Si(CH_2)_3]_2S$	163-164	73
$[N(CH_2CH_2O)_3SiO]_2Si(CH_3)_2$	240	15,71
$[N(CH_2CH_2O)_3SiOSi(CH_3)_2]_2O$	193-194	15,71
$[N(CH_2CH_2O)_3SiOSi(CH_3)_2O]_2Si(CH_3)_2$	139-140	15,71
$\{N[(CH_2CH_2O)_2(CH_2\dot{C}HO)]Si(OC_2H_5)\}_2$	254	15
$\{N[(CH_2CH_2O)_2(CH_2\dot{C}HO)]Si(C_6H_5)\}_2$	268	15
$[N(C_6H_4O)_2(\dot{C}_6H_4O)SiC_6H_5]_2$	500	78,79

* B.p., °C/p mm

Liquid Silatranes

Compound	B.p., °C/p,mm	n_D^{20}	d_4^{20}	ΔMR_D	Refer.
$CF_3(CH_2)_2Si(OCH_2CH_2)_2[OCH(CH_3)CH_2]N$	121-121.5/1	1.4393	1.2329	0.67	
$C_2H_5S(CH_2)_2Si(OCH_2CH_2)_2[OCH(CH_3)CH_2]N$	195-196/1.5	1.5150	1.1450	-0.27	
$C_2H_5S(CH_2)_2Si[OCH(CH_3)CH_2]_3N$	172-173/2	1.5045	1.1067	0.36	66
$(C_2H_5)_2P(O)CH_2Si(OCH_2CH_2)_2[OCH(CH_3)CH_2]N$	239-240/3	1.4832	1.2210	1.07	
$(C_2H_5O)_2P(O)CH_2Si[OCH(CH_3)CH_2]_3N$	229-230/4	1.4770	1.1800	-0.13	
$(C_2H_5O)_2P(O)(CH_2)_3Si[OCH(CH_3)CH_2]_3N$	184-186/0.1	1.4750	1.1234	-0.03	99
$C_2H_5Si(OCH_2CH_2)_2(CH_2CH_2CH_2)N$	102/3	1.4960	1.0958	0.85	89,90
$C_2H_5OSi(OCH_2CH_2)_2(CH_2CH_2CH_2)N$	120/2	1.4472	0.9855	0.4	89,90

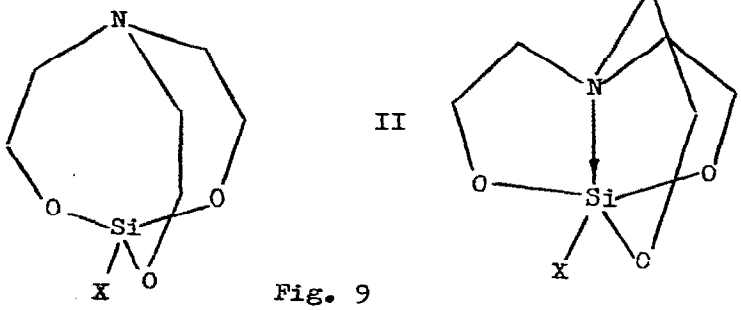


Fig. 9

calculated μ value for the exo-form was 0.9D and its vector was directed from silicon to nitrogen. The μ value calculated for the endo-form (Fig.9, II) without allowance for the transannular Si←N bond was 1.1D. Starting from this, the dipole moment of the coordinate Si←N bond in the endo-form was estimated to be 6.3D. If the electron transfer for the distance of N—Si (sp^3d) taken to be 1.84 Å, the dipole moment of the true coordinate Si←N bond is approximately 8.6 D. Due to this, the moment of the atrane skeleton $Si(OCH_2CH_2)_3N$ at the maximum transannular donor-acceptor interaction between the silicon and nitrogen atoms was evaluated to be 8.6-1.1 = 7.5 D. The lower measured dipole moment value for this group shows that the nitrogen electron pair transfer to the silicon atom is not complete (139).

Fairly high dipole moments are displayed also by silatrane analogs such as homosilatranes (4.7-7.5 D), boratranes (6 D), germatranes (6-3 D), and titanatranes (3 D)(10,12,137,138,142).

The independence of μ values on temperature has suggested a stronger coordinate Si←N bond in silatranes.

The comparatively high measured dipole moments of 1-organyl-2-carbasilatranes (4.2-4.9 D, Table 14) which exceed the calculated ones (0.17-0.84 D) also were attributed to the stable transannular Si←N bond. This bond is weaker than in silatranes, resulting in a lower exaltation of the dipole moments. The discrepancy between the measured (4.74-7.48 D) and the calculated (1.0-2.7 D) dipole moments for homosilatranes is explained in a similar way (Table 14).

In order to determine the influence of the replacement of hydrogen by methyl groups in positions 3-, 7-, and 10, the dipole moment of 3,7-dimethyl-1-phenylsilatrane was measured (141). A comparison between the measured values for this

Table 13

Dipole Moments of Si- and C-methyl-substituted Silatranes, $XSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$ at 25°C

X	n	μ,D obs.	μ,D vect.	Δμ,D	Solvent	Refer.
CH_3	3	5.30	0.66	4.64	C_6H_6	24,139
		7.57		6.91	$CHCl_3$	24,140
		5,64*		5,20		140
		5.46	4.08	1.38	C_6H_6	145
	0	4,92	4.08	0.84	C_6H_6	
C_2H_5	3	7.06			$CHCl_3$	24,140
$(CH_3)_2CH$	3	5.55	0.66	4.89	C_6H_6	24,139
$CH_2=CH$	3	5.88	0.5	5.38	C_6H_6	24,139
		7.38			$CHCl_3$	140
		6.04*				
		6.31	4.12	2,19	C_6H_6	
	0	5,64	4.19	1,52	C_6H_6	
C_6H_5	3	5.98	0.09	5.89	C_6H_6	139,24
		7.52			$CHCl_3$	24,140
		6.43*				140
	1	6.03	0.09	5,94	C_6H_6	141
C_2H_5O	3	6.29	0.49	5.80	C_6H_6	24,139
		8.31			$CHCl_3$	139
C_6H_5O	3	7.13			C_6H_6	24,139
		9.22			$CHCl_3$	24,140
		6.99*				24,140
$3\text{-}CH_3C_6H_4O$	3	9.01			$CHCl_3$	24,140
$4\text{-}(CH_3)_3CC_6H_4O$	3	8.66			$CHCl_3$	24,140
$5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3O$	3	8.34			$CHCl_3$	140
$4\text{-}ClC_6H_4O$	3	10.09			$CHCl_3$	24,140
$3\text{-}O_2NC_6H_4O$	3	11.45			$CHCl_3$	24,140
		9.71*				24,140
Cl_2CH	2	7.50	5.08	2.44	C_6H_6	145
	1	7,93	5.08	2.88	C_6H_6	145
	0	8.19	5.08	3.14	C_6H_6	145
CH_3CHCl	3	7.19	4.99	2.30	C_6H_6	145
	2	5.95	4.99	1.02	C_6H_6	145
	1	6.47	4.99	1.56	C_6H_6	145
	0	6.69	4.99	1.78	C_6H_6	145

Table 13 (continued)

ICH_2	0	6.77	4,85	1,99	CCl_4	145
$Cl(CH_2)_3$	3	6.99	6.34	2.03	CCl_4	146
$Br(CH_2)_3$	3	6.91	6.32	1.97	CCl_4	146
$I(CH_2)_3$	3	6.99	6.21	2.16	CCl_4	146
$C_2H_5SCH_2$	3	5.83	5.80	1.40	C_6H_6	146
	0	5.23	5.46	1.15	C_6H_6	146
$C_2H_5S(CH_2)_2$	3	6.66	6.28	1.76	C_6H_6	146
	0	6.31	5.75	1.94	C_6H_6	146
$\overline{CH_2(CH_2)_2\dot{N}CH_2}$	3	5.4			C_6H_6	38
$\overline{CH_2(CH_2)_3CH_2\dot{N}CH_2}$	3	5.56			C_6H_6	38
$\overline{CH_2(CH_2)_4CH_2\dot{N}CH_2}$	3	5.62			C_6H_6	38
$\overline{CH_2(CH_2)_2CH_2\dot{N}(CH_2)_3}$	3	5.23			C_6H_6	38
$\overline{CH_2(CH_2)_3CH_2\dot{N}(CH_2)_3}$	3	5.28			C_6H_6	38
$\overline{CH_2(CH_2)_4CH_2\dot{N}(CH_2)_3}$	3	5.08			C_6H_6	38

* measured in ethylacetate

compound and 1-phenylsilatrane showed that in this case the introduction of methyl groups did not change the dipole moment. Therefore, in the vector calculation of the dipole moments of C-methyl-substituted 3-homosilatranes the moments of two CH_3 groups were not taken into account (141). In the calculation of the dipole moments of Si- and C-substituted 3-homosilatranes the same values of the Si-O, C-O and C-N moments were used as in the case of silatranes (139,140). The moment of the $Si(NHCH_2CH_2)_3N$ group in Si-substituted 2,8,9-triazasilatranes, calculated using the vector scheme, was found to be 2.0 D and directed from the silicon toward the nitrogen atom (137). However, the measured dipole moment vector is directed from the nitrogen toward the silicon atom. That is confirmed by an increased μ value for $XSi(NHCH_2CH_2)_3N$ in going from X $=CH_3$ to X = CH_2=CH and X = C_6H_5. From these data the transannular Si→N bond moment was taken to be 4.3-4.9 D.

In determination of dipole moments of Si-substituted silatranes, $XSi(OCH_2CH_2)_3N$, where X = H, CH_3, C_2H_5, CH_2=CH, C_6H_5, C_6H_5O, 3-$CH_3C_6H_4O$, 4-$(CH_3)_3CC_6H_4O$, 5-CH_3-2$(CH_3)_2CHC_6H_3O$, 4-ClC_6H_4O, 3-$O_2NC_6H_4O$, in chloroform and ethyl acetate (Table 13)

Table 14

Dipole Moments of Silatrane Analogs (at 25°C, benzene)

X	R	μ, D obs.	vect.	Δμ, D	Refer.
		$XSi(OCHRCH_2)_2(OCH_2CH_2CH_2)N$			
CH_3	H	4.74	1.0	3.74	138
CH_3	CH_3	4.48	1.0	3.48	141
$CH_2=CH$	H	5.18	1.2	3.98	138
$CH_2=CH$	CH_3	4.85	1.2	3.65	141
CH_3O	H	5.8	2.0	3.80	138
CH_3O	CH_3	5.43	2.0	3.43	141
C_2H_5O	H	4,71	0.8	3.91	24, 143
C_6H_5	H	5.23	1.6	3.63	138
C_6H_5	CH_3	5.17	1.6	3.57	141
$3\text{-}ClC_6H_4$	CH_3	6.32	2.30	4.02	141
$4\text{-}ClC_6H_4$	CH_3	6.85	2.5	4.35	141
$4\text{-}BrC_6H_4$	H	7.48	2.7	5.78	138
$4\text{-}BrC_6H_4$	CH_3	6.70	2.7	4.00	141
C_6H_5*	H	4.91	0.17	4.74	90
		$XSi(NHCH_2CH_2)_3N$			
CH_3**		3.0	1.7	4.7	137
C_2H_5**		2.8	1.7	4.5	137
$CH_2=CH$**		3.3	1.6	4.9	137
C_6H_5**		3.2	1.1	4.3	137
C_6H_5***		5.10	3.34	1.76	

* $C_6H_5Si(OCH_2CH_2)_2(CH_2CH_2CH_2)N$

** Measured in dioxane

*** $C_6H_5Si(SCH_2CH_2)_3N$

it was attempted to explain the values obtained in terms of the electronic effect of substituents on transannular Si←N interaction. Predominance of the -I-effect of organoxy-groups over their +M-effect increases the dipole moments of 1-alkoxy- and 1-aroxysilatranes as compared with those of 1-alkylsilatranes and results in a larger moment of the Si←N bond (140). In general, changes in the silatrane dipole moments follow those in the electronegativity of the substituents at the silicon atom (140, 142,145).

Replacement of all oxygen atoms in 1-phenylsilatrane (μ = 5.98 D) by sulfur atoms or NH-groups gradually reduces the measured dipole moments to 5.1 and 3.2 D, respectively.

The increase in the silatrane dipole moments in chloroform solution is explained by the formation of a hydrogen bond with the solvent and this was later confirmed by NMR and IR data (148)

A drawback of the first calculations of silatrane dipole moments (80,139,140) carried out before the X-ray structural data were obtained was the use of an idealized molecular geometry and the arbitrary choice of some parameters such as the Si-O, Si-C, C-H bond momens and the Si→N distance. More recent calculations, however, were also based on the valence angle and bond moment values characteristic of acyclic compounds having a tetrahedral silicon atom.

The ideas of high polarity of the Si→N bond in silatrane molecules were first revised in 1975 (147). The dipole moments of the heterocyclic skeleton of silatranes, $Si(OCH_2CH_2)_3N$, calculated using the additive scheme and with allowance for X-ray structural (108,110) and conformational (130,131) analysis turned out to be appreciably higher than those reported previously (139). The dipole moment (with no account for the Si→N value) is about 3 D, and the changes caused by variations in the steric structure amount to $\pm$0.3 D. The dipole moments of the transannular Si→N bond of 1-methyl- and 1-phenylsilatrane are taken to be 2.2 D, which corresponds to the N→Si charge transfer of 0.2e (147).

The use of dipole moments of the Si-O (2.25 D) and Si-C bonds (1.48 D) in 1,3-dioxa-2-silacycloalkanes[143] and those of the H→C, C→Cl, and C→I bonds (0.28, 1.36, and 1.35 D, respectively) (150,151) as well as X-ray structural data (113) made it possible to evaluate the dipole moments of 1-halomethylsilatranes (Table 13)(145,146). The μ value for these compounds (Table 13) is a projection of the vector difference between measured and calculated dipole moments related to the symmetry axis of the silatrane skeleton. When asymmetric substituents are attached to the silicon atom it is this value rather than the scalar difference between the measured and calculated dipole moments which characterizes the Si→N bond polarity. In this case, the calculated dipole moment of the silatrane group is 2.88 D if its vector is directed toward the silicon atom. When calculated by the earlier used method, this value is 3.95 D and not 1.1 D as it was thought before

(139). The use of the measured interatomic Si—N distance (2.1-2.2 Å) gives the $\mu_{Si\leftarrow N}$ value in 1-methylsilatrane equal to 1.38 D which corresponds to an Si←N charge transfer of 0.1 e (145). An enhanced electronegativity of the substituent attached to the silicon atom leads to a greater $\mu_{Si\leftarrow N}$ value (to 3.14 D, for example, when X = Cl_2CH and n = 0 (Table 13)) and, consequently, to a greater charge transfer (in the example given it is 0.2 e).

Introduction of methyl groups into positions 3-, 7- and 10 results in a subsequent increase in the dipole moment value (145). The third methyl group produces a smaller increase in the dipole moment than the other two. According to the additive scheme, the replacement of the hydrogen atom by the methyl group should not change the dipole moment. So the observed higher μ values for C-methyl-substituted silatranes may be attributed to conformational distortions of the silatrane skeleton.

The dipole moment method was used to investigate rotational isomerism relative to simple bonds in the acyclic part of the molecules of 1-(3'-halopropyl)silatranes, $X(CH_2)_3Si(OCH_2CH_2)_3N$ (X = Cl, Br, I) and 1-(2'-ethylthioalkyl)silatranes, $C_2H_5S(CH_2)_2Si(OCHRCH_2)_3N$, with R = H, CH_3 (146). Five possible steric structures have been considered (Fig. 10). The moments of $-CH_2Si(OCH_2CH_2)_3N$ and $-CH_2Si[OCH(CH_3)CH_2]_3N$ have been taken to be equal to the measured dipole moments of 1-methylsilatranes (5.46 D) and

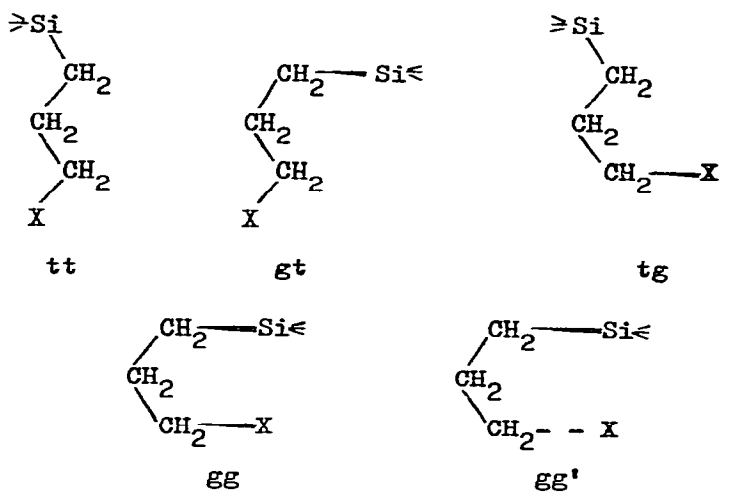


Fig.10

1,3,7,10-tetramethylsilatrane (4.92 D). The moments of C-X bonds (X = Cl, Br, I) are calculated from the dipole moments of the corresponding methyl halides and the S-CH_2 and C_2H_5S- moments are taken from the literature (150,151). The dipole moments of 1-(3'-halopropyl)silatranes and 1-(2'-ethylthioethyl)silatranes listed in Table 13 correspond to those calculated for gg- and gt-conformers, respectively.

According to X-ray structural data, the 1-(3'-chloropropyl)silatrane molecule exists in the tt'-conformation (Fig.10). Comparison between the measured and calculated dipole moments confirms that the energetically disadvantageous gg-conformers do not occur. The dipole moment method does not allow one to establish the existence of tt, tg, gt, and gg' conformations due to their equal polarity. Therefore, Kerr's constant (1363) was determined for 1-(3'-chloropropyl)silatrane, which turned out to be close to that calculated for the gg'-conformation (1338). The agreement between the two values shows that crystalline 1-(3'-chloropropyl)silatrane exists as the tt'-conformer, while in CCl_4 solution the gg'-conformation proves to be energetically most advantageous.

Thus, without rejecting the considerable influence of the transannular Si←N bond on many properties of silatranes (including the dipole moments), the above mentioned data (145-147) demonstrate the error of previous ideas on the extremely high polarity of the transannular Si←N bond.

4. Vibrational Spectra

Almost all vibrational frequencies in the IR absorption spectra of silatranes (9,10,152-154)(some of them are represented in Table 6) do not differ much from those observed in the spectra of usual organosilicon compounds (156-158).

The Si-H stretching frequency in the IR spectrum of silatrane (2137 cm^{-1} in $CHCl_3$ solution, 2117 cm^{-1} in methanol) is displaced from the region characteristic of organosilicon compounds bearing a $HSi(O)_3$-grouping (2190-2220 cm^{-1}) (9). This shift to the lower frequency is explained in terms of the electron-donor effect of the transannular Si←N bond (9, 152).

An important spectroscopic feature of the silatrane molecule of $HSi(OCHRCH_2)_3N$ (R = H, CH_3, CF_3) is the larger Si-H range depending on the polarity of the solvent, which is not common to other vibrations of the molecule and to the Si-H

of triethoxysilane (Table 15)(154a,155).

The intramolecular interaction of silatranes with solvents is of universal character with predominant contribution from the inductive-orientational forces. The lower νSi-H value

Table 15

The Solvent Effect on the νSi-H Frequency in the IR Spectra of $HSi(OCHRCH_2)_3N$ and $HSi(OC_2H_5)_3$

Solvent	ν Si-H, cm^{-1}			
	R = H	R = CH_3	R = CF_3	$HSi(OC_2H_5)_3$
CCl_4	2175	2166		2192
$CHCl_3$	2137	2132	2210	2197
CH_2Cl_2	2127	2118	2196	
C_6H_5Cl	2143	2136	2206	2192
$ClCH_2CH_2Cl$	2126	2118	2194	2194
CH_3CN	2116	2106	2171	2195
Solid or liquid (l)	2092	2115	2172	2194 (l)

with an increase in the solvent polarity in approximation of the three-centered bond model localized at the H-Si — N bonds explained by a greater Si→N interaction. The most probable reason for this is the shorter Si-N distance. The above silatranes as well as other polyhedral structures are characteristic of higher conductivity of the inductive effect displayed by the three-fold cyclic skeleton reflected by the following linear expression:

$$\nu Si\text{-}H = 2201(\pm 12) - 199(\pm 41)\frac{q-1}{2q+1} + 10(\pm 1)\Sigma\sigma^*$$

$$R = 0.991,\ r_1 = 0.969,\ r_2 = 0.990,\ r_3 = 0.967$$

The Si-C frequency in the spectra of 1-alkylsilatranes also is displaced to the lower frequency (152). This indicates a decreased electronegativity of the silicon atom and, consequently, a larger polarity of the Si-C bond. Absorption bands Si—X (X = F, Cl, Br) in the IR spectra of 1-halosilatranes also are displaced to the longer wave length (15).

A broad, moderately intense band previously assigned (10, 152,153) to stretching vibrations of the coordinate Si→N bond is observed in the 560-590 cm^{-1} region in the IR spectra of

1-organyl- and 1-organoxysilatranes (10,152,154). In assigning this band, methyltriethoxysilane and triethanolamine, whose spectra display no absorption in this region, were used as model compounds. However, this assignment was considered only as tentative since the ν_s(Si-O)frequency in the silatrane spectra may be observed in the 560-590 rather than 620-675 cm^{-1} region (152). An attempt was made to characterize quantitatively the Si N bond polarity on the basis of a spectroscopic investigation of 1-organoxysilatranes, $ROSi(OCH_2CH_2)_3N$ (R = CH_3, C_2H_5, n-C_4H_9, t-C_4H_9, n-C_5H_{11}, $CH_3S(CH_2)_2$, C_6H_5, 4-$CH_3C_6H_4$, 2-$H_2NC_6H_4$, etc.) (153). For this purpose, spectral characteristics of the band at 570-590 cm^{-1} assigned to Si←N, the apparent coefficient of molecular extinction (molecular absorption, ε) and the integral intensity, A, were determined. The data obtained led to the conclusion that the nature of the substituent R greatly affects the above parameters and, consequently, the polarity of the Si←N bond. However, a methodical error was made in this work (153) as variations of A, reverse to those of ε, were obtained for the same absorption band.

A detailed study of frequencies and intensities of the absorption bands of Si- and C-substituted silatranes in the 540-590 cm^{-1} region in their IR and Raman spectra has shown that these bands arise from skeletal vibrations of the silatranes (154). Measurements and an analysis of the absorption intensity values, A, for the silatrane skeleton of Si-substituted silatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_3, $(CH_3)_2CH$, CH_2=CH, C_6H_5, $ClCH_2$, Cl_2CH, ICH_2, $C_2H_5SCH_2$, $C_2H_5S(CH_2)_2$, C_2H_5O), C-methyl-substituted 1-ethylthiomethylsilatranes, $XSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$, (X = $C_2H_5SCH_2$) and 2-carbasilatranes, $XSi(OCH_2CH_2)_2(CH_2CH_2CH_2)_2N$, (X = C_2H_5O, C_6H_5, CH_3), led to the establishment of spectroscopic features of the electronic effects of the substituents X and to the assignment of some absorption bands in the IR spectra of silatranes and their analogs (154). As model compounds, not only the corresponding Si-substituted triethoxysilanes, $XSi(OC_2H_5)_3$ (X = CH_3, $ClCH_2$, CH_2=CH, C_2H_5O, C_6H_5), were spectroscopically studied, but boratrane, 3-homoboratrane, $B(OCH_2CH_2CH_2)_3N$, and and phenylsilabicyclo[2.2.2]-octane, $C_6H_5Si(OCH_2)_3CCH_3$, as well.

The spectra of the silatranes and 2-carbasilatranes studied show an absorption band splitting in the region of

the C-O and Si-O stretching modes with $\Delta\nu$ = 30-35 cm^{-1} and 10-15 cm^{-1}, respectively. When silatranes and 2-carbasilatranes go from solid state into solution, a rearrangement of the absorption band intensities is observed in the 1100 cm^{-1} region of the IR spectra. However, no changes are observed in this region for the C-methyl-substituted silatranes. Sensitivity of the bands in the 1100 cm^{-1} region to the state of aggregation suggests conformational changes in the silatrane skeleton of unsubstituted silatranes. On going from crystalline state into solutions the band intensities of the silatrane spectrum change by less than 30 %. This makes it possible to compare the vibrational intensities of the Si-O-C group in the spectra of crystalline silatranes and those of benzene solutions for the corresponding Si-substituted triethoxysilanes. The $A_{C-O}^{1/2}$ value in the $XSi(OCH_2CH_3)_3$ spectra is linearly related to the σ^* value of the substituent X:

$$A_{C-O}^{1/2} = 22.3 - 48.1\sigma^* \quad (r = 0.978,\ s = 6.0).$$

For the silatranes of the $XSi(OCH_2CH_2)_3N$ type with the exception of the compounds with X = H, CH_3, the $A_{C-O}^{1/2}$ value also correlates well with the σ^* value of X:

$$A_{C-O}^{1/2} = 160 - 22.2\sigma^* \quad (r = 0.967,\ s = 4.0)$$

The $\nu_{(C-N)}$ intensity is scarcely sensitive to variations in the substituents at the silicon atom. This indicates a relatively low transmission effect of the Si←N bond.

Introduction of methyl groups into positions 3-, 7-, and 10 increases the intensity and halth-width of the 540-570 cm^{-1} band and produces its splitting. In this region, absorption also is observed in the spectra of 2-carbasilatranes, 3-homosilatranes (138), 2,8,9-triazasilatranes (137). In the general case, the 540-600 cm^{-1} absorption band is always observed in the IR spectra of bicyclo-[3.3.3]undecane systems such as boratrane, $B(OCH_2CH_2)_3N$, 2,8,9-tricarbaboratrane, $B(CH_2CH_2CH_2)_3N$, (159), stannatranes, $XSn(OCH_2CH_2)_3N$ (160), various metalloatrane-3,7,10-triones, $M(OCOCH_2)_3N$ (M = Al, Ga, La, Bi, Cr, Fe, Ni, etc.)(163) and is usually associated with the atrane skeletal vibrations (159).

These considerations make it necessary to assign this absorption band in the spectra of silatranes and their analogs to deformational vibrations of the silatrane skeleton (154). In spite of this, in later publications, the absorption band

at 570-600 cm^{-1} in the spectra of 3-homosilatranes (138) and 2,8,9-triazasilatranes (137) was erroneously assigned to the symmetrical Si←N stretching vibrations. The above assignment of the band at 540-600 cm^{-1} permitted the use of IR-spectroscopy to confirm the structure of silatrane hydrochlorides which are, unlike azabicyclo[3.3.3]undecane (129) very sensetive to atmospheric moisture. So, the presence of the absorption band at 550 cm^{-1} in the IR spectrum of the adduct of 1,3,7,10-tetramethylsilatrane with hydrogen chloride indicates that the three-cyclic system does not change. The intense, broadened Si-O-C stretching modes undergo a negligible (by 10-20 cm^{-1}) shift toward shorter wave length (164).

The bands at 2500-2800 cm^{-1} characteristic for HCl-tertiary amine complexes are observed in the spectrum of both triisopropanolamine hydrochloride (2500-2700 cm^{-1}) and 1,3,7,10-tetramethylsilatrane hydrochloride (2560-2800 cm^{-1}). The order of the band arrangement may be associated with an increase in the degree of charge transfer in the $R_3N \cdot HCl$ system.

Thus no significant influence of Si←N transannular interaction in silatranes on their vibrational spectra has been observed so far.

5. Ultraviolet Spectra

UV absorption spectra of silatranes, $XSi(OCH_2CH_2)_3N$, with X = C_2H_5, n-C_3H_7, C_6H_5, $C_6H_5CH_2$, C_2H_5O and $(CH_3)_2CHO$, have been studied in the 180-240 nm region (165). The absorption band in the 170-240 nm region was assigned to the nitrogen atom and its surroundings and that in the ~170 nm region to the XSi group. The UV absorption spectrum for triethylamine was used for comparison. The long-wave length shift of the absorption band of 1-alkylsilatranes, X = C_2H_5, $(CH_3)_2CH$, relative to the absorption band of triethylamine is attributed to the Si←N transannular bond.

UV spectra of 3,4,6,7,10,11-tribenzosilatranes, $XSi(OC_6H_4)_3N$, show two absorption peaks at 284 and 277 nm for X = Cl, and at 285 and 277 nm for X = CH_3, C_6H_5, 4-$CH_3C_6H_4$ (166).

UV spectra of the 1-aroxysilatrane series, $XC_6H_4OSi(OCH_2CH_2)_3N$, (X = H, CH_3, Cl, CH_3O, $(CH_3)_3C$) have been studied in the 195-400 nm region (Table 16). The spectra of freshly prepared aqueous solutions of these compounds also display two absorption peaks at 212-225 nm and 270-288 nm (167).

In comparison with the 4-$XC_6H_4OCH_3$, the UV spectra of silatranes show a reduced intensity of the first band and a hypsochromic shift of the second band (Table 16).

Table 16

UV Absorption Spectra of XC_6H_4OY

X	Y	Solvent	Band I		Band II	
			λ,nm	$\varepsilon_1 \cdot 10^{-3}$ $l \cdot mol^{-1} cm^{-1}$	λ,nm	ε_1 10^{-3} $lmol^{-1} cm^{-1}$
H	$Si(OCH_2CH_2)_3N$	H_2O	270	1.3	212	6.20
CH_3	$Si(OCH_2CH_2)_3N$	H_2O	270	1.4	213	8.07
$(CH_3)_3C$	$Si(OCH_2CH_2)_3N$	H_2O	275	1.35	220	6.07
Cl	$Si(OCH_2CH_2)_3N$	H_2O	280	1.71	225	11.97
CH_3O	$Si(OCH_2CH_2)_3N$	H_2O	288	2.87	223	8.52
H	CH_3	H_2O	267	1.6	217	4.3
H	$Si(CH_3)_3$	C_6H_{12}	268	1.26	211	6.94
CH_3	CH_3	C_2H_5OH	277	2.10	226	9.7*
CH_3	$Si(CH_3)_3$	C_2H_5OH	274	1.39		
Cl	CH_3	C_2H_5OH	281	1.85	227	11.70*
Cl	$Si(CH_3)_3$	C_2H_5OH	277	1.18		

* In cyclohexane solution

The use of Pariser-Parr-Pople (PPP) method for the analysis of the UV long-wave bands permitted the electron-acceptor effect of the silicon atom to be rationalized in terms of the participation of one of the lowest vacant orbitals. It was also possible to characterize the disturbance from interaction of this orbital with an atomic orbital of oxygen which affects the electronic spectra of molecules having a C_6H_5OSi- group. In its electron withdrawing effect on the bound oxygen atom, the silatrane $-Si(OCH_2CH_2)_3N$ group is comparable with the $Si(CH_3)_3$ group.

Comparison of the UV spectra of tetraphenoxysilane, trimethylaroxysilanes and 1-aroxysilatranes shows that for the latter the Si←N coordination interaction does not affect the absorption in the 200-300 region.

6. NMR Spectra

NMR Spectra of silatranes have been studied in detail (10,13,70,75,137,168-187).

^{1}H NMR spectra of eight 1-organyl- and 1-organoxysilatranes, $XSi(OCH_2CH_2)_3N$, where X = CH_3, C_2H_5, i-C_3H_7, CH_2=CH, C_6H_5, CH_3O, C_2H_5O, n-C_3H_7O, were obtained for the first time in 1965 in chloroform medium using a 40 MHz spectrometer (168). The methylene proton signals of the silatrane skeleton appeared as two markedly broadened triplets forming the $(AA'XX')_3$ spin system. The splitting of lines in these spectra was nearly constant for all the compounds (5-6 Hz), but intensities are slightly different from those expected for the first order spectra. For the compounds studied, the proton chemical shifts are weakly dependent on the inductive effect of the substituent X (Table 17). This is explained in terms of $(p-d)_\pi$ interaction of the lone electron pair of the oxygen atoms with the silicon atom which compensates for the change in the chemical shifts of the $O-CH_2$ protons caused by variations in the substituent X. The difference between the proton chemical shifts of the OCH_2- and CH_2N-groups in silatranes and model compounds (organyltriethoxysilanes, triethanolamine and N,N-dimethylethanolamine) was attributed to the Si←N coordination bond.

In a further study of the ^{1}H NMR spectra of a large number of Si- and C-substituted silatranes the chemical shift values for some previously examined compounds were revised (Table 17) (169-171).

The δ_{CH_2N} values themselves cannot provide strong evidence for coordination interaction since screening constants of the CH_2N proton in silatrane spectra are only slightly lower than in those of acyclic and monocyclic silatrane analogs which display no coordination bond in the solvent (143). Thus, the paramagnetic resonance shift of N-methylene protons in the ^{1}H NMR spectra of 1-methylsilatrane in CCl_4 medium (δ_{NCH_2} = 2.71 p.p.m.) is greater only by 0.18 p.p.m. than that of 1,1-dimethylsila-5-methylaza-2,3-dioxacyclooctane (δ_{NCH_2} = 2.54 p.p.m.)(169). At the same time, if the nitrogen atom undergoes quarternization or participates with its unshared electron pair in the coordination bond, the N-methylene proton resonance usually shifts by 0.5-1 p.p.m. to lower field. Consequently, higher δ_{CH_2N} values do not show complete transfer of the nitrogen unshared electron pair to the vacant $3d_z2$-orbital of silicon. It was pointed out for the first time that lack of the basic properties of the nitrogen of silatranes is chiefly associated with the steric inaccessibility

Table 17

Proton Chemical Shifts in ^1H NMR Spectra of Si-Substituted Silatranes, $XSi(OCH_2CH_2)_3N$ (in Chloroform Solution)

X	δ, p.p.m.			Refer.
	OCH_2	CH_2N	X	
H	3.86	2.88	3.94	10,168,169
	3.81	2.85	3.87	160
CH_3	3.78	2.79	-0.12	10,169
	3.61	2.76	0.12	168,10
	3.78	2.88	-0.12	160
	3.47*	1.98	0.66	136
	3.59	2.64	-0.34	136
C_2H_5	3.76	2.79	0.30(α), 0.97(β)	169
	3.56	2.72	0.42(α), 0.98(β)	10,168
$(CH_3)_2CH$	3.75	2.77	0.92	10,169
C_6H_{11}	3.72	2.74	0.8-2.3	169
$CH_2=CH$	3.78	2.84	5.69	10,169
$ClCH_2$	3.84	2.90	2.66	46
	3.87	2.89	2.59	174
Cl_2CH	3.95	2.98	5.16	174
$Cl(CH_2)_3$	3.69	2.73	0.34(CH_2Si), 1.79(CH_2C) 3.40($ClCH_2$)	46
$BrCH_2$	3.84	2.89	2.31	46
$Br(CH_2)_3$	3.75	2.78	0.60(CH_2Si), 1.95(CH_2C) 3.37($BrCH_2$)	46
ICH_2	3.88	2.92	1.92	46
$I(CH_2)_3$	3.88	2.83	0.46 (CH_2Si), 1.96(CH_2C) 3.22(ICH_2)	45
$CH_2=CCl$	3.89	2.91	5.59,5.82	42
$ClCH=CH$	3.82	2.87	5.96(H-gem),6.49(H-cis)	42
$ClCH=CCl$	3.89	2.93	6.79	42
$Cl_2C=CH$	3.85	2.88	5.96	42
CH_3OCH_2	3.85	2.87	3.00(CH_2Si), 3.38(CH_3)	58
CH_3O	3.81	2.92	3.40	10,169
C_2H_5O	3.80	2.92	3.70(α), 1.13(β)	10,169
C_3H_7O	3.83	2.86	3.58(α), 1.42(β) 0,86(γ)	10,169
$(CH_3)_2CHO$	3.80	2.88	1.18(β)	169
$n\text{-}C_4H_9O$	3.82	2.88	3.66(α), 1.44-,-1.42(β,γ)	10,169
C_6H_5O	3.65	2.64	(in pyridine)	177
$(CH_3)_2CHCH_2O$	3.80	2.88	3.38(α),1.45(β) 0.85(γ)	169
$(CH_3)_3CO$	3.79	2.76	1.28	169
$(CH_3)_3CCH_2O$	3.81	2.84	3.30(α),0.86(γ)	169

Table 17 (continued)

$n\text{-}C_6H_{13}O$	3.84	2.85	3.55(α),1.25(β) 0.84(CH_3)	169
$C_6H_{11}O$	3.81	2.82	2.5-0.8	169
$n\text{-}C_{14}H_{29}O$	3.73	2.78	3.52(CH_2O),1.20(CH_2) 0.84(CH_3)	
$C_6H_5CH_2O$	3.82	2.71	4.74(CH_2O),7.29(C_6H_5)	169
$HSCH_2$	3.83	2.86	1.54(SCH_2)	64
$HS(CH_2)_2$	3.75	2.80	0.81(CH_2Si),2.62(SCH_2)	64
$HS(CH_2)_3$	3.75	2.79	0.48(CH_2Si),1.80(CH_2C) 2.54(SCH_2)	64
$NCS(CH_2)_3$	3.75	2.81	0.49(CH_2Si),1.88(CH_2C) 2.96(SCH_2)	56
C_6H_5	3.78	2.72	7.46-7.19	10,169
$4\text{-}CH_3C_6H_4$	3.74	2.68	7.55($H_{3,5}$),7.04($H_{2,6}$) 2.25(CH_3)	169
$2\text{-}ClC_6H_4$	3.74	2.70	7.6-7.0	169
$4\text{-}CH_3C_6H_4O$	3.80	2.82	2.19(CH_3),6.89(C_6H_4)	169
$3\text{-}CH_3C_6H_4O$	3.85	2.83	2.26(CH_3)	169
$2\text{-}CH_3C_6H_4O$	3.76	2.70	2.22(CH_3),6.81(C_6H_4)	169
$4\text{-}(CH_3)_3CC_6H_4O$	3.84	2.80	1.23(CH_3)	169
$4\text{-}ClC_6H_4O$	3.85	2.84	6.99($H_{2,6}$), 7.09($H_{3,5}$)	169
$2,4,6\text{-}Cl_3C_6H_2O$	3.82	2.89	7.17	169
$4\text{-}O_2NC_6H_4O$	3.87	2.94	6.99($H_{2,6}$), 7.97($H_{3,5}$)	169
$3\text{-}O_2NC_6H_4O$	3.88	2.92		1699
$2\text{-}O_2NC_6H_4O$	3.88	2.84		169
$C_6H_5OCH_2$	3.89	2.91	3.46	58
$2\text{-}CH_3OC_6H_4OCH_2$	3.82	2.82	3.45(CH_2Si),3.80(CH_3)	58
$\overbrace{CH_2(CH_2)_3N}CH_2$	3.74**	2.78	1.81($SiCH_2$)	38
	3.69***	2.74	1.65($SiCH_2$)	38
$\overbrace{CH_2(CH_2)_4N}CH_2$	3.75**	2.77	1.73($SiCH_2$)	38
$\overbrace{CH_2(CH_2)_5N}CH_2$	3.77**	2.79	1.97($SiCH_2$)	38
$\overbrace{CH_2(CH_2)_3N}(CH_2)_3$	3.76**	2.79	0.38($SiCH_2$)	38
$\overbrace{CH_2(CH_2)_4N}(CH_2)_3$	3.72**	2.76	0.29 ($SiCH_2$)	38
$\overbrace{CH_2(CH_2)_5N}(CH_2)_3$	3.75**	2.78	0.40 ($SiCH_2$)	38

* in C_6H_6
** in $CDCl_3$
*** in CCl_4

of its unshared electron pair oriented "inside" the silatrane skeleton, rather than with reduced electronic density (169).

An analysis of the ^1H NMR spectra of a large number of silatranes has shown (169) that the screening constant value for OCH_2- and CH_2N-protons depends on the nature of the substituent on the silicon atom. In the NMR spectra the difference between OCH_2 and NCH_2 chemical shifts is nearly constant amounting to approximately 1 p.p.m. on the average (Table 17).

The invariability of this value indicates that the electronic effects of the substituent attached to the silicon atom are transmitted to the OCH_2- and CH_2N-fragments not only through the σ-bonding system of the atrane half-rings, Si-O-C-C-N, but also through the Si→N transannular bond.

For molecules of the series $XSi(OCH_2CH_2)_3N$ with X = H, CH_3, C_2H_5, $(CH_3)_2CH$ and CH_2=CH, the chemical shifts of ring protons are linearly related to the Taft inductive constants of the substituent X:

$$\delta_{CH_2N} = 2.79 - 0.177\sigma^*_X \quad (r = 0.97)$$

$$\delta_{CH_2O} = 3.77 - 0.180\sigma^*_X \quad (r = 0.98)$$

The parameters of these equations later were made more exact by inclusion of chemical shifts of 1-diethylaminomethylsilatrane methiodide (171):

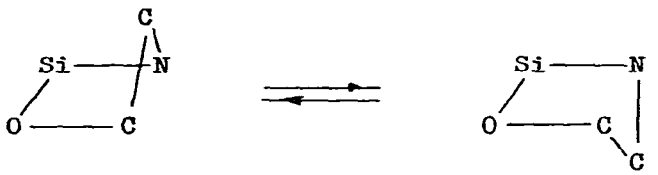
$$\delta_{CH_2N} = 2.79 - 0.161\sigma^*_X \quad (r = 0.99)$$

$$\delta_{CH_2O} = 3.76 - 0.064\sigma^*_X \quad (r = 0.97)$$

Silatranes containing an aryl- or organoxy-group in position 1 do not obey these relationships. This seems to be due to an additional effect, their $(p\text{-}d)_\pi$-interaction with the silicon atom. The steric interaction of the substituent at the silicon atom influences the electron density distribution more strongly than the inductive effect of the substituent does (169). More bulky substituents decrease the degree of Si→N interaction due to distortion of the SiO_3-group configuration (a decrease in the planar character of the SiO_3-group).

From an X-ray structural analysis (106) it has been established that the SiOCCN units of Si-substituted silatranes have an envelope shape. As a rule, α-carbon atoms come

out of the plane of other atoms of the silatrane half-rings. According to the ^1H NMR data, the inversion rate of these five-membered heterocycles is extremely high. Thus, for the inversion equilibrium,



a decrease in the temperature of 1-ethoxysilatrane solution in CH_2Cl_2 to -80° does not "freeze" out these conformational transitions.

In ^1H NMR spectra of 3-methyl-substituted silatranes the proton signals of the substituted atrane half-rings are characterized by a multiplet of the $ABXM_3$ type with zero spin-spin coupling (SSC) constant between the proton separated by four bonds (170). These spectra show that the introduction of the CH_3-group "freezes" the conformational transitions (169) of both substituted (170) and unsubstituted (170,184) half-rings. The proton spectrum of the latter is of the type $(ABXY)_2$. The 3-substituent displays a pseudo-equatorial orientation (170,184).

The geminal coupling constants of the protons of the substituted atrane ring in the PMR spectra of 1,3-dimethylsilatrane and 1-phenyl-3-methylsilatrane were used to confirm that the molecules of these compounds exist in the endo-form and have an Si←N bond. A distinguishing character of the ^1H NMR spectra of 3-methyl-substituted metalloatranes is that the $^2J_{AB}$ and $\Delta\delta_{AB}$ values of the geminal protons change in line when the silicon atom is replaced by boron, germanium or vanadium (170).

A decrease in the $^2J_{AB}$ and $\Delta\delta_{AB}$ values shows that the deviation of the considered fragments from the planar structure decreases in the following order B>RSi>V=O.

From the chemical shifts of CH_2N protons of the unsubstituted rings it is seen that the introduction of the CH_3 group into the silatrane skeleton hardly affects the degree of the Si←N transannular interaction.

Unlike the ^1H NMR spectra of the atrane skeleton of Si-substituted silatranes (type AA'XX'), the spectra of C-substituted derivatives of type $XSi(OCH_2CH_2)_{3-n}(OCHRCH_2)_nN$,

where X = CH_3, $ClCH_2$, CH_3CHCl; R = CH_3, CF_3; n = 1-3, are extremely complicated. In the simplest case with n = 1, there is overlapping of three groups of spin-systems, $ABXM_3$, A'B'X'Y' and A"B"X"Y" (179,184). In the ^1H NMR spectra of 3,7,10-trimethyl-substituted silatranes the signals of the ring protons are represented by four spin multiplets of the $ABXM_3$ type and equal intensity (A and B correspond to CH_2N and X-OCH_2 and M_3 to the protons of methyl groups) (184). The molecules of C-methyl-substituted silatranes, $XSi(OCH_2CH_2)_{3-n}[OCH(CH_3)CH_2]_nN$, where n = 2,3, are a mixture of diastereoisomers (Fig. 11).

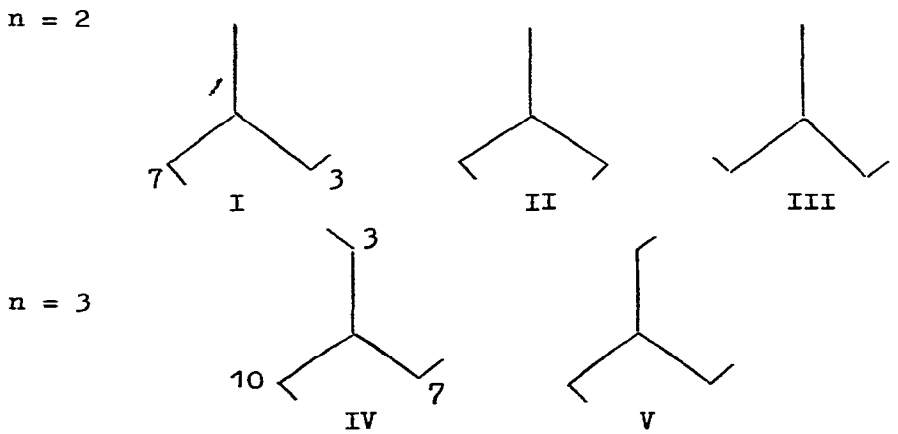


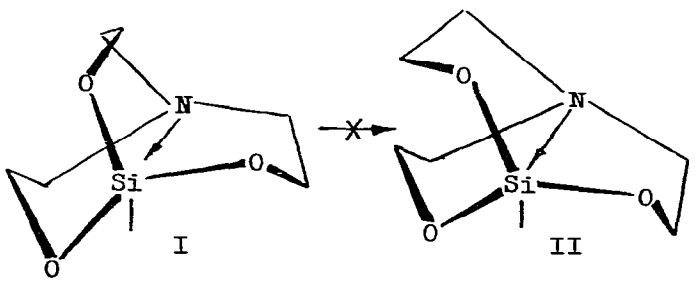
Fig. 11

When statistical distribution is the case, the isomer ratio should be as follows: I:II:III = 2:1:1 and IV:V = 1:3. In the ^1H NMR spectrum of 3,7,10-trimethyl-1-iodomethylsilatrane (n = 3) the isomer ratio corresponds to the statistical one, whereas in that of 3,7-dimethyl-1-iodomethylsilatrane (n = 2) a considerable deviation favoring the less strained form, I, is observed (184).

In diastereoisomers I and IV all exo-substituents are in the pseudoequatorial position; in V two substituents are in the pseudoequatorial position and one in pseudoaxial (184). The conformational rigidity of molecules I, IV and V is caused by a significant energy gain of the cycles with e-oriented C-substituents.

Equivalence of 3,7-substituted rings (184) in each diastereoisomer, II and III, as well as the values of spin-spin coupling between the A, B, and X protons indicate a high con-

formational lability of their molecules. Methyl groups of diastereoisomers II and III undergo fast ea ⇌ ae conformational transitions. A temperature change from -80 to +200°C in 3,7-dimethyl- and 3,7,10-trimethylsilatrane solutions does not influence the line arrangement in the ^{1}H NMR spectra. This is the equatorial-axial orientation of 3,7-substituents in isomers II and III rather than the equatorial-equatorial one. This confirms that the unconcerted inversion of three five-membered rings of the type below is not allowed due to large energy strains in structure I (184). This also is true for



conformations of unsubstituted silatrane half-rings (132) and agrees well with the literature data for the related bicyclo-[3.3.3]undecane systems (manxane XVI and manxine XVII structures, Chapter II, Section 1) (126-129).

Thus, the conformational transitions in silatrane molecules are collective transitions which occur with retention of the C_3 symmetry (184).

^{1}H NMR spectra of the ring protons of silatrane analogs (Table 18) differ only slightly from the above described spectra of Si- and C-substituted silatranes. The differences between the proton chemical shifts of the NCH_2 and OCH_2 groups in 3-homosilatranes (independent of the nature of the substituent X) are almost constant, amounting to approximately 1 p.p.m., on the average (38,139). ^{1}H NMR spectra of 2,8,9-triazasilatranes (except the protons of the substituent X) contain an NH-proton singlet and two multiplets which are the components of the AA'BB' system. In the spectrum of 1-methyl-2,8,9-triazasilatrane an increase in proton screening of the methyl group and a decrease in the spin-spin coupling value, $^1J_{CH}$, as compared with those of methyl-tris-(dimethylamino)silane, are observed (137,187).

In spectra of silatrane-3-ones the signals due to the OCH_2-protons are triplets and the NCH_2 proton resonance is a

Table 18

Chemical Shifts of the Ring System Protons of Si-Substituted Silatrane Analogs

	Chemical Shift, δ, p.p.m.				Solvent	Refer.
	OCH_2(n)*	NCH_2(n)*	CH_2(n)*	X		
			$XSi(OCH_2CH_2)_2(CH_2CH_2CH_2)N$			
CH_3	3.70	2.71	0.55(2) 1.60(3) 2.60(4)	-0.14	$CHCl_3$	169
	3.60	2.67	0.45(2) 1.58(3) 2.54(4)	-0.29	CCl_4	
C_2H_5	3.72	2.74	0.58(2) 1.63(3) 2.59(4)	0.35 0.95	$CHCl_3$	169
	3.61	2.63	0.44(2) 1.57(3) 2.53(4)	0.20 0.82	CCl_4	
C_6H_5	3.85	2.70	0.82(2) 1.70(3) 2.64(4)	7.2-7.5	$CHCl_3$	169
	3.70	2.66	0.64(2) 1.62(3) 2.52(4)	7.1-7.4	CCl_4	
C_2H_5O	3.81	2.77	0.67(2) 1.67(3) 2.63(4)	1.16(CH_3) 3.69(CH_2)	$CHCl_3$	169

	3.60	2.24	0.86 (2) 1.98 (4)	1.34 (CH_3) 4.10 (CH_2)	CCl_4	169
		$XSi(OCH_2CH_2)_2(OCH_2CH_2CH_2)N$				
CH_3	3.95 (3) 3.76 (8,11)	2.93 (5) 2.86 (7,12)	1.67 (4)	-0.22	CCl_4	138
$ClCH_2$	4.02 (3) 3.90 (8,11)	3.01 (5) 2.73 (7,12)	1.74 (4)	2.35	CCl_4	138
$CH_2=CH$	3.95 (3) 3.82 (8,11)	2.96 (5) 2.70 (7,12)	1.67 (4)	5.67	CCl_4	138
C_6H_5	4.08 (3) 3,89 (8,11)	2.98 (5) 2,72 (7,12)	1.73 (4)	7.56 (α) 7.18 (β,γ)	CCl_4	138
$4\text{-}BrC_6H_4$	4.08 (3) 3.90 (8,11)	2.98 (5) 2.72 (7,12)	1.72 (4)	7.4 (α) 7.32 (β,γ)	CCl_4	138
$4\text{-}ClC_6H_4$	4.09 (3) 3.90 (8,11)	3.00 (5) 8.74 (7,12)	1.70 (4)	7.1 (α) 7.45 (β,γ)	CCl_4	138
$3\text{-}ClC_6H_4$	4.06 (3) 3.89 (8,11)	2.94 (5) 2,70 (7,12)	1.70 (4)	7.0-7.4	CCl_4	138
CH_3O	3.99 (3) 3.82 (8,11)	2.95 (5) 2.63 (7,12)	1.68 (4)	3.27	CCl_4	138
		$XSi(NHCH_2CH_2)_3N$				
H		2.95	2,69 (3,7,10)	3.77	CCl_4	137
CH_3		2.88	2.57 (3,7,10)	- 0.54	CCl_4	137
C_2H_5		2.92	2.59 (3,7,10)	- 0.01; 0.82	CCl_4	137
$CH_2=CH$		2,97	2.69 (3,7,10)	5,55	CCl_4	137
C_6H_5		3.07	2.68 (3,7,10)	7.47(α),7.08(β,γ)	CCl_4	137

Table 18 (continued)

$XSi(OCH_2CH_2)_2(OCOCH_2)N$						
CH_3	3.65	2.99 (A)** 2.77 (B)**	3.59 (4)	-0.3	DMSO	75
C_2H_5	3.65	2.96 (A) 2.77 (B)	3.58 (4)	0.23	DMSO	75
$n\text{-}C_4H_9$	3.65	2.96 (A) 2.74 (B)	3.58 (4)		DMSO	75
$C_6H_5CH_2$	3.69	2.86 (A) 2.68 (B)	3.35 (4)		$CDCl_3$	75
	3.65	2.98 (A) 2.78 (B)	3.60 (4)		DMSO	75
$3\text{-}CH_3C_6H_4$	3.75	3.05 (A) 2.85 (B)	3.69 (4)		DMSO	75
$3\text{-}ClC_6H_4$	3.75	3.08 (A) 2.90 (B)	3.71 (4)		DMSO	75
$4\text{-}FC_6H_4$	3.78	3.10 (A) 2.90 (B)	3.73 (4)		DMSO	75
$3\text{-}CF_3C_6H_4$	3.82	3.14 (A) 2.96 (B)	3.78 (4)		DMSO	75
$4\text{-}ClC_6H_4$	3.80	3.12 (A) 2.92 (B)	3.75 (4)		DMSO	75

* n denotes the methylene group position in the heterocyclic skeleton

** Multiplet centers of diastereotropic NCH_2-protons

complex multiplet (75). As seen from Tables 17 and 18, the nature of the solvent greatly affects the values of the proton chemical shifts.

^{1}H NMR spectra of 2-carbasilatranes are characterized by markedly greater screening constants for the substituent X protons and the protons of the OCH_2CH_2N-fragment than those of the corresponding silatranes. As with silatranes, the splitting pattern of the resonance lines in the ^{1}H NMR spectra of 2-carbasilatranes demonstrates their high conformational lability. A comparison of the spectra of silatranes and the corresponding 2-carbasilatranes reveals that in the latter the N-methylene proton resonance is less sensitive to variations in the nature of the substituent X. Thus, the proton chemical shift in 1-ethoxysilatrane is lower by 0.13 p.p.m. than that in 1-methylsilatrane (in $CHCl_3$). A similar change in the substituents in the series of Si-substituted 2-carbasilatranes shifts the resonance by 0.03 p.p.m. (169). This seems to be associated with the fact that the replacement of the oxygen atom in the silatrane molecule by a methylene group having lower electronegativity and another steric structure reduces the electron-withdrawing properties of the silicon atom in 2-carbasilatranes and, consequently, the Si←N transannular interaction.

Recently $Eu(DPM)_3$-induced chemical shifts of the proton signals in the ^{1}H NMR spectra of 1-methylsilatrane ($CHCl_3$ and $CHCl_3$-CS_2 mixture) (181) and 1-methyl-3-homosilatrane (CCl_4) (138) have been measured.

In order to interpret the $Eu(DPM)_3$-induced paramagnetic shifts, δ, in the ^{1}H NMR spectrum of 1-methylsilatrane, the δ values were compared (185) with the paramagnetic shifts, δ_m, calculated by means of the following formula (183).

$\delta_m = K\frac{3\cos^2\theta-1}{r^3}$, where θ = the angle between the main magnetic axis of the paramagnetic complex and the direction to the nucleus, r = the distance from the coordinating ion to the resonance nucleus, and K = the constant for 1-methylsilatrane at given temperature.

The δ and δ_m values were compared, with allowance for the following conditions: 1) The silatrane molecule has four electron-donating heteroatoms which may be considered as possible coordination centers, three of them (oxygen atoms) being equivalent; 2) In accordance with the molecular geo-

metry of silatranes and $Eu(DPM)_3$ coordination to the oxygen, the europium atom should be in the plane formed by the silicon, oxygen, nitrogen and one of the carbon atoms of the silatrane ring; 3) The calculation is checked by the conformity factor,R.

Under the condition that complexation occurs only via the oxygen atoms, no agreement between the δ and δ_m values was achieved. Further interpretation of the paramagnetic shifts observed was made on the basis of the suggestion of N-coordination of 1-methylsilatrane with $Eu(DPM)_3$. This suggestion was based on the data that an HCl-1,3,7,10-tetramethylsilatrane complex formed via the N atom was obtained (164) despite the existing ideas on inactivity of this silatrane due to steric inaccessibility of the unshared electron pair and the participation of the latter in transannular interaction with the silicon atom (168). In calculations of the δ_m values for N—$Eu(DPM)_3$ coordination, the main magnetic axis was taken to be coincident with the Si—N direction. The analysis carried out showed that the R value which is adequate within experimental accuracy was reached if it was assumed that the O-coordinated molecules amounted to 90%, the other 10% having the nitrogen atom as the coordination center. The Eu-O distance was 2.69 Å. The results obtained may be explained in two ways: 1) N-coordination occurs in the exo-conformation of the silatrane which is in equilibrium with the endo-conformer; 2) N-coordination occurs without inversion of the endo-form (or the form approaching the latter). In this case, the association is due to rehybridization of the unshared electron pair of the nitrogen electron pair caused by the $N(CH_2)_3$-flattening. The calculations carried out confirm the second hypothesis. In the coordination without transition of the endo-form into the exo-form, the Eu-N distance is 2.15 Å. In the case of exo-conformation, the agreement between the δ and δ_m values requires the Eu-N distance to be 1.5 Å, which is considerably less than the normal Eu-N distance (2.65 Å) (188).

The distortion of nitrogen sp^3-hybridization in silatrane molecules may be explained by specific conformation of bicyclo[3.3.3]undecane systems which is observed, in particular, in 5-azabicyclo[3.3.3]undecane (XVII) and its derivatives (126,128,129).

^{13}C NMR spectra of silatranes have not been studied in detail. The screening of ^{13}C nuclei of the silatrane skeleton

is higher than that in acyclic Si-substituted tris(2-aminoethoxy)silanes. This is due to the cyclization effect and, possibly, to the intraannular compression in the $N(CH_2)_3$ fragment of the silatrane molecules (173). As a result of an increase in the electronic density in the silatrane molecules due to the transfer through the X-Si-N bonds, the ^{13}C resonances of the carbon atoms (which are in the β-position or even more distant from the silicon atom) are observed at higher field than that of the corresponding Si-substituted triethoxysilanes. According to (178a), the deshielding of the carbon atoms attached to silicon in phenyl- and vinylsilatranes and the shielding of the C_{para} in phenylsilatrane with respect to the corresponding Si-substituted triethoxysilanes were explained in terms of the changes in the electronic structure in the Si-Ph bond and can be understood in terms of the loss of p_π-d_π bonding. Utilization of the ^{13}C chemical shifts of 1-phenylsilatrane and phenyltriethoxysilane, as well as least-square correlation equations related to inductive and resonance constants of the substituents in the aromatic ring of monosubstituted benzene, C_6H_5X, with the meta- and para carbon atom screening constants ($\sigma_i = a_o + a\sigma_{C_m} + a_2\sigma_{C_p}$) made it possible to calculate the corresponding σ_I constants for the silatranyl- and triethoxysilyl groups (187b):

	σ_I	σ_R	σ_R^o	σ_R^+	σ_R^-	σ^*
$Si(OCH_2CH_2)_3N$	-0.40	0.02	0.02	-0.09	0.17	-0.89
$Si(OC_2H_5)_3$	-0.18	0.10	0.08	0.21	0.17	-0.19

Nearly the same σ^+ values for the silatranyl- (-0.08) and triethoxysilyl (0.17) groups were estimated from the relationship between σ^+ and σ_{C_p} (178b). The analysis of their values proves that the extension of the heteroatom coordination number in silatrane molecules considerably increases the electron donor properties of the silicon atom.

Changes in a number of other spectral characteristics of silatranes including a decrease in the coupling constant, $^1J_{^{13}CH}$, (115.6 Hz) and an increase in $^1J_{^{29}SiC}$,(106.9 Hz) for methyl groups as compared with those observed for methyltriethoxysilane ($^1J_{^{13}CH}$ = 118.9 Hz, $^1J_{^{29}SiC}$ = 97.0 Hz) also are connected with rehybridization of the silicon atom in sil-

atrane molecules. These results are similar for pentacoordinate tin derivatives and seem to reflect general regularities related to the fact that the Group IVB elements extend their coordination number.

1-(4'-Fluorophenyl)silatrane (175), 1-(4'-fluorobenzyl)- and 1-(3'-fluorobenzyl)silatranes (176) were investigated by ^{19}F NMR. For comparison, ^{19}F NMR spectra of the corresponding Si-substituted trialkyl- and trialkoxysilanes were studied (Table 19). Correlation equations for compounds of these series 3- and 4-XC_6H_4F permitted the determination of the inductive (σ_I= -0.36) and resonance (σ_R = -0.21) constants of the $CH_2Si(OCH_2CH_2)_3N$ group. A higher δ_F value for 1-(4'-fluorophenyl)silatrane as compared with 4-fluorophenyltriethoxysilane was explained in terms of an Si←N coordination interaction. A longe-range spin-spin coupling through space between the fluorine atoms separated by eight valence bonds in 1-methyl-3,7-bis(trifluoromethyl)silatrane and 1-methyl-3,7,10-tris(trifluoromethyl)silatrane was observed (182).

Coupling constants between the fluorine nuclei of the magnetically nonequivalent 3-$^{12}CF_3$- and 7-$^{13}CF_3$ groups isomer (II) and of 3- and 7-CF_3groups of isomer (V) (Fig. 11) of the above molecules were determined to be $^8J_{FF}$ = 1.6 Hz (182). This value corresponds to an F-F distance of ~4.2 Å (182a).

Low sensitivity of the ^{14}N isotope (0.001 of the proton sensitivity at constant field) and the influence of quadrupole line broadening (spin number, i, is 1) make investigations of organic and elementoorganic compounds by the ^{14}N NMR method very difficult. The i value for the ^{15}N isotope is 1/2. However, its natural abundance is extremely low. This is why only one study (180) has been devoted to ^{14}N NMR spectra of silatranes. The ^{14}N resonances of 1-hydrosilatrane and 1-methylsilatrane are at higher field relative to that of triethylamine (Table 20). A considerably different ^{14}N relaxation time in the silatranes studied indicates a substantial influence of the substituent at the silicon atom on the elctronic surroundings of the nitrogen atom. This affords evidence for the interaction of the nitrogen unshared electron pair with the silicon atom, but not excluding the influence of stereochemical factors such as deviation of the $N(CH_2)_3$- valence angles from the tetrahedral value. In 1-methylsilatrane the ^{14}N shift to lower field by 9 p.p.m. relative to that observed in alkylamines when the hydrogen atom of the

Table 19

^{19}F Chemical Shifts of Compounds FC_6H_4X*

X	δ_F, p.p.m	σ_I	σ_R^o	Solvent	Refer.
4-$Si(OCH_2CH_2)_3N$	2.43			CCl_4, C_6H_5F	175
4-$CH_2Si(OCH_2CH_2)_3N$	9.32		-0.21	$CDCl_3$	176
3-$CH_2Si(OCH_2CH_2)_3N$	3.15	-0.36		$CDCl_3$	176
4-$CH_2Si(CH_3)_3$	7.06		-0.20	CCl_4	176
3-$CH_2Si(CH_3)_3$	1.14		0.08	CCl_4	176

* Relative to fluorobenzene

Table 20

Chemical Shifts in the ^{14}N NMR Spectra of Silatranes and Model Compounds

Compound	δ_N, p.p.m.*	$\Delta\nu_{1/2}$, Hz
$HSi(OCH_2CH_2)_3N$	-354.7 ± 4.4	638 ±68
$CH_3Si(OCH_2CH_2)_3N$	-346.2 ± 3.6	2211 ±103
$B(OCH_2CH_2)_3N$	-325.0 ± 4.9	543 ±71
$(C_2H_5)_3N$	-327.0 ± 2	320 ±10

* The negative δ_N values show a higher field resonance shift as compared to the CH_3NO_2 standard (in CH_2Cl_2)

H-C-N group is replaced by a methyl group (189).

^{29}Si NMR spectra of Si-substituted silatranes and triethoxysilane have been studied recently (Tables 21, 22). It is known that the δ_{Si} value in the NMR spectra of silane derivatives is determined by a whole complex of different factors including the inductive, resonance and steric effects of substituents (186).

The δ_{Si} dependence on the nature of the substituent X for triethoxysilane and substituted silatrane is nearly the same. As the electronegativity of the substituent X increases, the ^{29}Si resonance of these compounds shifts to higher field. This is, in principle, consistent with the theory of ^{29}Si screening. When the substituent X in molecules of the

Table 21

^{29}Si Chemical Shifts in the NMR Spectra of Si-Substituted Silatranes, $XSi(OCH_2CH_2)_3N$

X	$\delta^{29}Si$, p.p.m.	X	$\delta^{29}Si$, p.p.m.
$(CH_3)_2CH$	-65.0	$(CH_3)_2CHCH_2O$	-95.2
$CH_3(CH_2)_4$	-65.4	$(CH_3)_3CO$	-94.9
C_6H_{11}	-65.4	$CH_3(CH_2)_4O$	-95.1
$Cl(CH_2)_3$	-68.2	C_6H_5O	-99.3
$Br(CH_2)_3$	-68.5	$4\text{-}(CH_3)_3CC_6H_4O$	-98.9
$I(CH_2)_3$	-69.5	$2\text{-}CH_3C_6H_4O$	-99.1
$[(C_2H_5)_2CH_3\overset{+}{N}]CH_2$	-84.7	$3\text{-}CH_3C_6H_4O$	-99.5
$\overline{CH_2(CH_2)_4\overset{+}{N}CH_2}$	-84.1	$4\text{-}CH_3C_6H_4O$	-99.1
CH_3O	-95.4	$4\text{-}ClC_6H_4O$	-99.7
$(CH_3)_2CHO$	-95.0	$3\text{-}O_2NC_6H_4O$	-99.5
$CH_3(CH_2)_3O$	-95.0	$4\text{-}O_2NC_6H_4O$	-99.6

$XSi(OCH_2CH_2)_3N$ and $XSi(OCH_2CH_3)_3$ type changes, a linear relationship between the δ_{Si} values and the inductive aliphatic Taft constants, σ^*_X, of the substituent X holds: (equations 1 and 2, respectively) (187a)

$$\delta_{Si} = -67.10(0.6) - 11.3(1.1)\sigma^*_X;\ r = 0.992,\ s = 0.768 \quad (1)$$

$$\delta_{Si} = -45.3(1.7) - 11.3(1.8)\sigma^*_X;\ r = 0.998\ \ s = 1.28 \quad (2)$$

Judging from equations (1) and (2), the indicator center sensitivity to the substituent effect in these two series is nearly the same. The absolute δ_{Si} values for the corresponding Si-substituted silatranes and triethoxysilanes with X = H, $C_nH_{2n+1}O$, RC_6H_4O, RC_6H_4, $CH_2{=}CH$ are essentially higher than those calculated from equations 1 and 2. This deviation results from the non-linear character of the dependence of δ_{Si} on the electronegativity of the substituents of the silane derivatives (186), as well as from the influence of conjugative contributions.

When the substituents change, both classes of the compounds studied display the same order in the deviation of the δ_{Si} values from those calculated from equations (1) and (2):

Table 22

^{29}Si Chemical Shifts in the NMR Spectra of Si-Substituted Silatranes and Triethoxysilanes

X	$\delta^{29}Si$, p.p.m.		$\Delta\delta Si$, p.p.m.	Refer.
	$XSi(OCH_2CH_2)_3N$	$XSi(OCH_2CH_3)_3$		
H	-83.6	-66.0	17.6	187a
	-83.6	-59.5	24.1	178a
CH_3	-65.7	-44.0	21.7	187a
	-64.8	-44.2	20.6	178a
	-66.6			179a
C_2H_5	-67.1	-45.9	21.2	187a
$ClCH_2$	-77.2	-56.1	21.2	187a
Cl_2CH	-83.2	-68.4	14.8	187a
$BrCH_2$	-77.7	-56.2	21.5	187a
ICH_2	-77.0	-54.7	22.3	187a
$CH_2=CH$	-83.5	-60.3	23.2	187a
	-81.6			178a
$C_6H_5C\equiv C$	-94.7	-69.5	25.2	187a
C_2H_5O	-94.7	-82.6	12.3	187a
C_6H_5	-80.5	-59.4	21.1	187a
	-81.7	-58.4	23.3	178a
$C_6H_5OCH_2$	-75.9	-53.9	22.0	187a
$\overline{CH_2(CH_2)_4NCH_2}$	-72.8	-50.2	22.6	187a

$C_nH_{2n+1}O \sim C_6H_5C\equiv C > CH_2=CH \sim H > C_6H_5$. In the case of Si-substituted silatranes the deviations are smaller than for the corresponding triethoxysilane derivatives. The similar δ_{Si} dependence on the substituent X in these two series shows that the determining role in the ^{29}Si-screening of silatranes belongs to the total charge of the silicon atom.

Having studied ^{29}Si NMR spectra of four silatranes, $XSi(OCH_2CH_2)_3N$, (X = H, Me, Vi, Ph), Harris (178a) suggested that the substituent effects on ^{29}Si chemical shifts pointed to a dependence on p_π-d_π interaction of three oxygen atoms which is greater than that on the Si←N coordination charge in silatrane formation.

A specific feature of the Si-substituted silatranes is

the considerable (14-25 p.p.m.) higher field shift of the ^{29}Si resonance in their NMR spectra as compared with that observed for the corresponding triethoxysilanes (Table 22). This is not related to the "cyclization effect" (186) leading to a lower-field shift of signals. The effect of the nitrogen atom may also be neglected as the ^{29}Si screening in methyltris(2-aminoethoxy)silane is lower than in methyltriethoxysilane by only 3 p.p.m. The observed difference in the δ_{Si} values for the corresponding triethoxysilanes and silatranes is caused by a change in the Si atom hybridization. It is suggested that the extension of the coordination number of the silicon atom in silatrane molecules and, consequently, its rehybridization are accompanied by an additional positive contribution, $\delta_{coord.}$, to the ^{29}Si screening constant. The greater the degree of Si←N interaction in silatranes, the greater is the value of the $\delta_{coord.}$ contribution. Thus, the observed difference in the ^{29}Si chemical shifts of the corresponding Si-substituted silatranes and triethoxysilanes, $\Delta\delta_{Si} = \delta^{A}_{Si} - \delta^{S}_{Si}$, reflects the mutual change in both the total charge, $\Delta\delta_{q} = \delta^{A}_{q} - \delta^{S}_{q}$, and the Si coordination number, $\delta_{coord.}$. The $\Delta\delta_{q}$ and $\delta_{coord.}$ values have opposite signs and depend in different ways on the substituent X electronegativity. Their absolute values should rise with an increase in the electronegativity of X. According to the experimental data, the absolute $\Delta\delta_{q}$ value is somewhat lower than $\delta_{coord.}$. In the series studied the $\Delta\delta_{q}$ varies in a greater range than the $\delta_{coord.}$.

The $\Delta\delta_{q}$ value for 1-hydrosilatrane and triethoxysilane is evaluated to be +22 p.p.m. (the plus sigh denotes a lower-field resonance shift). As the experimental difference in the ^{29}Si screening of these compounds, -17.6 p.p.m., is $\Delta\delta_{Si} = \delta^{A}_{Si} - \Delta\delta_{q} + \delta_{coord.}$, the $\delta_{coord.}$ should be -39 p.p.m. If the difference in the silicon atom charge in 1-ethoxysilatrane and tetraethoxysilane is assumed to be 0.12 e, the $\Delta\delta_{q}$ value attains + 34 p.p.m. On this assumption, the difference in the δ_{Si} values observed in the NMR spectra of the above compounds corresponds to a $\delta_{coord.}$ value of -46 p.p.m.

In silatranes having a low degree of Si←N interaction the $\delta_{coord.}$ contribution to the ^{29}Si screening is significantly lower. So a larger $\Delta\delta_{Si}$ value with X = $C_6H_5C{\equiv}C$ in comparison with X = C_2H_5O (Table 22) indicates a stronger transannular Si←N interaction in the 1-phenylethynylsilatrane molecule.

The ^{29}Si chemical shifts in Si-substituted silatranes are determined by the total charge on the silicon atom which depends, in particular, upon the degree of Si←N transannular interaction, and by the Si rehybridization. However, the interaction of the two factors, as well as their dependence on the nature of the substituent at the silicon atom, are rather complicated. Therefore, without a thorough analysis of the theory of ^{29}Si screening and quantum-chemical calculations it is not possible to obtain any quantitative information from the ^{29}Si NMR spectra.

Recently, ^{1}H, ^{13}C, and ^{29}Si NMR spectra of methyl-2,8,9-triazasilatrane have been investigated (187). The Si←N transannular interaction in this compound results in an increased screening of the ^{1}H and ^{29}Si nuclei in the CH_3-Si fragment (compared with $CH_3Si[N(CH_3)_2]_3$). The difference in the ^{29}Si chemical shifts of these compounds also is caused by the paramagnetic contribution (+16 p.p.m.) from the other three "extra" methyl groups at the silicon atom in the model acyclic compounds. Thus, the contribution from the Si←N transannular bond to the screening in 1-methyl-2,8,9-triazasilatrane is about 34 p.p.m. Since the difference in chemical shifts of 1-methylsilatrane and methyltriethoxysilane is 22 p.p.m., it may be suggested that the Si←N transannular interaction is stronger in 2,8,9-triazasilatrane than in silatranes (187).

7. NQR Spectra

Nuclear quadrupole resonance (NQR) spectra of silatranes are considered in only one publication (174) where ^{35}Cl NQR frequences of some 1-(chloroalkyl)- and 1-(chlorovinyl)silatranes are discussed (Table 23). These frequencies were used for evaluation of the σ^* constants of the $Si(OCH_2CH_2)_3N$ group.

Spectra of 1-chloromethyl-, 1-(3'chloropropyl)-, 1-(α-chlorovinyl)-, 1-(α,β-dichlorovinyl)silatranes and of C-substituted 1-chloromethyl- and 1-(dichloromethyl)silatranes show one signal with $\Delta\nu \sim 0.1$ MHz. The NQR spectra of 1-(dichloromethyl)- and 1-(dichlromethyl)-3-methylsilatranes showed a doublet. The intensity and width ($\Delta\nu \simeq 0.06$ and 0.04 MHz, respectively) of both the lines were practically the same. No NQR signals of 1-chlrosilatrane, 1-(1'-chloroethyl)silatrane and some C-methyl-substituted 1-(chloroalkyl)-silatranes have been observed.

A decrease in NQR frequencies of 1-(chloroalkyl)silatranes in comparison with the corresponding (chloroalkyl)triethoxysilanes is in agreement with the donor effect of the Si←N transannular bond and the silatrane group as a whole.

In compounds of the series $X(CH_2)_nCl$ the effect of the substituent X on the ch orine atom with $n \geq 3$ is negligible. The ^{35}Cl NQR frequency of compounds of this type is close to $\nu^{77} \approx 33.0$ MHz, being 33.090 MHz for $Cl(CH_2)_3SiCl_3$, 33.19 MHz for $Cl(CH_2)_3SiCH_3Cl_2$, 32.958 MHz for $Cl(CH_2)_3Si(CH_3)_3$, etc. Nevertheless, the NQR frequency of 1-(3'-chloropropyl)silatrane, $\nu^{77} = 31.552$ MHz, is considerably lower than the above values. Previously, this was attributed to a coordination interaction between the chlorine and silicon or oxygen atoms.

This suggestion was not confirmed, however, since X-ray structural data (116), dipole moments and Kerr's constants (146) for 1-(3'-chloropropyl)silatranes showed that the $Si(CH_2)_3Cl$ fragment in the crystalline state is a flat zigzag chain and that the chlorine atom is considerably (by 5 Å) distant from the planar $Si(O)_3$ group. Therefore, this low ^{35}Cl NQR frequency of 1-(3'-chloropropyl)silatrane most likely is due to the powerful +I-effect of the silatrane group. A higher ^{35}Cl NQR frequency of 1-(chloromethyl)silatrane seems to be due to geminal interaction between the silicon atom and the C-Cl bond (α-effect).

As should be expected, the NQR frequencies of 1-(chloromethyl)- and 1-(chloromethyl)-3-methylsilatranes are lower than those of the corresponding (dichloromethyl)silatranes (Table 23). This agrees with the inductive effects of the chlorine and hydrogen atoms.

NQR frequencies of compounds of the series $CH_2=CClSiR_3$ show a linear correlation of ^{35}Cl NQR frequencies of compounds of the series $H_2C=CClX$ with the σ^* inductive constants of substituents

$$\nu^{77} = 33.001 + 1.235\,\sigma^* \quad (r = 0.989)$$

The σ^* constant value for the $Si(OCH_2CH_2)_3N$ group calculated using the above equation from the ^{35}Cl NQR frequency of 1-(α-chlorovinyl)silatrane is -1.18. This is close to the σ^* value of $Si(OCH_2CH_2)_3N$ (-1.21) calculated from the ^{35}Cl NQR frequency of 1-(dichloromethyl)silatrane by the following equation:

$$\nu^{77} = 35.215 + 0.959\,\sigma^{*} \quad (r = 0.932)$$

for compounds of the series XYZCCl.

The increase in NQR frequencies in C-methyl-substituted 1-(chloromethyl)silatranes is associated with a distortion of the molecular geometry. This also is confirmed by the considerable decrease in the δ_{OCH_2} and δ_{NCH_2} values in the NMR spectra of C-methyl-substituted silatranes (170) and 2-carbasilatranes (Table 1) as compared with unsubtituted silatranes (Table 17).

In the spectrum of 1,3,7,10-tetramethylsilatrane hydrochloride the ^{35}Cl NQR signal (ν^{77} = 17.93 MHz) is shifted to the low-frequency region as compared to the signal of triisopropanolamine (ν_m^{77} = 22.6 MHz) (164).

8. Mass Spectra

A mass spectrometric investigation of silatranes was first carried out with 1-methyl- and 1-phenylsilatranes (190). Later on, mass spectra of a larger number of Si- and C-substituted silatranes were examined with the aim of determining their structure and molecular weight and the mechanism of

Table 23

^{35}Cl NQR Frequencies of 1-Chloroalkyl, 1-Chlorovinylsilatranes and Related Si-Substituted Triethoxysilanes at 77°K

$XSi(OCH_2CH_2)_3N$ X	ν_{77}, MHz	$XSi(OC_2H_5)_3$ X	ν_{77}, MHz
$ClCH_2$	32.702	$ClCH_2$	35.122
$ClCH_2$*	33.380		
Cl_2CH	34.649	Cl_2CH	36.231
	34.394		36.114
			35.784
Cl_2CH *	34.55		
	35.17		
Cl_2CH **	35.01		
$Cl(CH_2)_3$	31.552		
$CH_2=CCl$	31.545	$CH_2=CCl$	33.074
$ClCH=CCl$	33.487		

* 3-methylsilatrane derivative

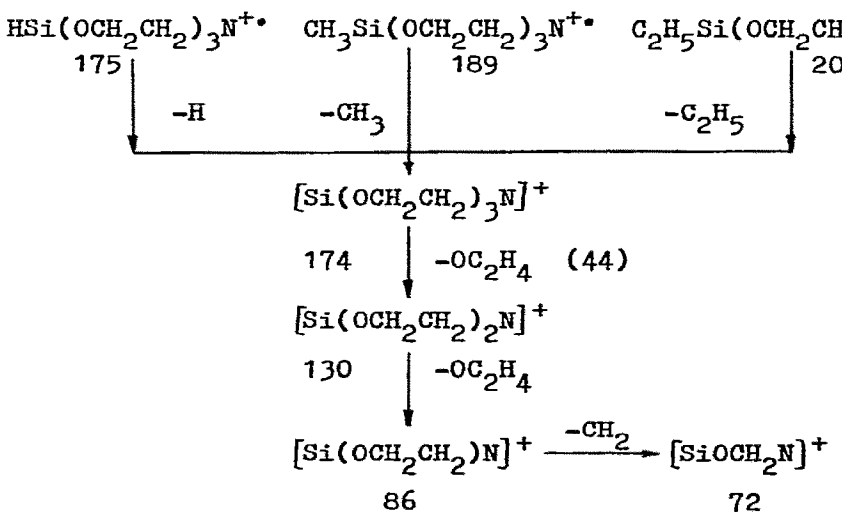
** 3,7-dimethylsilatrane derivative

their electron impact-induced fragmentation (138,160,190-193).

The common feature of mass spectra of silatrane, $HSi(OCH_2CH_2)_3N$, and its derivatives is the most intense ion peak at m/e 174. This ion of the silatrane skeleton, $[Si(OCH_2CH_2)_3N]^+$, is formed by dissociative ionization of the H-Si≡ or C-Si≡ bonds. It amounts for 1-alkylsilatranes from 5 to 12% of the total ion current.

The subsequent fragmentation of the silatrane skeleton proceeds step-wise and involves elimination of the $(OCH_2CH_2)^+$ groups and the formation of the following fragment ions: m/e 130, $[Si(OCH_2CH_2)_2N]^+$, intensity 19-26%; m/e 86 $[Si(OCH_2CH_2)N]^+$, 2.3-3.7%; m/e 72 $[SiOC_2H_4]^+$, 5-19% which are typical for 1-alkylsilatranes only (190-191). These ions are likely to form by simple cleavage of the C-C, C-H and Si-O bonds. However, every mass spectrum shows rearrangement ions resulting from hydrogen migration (m/e 176, 5-12% of the maximum ion). The intense ions observed in the mass spectra of alkylsilatranes, m/e 89, $[SiC_2H_5O_2]^+$ (6-25%), m/e 102 $[SiC_2H_4O_2N]^+$ (5-24%) and m/e 132 $[SiC_4H_{10}O_2N]^+$ (3-88%), are formed by consecutive and partial cleavage of the $(OCH_2CH_2)^+$ group of the silatrane skeleton (confirmed by metastable transitions).

The mechanism of dissociation ionization of 1-alkylsilatranes may be represented by the following simplified scheme:



Scheme 1

As the molecular weights of the silatranes increase, the stability to electron impact is reduced from 7.1% (1-hydro-

silatrane) to 0.7% (1-ethylsilatrane)(191).

Together with the molecular ions, mass spectra of 1-aryl-, 1-alkenyl-, and 1-alkoxysilatranes show fragment ions (over 92%), rearrangement ions and metastable species (192). The second stage of the dissociation process is common for all the silatranes studied.

Mass spectra of 1-(chloromethyl)silatranes of general formula $ClCH_2Si(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$ made it possible not only to study the mechanism of electron impact-induced fragmentation but also to follow the influence of the Si←N transannular bond and CH_3 groups in the 3, 7 and 10 positions on the molecular stability (193). The mass spectrum of 1-chloromethylsilatrane also shows the most intense peak that corresponds to $[Si(OCH_2CH_2)_3N]^+$ (m/e 174). The relative intensity,I, of the ion peak is 48.5% of the total ion current. The presence of a metastable transition of the m/e 174 ion to the m/e 130 ion (apparent mass 97.1) indicates that the latter is formed by elimination of the OCH_2CH_2 group. Further fragmentation of the m/e 130 ion involves elimination of the methylene groups and formation of characteristic fragment ions (m/e 116, 102 and 89). The second route of 1-(chloromethyl)silatrane fragmentation is conditioned by the initial elimination of the $-OCH_2CH$ group from the silatrane ring with migration of the hydrogen atom to nitrogen. Relative intensity of the $[ClCH_2Si(OCH_2CH_2)_2NH]^+$ ion peak is 4.5% of the total ion current. Subsequent fragmentation leads to the m/e 150, 136, 88 ions. Besides, doubly-charged 179^{++}, 175^{++}, 173^{++} and 145^{++} ions are observed in the mass spectrum of silatrane.

The presence of two methyl substituents in the 3- and 7-positions of the silatrane ring, 1-(chloromethyl)-3,7-dimethylsilatrane, changes not only the mass of the most ions formed, but reduces the fragmentation selectivity. The most intense peak, $[M-CH_2Cl]^+$, is 34.9% of the total ion current. Metastable transition of the m/e 202 ion to m/e 158 (apparent mass 123.6) indicates abstraction of the $-OCH(CH_3)CH_2$ group, first of all, from the silatrane ring. This shows that the $OCH(CH_3)CH_2$ group is more weakly bound in the silatrane skeleton than OCH_2CH_2 group. 1-(Chloromethyl)-3,7,10-trimethylsilatrane fragments in a similar way. The most intense $[M-CH_2Cl]^+$ peak is 33.9% of the total ion current. The high intensity of the $[M-CH_2Cl]^+$ ions (48.5-33.9%) formed from all the sila-

tranes investigated gives evidence for the stability of the silatrane ring under electron impact. This seems to be explained by the fact that abstraction of the CH_2Cl-substituent converts the weak Si←N annular bond into the strong covalent Si—N bond and thus stabilizes the silatrane skeleton.

An increase in the electron density of the silatrane ring on introduction of methyl groups scarcely affects the stability of the molecular ion (the molecular peak/total ion current ratio for all 1-(chloromethyl)silatranes being 0.4, 0.3, 0.5, and 0.3%). This may be caused by localization of the positive charge in the molecular ion. However, methyl substituents in the silatrane ring greatly affect the relative intensity of the $[M-CH_2Cl]^+$ ion. As the number of methyl groups in the silatrane ring increases, the intensity falls linearly (ρ = -4.98; z = 0.96, s_o = 0.22; I = 48.5, 40.9, 34.9, 33.9%, respectively). This indicates the corresponding increase in the Si-C bond strength due to the increasing electron density at the silicon atom.

The decrease in selectivity of dissociative ionization of the 1-(chloromethyl)silatranes studied is manifested in the relative intensity of the total peaks of characteristic fragment ions (Σ = 205.8, 244.3, 286.9, 294.7, respectively).

The molecular fragmentation with initial elimination of $OCHRCH_2$ (R = H, CH_3) from the silatrane ring of the molecular ion is expressed much weaker (I = 2.2, 3.0, 2.4, 1.3, respectively). The intensity of $[M-44]^+$ ions for 1-(chloromethyl)-, 1-(chloromethyl)-3-methylsilatranes and the $[M-58]^+$ ions for 1-(chloromethyl)-3,7,10-trimethylsilatrane may be related to the rate of hydrolythic decomposition of these compounds.

The silatranes whose mass spectra display a higher relative intensity of the above ions have greater constants of acidic hydrolysis rate (194). It is more reasonable, however, to relate these hydrolysis rate to the relative intensity of the $[M-CH_2Cl]^+$ ions since these values bear a fairly linear relationship described by the following equation $I = 61.84k_2^{25} - 5.44$; r = 0.99, s_o = 0.13. The relative intensity of these chracteristic ions may, undoubtedly, be used for evaluating the reactivity of silatranes.

In mass spectra of exo-trifluoromethyl-substituted 1-(chloroalkyl)silatranes the molecular ion peak is weak (< 1%

of the maximum). The main fragmentation route also is elimination of the chloroalkyl substituent, which leads to the formation of the most stable and intense peak of the silatrane skeleton $[M-X]^+$. Mass spectra of C-trifluoromethyl-substituted 1-organylsilatranes show the predominance of the silatrane skeleton ions, on one hand, and the absence of the fragment ions, on the other hand. This points to a higher stability of the silatrane skeleton of these compounds in comparison with the corresponding C-methyl-substituted silatranes (182a).

According to thermogravimetric data, the initial decomposition temperature of all these silatranes studied (in air) exceeds 250°C. This excludes the possibility of thermal decomposition of these compounds under mass-spectrometric investigations.

Thus, the introduction of the CH_3- and CF_3-groups into the silatrane ring scarcely changes the molecular ion stability. At the same time, these substituents do affect the relative intensity of the $[M-CH_2Cl]^+$ ion, and seems to be connected with both the change in the geometry and stereochemical factors stabilizing the silatrane molecules.

9. Studies by Other Physical Methods

$SiK\alpha_{1,2}$ chemical shifts in X-ray emission spectra of silatranes of type $XSi(OCH_2CH_2)_3N$ where X = R, C_2H_5, CH_2=CH, C_6H_5, etc., have been determined (195-198).

In all cases when the local symmetry of the silicon atom in the molecule is lower than $T_d(C_{3v}, C_{2v})$, the contributions from 3p atomic orbitals of silicon to molecular σ- and π-orbitals are comparable. Consequently, the stereochemically peculiar features of these molecules are caused predominantly by p_π-p_π interaction between the silicon atom and the nearest neighboring atoms (198). The SiKß spectra of silatranes and $[SiO_4]^{4-}$ groups are similar both in shape and energy state, which indicates the prevailing localization of silicon 3p-electrons at the σ-Si-O bonds. The SiK X-ray emission spectra of silatranes are composed of three components, these are $K\beta'$, $K\beta_1$ and $K\beta_\pi$ lines (Table 24). The presence of Kß' lines (transition from the a_1 + e level) gives evidence for 3p(Si)-2s(O) interaction. The role of $(p-d)_\pi$-bonding in silatranes is suggested to be extremely small. At the same time, as the X-Si-O angle approaches 90°, the $3p_\pi(Si)$ -$2p_\pi(O)$

interaction grows stronger (197,198). The effective charge of the silicon atom, q, in the silatranes studied points to the existence of the Si←N transannular bond.

Table 24

K-Spectral Data of 1-Organylsilatranes, $XSi(OCH_2CH_2)_3N$

X	$\Delta E_{ad.}$, ev	$\Delta E_{obs.}$, ev	q, a.u.	$E_{K\beta_1}$, ev	$E_{K\beta_1-K\beta'}$, ev	$\frac{I_{K\beta'}}{I_{K\beta_1}}$	$\frac{I_{K\beta_{II}}}{I_{K\beta_1}}$
H	0.47	0.375	0.65	1832.2	13.9	0.18	0.32
CH_3	0.50	0.307	0.53	1832.2	14.3	0.20	0.32
C_2H_5	0.50	0.370	0.64	1832.3	14.2	0.20	0.38
$(CH_3)_2CH$	0.50	0.346	0.60	1832.3	13.8	0.20	0.48
C_6H_{11}	0.50	0.270	0.46	1832.0	13.8	0.20	0.35
$CH_2=CH$	0.50	0.354	0.61	1832.2	14.1	0.21	0.50
C_6H_5	0.50	0.372	0.65	1832.0	14.0	0.20	0.50

The Si 2p and N 1s binding energies have been measured for silatranes, $XSi(OCH_2CH_2)_3N$, and compared with Si 2p binding energies for other organosilicon compounds (199). Chemical shifts of N and Si correlate well with each other providing evidence for a strong Si←N interaction. Considerable transfer of charge from N to Si is observed when the Si atom is bound to a very electronegative substituent X. If X is an aliphatic group, the observed shifts can be explained by the inductive effect of the substituent. In 1-arylsilatranes, the effect of the substituent in para-position is transmitted to the nitrogen atom through π-conjugation between the silicon atom and the aromatic ring.

Photoelecton spectra (PES) of boratrane and three silatranes, $XSi(OCH_2CH_2)_3N$, with X = H, CH_3 and C_2H_5O have been investigated. Triethanolamine, triethoxysilane and its corresponding derivatives were used as model compounds (200). Two bands at 10.4 and 11.2 ev (X = H) and at 10.0 and 11.0 ev ($X = C_2H_5O$) are observed in the spectra of silatranes. In the PES of triethanolamine the band due to the nitrogen lone electron pair appears at 8.7 ev. In the spectra of 1-ethoxysilatrane and boratrane no bands below 9.5 ev were observed. This indicates that the nitrogen lone pair is more tightly bound in these compounds. The spectrum of 1-methylsilatrane shows a broad band at 8.7 ev which seems to be caused by the

methyl group inductive effect decreasing the positive charge on the silicon atom and thus interfering the Si←N transannular interaction. However, this band is most likely to be caused by the triethanolamine impurity.

The spectra of triethoxysilane and its derivatives show a relatively sharp strong band near 10.8 ev which is probably due to the oxygen 2p lone pair levels.

Comparison of chemical shifts of the oxygen lone pair in the photoelectron spectra of $XSi(OCH_2CH_3)_3$ and $XSi(OCH_2CH_2)_3N$ shows that inclusion of the Si-O bonds into the heterocyclic silatrane system interferes in their achieving the most advantageous orientation realizable in triethoxysilane and its Si-derivatives.

Utilization of Kerr's effect (together with the dipole moment method) enabled us to determine conformation of the $Cl(CH_2)_3Si$-fragment in the 1-(3'-chloropropyl)silatrane molecule in CCl_4 solution (gg'). For this purpose, Kerr's constant (K_m = 1363) was compared with the calculated K_c values for conformations tt (1208), tg (1136), gt (839), gg (524) and gg' (1338) (146).

An attempt was made to determine Kerr's molar constant, total polarization, and molecular anisotropy of 1-methylsilatrane molecules (202). Anizotropy polarizability of oxygen-containing organosilicon compounds had not been studied before, therefore the Si-O bond parameters were determined first of all. Hexamethyldisiloxane and trimethylmethoxysilane were used as model compounds. The additive scheme can be used only on assumption of both isotropy of the C-H bonds ($\gamma_{C-H} = 0$) and an idealized silatrane structure. A considerable distortion of the tetrahedral arrangement of the bonds and valence angles gives rise to a supplementary deviation from additivity.

The possibility of using the additive scheme in determining anisotropy of the 1-methylsilatrane polarizability also is conditioned by the choice of an arbitrary anisotropy for one of the Si-O or Si-C bonds. Nevertheless, the new additive scheme of polarizability of bonds (202) permitted the determination of the contribution of Si←N transannular interaction to the polarizability ellipsoid of 1-methylsilatrane, $b_L = 2.78$ Å^3, $b_T = b_V = 0.11$ Å^3. This indicates a significant anisotropy of the nitrogen electron pair polarizability.

Chapter III. Chemical Properties

3.1. Reactions Involving Cleavage of the Silatrane Ring.

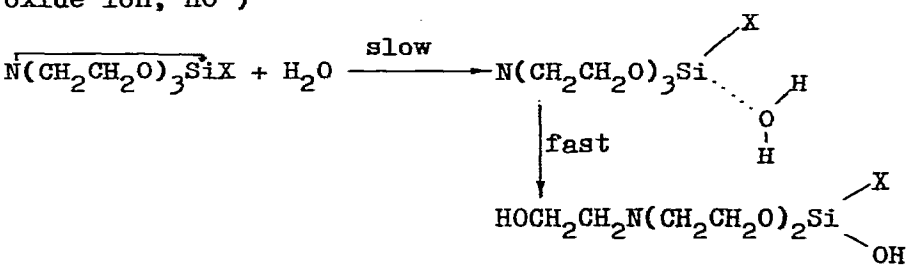
3.1.1. Hydrolysis Reactions

The facility with which organosilicon compounds which have an Si-O bond hydrolyze is well known and widely used in practice (24). It was pointed out long ago that silatranes were relatively stable to the atmospheric moisture and more difficult to hydrolyze than the corresponding derivatives of triethoxysilane, $XSi(OC_2H_5)_3$, and tris-(2-aminoethoxy)silane, $XSi(OCH_2CH_2NH_2)_3$. Hydrolysis of 1-organyl- and 1-organoxysilatranes was quantitatively studied for the first time in 1967. The dependence of the rate of neutral hydrolysis of $XSi(OCH_2CH_2)_3N$ on the nature of the substituent X (X = H, CH_2=CH, CH_3, C_2H_5, C_3H_7, C_6H_5, CH_3O, C_2H_5O, C_6H_5O, etc.) was determined. Hydrolysis kinetics was investigated in aqueous 0.01 M solution of silatranes at 20°C. The hydrolysis, which is a combination of a number of parallel-successive reactions, is a first order reaction (203). The hydrolysis rate of silatranes falls in the following order of change in the substituent X:

I $H > CH_2=CH > CH_3 > n\text{-}C_3H_7 = C_6H_5 > C_2H_5 > (CH_3)_2CH$

II $CH_3O > C_2H_5O > n\text{-}C_4H_9O > n\text{-}C_3H_7O > i\text{-}C_3H_7O > (CH_3)_3CO$

Thus, the silatranes studied are subdivided into two reaction series: I with X = R (alkyl) and II with X = RO (alkoxy) where a good linear correlation between the logK and σ^* is observed. In series I, an increase in the inductive constant of R makes the hydrolysis faster ($\rho^* > 0$). This indicates that the total rate of multi-stage hydrolysis of alkylsilatranes is determined by nucleophilic attack at the reaction center of the silatrane molecule by a water molecule (or by hydroxide ion, HO^-)



The high absolute value of ρ^* (+4.76) is indicative of a considerable degree of polarity in the transition state at

the kinetic stage where the reaction center (the silicon atom) acquires a significant negative charge.

The steric effect of the substituent on the hydrolysis rate of 1-alkylsilatranes is not likely to be overly important. 1-Hydroxysilatrane (X = H) also belongs to reaction series I. A deviation of the logK value from the correlation line may be explained in terms of the competitive hydrolysis of the Si-H bond in addition to cleavage of the Si-O-C group. The logK values of 1-vinyl- and 1-phenylsilatranes markedly deviate from the correlation line and the hydrolysis rate proves to be much lower than expected. This seems to be due to $(p-d)_{\pi}$-interaction of the above substituents with the silicon atom, leading to a considerable reduction of the electron-withdrawing effect (from σ^*_X = 0.40 and 0.60 to σ^*_{eff} = 0.1 and -0.05, respectively) (203).

The hydrolysis rate of 1-alkoxysilatranes (series II) is much lower than expected. Such hydrolytic stability may be explained in terms of two factors. 1) The presence of an Si←N transannular interaction which decreases the effective positive charge on the silicon atom and which thus hinders nucleophilic attack by the water molecule or the OH^- ion. 2) $(p-d)_{\pi}$ interaction between the oxygen and silicon atoms.

Of four Si-O bonds the silatrane molecule, the siloxy bonds of the ring are first to hydrolyze. This may result from a lesser steric hindrance and a greater length (1.65-1.70 Å) of the endo-cyclic Si-O bonds as compared with the exo-cyclic siloxy Si-OR bond (1.63-1.64 Å)(24).

Unlike 1-alkoxysilatranes, the hydrolysis rate of para-substituted 1-aroxysilatranes falls with an increase in electron-withdrawing properties of the substituent in the aromatic ring. The logK values of these compounds are linearly correlated to the σ_p values, or, even better, with the σ^*_p values of the aromatic group. The reaction constant in this series is negative which supports the nucleophilic mechanism of 1-aroxysilatrane hydrolysis. The low ρ^* value (-0.40) shows that the effect of the substituent in the aromatic ring on the reaction rate is small.

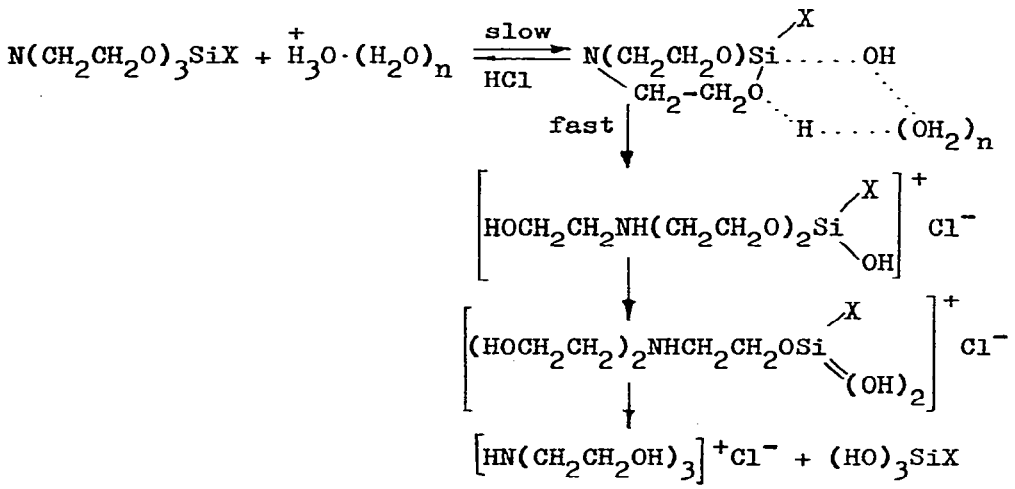
Unlike hydrolytic cleavage in neutral medium (203), acid hydrolysis of 1-organoxysilatranes is described by a kinetic equation of the second order. The hydrolysis was studied in dilute aqueous solutions at 25°C in the presence of HCl and KCl. No salt effect was observed at KCl concentrations from 0.05 to 0.25 mole/l (204).

All the compounds studied are subdivided into two reaction series. 1-Alkoxysilatranes are included in the first series and 1-aroxysilatranes and 1-benzyloxysilatrane are included in the second. In series I, where $\rho^* = -1.26$ [R = C_2H_5, C_3H_7, $(CH_3)_2CH$, $(CH_3)_3C$, $(CH_3)_3CCH_2$], and in series II (R = C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-ClC_6H_4, $C_6H_5CH_2$), where $\rho = 0.23$, the reaction rate falls with an increase in the inductive effect, δ^*_{OR}, indicate that a positive charge is generated at the reaction center in the transition state. The logK values for 1-tert-butoxysilatrane deviate strongly from the correlation line (the hydrolysis rate proves to be much lower than the expected one), and this is caused by the substituent steric effect. The linear dependence of the hydrolysis rate on pH shows that the rate limiting step for both the series is electrophilic attack of the reaction center by a hydroxonium ion. The subsequent steps of cleavage of the endo-cyclic Si-O bonds proceed very fast to form triethanolamine hydrochloride as the main reaction product. It should be noted that a decrease in hydrolytic stability of 1-aroxysilatranes reduces their toxicity.

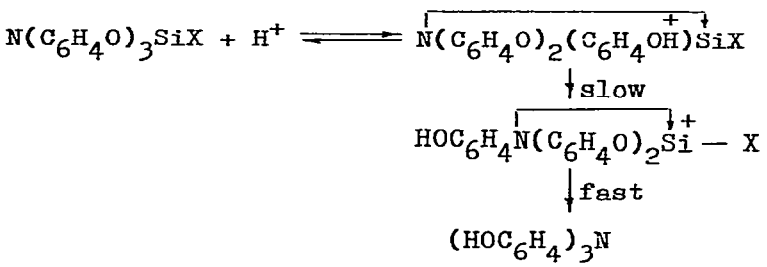
The hydrolysis of 1-(chloroalkyl)silatranes of type $XSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$ where X = $ClCH_2$, Cl_2CH, CH_3ClCH; n = 1-3, has been studied in neutral, acidic and aqueous-alcohol media (194). The rate of hydrolysis of 1-(chloromethyl)silatrane in acidic medium is significantly higher than in neutral showing a good linear dependence on pH (with [HCl] = $1 \cdot 10^{-3}$, $1.5 \cdot 10^{-3}$ and $2.5 \cdot 10^{-3}$ mole$\cdot l^{-1} \cdot sec^{-1}$, k_2^{25} = 0.44 ± 0.01, 0.66 ± 0.01 and 0.87 ± 0.02 mole$\cdot l^{-1} \cdot sec^{-1}$, respectively) (194). Such a large change in the rate in the presence of HCl indicates that the limiting step of the process is electrophilic attack of the reaction center by the hydroxonium ion with simultaneous transfer of the hydration shell to the silicon atom.

The hydrolysis of 1-(chloromethyl)silatrane using $H_2{}^{18}O$ shows that this process involves cleavage of the Si-O rather than of the O-C bond (194).

The presence of methyl groups in positions 3,7,10 of the silatrane skeleton decreases the hydrolysis rate considerably (194). This appears to result from decreased steric accessibility of the oxygen atom. As the electronegativity of the substituent at the silicon atom increases, the hydrolysis rate constant of 1-(chloroalkyl)silatranes also decreases markedly.



In the acid-catalyzed hydrolysis of 1-organyltribenzosilatranes, $XSi(OC_6H_4)_3N$ (X = CH_3, C_6H_5, 4-$CH_3C_6H_4$) and $[N(C_6H_4O)_3Si]_2O$, the rate-determining step also involves rapid protonation of an oxygen atom followed by breakage of the Si-O bond. Protonation of the nitrogen atom is rejected as a mechanistic path since the nitrogen has been shown to be non-basic and such protonation is not expected to promote Si-O bond cleavage (166).



When X is Cl, the reaction proceeds via the ion pair stabilized by $(p\text{-}d)_{\pi}$ bonding in the siliconium ion (166).

A kinetic study of the acid-catalyzed hydrolysis of 1-benzylsilatrane as well as 4- and 3-substituted 1-phenylsilatranes using D_2O as solvent suggested that the rate-determining step involves slow protonation of the nitrogen atom concerted with fission of the Si←N bond (205) rather than breakage of an endocyclic Si-O bond as proposed previously (166).

3.1.2. Other Reactions

Cleavage of 1-organylsilatranes by aqueous solutions of heavy metal salts containing fluoride ion leads to the formation of the corresponding organometallic compounds (190, 206-208).

$$RSi(OCH_2CH_2)_3N + HgCl_2 + NH_4F \longrightarrow RHgCl + SiO_2 + [(HOCH_2CH_2)_3NH]F + NH_4Cl \quad (49)$$

$$RSi(OCH_2CH_2)_3N + Hg_2F_2 + 2H_2O \longrightarrow RHgF + Hg + SiO_2 + [(HOCH_2CH_2)_3NH]F \quad (50)$$

$R = CH_3,\ CH_2{=}CH,\ C_6H_5$

$$3RSi(OCH_2CH_2)_3N + Pb(OCOCH_3)_4 + NH_4F + 6H_2O \downarrow R_3PbF + 3SiO_2 + 3[(HOCH_2CH_2)_3NH]OOCCH_3 + NH_4OCOCH_3 \quad (51)$$

$$2RSi(OCH_2CH_2)_3N + Pb(OCOCH_3)_4 + NH_4F + 4H_2O \downarrow R_2PbF_2 + 2SiO_2 + 2[(HOCH_2CH_2)_3NH]OOCCH_3 + NH_4OCOCH_3 \quad (52)$$

$$2RSi(OCH_2CH_2)_3N + SbF_3 + 8HF + 4NH_4F \downarrow R_2SbF + 2(NH_4)_2SiF_6 + 2[(HOCH_2CH_2)_3NH]F \quad (53)$$

$$3RSi(OCH_2CH_2)_3N + Bi(OH)_3 + 6NH_4F + 12HF \downarrow BiR_3 + 3[(HOCH_2CH_2)_3NH]F + 3(NH_4)_2SiF_6 + 3H_2O \quad (54)$$

$R = C_6H_5$

These reactions are based on the initial hydrolytic fission of a Si-O bond of the silatrane skeleton according to the following scheme:

$$CH_3Si(OCH_2CH_2)_3N + 3H_2O \longrightarrow CH_3Si(OH)_3 + N(CH_2CH_2OH)_3 \quad (55)$$

$$CH_3Si(OH)_3 + 5NH_4F \longrightarrow (NH_4)_2[CH_3SiF_5] + 3NH_4OH$$

$$(NH_4)_2[CH_3SiF_5] + HgCl_2 \longrightarrow CH_3HgCl + (NH_2)_2[SiF_5Cl] \downarrow NH_4F \rightarrow (NH_4)_2[SiF_6]$$

The reaction of 1-organylsilatranes with aqueous solutions of antimony trifluoride gives predominantly diorganylfluorostibines (scheme 53), but in the absence of water, stibatrane and the corresponding organyltrifluorosilane are formed (208).

$$XSi(OCH_2CH_2)_3N + SbF_3 \longrightarrow XSiF_3 + Sb(OCH_2CH_2)_3N \qquad (56)$$

$X = CH_3,\ CH_2{=}CH$

The primary product of the reaction of 1-ethoxysilatrane with AgF seems to be 1-fluorosilatrane (190)

$$2C_2H_5OSi(OCH_2CH_2)_3N + 2AgF \longrightarrow 2AgOC_2H_5 + 2FSi(OCH_2CH_2)_3N$$

$$\downarrow 2H_2O$$

$$Ag_2O + 2C_2H_5OH$$

$$\downarrow$$

$$2Ag + 1/2\ O_2$$

In the presence of HCl, 1-organylsilatranes are decomposed by alcohols to give the corresponding organyltrialkoxysilanes (209).

$$XSi(OCH_2CH_2)_3N + ROH \xrightarrow{HCl} XSi(OR)_3 + (HOCH_2CH_2)_3N\cdot HCl \qquad (58)$$

$R = CH_3,\ C_2H_5;\ X = CH_3,\ C_6H_5,\ CH_2{=}CH,\ CH_3COOCH_2$

3.2. Reactions with Retention of the Silatrane Ring

3.2.1. Complexation Reactions

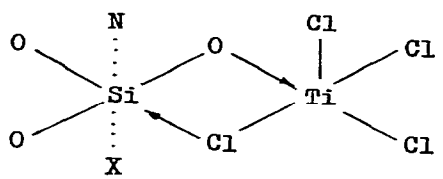
The peculiar character of the molecular structure of silatranes accounts for their lack of clearly distinguished basic properties. This may be explained in terms of steric inaccessibility of the nitrogen lone electron pair involved, in addition, the Si←N transannular interaction. In fact, silatranes are not neutralized immediately by glacial acetic acid and are only titrated slowly at 100°C in the same medium (9,15).

The steric factors in the silatrane molecule are so important that despite considerably lesser σ-electron release from nitrogen than in boratranes, silatranes do not form complexes with methyl iodide (143) (unlike boratranes (200), stannatranes (160), and 5-azabicyclo[3.3.3]undecane (manxine) (128, 129).

Nevertheless, recently it has been found that the nitrogen atom in silatranes is able to form ammonium salts. This appears to be due to isomerization of the endo-form of the silatrane into the exo-form having a nearly planar $N(CH_2)_3$ group (164). This isomerization is confirmed by anhydrous potentiometric titrations of some 1-organylsilatranes in acetonitrile and dimethyl sulfoxide (164). As the hydrolysis of the silatranes is much slower than these titrations, it was suggested that silatranes react with acids to give nitrogen complexes (164). The observed similarity in the semi-neutralization potentials of $HClO_4$-silatrane complexes and the analogous tri(2-oxyalkyl)amine salts shows a negligible effect of the silicon atom on the atom-base properties of nitrogen in the exo-form. The limiting stage of salt-formation is the endo/exo-form conversion. The silatrane/$HClO_4$ adduct is consistent with 1:1 composition.

A comparison of the dipole moments of silatranes measured in benzene, chloroform, and ethyl acetate indicates that silatranes form hydrogen bonds with chloroform (139-142). This also is confirmed by IR and NMR data (149,169) and by the dielectric loss method as well (210). Isotherms of dielectric loss of the systems benzene-chloroform-silatrane, $XSi(OCH_2CH_2)_3N$, (X = C_2H_5, C_2H_5O, C_6H_5) show that chloroform forms an intermolecular hydrogen bond with silatranes involving the oxygen atoms (210).

Silatranes, $XSi(OCH_2CH_2)_3N$, where X = C_2H_5, C_2H_5O, C_6H_5, 3-$CH_3C_6H_4$) form complexes with Lewis acids (1:1 complexes with $AlBr_3$ and $TiCl_4$ and 1:2 with $TiCl_4$ (211). The donor



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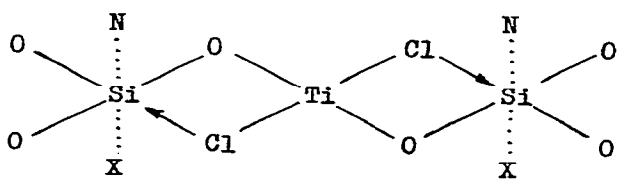


b

centers of the complexes considered are thought to be the oxygen atoms. The halogen atoms are arranged in the plane of three oxygen atoms, thus changing the trigonal pyramidal configuration to octahedral.

Such complexation shifts the ν_{as}(Si-O) band to the shorter wave length by approximately 10 cm^{-1}. The unchanged band at 568-590 cm^{-1} suggests that there is no participation of the nitrogen atom in the donor-acceptor interaction with Lewis acid (211). However, these data do not allow one to make a unique conclusion concerning the structure of the complex.

Recently, it has been possible to isolate 1-organyl-3,7,-10-trimethylsilatrane hydrochlorides of the type $XSi[OCH(CH_3)CH_2]_3N \cdot HCl$ (X = CH_3, CH_2=CH, $ClCH_2$) which are formed when dry hydrogen chloride is passed through chloroform solutions of the corresponding silatranes at room temperature or below (164). These are white powdery substances, insoluble in non-polar and weakly polar organic solvents. All the hydrochlorides are soluble in acetonitrile and water. The latter hydrolyzes them to give immediately tris(2-oxypropyl)amine hydrochloride and polyorganylsesquioxane, $RSiO_{1.5}$. These hydrochlorides melt with decomposition, HCl being evolved. When heated in vacuum, they sublime, decomposing into the initial components.

According to NMR data, 1-methylsilatrane is capable of coordination with europium tris(dipivaloylmethanate), $Eu(DPM)_3$ (181,185).

1-Phenyl- and 1-benzylsilatranes form charge-transfer complexes with tetracyanoethylene (176). In these complexes coordination is effected via the benzene ring of the aromatic substituent. A study of UV spectra of dichloroethane solutions of silatranes (1-methyl- and 1-chloromethylsilatrane and their 3,7,10-substituted derivatives) containing tetracyanoethylene suggested complexing between the components (164). The donor center of silatrane was believed to be the nitrogen atom whose lone elctron pair might be involved in complexing with tetracyanoethylene via the endo-exo transfer of the silatrane skeleton. Later it was established (220) that the UV absorption in the 20000-25000 cm^{-1} region belonged to the tetracyanoethylene anion-radical rather than to the silatrane-tetracyanoethylene complex, as the EPR and UV spectra of the former were consistent with those reported in the

literature. The formation of the anion-radical is due to electron-transfer from the nitrogen atom of triethanolamine molecule and the products of uncompleted silylation of the latter contained as trace impurities. The nitrogen atom of the silatrane does not react with tetracyanoethylene. That is confirmed by the absence of an EPR signal and characteristic colour of saturated solutions of the above silatranes and tetracyanoethylene thoroughly purified by multiple recrystallization in benzene followed by sublimation in vacuum. The results obtained are in agreement with chemical data on the inertness of the silatrane nitrogen atom (10) and with quantum-chemical calculation of the Si←N bond energy as well.

3.2.2. Other Reactions

Most chemical transformations of silatranes which involve no cleavage of the silatrane skeleton have been described already in subsections 2.1-2.5, Section 1. Therefore, the above reactions are only briefly considered here.

Although the classical S_N2 mechanism of nucleophilic substitution is not applicable to silatranes since back-side attack at the silicon atom is impossible, silicon-functional silatranes are readily involved into different reactions of nucleophilic substitution. Thus 1-alkoxysilatranes undergo exchange reactions by higher alcohols, glycols and glycerine according to scheme 25 (27,72), by phenols (73,77), triethanolamine (15), triphenylsilanol (scheme 27)(15) and some carboxylic acids according to scheme 26 (15).

The alkoxy group in 1-alkoxysilatranes and hydrogen atom in 1-hydrosilatranes are easily replaced by halogen atoms in reactions with hydrogen halides HX (X = F, Cl, Br) (15). (schemes 28 and 37), with phosphorus and sulfur halides, $M(O)X_2$, where M = P,S, CH_3P; X = Br, Cl, F (91); with free halogens (schemes 35,36) (15,96) and N-halosuccinimides (scheme 38) (15).

The dehydrocondensation reactions of hydrosilatrane and its C-substituted derivatives with alcohols, phenols (94), alkanediols (72,93), acids (94), carbohydrates (95,95a) and cholesterine (95b) proceed readily according to schemes 33 and 34. The high reactivity of the Si-H bond in the silatrane allowed it to be used as a reducing agent for benzyl bromide, benzoyl chloride, acetone, some aldehydes, and azo- and nitrocompounds of the aromatic series (212).

1-Hydroxysilatrane enters characteristic reactions for normal silatranes (30) and (31) (15,71).

Chemical transformations of 1-halosilatranes have not been studied in detail. Only the reaction of 1-chlorotribenzosilatrane with phenol has been described (79).

1-Vinylsilatrane can be hydrosilylated in the presence of chloroplatinic acid as catalyst (102, 103). 3-Methylsubstituted 1-vinylsilatrane displays a higher reactivity in reactions with perfluoroorganyl iodides according to scheme 44 (101,213), various mercaptans (scheme 46) (60,61,214,215), thioacetic and thiobenzoic acids than unsubstituted vinylsilatrane.

1-(Haloalkyl)silatranes react rather easily with alkali methal mercaptides according to scheme 40 (61,97,214) and with sodium iodide. They also form phosphonic salts in reactions with triorganylphosphines (42) and undergo the Arbuzov reaction with trialkyl phosphites (scheme 41) (55,94,98). The iodo derivatives have proved to be most reactive in these reactions.

1-Aminoalkylsilatranes easily form methiodides (35). The amine group in 1-(3'-aminopropyl)silatrane is readily acylated and alkylated (35,104) and enters the condensation reaction with aldehydes as well (35a).

(Mercaptoalkyl)silatranes of type $HS(CH_2)_nSi(OCH_2CH_2)_3N$ (n = 2-6), when heated with sulfur, form the corresponding bissilatranylalkylpolysulfides, $[N(CH_2CH_2O)_3Si(CH_2)_n]_2S_m$ where m = 2-6 (215).

The data of the first author's investigations in the field of chemistry of silatranes were reported at numerous international symposia and conferences (221-244). The results on biological activity of silatranes are summarized in several reviews and monographs (1, 4,10,11,16,21,245,246).

We thank Dr. V.A. Pestunovich for several interesting discussions and valuable interpretation of physical data. We also are grateful to Drs. Yu.L. Frolov and E.I. Brodskaya for their kind help in writing the spectroscopic sections of the present review.

APPENDIX

Since the publication of the present review was somewhat delayed and the investigations in the field of chemistry, physics and biology of silatranes have developed rather extensively, the authors consider it desirable to complement this work with up- dated literature data which has appeared until the end of 1980.

Recently a monograph "Silatranes" and a review by M.G.Voronkov and V.M.Dyakov (247,248), a review by V.F.Sidorkin, V.A. Pestunovich and M.G.Voronkov (249) devoted to the physical chemistry of silatranes have been published in the USSR. The biological activity of silatranes has been elucidated in detail in a review by M.G.Voronkov (4a, 250).

The up-to-date material is presented in the Appendix in the same order as in the main text of the review, the numeration of the list of references continuing that in the main text.

Chapter I. METHODS OF PREPARATION

I.1.Transesterification of Si-Substituted Trialkoxysilanes

Transesterification of unsaturated organyltrialkoxysilanes by triethanolamine without a catalyst leads to the 1-organylsilatranes, X-Si(OCH_2CH_2)$_3$N having a double or triple bond or, in some cases, a triorganyl- or diorganylsilyl group in a hydrocarbon radical at the silicon atom (X = HC≡C, H_2C=CC≡C, C_6H_5C≡C, C_6H_5CH=CH, $(CH_3)_3SiC$≡C, $(CH_3)_3SiCH$=CH, $C_6H_5(CH_3)_2Si$-CH=CH, HC≡C$(CH_3)_2SiCH$=CH, $(CH_3)_3SiCH$=CHSi$(CH_3)_2C$≡C, $(CH_3)_3Si$-CH=CHSi$(CH_3)_2CH$=CH). The reaction was carried out in anisole on cooling or under slight heating (251).

The reaction of 4-alkaryltriethoxysilanes with triethanolamine in the presence of its sodium alkoxide has given the corresponding 1-(4'-alkaryl)silatranes, 4-R-$C_6H_4Si(OCH_2CH_2)_3N$ (R = C_2H_5, $(CH_3)_2CH$) in 90% yield (252). The same method has been used for the synthesis of 1-(4'-vinylphenyl)silatrane (253).

A number of 3-substituted silatranes have been obtained by the reaction of organyltrialkoxysilanes with trialkanolamines (254).

$$XSi(OR)_3 + (HOCH_2CH_2)_2(HOCHR'CH_2)N \rightarrow XSi(OCH_2CH_2)_2(OCHR'CH_2)N$$

X = CH_3, R' = C_6H_5; X = C_2H_5, R' = $ClCH_2$, C_6H_5;

$X = CH_2{=}CH$, $R' = ClCH_2$, C_6H_5; $X = ClCH_2$, $R' = CH_2{=}CH$, $ClCH_2$;
$X = CH_3O$, $R' = C_6H_5$; $X = C_6H_5$, $R' = CH_2{=}CH$, C_6H_5, $ClCH_2$;
$X = C_6H_5CH_2$, $R' = C_6H_5$

A series of 1-organylsilatranes which are adamantyl substituted was prepared by treating the corresponding organyltrialkoxysilanes with triethanolamine (255).

$$AdR'Si(OC_2H_5)_3 + (HOCH_2CH_2)_3N \longrightarrow AdR'Si(OCH_2CH_2)_3N$$

$R' = -CH_2CH_2-$, $-C_6H_4-$, $-C_4H_2S-$ (thienyl)

Ad = 

Treatment of tetraethoxysilane with triethanolamine and substituted phenols has afforded phenoxysilatranes of general formula $R-C_6H_4OSi(OCH_2CH_2)_3N$ ($R = C_2H_5OOC$, C_3H_7OOC (256), $R = CH_3$, C_2H_5, $(CH_3)_2CH$, $CH_2{=}CHCH_2$, Cl, Br, CH_3O, NO_2, NH_2 (257) or $2,4,6\text{-}R_3C_6H_2Si(OCH_2CH_2)_3N$ ($R = CH_3$) (258).

3-Methyl-, 3,7-dimethyl- and 3,7,10-trimethyl derivatives of 1-(iodomethyl)silatrane have been prepared by transesterification of iodomethyltrimethoxysilane with the corresponding trialkanolamines (259).

The alkali hydroxide-catalyzed reaction of dichloromethyltrialkoxysilanes or dichloromethylalkyldiethoxysilanes with triethanolamine involves loss of a Cl_2CH group leading to the formation of 1-alkoxy- or 1-alkylsilatranes, respectively, in quantitative yield (260, 261).

$$Cl_2CHSi(OR)_3 + (HOCH_2CH_2)_3N \longrightarrow ROSi(OCH_2CH_2)_3N + CH_2Cl_2$$
$$Cl_2CHRSi(OR')_2 + (HOCH_2CH_2)_3N \longrightarrow RSi(OCH_2CH_2)_3N + CH_2Cl_2$$

The reaction of triethanolamine with 1-cyanoethyltrimethoxysilane and 1-carbomethoxyethyltrimethoxysilane proceeds anomalously to give 1-methoxysilatrane (262).

$$CH_3CHXSi(OCH_3)_3 + (HOCH_2CH_2)_3N \longrightarrow CH_3OSi(OCH_2CH_2)_3N + C_2H_5X$$

$X = CN$, CH_3OCO

This reaction is another example of the formation of a silatrane ring due to loss of the electronegative organic group from silicon by cleavage of the Si-C bond. Especially interesting is the fact that the Si-C bond breaks more easily than the Si-O bond.

An attempt to synthesize 1-organylsilylmethylsilatrane, $R_3SiCH_2Si(OCH_2CH_2)_3N$, having a methylene group between two silicon atoms, was unsuccesful due to Si-C bond cleavage in the presence of an alkali catalyst (263). The main reaction product is 1-methylsilatrane.

$$CH_3(C_2H_5O)_2SiCH_2Si(OC_2H_5)_3 + (HOCH_2CH_2)_3N \rightarrow CH_3Si(OCH_2CH_2)_3N$$

1-(2'-O,O-Dialkylphosphonmethyl)silatranes have been obtained by treatment of 2-(O,O-dialkylphosphonmethyl)trialkoxysilanes with tris(2-oxyalkyl)amine in the presence of alkali alkoxide as a catalyst (264).

$$(RO)_2P(O)CH_2CH_2Si(OAlk)_3 + (HOCHR'CH_2)_3N \downarrow$$

$$(RO)_2P(O)CH_2CH_2Si(OCHR'CH_2)_3N$$

$R = C_2H_5$, $R' = CH_3$

Unlike the corresponding organylthiomethyltrialkoxysilanes, transesterification of alkyl(methyl)trialkoxysilylmethylsulfonium iodides by triethanolamine requires no catalyst and leads to sulfonium salts of the silatrane series (243,265,266).

$$^-IR(CH_3)\overset{+}{S}CH_2Si(OR')_3 + (HOCH_2CH_2)_3N \rightarrow {}^-IR(CH_3)\overset{+}{S}CH_2Si(OCH_2CH_2)_3N$$

$R = CH_3$, C_2H_5; $R' = CH_3$

A side-product of the reaction is alkyldimethylsulfonium iodide, $^-IR(CH_3)_2S^+$. The formation of this substance seems to be due to decomposition of the silatrane sulfonium salts obtained under the action of triethanolamine or the alcohol evolved during the reaction.

Treatment of ethylthioethyltrimethoxysilane methiodide by triethanolamine in an alcohol medium resulted in only β-cleavage and formation of triethanolamine iodohydride (265).

Bissilatranylalkylpolysulfides, $[N(CH_2CH_2O)_3Si(CH_2)_n]_2S_m$ can be obtained from the corresponding trialkoxy derivatives and triethanolamine (267).

Furyl- and thienylsilatranes, $X\text{-}Si(OCH_2CH_2)_3N$ (X = furyl, 5-methylfuryl, 2-furylethyl, thienyl) were prepared by transesterification of corresponding heteryltrialkoxysilanes with triethanolamine (268).

Heating of carbofunctional organyltriethoxysilanes, $X(CH_2)_nSi(OC_2H_5)_3$ (n = 1-3, X = N-heterocyclic substituent or acetamido group) with triethanolamine in benzene or xylole

has led to the corresponding organylsilatranes (35a).

$$X(CH_2)_nSi(OC_2H_5)_3 + (HOCH_2CH_2)_3N \longrightarrow X(CH_2)_nSi(OCH_2CH_2)_3N$$

X = aziridinyl, n = 2; X = morpholinyl, n = 1,3; X=pyridazinyl, n = 3; X = phthalazinyl, n = 3; X = $C_4H_9(CH_3CO)N$, n = 1; X = CH_3CONH, n = 3

Glycosyl silatrane acetates have been prepared by transesterification of corresponding triethoxysilyl derivatives of glucose, galactose and xylose acetates with triethanolamine (269).

1.2. From Other Compounds of Type $RSiX_3$

A series of C-substituted 1-organylsilatranes can be readily obtained from the corresponding organyltrichlorosilanes and tris(2-oxyalkyl)amines or their hydrochlorides (270).

$$RSiCl_3 + [HOCH(CH_3)CH_2]_n(HOCH_2CH_2)_{3-n}N \cdot mHCl \downarrow$$

$$RSi[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}N + (3+m)HCl$$

R = CH_3, C_2H_5, $ClCH_2$, $Cl(CH_2)_3$; n = 1-3, m = 0-1

When m = 0 the reaction is catalyzed by the compounds capable to generate hydrogen chloride (alcohols, alkanolamine hydrochlorides) while reacting with chlorosilanes. This reaction proceeds mainly at 140-180°C or at the boiling point of the initial organyltrichlorosilane. However, when m = 1 the reaction proceeds without a catalyst even at room temperature and completes by heating the reaction mixture in vacuum. If an organic group at silicon is readily cleaved by HCl the reaction of $RSiCl_3$ with tris(2-oxyalkyl)amines or their hydrochlorides affords the corresponding C-methylsubstituted 1-chlorosilatranes (270).

$$RSiCl_3 + [HOCH(CH_3)CH_2]_n(HOCH_2CH_2)_{3-n}N \cdot mHCl \downarrow$$

$$ClSi[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}N + RH + (2+m)HCl$$

R = CH_2=CH, C_6H_5

The above compounds are also the products of the reaction of tris(2-oxyalkyl)amine hydrochlorides with 2-chloroethyltrichlorosilane due to β-elimination of the initial silane.

$$ClCH_2CH_2SiCl_3 + [HOCH(CH_3)CH_2]_n(HOCH_2CH_2)_{3-n}N \xrightarrow{mHCl}$$

$$ClSi[OCH(CH_3)CH_2]_n(OCH_2CH_2)_{3-n}N + CH_2{=}CH_2$$

A new synthetic route to 1-organylsilatranes is the hydrocondensation of organylsilanes with triethanolamine in the absence or presence of transition metals, for example, cobalt tetracarbonyl (271).

$$RSiH_3 + (HOCH_2CH_2)_3N \longrightarrow RSi(OCH_2CH_2)_3N + 3H_2$$

R = CH_3, n-C_8H_{17}, C_6H_5, $C_6H_5CH_2$, 4-ClC_6H_4, 4-$CH_3OC_6H_4$, 4-$(CH_3)_2NC_6H_4$, 3-$F_3CC_6H_4$, 4-$CH_3C_6H_4CH_2$

However, this method is mainly of theoretical interest.

Treatment of organyltrifluorosilanes by tris(2-trimethylsiloxyethyl)amine has led to the corresponding organylsilatranes (272-274).

$$RSiF_3 + [(CH_3)_3SiOCHR'CH_2]_3N \longrightarrow RSi(OCHR'CH_2)_3N + 3(CH_3)_3SiF$$

R = $C_6H_5COOCH_2$, $CH_3C_6H_4COOCH_2$, $FC_6H_4COOCH_2$; R' = H, CH_3

A similar reaction of 3-perfluoroacyloxypropyltrifluorosilanes with tris(2-trimethylsiloxyalkyl)amines has been used for the preparation of 1-(3'-perfluoroacyloxypropyl)silatranes (275).

$$R_FCOO(CH_2)_3SiF_3 + [(CH_3)_3SiOCHRCH_2]_3N \rightarrow$$

$$R_FCOO(CH_2)_3Si(OCHRCH_2)_3N + 3(CH_3)_3SiF$$

R_F = CF_3, C_3F_7; R = H, CH_3

These compounds could not be synthesized according to the classical scheme from the corresponding organyltrialkoxysilanes and tris(2-oxyethyl)amines.

Treatment of organyltris(dimethylamino)silanes with the corresponding trialkanolamines has afforded 3-substituted silatranes (254).

$$XSi[N(CH_3)_2]_3 + (HOCH_2CH_2)_2(HOCHRCH_2)N \rightarrow$$

$$XSi(OCH_2CH_2)_2(OCHRCH_2)N$$

X = CH_3, R = C_6H_5; X = R = C_6H_5

Silatranes with a germatranyl group in the α-position to

silicon have been prepared according to scheme (263):

$$[(CH_3)_2N]_3SiCH_2Ge[N(CH_3)_2]_3 + (HOCH_2CH_2)_3N \longrightarrow N(CH_2CH_2O)_3SiCH_2Ge(OCH_2CH_2)_3N$$

The low yield (30%) of the above compound seems to be due to steric hindrance. The steric factors are likely to be responsible for failure in attempts to synthesize bis(silatranyl)-methane by the same method (263).

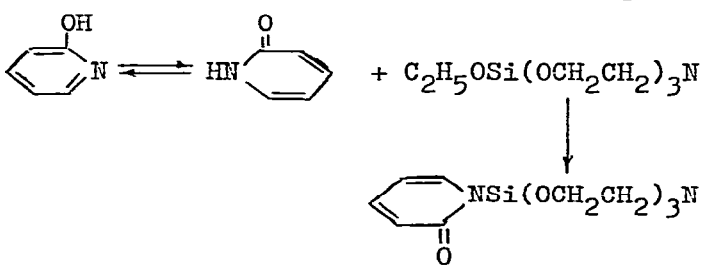
2.1. Transformations of 1-Alkoxy- and 1-Oxysilatranes

Transesterification of 1-ethoxysilatrane by ethanolamine and its N-alkyl derivatives, $R_2NCH_2CH_2OH$ (R = H, CH_3, C_2H_5) as well as by aminophenol affords the corresponding 1-(2'-aminoorganoxy)silatranes (276).

$$C_2H_5OSi(OCH_2CH_2)_3N + ROH \longrightarrow ROSi(OCH_2CH_2)_3N$$

R = $(CH_3)_2NCH_2CH_2$, $(C_2H_5)_2NCH_2CH_2$, $H_2NCH_2CH_2$, $2\text{-}H_2NC_6H_4$

The reaction occurs without solvent in the presence of sodium ethoxide as the catalyst. Use of 2-oxypyridine in this reaction has made it possible to obtain 1-(2'-pyridonyl)silatrane, the first compound of the silatrane series with the silicon atom directly bound to the nitrogen atom (276).



2.2. Reactions of 1-Hydrosilatrane

The exchange reaction of 1-hydrosilatrane with triphenylhalomethanes provides a convenient method for the synthesis of 1-halosilatranes (116a, 277).

$$HSi(OCH_2CH_2)_3N + (C_6H_5)_3CX \longrightarrow XSi(OCH_2CH_2)_3N + (C_6H_5)_3CH$$

X = Cl, Br

At room temperature and in CH_2X_2, the reaction proceeds via an ionic mechanism and is of second order. With X = Br the exchange rate of $(C_6H_5)_3CX$ with hydrosilatrane is higher

than with X=Cl that is consistent with different dissociating ability of these halides. A radical mechanism is suggested for the above reaction in benzene at 80°C. The EPR spectrum displays a $(C_6H_5)_3C^\bullet$ signal only in the presence of 1-hydrosilatrene. The latter shows the reaction to involve a silatranyl radical (278).

$$HSi(OCH_2CH_2)_3N \longrightarrow {}^\bullet Si(OCH_2CH_2)_3N + H^\bullet$$

$${}^\bullet Si(OCH_2CH_2)_3N + (C_6H_5)_3CX \longrightarrow XSi(OCH_2CH_2)_3N + (C_6H_5)_3C^\bullet$$

$$HSi(OCH_2CH_2)_3N + (C_6H_5)_3C^\bullet \longrightarrow {}^\bullet Si(OCH_2CH_2)_3N + (C_6H_5)_3CH$$

1-Hydrosilatrane reacts with polyhalomethanes (CH_2Cl_2, $CHCl_3$, $CHBr_3$) in the presence of tert-butyl or benzoyl peroxide to give the corresponding 1-halosilatranes (278,279). The latter are also obtained by treatment of 1-hydrosilatrane with trimethylchloro- or trimethylbromosilane in the presence of quinoline (277).

$$HSi(OCH_2CH_2)_3N + (CH_3)_3SiX \longrightarrow XSi(OCH_2CH_2)_3N + (CH_3)_3SiH$$

X = Cl, Br

2.3. Reactions of Halo- and Haloalkylsilatranes

The exchange of halogen atoms between 1-chlorosilatranes and potassium fluoride occurs in HMPT at 100°C (277).

$$ClSi\left[OCH(CH_3)CH_2\right]_n(OCH_2CH_2)_{3-n}N + KF \downarrow$$

$$FSi\left[OCH(CH_3)CH_2\right]_n(OCH_2CH_2)_{3-n}N + KCl$$

n = 0-3

The reaction of 1-iodomethylsilatrane with tertiary amines has given the corresponding quartenary ammonium salts (280).

$$ICH_2Si(OCH_2CH_2)_3N + B \longrightarrow {}^-I\overset{+}{B}CH_2Si(OCH_2CH_2)_3N$$

B = $(CH_3)_3N$, $(CH_3)_2NCH_2CH_2N(CH_3)_2$, $\overline{CH_2(CH_2)_4N}$, $O(CH_2CH_2)_2NH$, C_5H_5N (pyridine), C_9H_7N (quinoline), $C_6H_5NH_2$

The action of dimethylethanolamine on 1-iodomethylsilatrane causes cleavage of the Si-C bond and formation of 1-(2'-dimethylaminoethoxy)silatrane methiodide (280).

$$(CH_3)_2NCH_2CH_2OH + ICH_2Si(OCH_2CH_2)_3N \downarrow$$

$${}^-I\overset{+}{(CH_3)_2N}CH_2CH_2OSi(OCH_2CH_2)_3N$$

In contrast to this, treatment of 1-iodomethylsilatrane with acetylcholine yields the corresponding quartenary ammonium salt, $^{-}ICH_3COOCH_2CH_2(CH_3)_2NCH_2 \cdot i(OCH_2CH_2)_3N$ (280).

Treatment of 1-(haloalkyl)silatranes with thiourea has led to the corresponding isothiuronium salts of silatranes (281).

2.4. Addition to 1-Vinylsilatranes

Furyl- and thienylsilatranes containing a second silicon atom between the silatranyl group and the heterocycle have been prepared by hydrosilylation of 1-vinylsilatrane with the corresponding heterylhydrosilanes (268). The reaction were carried out in benzene in the presence of H_2PtCl_6 as catalyst.

$$(CH_3)_{3-n}R_nSiH + CH_2{=}CHSi(OCH_2CH_2)_3N \downarrow$$

$$(CH_3)_{3-n}R_nCH_2CH_2Si(OCH_2CH_2)_3N$$

R = 2-furyl, 2-thienyl, n = 1-2

Addition of 2,5-bis(dimethylsilyl)thiophene to 1-vinylsilatrane leads to the compound having two silatranyl groups (268).

$$H(CH_3)_2Si\text{-}R\text{-}Si(CH_3)_2H + 2CH_2{=}CHSi(OCH_2CH_2)_3N \downarrow$$

$$N(CH_2CH_2O)_3SiCH_2CH_2Si(CH_3)_2\text{-}R\text{-}Si(CH_3)_2CH_2CH_2Si(OCH_2CH_2)_3N$$

R = C_4H_2S (2,5-thienyl)

The addition of α,ω-alkanedithiols to vinylsilatranes is initiated facily by not only UV irradiation, but also by exposure to diffused daylight (in the latter case the reaction proceeds much slower) (281, 282). Diadducts are formed when the initial reagent molar ratio is 1 : 2 (281, 282).

$$HS(CH_2)_nSH + 2CH_2{=}CHSi\left[OCH(CH_3)CH_2\right]_3N \downarrow$$

$$N\left[CH_2CH(CH_3)O\right]_3SiCH_2CH_2S(CH_2)_nSCH_2CH_2Si\left[OCH(CH_3)CH_2\right]_3N$$

n = 1-2

Phosphorus-containing 1-ethylsilatrane derivatives have been obtained by the addition of diphenylphosphine to 1-vinylsilatranes in the presence of radical initiators (264). With R = CH_3, the reaction may occur without initiators.

$$(C_6H_5)_2PH + CH_2{=}CHSi(OCHRCH_2)_3N \longrightarrow (C_6H_5)_2PCH_2CH_2Si(OCHRCH_2)_3N$$

R = H, CH_3

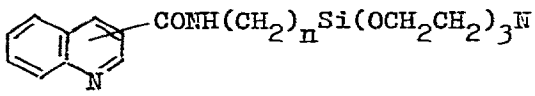
2.5. Reactions of Aminoalkylsilatranes

1-(3'-Aminopropyl)silatrane was used as starting material for the synthesis of 1-[3'-(arylidenamino)propyl]silatranes(35a).

$$H_2N(CH_2)_3Si(OCH_2CH_2)_3N + RCHO \longrightarrow RCH{=}N(CH_2)_3Si(OCH_2CH_2)_3N$$

R = 4-$CH_3OC_6H_4$, 4-$O_2NC_6H_4$, 4-ClC_6H_4, 4-HOC_6H_4, 4-$(C_2H_5)_2NC_6H_4$

Aminoalkylsilatranes, $H_2N(CH_2)_nSi(OCH_2CH_2)_3N$ (n = 1,3), react with hydrochlorides of 2-, 3-, and 4-quinoline carboxylic acids to form the corresponding amides (283):



1-(3'-Aminopropyl)silatranes are involved in the addition-cyclization reaction with divinylsulfoxide (284). The reaction occurs in ethanol at 40-60°C in 92% yield.

$$H_2N(CH_2)_3Si(OCH_2CH_2)_n(OCHRCH_2)_{3-n}N + CH_2{=}CHS(O)CH{=}CH_2$$

$$\downarrow$$

$$O{=}S(CH_2CH_2)_2N(CH_2)_3Si(OCH_2CH_2)_n(OCHRCH_2)_{3-n}N$$

R= H, CH_3

Chapter 2. STRUCTURE AND PHYSICAL PROPERTIES

2.1. Molecular Structure

New data on the effect of Si- and C -substituents on the silatrane structure have been obtained by X-ray diffraction.

The Si-N bond length and the extent of transannular interaction are not affected much by the substituents in position 3,7,10 of the atrane skeleton. Thus, the r_{Si-N} value in 1-(chloromethyl)-3,7-dimethyl- and 1-(chloromethyl)-3,7,10-trimethylsilatrane is the same (2.12Å) as that in the unsubstituted analog (115a, 285). In the molecule of 1-(chloromethyl)-3,7-dimethylsilatrane the conformation of the silicon atom is trigonal bipyramidal. The NC_3 group displays a flattened tetrahedron with the C-N-C and Si-N-C angles being 113° and 105°, respectively (115a). The average values of valence angle at the carbon atoms exceed those of tetrahedral angles (the N-C-C and C-C-O values are 112° and 114°, respectively). The average value of the Si-O bond length in 3,7-dimethyl derivative silatrane is slightly smaller than that in unsubstituted 1-(chloromethyl)silatrane (1.64 and 1.66Å, respectively).

A significant difference of the C-C bond length (especially endocyclic)from normal values and the analysis of anisotropic temperature factors suggest that most O and C atoms are involved in vibrations with large amplitudes and high enharmonicity.

In the molecule of 3,7,10-trimethylsilatrane the Si - N distance is 2.146 Å, i.e., it is within the limits of normal values for silatranes(286). The silicon atom is in the centre of a slightly distorted trigonal bipyramid. The mean values of H-Si-O, N-Si-O and O-Si-O angles are 96.0, 84.0 and 118.9°, respectively. The atoms of silicon and nitrogen are displaced from the plane of the three oxygen atoms by 0.167 and 1.973 Å, respectively. The nitrogen atom lies by 0.369 Å out of the plane of the attached carbon atoms. The Si-O bonds in the molecule are shorter (1.594 Å) than in other silatranes studied by the X-ray method. Five-membered half-rings have a clearly displayed C_β-envelope configuration. The β-carbon atoms are displaced from the half-ring plane by in average 0.51 Å. The "envelope" character is determined by H...H repulsion of hydrogen atoms in different half-rings. The C_α-envelope is energetically most favourable for the silatranes having no substituents at endocyclic carbon atoms. With endocyclic methyl groups, the distance between the hydrogen atoms at α-carbon atoms and those of the methyl groups is too short for such a conformation. Owing to this, the C_β-envelope conformation is energetically more advantageous.

The molecular structure of two silatranone derivatives, $X\text{-}Si(OCH_2CH_2)_2(OCOCH_2)N$ (X = 4-F-C_6H_4, 3-CF_3-C_6H_4) have been investigated to reveal the effect of the carbonyl group upon the geometry of the silatrane skeleton (287, 288). The C=O group does not affect muchthe Si - N distance. The lengths of the Si - N transannular bond are 2.106 (X = $CF_3C_6H_4$) and 2.129 Å (X = FC_6H_4). The silicon atom deviates from the plane of the three equatorial oxygen atoms by 0.186 Å (X = $CF_3C_6H_4$) and 0.196 Å (X = FC_6H_4) in opposite direction to the nitrogen. The distances of nitrogen atom from the plane of the adjacent carbon atoms are 0.385 and 0.386 Å for X = $CF_3C_6H_4$ and FC_6H_4, respectively. In both compounds the Si-O bond in the Si-O-CO moiety is longer than the other two. The carbonyl group seems to reduce the interaction between the silicon and oxygen atoms and also strengthen the O-C bond in the Si-O-CO unit. The O-C

bond is nearly 0.1 Å shorter than the other two . Nevertheless the C=O double bond is well localized. The trifluoromethylphenyl derivative contains a disordered CF_3 group.

The Si - N bond length is rather sensitive to the electronic effect of the substituent X at silicon (116a, 287-289). The dependence of the Si - N bond length (r_{Si-N}) in silatranes on the σ^*_X constants is described by the following equation (116a):

$$r_{Si-N} = 2.20(\pm 0.01) - 0.063(\pm 0.006)\sigma^*_X;\ r = 0.947$$

A shorter Si - N distance (2.02 Å) has been found in the 1-chlorosilatrane molecule where the SiO_3 group is nearly planar (116a). The Si-Cl length (2.15 Å) is by 0.13 Å greater than in molecules with a tetrahedral silicon atom. These data agree with the theory of the hypervalent X-Si-N bond in the silatrane molecule.

The Si-N bond length in 1-phenyl-3,7-dimethylhomosilatrane attains 2.42 Å (290).

The structure of 1-methylsilatrane has been investigated by gas-phase electron diffraction at 185°C (291). The results is quite different from the solid-state results. The most drastic difference is the distance between the Si and N atoms. It appears that the gas-phase molecule exhibits weaker interaction between the silicon and nitrogen atoms. The Si-N bond length is much longer compared with the solid-state structure (2.45 and 2.17 Å, respectively). The other distance parameters, with the single exception of the C-C distance, are systematically smaller than the comparable parameters obtained by X-ray. The geometry at the nitrogen atom is remarkably similar to the structure of trimethylamine. The geometry at the silicon atom is more nearly tetrahedral in the gas phase than the proposed trigonal bipyramidal geometry associated with pentacoordinate silicon.

A model for the mechanism of a hypothetic nucleophilic displacement reaction at the tetrahedral silicon atom with a stable trigonal-bipyramidal intermediate has been obtained from X-ray data of Si-substituted silatranes (292). It is shown that the order of the hypervalent X-Si-N bond in the silatrane molecule is a constant value and the substituent X influences the valent state of silicon and nitrogen to the same extent.

INDO computations of the 1-methylsilatrane molecule with or without 3d orbitals of the silicon atom have confirmed the

presence of the transannular Si←N bond (293).

2.3. Dipole Moments

Dipole moments of a number of silatranes, $X\text{-}Si(OCH_2CH_2)_3N$ ($X = CH_3$, C_2H_5O, C_6H_5, C_6H_5O, $4\text{-}ClC_6H_4O$) have been measured in benzene at 25°C (289, 294). The dipole moment of the silatrane molecule increases with increasing electronegativity of the substituent X.

The temperature dependence of dipole moments for three of these silatranes ($X = CH_3$, C_6H_5O, $4\text{-}ClC_6H_4O$) has been investigated within the 20–70°C range. When the temperature rises the dipole moment of 1-methylsilatrane decreases slightly, that of 1-(4'-chlorophenoxy)silatrane increases, and that of 1-phenoxysilatrane apparently does not change. This enables one to suggest that the increase in temperature results in lengthening of the Si←N bond in 1-methylsilatrane; however, a more significant effect is produced by a decrease of "point" charge. On the other hand, in 1-(4'-chlorophenoxy)silatrane, the Si←N bond length is shorter and the "point" charges are higher than in 1-methylsilatrane and the lengthening of this bond due to temperature increase is not sufficient to reduce the dipole moment. In the case of 1-phenoxysilatrane, the influences of the two opposite effects are cancelled.

From the dipole moments and X-ray structural data of silatranes, $XSi(OCH_2CH_2)_3N$, it was possible to calculate the dipole moments of the silatrane skeleton (3.0, 2.7, 2.7 and 3.0 D for $X = CH_3$, $CH_2{=}CH$, C_6H_5, $ClCH_2$, respectively) and the transannular Si←N bond (1.4, 2.3, 2.4 and 3.0 D for the same X, respectively) (295, 296). As the electronegativity of the substituent X at the silicon atom increases, the dipole moment of the Si←N bond increases and is indicative of an increasing charge-transfer from nitrogen to silicon.

The dipole moments of 1-(ethylthioalkyl)silatranes, $C_2H_5S(CH_2)_nSi(OCHRCH_2)_mN$ ($n = 1\text{-}2$, $R = H$, CH_3), have been measured (297). The dipole moments of C-methyl substututed silatranes are slightly higher than those of the corresponding unsubstituted analogs.

The calculated dipole moments of the Si←N bond in 2-homosilatranes, $XSi(OCH_2CH_2)_2(OCH_2CH_2CH_2)N$ ($X = CH_3$, $CH_2{=}CH$, C_6H_5, $ClCH_2$) show that the polarity of this bond is appoximately by 1D lower than that in the corresponding silatranes (296).

The above dipole moment values of the Si←N bond for the

same organylsilatranes and 2-homosilatranes were used in the estimation of the heats of the formation ($-\Delta H$) of this bond. Depending on the nature of the substituent attached to the silicon atom, the heat of formation values are 5-15 kcal/mol for silatranes and 3-11 kcal/mol for homosilatranes (296). The lower Si←N heat of formation for 2-homosilatranes is likely to be related to a Si←N bond lengthening (i.e., a lower charge transfer as compared to that in silatranes) due to steric repulsion of the nitrogen atom on insertion of a CH_2-group in one of the half-rings of the silatrane skeleton.

The dipole moment of the Si-N transannular bond in 1-organylsilatranes has been estimated to be 2.3 D, which is consistent with a charge transfer from nitrogen to silicon of 0.27 ± 0.05 e (298, 299).

2.4. Vibrational Spectra

The IR spectra of furylsilatranes, $R(CH_2)_nSi(OCH_2CH_2)_3N$ (R = 2-furyl, 5-methylfuryl, n = 0-2), have been discussed in terms of Si←N interaction and, in the case of corresponding 2-furylalkoxy- and 2-furyl(aminoalkoxy)silanes, $(p\text{-}d)_\pi$ interactions (300).

The IR and Raman spectra of silatranes do not change in going from the crystalline to the liquid state (301).

It has been concluded that ν_{Si-N} stretching vibrations in silatranes should be in a region lower 400 cm^{-1} (301-302). However, even the simplest spectrum of 1-hydrosilatrane displays no well-defined bands. Therefore, the assignment of band can be a rather approximated one. Although calculations give a ν_{Si-N} value of 334 cm^{-1}, it is not possible to assign any certain frequency in the low-frequency region to the ν_{Si-N} stretching.

A comparison of IR spectra of silatranes, $XSi(OCH_2CH_2)_3N$ and analogous ^{15}N-labelled compounds has enabled a band in the 320-390 cm^{-1} region to be assigned to absorption of the Si←N bond (with X = CH_3, CH_2=CH, C_6H_5, $ClCH_2$, CH_3O, the ν_{Si-N} value is 351, 386, 359, 320, 377 cm^{-1}, respectively) (296).

The Si←N vibrational frequency is a linear function of the bond length. However, the assignment of the band using its isotopic shift is not sufficiently reliable if the mode of vibration is unknown and no complete calculation of the vibration is available. Therefore, the conclusion drawn in (296) needs further confirmation.

Si←N force constants and bond energies have been estimated to be 0.565-0.790 dyne/cm and 23.5-27.4 kcal/mol, respectively (296). On the basis of IR data the force constant (0.5dyne/cm) and energy of the transannular Si←N bond in 1-organylsilatranes (22±2 kcal/mol) have been calculated (298, 299). These data are in good agreement with a previous quantum-chemical calculation (133).

IR spectra of compounds of the type Z-$ArOCH_2COOCH_2Si(OCH_2CH_2)_3N$ (Z = 4-Cl, 2,4,5-Cl_3) have been studied and the carbonyl group stretching intensity has been measured (303,304).

2.5. Ultraviolet Spectra

According to the data of electronic spectroscopy, silatranes, $XSi[OCH(CH_3)CH_2]_3N$ with X = CH_3, CH_2=CH, $NCCH_2CH_2$ form hydrogen bonds with phenol (305). The associates are consistent with a 1 : 1 composition. Equilibrium constants, free energies, enthalpies (6.0-7.5 kcal/mol) and the entropy of hydrogen bond formation have been determined. The data obtained do not solve unambiguously the question concerning the centre of phenol-silatrane coordination, although it is almost certain that it is the oxygen atoms.

The electronic spectra of tetracyanoethylene complexes with 1-(organylthioalkyl)silatranes, $RS(CH_2)_mSi(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N$ (R = CH_3, C_2H_5, C_3H_7, n-C_4H_9, t-C_4H_9, CH_2=$CHCH_2$, m = 1, n = 3; R = $C_6H_5CH_2$, m = 1, n = 1,2; R = C_6H_5, m = 2, n = 3) were compared with the spectra of TCNE-$RS(CH_2)_mSi(OR')_3$ (R' = CH_3, C_2H_5) complexes (306). The charge-transfer bands of the former appear at longer wave-lengths than those of the latter. This has been explained by the Si←N interaction. The ionization potentials of the donor were calculated from the charge-transfer band frequencies and were correlated with inductive and steric constants of substituents at silicon.

The UV spectra of silatranylmethyl esters of aroxyacetic acid have been studied and compared with those of the corresponding trialkoxysilyl derivatives (304).

2.6. NMR Spectra

The linear dependence between the CH_2N chemical shifts and the Si←N bond length in the molecule of silatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_3, C_2H_5, C_6H_5, $ClCH_2$, $Cl(CH_2)_3$) is observed (307).

For a series of silatranes, $XSi(OCH_2CH_2)_3N$ (X = H, CH_3, C_2H_5, Cl, Br, HO, CH_3O, C_2H_5O, C_6H_5O) the relation between the ring proton chemical shifts and the σ_I and σ_R° constants is described by the following equations (307):

$\delta_{OCH_2} = 3.823 + 0.465\sigma_I + 0.261\sigma_R^\circ$; r = 0.989, s = 0.014

$\delta_{NCH_2} = 2.866 + 0.433\sigma_I + 0.342\sigma_R^\circ$; r = 0.989, s = 0.015

The above correlations show that both the inductive and resonance effects of the substituent at silicon do affect the extent of Si←N transannular bonding.

The chemical shifts in the ^1H NMR spectra of a series of sulfur-containing 1-organylsilatranes, $YCH_2Si(OCH_2CH_2)_3N$ [Y = CH_3S, C_2H_5S, t-C_4H_9S, $C_6H_5CH_2S$, $CH_3S(O)$, $C_6H_5CH_2S(O)$], and the corresponding sulfonium salts have been shown to be determined by steric hindrance of the substituent at silicon and sulfur valency (184a, 307, 308).

The NMR shifts induced in 1-chloro-, 1-methyl-, and 1-(chloromethyl)silatrane by complexes of 1-ethylimidazole with $NiCl_2$ or $CoCl_2$ indicate that coordination of the silatranes to the metal ions involved the nitrogen atom (309, 310).

The basicity of oxygen atoms in 1-methylsilatrane and 1-methylhomosilatrane has been determined using a paramagnetic $Eu(DPM)_3$ shifting reagent and shown to increase in the following order: methyltriethoxysilane < 1-methylhomosilatrane < 1-methylsilatrane (138).

^{19}F Chemical shifts to higher field relative to $CFCl_3$ are observed in NMR spectra of 1-fluoro- and 1-fluoro-3,7,10-trimethylsilatranes at 142.8 and, respectively, 141.1 (asymmetrical diastereomer) and 140.2 (symmetrical diastereomer) p.p.m. (178). A lower $^1J_{Si-F}$ value for 1-fluoro-3,7,10-trimethylsilatrane (131.2 Hz) as compared with that for fluorotriethoxysilane (199.1 Hz) is due to a decreased s-character of the Si-F bond of the former.

^1H, ^{13}C, ^{15}N and ^{29}Si NMR spectra of ^{15}N-labelled silatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_3, CH_2=CH, C_6H_5, $ClCH_2$, CH_3O, C_2H_5O) confirm the presence of the Si←N transannular bond (295, 311, 312, 313). The $\delta_{^{15}N}$ chemical shifts correlate with the Taft inductive constants of substituents X at the silicon atom (295, 311) and the calculated Si←N dipole moments (295). This shows that the change in the nitrogen nucleus shielding is mainly explained by charge transfer from nitrogen to silicon.

Measurement of the direct ^{15}N-^{29}Si spin-spin coupling constant in 1-chloromethylsilatrane (1.5 Hz) is the most reliable experimental confirmation of the donor-withdrawing Si←N bond in silatranes (311). Evidently, this constant reflects transmission of the spin information through the Si←N bond since it is unlikely that the interaction of such a value can be transmitted through a system of ^{15}N-C-C-O-^{29}Si bonds.

The solvent effects on the chemical shifts in ^{15}N and ^{29}Si NMR spectra of Si-substituted silatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_3, CH_2=CH, $ClCH_2$, C_2H_5O) have been investigated in detail (311, 312, 314, 315). It has been shown that the linear relationship between $\delta_{^{15}N}$ and $\delta_{^{29}Si}$ measured in various solvents exists not only for the 1-methylsilatrane (314) but also for 1-vinyl-, 1-chloromethyl and 1-ethoxy derivatives of silatrane (315). The nitrogen-15 chemical shifts of these silatranes depend on the polarity and electrophilic affinity of the solvent (313, 315). The investigation of the ^{29}Si NMR spectra of polycrystalline silatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_3, C_2H_5, CH_2=CH, C_6H_5, C_2H_5O, $ClCH_2$, Cl_2CH, ICH_2,F) shows that the influence of the crystalline field on the extent of transannular interaction, peculiar to silatranes in the solid state, does not exceed the effect of a highly polar solvent (DMSO, H_2O) (316). At the same time, the increase in the Si←N bond strength under the substituent effect is accompanied by the decrease in the solvent effect on the ^{15}N and ^{29}Si NMR chemical shifts of silatranes (315, 316). These data were explained by the lowering of transannular Si←N interaction in going from the solid to the solution state. Such a weakening of the Si←N bond has been found to be greater the less strong is this bond and the less is the polar and electrophilic ability of the solvent used (315).

Investigation of the ^{13}C, ^{15}N and ^{29}Si NMR spectra of C-substituted silatranes, $C_6H_5Si(OCHRCH_2)(OCH_2CH_2)_2N$ (R = CH_3, CH_2=CH, C_6H_5, $ClCH_2$) has shown that endocyclic substituents enhance the Si←N transannular bond due to hindered conformation transitions (317).

Investigation of silatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_3, C_6H_5, C_2H_5O, C_6H_5O, 4-ClC_6H_4O, 4-$O_2NC_6H_4$) has been performed (289, 318). The data for aryloxysilatranes indicate that the effect of the substituent in para position on the ^{29}Si chemical shifts can be practically neglected.

According to ^{13}C, ^{15}N and ^{29}Si NMR data for homosilatranes $XSi(OCH_2CH_2CH_2)(OCH_2CH_2)_2N$ (X = CH_3, CH_2=CH, C_6H_5, CH_2Cl, 4-BrC_6H_4) and carbasilatranes $XSi(CH_2CH_2CH_2)(OCH_2CH_2)_2N$ (X = CH_3, C_6H_5), the expansion of one of the rings or substitution of oxygen in the silatrane skeleton make the Si←N bond weaker (317).

2.8. Mass Spectra

Mass spectral fragmentation of Si-substituted silatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_2=CH, CH_2=CCl, HC≡C, C_6H_5C≡C, C_6H_5, C_6F_5), depends on the nature of the substituent X and may proceed in two directions: 1) loss of the substituent X to give an ion of the silatrane skeleton; 2)cleavage of the silatrane ring with retention of the X-Si bond (319). The first route is more characteristic for silatranes with X = CH_2=CH, CH_2=CCl, C_6H_5, C_6F_5. The molecular ion intensity is very low. The second route is observed in silatranes with a C≡C bond.

In the mass spectra of Si-substituted homosilatranes, $XSi(OCHRCH_2)_2(OCH_2CH_2CH_2)N$ (R = H, CH_3, X = CH_3, CH_2=CH, C_6H_5, OCH_3) and 2,8,9-triazasilatranes, $XSi(NHCH_2CH_2)_3N$ (X = CH_3, CH_2=CH, C_6H_5), the molecular ion peak is low intense (320, 321). In spectra of most compounds (exept homosilatrane with R = H, X = CH_2=CH and OCH_3 and 2,8,9-triazasilatranes with X = CH_2=CH) the $M-X^+$ peak is most intense. Further fragmentation of this ion proceeds stepwise, in several parallel routes involving elimination of neutral molecules of ethylene,ethylene oxide and propylene oxide.

The fragmentation of Si-substituted homosilatranes with R = CH_3 proceeds in a similar way. The first step also is a breakage of the substituent X from the silicon atom. This is followed by cleavage of the silatrane ring occurring in several directions. Prior to fragmentation, the molecular ion of homosilatrane derivatives with R = CH_3 is likely to undergo isomerization with the 5-membered ring being enlarged by inclusion of the methyl group.

Along with above cleavage of the X-Si bond, methoxyhomosilatranes with R = H and CH_3 undergo loss of neutral $C_2H_3O^\bullet$ and $C_3H_5O^\bullet$ species without previous abstraction of the CH_3O group from silicon.

Loss of the substituent X in the triazasilatrane molecule is followed by cleavage of silatrane skeleton with a consecu-

tive elimination of two ethylenimine molecules (320).

2.9. Studies by Other Physical Methods

K_α-spectra of Si- and C-substituted silatranes, $XSi(OCHRCH_2)_3N$ (X = H, CH_3, R = H; X = R = CH_3) as well as those of a number of model compounds, i.e., organyltriethoxysilanes and monocyclic compounds, $(CH_3)_2Si(OCH_2CH_2)_2Y$ (Y = O, NCH_3), have been obtained using the X-ray fluorescence method (322). The change in hybridization of the central silicon atom from sp^3 in organyltriethoxysilanes to trigonal-bipyramidal in silatranes and the formation of transannular Si←N bond are accompanied by a considerable increase (by 25%) in the positive charge on the silicon atom. Introduction of three methyl groups in the position 3, 7, 10 of the silatrane skeleton causes no additional change in the charge on the silicon atom.

X-ray fluorescence K_α- and K_β-spectra of the sulfur atom in 1-organylthiomethylsilatranes and their sulfonium salts have been studied (323). Silatranyl carbohydrates have been analyzed using gel chromatography (324). The applicability of gas chromatography to the resolution of silatranes at 200–250°C has been demonstrated (325–328). Retention indices were measured for 48 compounds of this class. The relationship between the observed retention characteristics and silatrane structure has been examined. The retention values observed correlate well with both the inductive constants of substituents at the silicon atom and the dipole moments of silatranes. The extremely strong interaction of silatrane molecules with the stationary phase has been attributed to the influence of the transannular Si←N bond (327).

3,7-Dimethyl-, 3,7,10-trimethyl-, and 3,7-diphenylsilatrane diastereomers were resolved by gas chromatography on medium-polarity columns (326). Individual diastereomers of 1-methyl-3,7,10-tris(trifluoromethyl)silatrane have been separated by GLC (329). The symmetrical isomer, m.p. 90°C was the first to eluate. The unsymmetrical isomer has a melting point of 157°C.

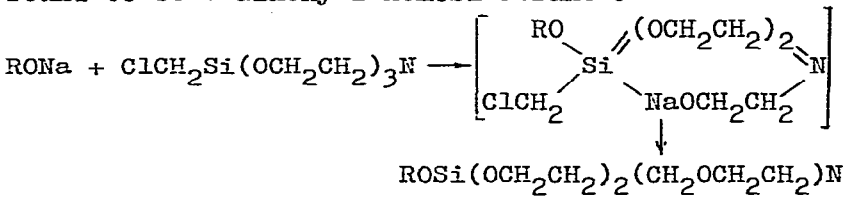
Chapter III. CHEMICAL PROPERTIES

3.1. Reactions Involving Cleavage of the Silatrane Ring

The investigation of the effect of substituent nature in the aromatic ring, temperature, solvent and pH of the medium on the hydrolysis rate of 1-aryloxysilatranes, $RC_6H_4OSi(OCH_2-$

$-CH_2)_3N$, has enabled one to suggest that the reaction conforms to a mechanism of the S_N2-type (330, 331). The hydrolysis kinetics of $2,4,6-(CH_3)_3C_6H_2OSi(OCH_2CH_2)_3N$ has been examined by spectrophotometry (258).

It is remarkable that the reaction of 1-chloromethylsilatrane with sodium or potassium alkoxides of primary, secondary and tertiary alcohols does not lead to the corresponding 1-alkoxymethylsilatranes (332). The reaction products are found to be 1-alkoxy-2-homosilatranes.



The intermediate seems to result from cleavage of a siloxane bond of the silatrane cycle by the alkoxide ion. The above reaction was used to obtain a series of monosaccharide homosilatrane derivatives such as glucose, fructose, sorbose, etc. (332).

Pyrolysis of 1-aroxysilatranes at 220-350°C has been studied using differential thermal analysis (333).

3.2. Reactions with Retention of the Silatrane Ring

1-Hydrosilatrane reacts with triphenylhalomethanes (116a, 277-279), polyhalomethanes (278) and trimethylhalosilanes (277) to give the corresponding 1-halosilatranes. The dehydrocondensation of 1-hydrosilatrane with carbohydrates proceeds readily (334, 335).

The exchange reaction of 1-chlorosilatrane with KF affords 1-fluorosilatrane (277).

1-Vinylsilatrane adds dialkylphosphites more readily in the presence of sodium alkoxide than under UV-irradiation (264). Introduction of methyl groups into the 3, 7 and 10 positions of the silatrane skeleton markedly activates the double bond, thus increasing the yield of adducts (264). So, 1-vinylsilatrane fails to react with dipropylphosphite upon UV-irradiation. Under similar conditions, 3,7,10-trimethyl-1-vinylsilatrane easily adds dipropylphosphite in 68% yield. With or without radical initiators, diphenylphosphine forms β-adduct with 1-vinylsilatrane and its C-methyl derivatives (264). 1-(4'-Vinyl)phenylsilatrane is polymerized by trifluoroboron etherate to afford a viscous, non-melting polymer. The sil-

atrane skeleton is likely to remain in the course of polymerization (253).

The reaction of 1-(2'-aminoethoxy)silatranes with methyl iodide gives the quarternary salts (276). 1-(Aminoalkyl)silatranes are involved in reactions with aldehydes (35a), hydrochlorides of quinoline carboxylic acids (283) and divinylsulfoxide (284).

Alkylthioalkylsilatranes, $RS(CH_2)_nSi(OCH_2CH_2)_3N$ are oxidized by hydrogen peroxide to the corresponding S-oxides or S-dioxides (266). The reaction of 1-(organylthioalkyl)silatranes with alkylhalides yields sulfonium salts (267).

Chapter IV. BIOLOGICAL ACTIVITY

Silatranes are compounds having high and specific biological activity. They are of great interest in biology, physiology, pharmacology, medicine and agriculture.

The data on the biological activity of silatranes have been published in two English reviews by M.G.Voronkov (4a, 250) and in the Russian edition of the monograph "Silatranes" (247). To avoid duplication of these earlier reviews, we have therefore restricted our attention, in the main, to a consideration of recent publications dealing with the biological activity of silatranes.

The toxicity of new 1-(4'-alkaryl)silatranes, $4\text{-}R\text{-}C_6H_4\text{-}Si(OCH_2CH_2)_3N$ ($R = C_2H_5$, $i\text{-}C_3H_7$) has been determined (252). The compounds were intravenously administrated to white male mices as a solution in DMSO. The LD_{50} values for these compounds are much lower (100 and 15.2 mg/kg, respectively) than for 1-phenyl- and 1-(4'-methylphenyl)silatrane (0.1 and 0.3 mg/kg, respectively) (4a, 247, 250). Thus, the substitution of a methyl group in 1-(4'-methylphenyl)silatrane by a longer ethyl or more branched isopropyl one only decreases the toxicity (252). An analogous effect is produced by the substitution of the silicon atom in silatranes by other heteroatoms (P, As, Ge) (252, 336, 337).

A more detailed investigation of the toxicity of sulfur-containing silatranes has shown that the LD_{50} values for 1-(organylthioalkyl)silatranes, $RS(CH_2)_nSi(OCH_2CH_2)_m[OCH(CH_3)\text{-}CH_2]_{3-m}N$, vary greatly depending on R, n, and m: from 6 mg/kg for 1-(2'-ethylthioethyl)silatrane to 3000 mg/kg for 1-(benzylthiomethyl)-3-methylsilatrane and more than 3000 mg/kg for

1-(naphthylthiomethyl)- and 1-(carbomethoxymethylthiomethyl)-silatranes (297). For the LD_{50} values of 1-(alkylthioalkyl)-silatranes of the series $H(CH_2)_xSCH_2Si(OCH_2CH_2)_3N$, an alternation phenomenon is observed. The members of this series having an even x value are less toxic than the subsequent member with an odd x value. An analogous phenomenon takes place if the n-alkyl chain contains a side methyl group. Accordingly, the toxicity of silatranes with R = $(CH_3)_3C$ and $CH_3(CH_2)_3$ is similar and fairly high (LD_{50} = 310 and 400mg/kg, respectively) whereas the compound with R = $(CH_3)_2CHCH_2$ has low toxicity (LD_{50} 2000 mg/kg). In general, the lengthening of the alkyl radical attached to the sulfur atom, i.e., increase in the x value, decreases the toxicity. A similar periodic relationship between the LD_{50} and n values is observed in the series $RS(CH_2)_nSi(OCH_2CH_2)_3N$. Thus, when R = C_2H_5, the compound with an even n value (n = 1) is less toxic than the homologue with n = 2. The toxicity of C-methyl substituted silatranes is usually lower than that of their unsubstituted analogues (338).

All the 1-(alkylthioalkyl)silatranes studied cause death of animals in "the pose of prayer". In the case of highly toxic silatranes, the animals die 3-7 minutes after administration of the highest dose. The less toxic 1-(propylthiomethyl)silatrane, when introduced at the highest dose, causes death in only 50% of all the mice. In this case the animals display depression, strong convulsion, retainment of all reflexes. As a rule, the highest doses of the highly toxic 1-(alkylthioalkyl)silatranes bring about stimulation, convulsion attack and death. Low doses of these compounds (120 and 24 mg/kg) cause depression.

The toxicity of diorganyl(silatran-1-yl-methyl)sulfonium halides may be higher or lower than that of the initial 1-(organylthioalkyl)silatranes (297). Thus, for example, in going from 1-(benzylthiomethyl)silatrane and its methiodide the LD_{50} values falls from 2000 to 24 mg/kg. On the contrary, the LD_{50} values for 1-(ethylthiomethyl)silatrane and its methiodide are 30 and 267 mg/kg, respectively. The toxicity of iodo derivatives is commonly somewhat higher than that of the corresponding sulfonium bromides.

The influence of 1-organylsilatranes, $XSi(OCH_2CH_2)_3N$ (X = CH_3, CH_3O, C_2H_5O, $(CH_3)_2CHO$, $(CH_3)_3CO$, $ClCH_2$, $C_3F_7COO(CH_2)_3$,

$(C_2H_5O)_2P(O)CH_2$, $C_2H_5S(O)CH_2$, $^-YR_2S^+CH_2$) on the proliferative-reparative function of connective tissue, healing of wounds and histamine-induced ulcers, inflamation processes (339-347), the pylotropic activity of silatranes with X = CH_3, C_2H_5, $ClCH_2$, C_4H_9, C_2H_5O, $(CH_3)_2CHO$ (348-349), the effect of 1-propoxysilatrane on the biosynthesis of collagen and noncollagen proteins in granulative fibrous tissue (350) have been studied in detail. The influence of 1-ethoxysilatrane on the external secretion of liver as well as the activity of some blood enzymes of rats in normal conditions and with hepatitis have been examined (351, 352). The change in the functional activity of thrombocytes and biophysical properties of erythrocytes under the action of a series of silatranes has been extensively investigated (353-358).

1-(Iodomethyl)silatrane inhibits growth of Geren carcinoma and sarcoma 180 by 52 and 32%, respectively. 1-(3'-Aminopropyl)-3-methylsilatrane exhibits a similar action (359).

$H_2N(CH_2)_3Si(OCH_2CH_2)_3N$ combined with antitumorous preparations inhibits the growth of sarcoma 180 by 70%. The life span of mice with Erlich ascites tumour treated with this composition was found to be 1.5 times as long as in control (360,361).

N-Silatranyl alkyl derivatives of quinoline carboxylic acids inhibit the growth of adenocarcinoma 755 by 35-50% (283) and increase the life span of mice with sarcoma 37 and Erlich ascites tumour by 30-40% (362). As it has been shown by two years tests with white mice, 1-chloromethylsilatrane displays no blastomogenic effect producing, on the contrary, antitumorous activity (363).

A favourable effect of 1-(2'-perfluoroalkyl-1'-iodoethyl)-silatranes on the immunobiological system of the organism has been established (364).

1-Ethoxysilatrane exhibits a wide spectrum of adaptogenic action (365, 366). In particular, it increases the tolerance of animals to intense physical load, acute hypobaric hypoxia and hypothermia, and inhibits the formation of free radicals in the organism. At the same time, this compound does not influence A_2 phospholipase activity, potential change and activity of H^+-ATF-ase of submitochondrial particles. Thus, the mechanism of the adaptogenic action of 1-ethoxysilatrane is not related to suppression of A_2 phospholipase and mitochondrial breath.

1-(3'-Perfluoroacyloxypropyl)silatranes, $R_FCOO(CH_2)_3Si$-

$-(OCH_2CH_2)_3N$ possess a neurotropic activity (275). The compounds with $R_F = CF_3$ and C_4F_9 prolong the action of hexenal narcosis by a factor of 1.5 and 2, respectively. Heptafluorobutyroxypropylsilatrane exhibits an antistress effect (367). N-Silatranylmethylbutyrolactam shows sedative and tranquilizating effect (368).

Some 1-(organylthioalkyl)silatranes, $RS(CH_2)_nSi(OCH_2CH_2)_m-[OCH(CH_3)CH_2]_{3-m}N$ (R = C_2H_5, n = 1-3, m = 2-3) at low doses produce partial or complete depression of the painful reflex, other reflexes remaining normal (297). The derivatives with R = C_2H_5 (n = 1, m = 1,3) cause sharp exacerbation of reflexes. In the case of compounds with R = $C_6H_5CH_2$ (n = 1, m = 1-3) only a blunted painful reflex was observed.

Furyl- and thienyl derivatives of silatranes, $XSi(OCH_2CH_2)_3N$ (X = 2-furyl-, 2-thienyl-, 2-(2'-furylethyl)-, 3-furyl-, 3-thienyl-) display a neurotropic action of the depressive type (369, 370).

1-(4'-Carbalkoxyphenoxy)silatranes and 1-aroxysilatranes exhibit antimicrobial activity against various microorganisms (256, 371). The bactericidal properties of the latter do not correlate with the analogous activity of the corresponding phenols formed upon hydrolysis (371).

1-Chloromethylsilatrane stimulates the sprouting of seeds, rootlet growth, the morphogenesis processes, and the ripening of fruits and seeds (372-375). A number of silatranes intensify metabolic processes in the silkworm (376).

Chapter V. PRACTICAL APPLICATION

This chapter considers the possibility of practical application of silatranes in fields other than agriculture. Even the first American patents on silatranes (8, 27, 28) reported the possibility of application of these compounds and their composites with polyols for curing a number of synthetic resins.

Some carbofunctional derivatives of 1-alkylsilatranes, $X(CH_2)_nSi(OCH_2CH_2)_3N$ with n = 1-4, X = CH_2=CHCOO, CH_2=C(CH_3)-COO, C_6H_9O (3,4-epoxycyclohexyl), NC, C_6H_5NH, HS, etc., have been proposed as emulsion components for polymer modification, glass fibre and textile couplings, and agents for antistatic treatment of different materials and improvement of polyester, epoxyde and phenolformaldehyde resins (48, 49, 65).

The products of the copolymerization of polyfluoroamido-

alkylsilatranes, $CF_3(CF_2)_nC(O)NH(CH_2)_3Si(OCH_2CH_2)_3N$ (n=0-20) and epoxyalkyltrialkoxysilanes have been suggested as water- and oil-repellents for different fibres and solid materials (37). The treatment may be performed using rollers or by dipping the material into water solutions of polyfluoroamido-alkylsilatrane compositions. Articles made of wool, leather, textile (carpets, for example) or synthetic fibre can be treated in a similar way.

Some silatranes inhibit corrosion of iron (377). At an optimal concentration of 2×10^{-4} M, the protective properties of silatranes were evaluated by means of the inhibition coefficient, $K = i_o/i$, where i_o and i are the rate of metal corrosion in pure and inhibited acids, respectively.

Silatranes are of certain practical interest as suitable alkylating, alkenylating and arylating agents, for the preparation of very pure organic derivatives of heavy metals (206).

1-(4'-Carbalkoxyphenoxy)silatranes possessing bactericidal activity, have been proposed as fish conservation agents (33). They prolong the conservation time approximately two-fold.

Silatranes are used as components of a catalyst for the removal of butadiene in the purification of the C_4 hydrocarbon fraction from the cracking and pyrolysis of oil (378).

The possibilities of practical application of silatranes are not limited, of course, to those mentioned above. Even in the near future, we can expect new fields in which silatranes will prove useful and widely applicable.

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