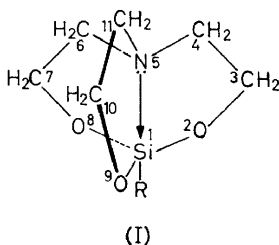


SILATRANES: INTRA-COMPLEX HETEROCYCLIC COMPOUNDS OF PENTACOORDINATED SILICON

M. G. VORONKOV†

*Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR,
Rīga (USSR)*

In recent years a number of authors have evinced interest in intra-complex heterocyclic inorganic esters and alcoholates of triethanolamine and its derivatives of the type $R_{n-3}M(OCH_2CH_2)_3N$ (I), where M = an atom of tri- or multivalent element with an incomplete p - or d -valency shell; n = its valency; and R = an organic radical, hydrogen or any other substituent. The growing interest in this type of compounds is prompted by



both theoretical and practical reasons. At the present time the following compounds of the above indicated structure are already known: with M = boron¹⁻²¹, aluminium²²⁻²⁴, silicon²⁵⁻³⁶, titanium and zirconium³⁷⁻⁴⁴, bismuth⁴⁵; and vanadyl⁴⁶ and iron⁴⁷⁻⁵⁰.

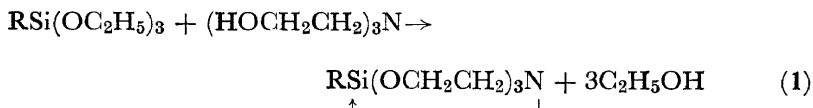
We would suggest that all compounds of the type (I) should be unified under one name "atranes" and that the various substances should be named depending on the substituent M , e.g. "silatrane"—($M=Si$, $R=H$)—2,2',2''-aminotriethoxysilane; "boratrane"—($M=B$)—2,2',2''-aminotriethoxyboron; "alumatrane"—($M=Al$)—2,2',2''-aminotriethoxyaluminium, etc.

The silatranes containing a coordinate link to nitrogen from a pentacoordinated silicon atom, are of special interest because of the formation of stable coordinated complexes between alkoxyasilanes and tertiary amines. Such compounds have not been reported so far, nor did we succeed in gathering sufficient evidence, by means of physico-chemical analyses,

† in collaboration with G. I. Zelčans, I. B. Mažeika, J. J. Baltkajs, J. P. Jegorov, and V. A. Pestunovich

molecular or n.m.r. spectroscopy, for a possible coexistence of alkoxy silanes with tertiary amines in a solution. Silatranes of a general formula (I) have been only rarely mentioned in the literature. Some patents²⁵⁻²⁷, a letter to the editor²⁶, one publication³⁵ with only a passing mention about 1-vinylsilatrane, and a reference to unpublished data³⁶ have appeared recently; all this material contains just a minimum of information and no descriptions of experimental results†.

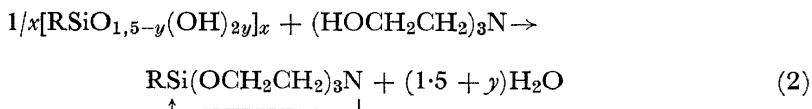
Synthesis of similar compounds is always done by trans-esterification of the corresponding Si-substituted triethoxysilanes according to the reaction given in equation (1).



where R = alkyl, alkenyl, aryl, or alkoxy.

1-ORGANYLSILATRANES

We have found a simple and convenient method for the synthesis of 1-organylsilatranes^{28, 30} using more accessible starting reagents than the corresponding organyltriethoxysilanes. This method is based on triethanolamine cleavage reaction on organyltrichlorosilanes hydrolysis products, namely polyorganylsesquisiloxanes $(\text{RSiO}_{1.5})_x$ or polyorganylsiloxanols $[\text{RSiO}_{1.5-y}(\text{OH})_{2y}]_x$ ($y = 0-1.5$), in the presence of catalytic quantities of alkali metal hydroxide (preferably KOH). Equation (2) illustrates the course of the reaction:



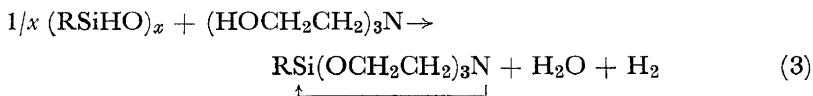
Water lost during this process is gradually eliminated by azeotropic distillation with a suitable inert solvent (xylene). The volume of water distilled over enables the course of the reaction to be followed till its completion. The velocity of the reaction increases with diminishing degree of condensation of the starting siloxanols. Vinyl and phenyl derivatives react with triethanolamine considerably faster than the alkyl derivatives. The alkylsilatranes synthesis is complete in 4-8 h; in the case of vinyl or phenyl derivatives it is complete in 0.5-1.5 hour. On cooling 1-organylsilatranes precipitate in crystals and are purified by recrystallization; yields 60-90 per cent.

Polyorganylsiloxanes of the type $(\text{RSiHO})_x$ or $\text{HO}(\text{RSiHO})_x\text{H}$, obtained by hydrolysis of corresponding organyldichlorosilanes when used as starting materials for 1-organylsilatrane synthesis give also high yields.

† Some of these communications appeared after our articles were either published or in press.

SILATRANES

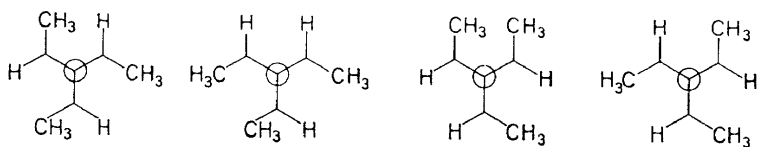
The reaction takes place under the same conditions and is illustrated in equation (3).



In the reaction of triethanolamine with polyorganylhydrosiloxanes the first to react is the Si-H bond which results in the liberation of hydrogen; the theoretical quantity of hydrogen is eliminated long before the end of the whole process. This is followed by the cleavage of the siloxane bonds with consequent water formation. It is therefore not the completion of hydrogen elimination but the termination of water formation that indicates the end of the reaction. The completion of the reaction in this case does not exceed 1.5-2 hours as against 4-8 h when polyalkylsesquioxanes or polyalkylsiloxanols are used as the starting materials.

The nine 1-organylsilatrane (four of which have not been previously known) synthesized by both these methods along with their yields, melting points, water-solubility, analytical data and molecular weights are given in *Table 1*. Among the products listed are also 3-methyl-, 3,7-dimethyl-, and 3,7,10-trimethyl-1-phenylsilatrane obtained by reacting polyphenylsesquioxane with isopropanoldiethanolamine, diisopropanolethanolamine and triisopropanolamine respectively.

All 1-organylsilatrane form colourless pretty crystals mostly needle-shaped with sharp melting points. In substituted 1-phenylsilatrane the occurrence of stereoisomeric forms can be attributed to the presence of asymmetric carbon atoms. 3-Methyl-, 3,7-dimethyl-, and 3,7,10-trimethyl-1-phenylsilatrane can have, depending on the number of asymmetric hydrocarbon atoms, two, three and four stereoisomers respectively. In the last case they may be presented as follows.



(II)

In this connection we would like to indicate that we obtained 3,7-dimethyl-1-phenylsilatrane in two crystal forms (in needles with m.p. 90.4-91.4°; and in platelets with m.p. 94.5-95.8°).

1-Methylsilatrane is a polymorphic compound and has a double melting point. After recrystallization from xylene its m.p. is 142-143°, but after fast cooling of the melt the m.p. is raised to 151.5-152.5°. This more stable form, which does not change after repeated cooling and heating, is sometimes obtained by recrystallization of the mentioned compound from *n*-heptane or xylene. These data disagree with another report²⁶ according to which on recrystallization of 1-methylsilatrane from the melt a low temperature melting form (m.p. 123-125°) is obtained.

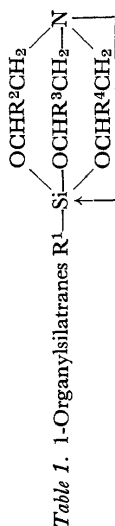


Table 1. 1-Organosilyltranes

R ¹	R ²	R ³	R ⁴	m.p. (°C)	Solubility in water (g/100g soln)	Neutralization equivalent		Mol. wt (cryoscopic, in PhNO ₂)		Mol. formula	Found (%)		Calculated (%)		Yield of unre-fined product (%)	
						Found	Calc.	Found	Calc.		Si	C	H	Si		C
H	H	H	H	256-58 142-43	—	177	175	187	189	C ₄ H ₁₂ NO ₃ Si	16.07 15.95 14.63	41.50	16.03	41.12	7.48	81§ 80
CH ₃	H	H	H	151.5-52.5	17.0	190	189	187	189	C ₇ H ₁₂ NO ₃ Si	13.82 13.71	44.65	14.83	44.42	7.99	80¶ 88
C ₂ H ₅	H	H	H	132-33.5†	20.0	204	203	197	203	C ₈ H ₁₇ NO ₃ Si	12.60 12.66	47.73	13.81	47.26	8.43	93¶
(CH ₃) ₂ CH	H	H	H	106.5-107.5†	4.5	218	217	210 212 212‡ 222	217	C ₄ H ₁₃ NO ₃ Si	13.98 14.06	49.87	12.92	49.74	8.81	87
CH ₂ =CH	H	H	H	165-66.2	8.4	203	201	202 242	201	C ₆ H ₁₂ NO ₃ Si	11.15 11.19	47.85	13.94	47.73	7.51	92
C ₆ H ₅	H	H	H	210.3-211.3	0.5	253	251	244	252	C ₁₂ H ₁₇ NO ₃ Si	10.50 10.62	57.05	11.17	57.34	6.82	83
C ₆ H ₅	CH ₃	H	H	95-96	—	263	265	273 275	279	C ₁₉ H ₂₄ NO ₃ Si	10.15 10.33	58.96	10.58	58.84	7.22	63
C ₆ H ₅	CH ₃	CH ₃	H	86.5-89†	0.7	280	279	275	279	C ₁₄ H ₂₁ NO ₃ Si	9.05 9.00	60.66	10.05	60.18	7.58	80
C ₆ H ₅	CH ₃	CH ₃	CH ₃	133-34†	—	305	309	305	309	C ₁₆ H ₂₃ NO ₃ Si	9.00	61.12	9.08	61.40	7.90	93

† A new compound.

‡ In benzene.

§ Method of synthesis will be published elsewhere.

¶ From (RSiHO)₂.

SILATRANES

All 1-organylsilatrane synthesized are sufficiently thermostable to be distilled *in vacuo*, or even at normal pressure, without decomposing. They are monomers, a fact confirmed by cryoscopic data on their molecular weights in nitrobenzene or benzene (*Table I*).

These substances are readily soluble in halogenated hydrocarbons, nitrobenzene, dimethylformamide, and acetonitrile. Methyl and ethyl derivatives are fairly soluble in water, which cannot be said about arylsilatrane (cf. *Table I*). The nature of the hydrocarbon radical bound to the silicon atom also influences substantially the degree of solubility of 1-organylsilatrane in organic solvents. Thus, for instance, 1-methylsilatrane is practically insoluble in diethyl ether; its nearest homologues, however, such as 1-ethyl- and 1-isopropylsilatrane are readily dissolved in the same solvent. The solubility of 1-ethylsilatrane in xylene is less but in water it is more as compared to the isopropyl derivative. As a rule, 1-arylsilatrane dissolve less readily in any solvent than do the 1-alkylsilatrane.

In contrast to the organyltriethoxysilane $\text{RSi}(\text{OCH}_2\text{CH}_3)_3$ which are hydrolyzed readily the 1-organylsilatrane are quite resistant to humidity (and atmospheric oxygen). A notable hydrolytic decomposition of 1-methylsilatrane can be observed after its exposure to 50 per cent relative humidity during 28 days; 1-isopropyl- or 1-phenylsilatrane, kept under the same conditions for almost two years, remained unchanged.

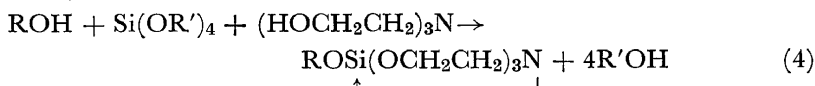
One of the characteristic properties of the 1-organylsilatrane (especially of 1-isopropylsilatrane) is the ability of their crystals to develop intensive contact movements when put on the surface of a fluid (water, benzene, etc.).

1-Organylsilatrane do not give ammonium bases with methyl iodide at its boiling temperature. 1-Phenylsilatrane does not react with iodine solution in boiling chloroform, but decolorizes a bromine solution. 1-Vinylsilatrane reacts with bromine in cold.

1-ORGANOXYLSILATRANES

Three compounds belonging to the group of 1-organoxy-silatrane have already been described in literature (1-ethoxy²⁵⁻²⁷, 3,7,10-trimethyl-1-ethoxy²⁷- and 1-menthoxy-silatrane²⁶) and have been prepared according to scheme (1) from the corresponding organoxytriethoxysilane. To consider this as the general method of synthesis is not feasible because it necessitates a previous preparation of the already mentioned organoxytriethoxysilane.

We have found a new general method for synthesis of 1-organoxy-silatrane^{29, 33} based on trans-esterification of the lower tetralkoxysilane, $\text{Si}(\text{OR}')_4$ [$\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$] by an equimolar mixture of triethanolamine and a corresponding hydroxyl containing organic compound (ROH). The reaction takes place mostly in the presence of an alkali catalyst (an alkali metal hydroxide) which speeds up the process and ensures better yields of the end product. Some of the 1-alkoxy-silatrane [$\text{R} = (\text{CH}_3)_2\text{CH}, (\text{CH}_3)_3\text{C}$] cannot be prepared in the absence of alkali. The reaction proceeds according to the equation (4).



where R = alkyl, cycloalkyl, aralkyl, aryl; and R' = CH₃, C₂H₅.

The synthesis is achieved by preparing an equimolecular mixture of tetraethoxysilane (or tetramethoxysilane), triethanolamine, a corresponding alcohol or phenol and a catalyst; the whole mixture is then heated until ethanol (or methanol) is completely distilled off (0.5–1.5 h). 1-Organoxysilatranes are crystallized directly from the reaction mixture or are separated from it after evaporation of the solvent and then purified by recrystallization. 1-Alkoxy- and 1-cycloalkoxysilatranes are crystallized from *n*-heptane (1-methoxy- and 1-cyclohexoxy derivatives can be also crystallized from xylene), and 1-aralkoxy- and 1-aroxy-silatranes from xylene, a mixture of chloroform and *n*-heptane, or from carbon tetrachloride and chloroform.

1-Organoxysilatranes thus obtained, their melting points, analytical data, molecular weights, neutralization equivalents, and yields are given in *Tables 2 and 3*.

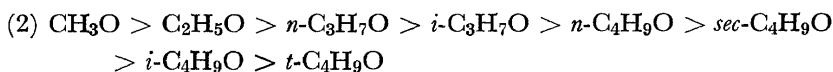
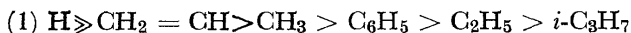
Like 1-organylsilatranes all these compounds represent colourless (with the exception of the yellow 1-nitrophenoxysilatranes) solid substances and after crystallization acquire the form of small, mostly flake-like crystals. 1-Alkoxy-silatranes dissolve readily in water and in most organic solvents, like chloroform, dioxane, acetone, ethyl acetate, alcohol, aromatic hydrocarbons, diethyl ether, carbon tetrachloride, but do not dissolve in cold petroleum ether. 1-*n*-Tetradecoxysilatrane, on the contrary, is not soluble in water, but soluble in cold petroleum ether; 1-methoxysilatrane is only slightly soluble in cold benzene, toluene, xylene and completely insoluble in diethyl ether and carbon tetrachloride. 1-Aroxy-silatranes are only slightly soluble in water and in many organic solvents with the exception of halogenated hydrocarbons, nitrobenzene, dimethylformamide, acetonitrile, and alcohol, in which they easily dissolve.

1-Organoxysilatranes as well as 1-organylsilatranes are monomers (cf. *Table 2*). They get gradually hydrolyzed in atmosphere. 1-*p*-Nitrophenoxysilatrane, like *p*-nitrophenol has indicator properties. 1-Organoxysilatranes can be recommended as crystalline derivatives for identification of various alcohols and phenols.

By replacing the alcohol with the corresponding monocarboxylic acid we synthesized crystalline 1-acyloxysilatranes—new compounds not described previously in the literature. These compounds are extremely unstable which makes their purification a matter of considerable difficulty. Aliphatic carboxylic acid derivatives are easily transformed into polymers, even in the absence of air humidity and at room temperature; aromatic and heterocyclic acid derivatives polymerize in the process of crystallization.

KINETICS OF HYDROLYSIS

The hydrolysis of silatrane in an aqueous solution is a first order reaction. The decrease in speed in silatrane (I) hydrolysis with change in substituent R at the silicon atom can be expressed by the following series:



SILATRANES

Table 2. 1-Alkoxysilatrane ROSi(OCH₂CH₂)₃N

R	m.p. (°C)	Mol. wt. (Cryoscopic, in PhNO ₂)		Mol. formula	Found (%)			Calculated (%)			Neutralization equivalent		Yields of unrefined products (%)
		Found	Calc.		Si	C	H	Si	C	H	Found	Calc.	
CH ₃	155-56	206, 210	205-29	C ₇ H ₁₅ NO ₄ Si	13.97	41.03	7.29	13.68	40.96	7.37	203	205	89
CH ₃ CH ₂	102-103†	220, 224	219-31	C ₈ H ₁₇ NO ₄ Si	13.45	43.76	7.57	12.81	43.81	7.81	224	219	65†
CH ₃ CH ₂ CH ₂	79-80			C ₉ H ₁₉ NO ₄ Si	12.75	45.87	8.03	12.04	46.33	8.21	231	233	26†
(CH ₂) ₂ CH	129.5-131.0	222, 246	233-34	C ₈ H ₁₅ NO ₄ Si	12.11	45.80	8.20	12.04	46.33	8.21	229	233	52
CH ₃ (CH ₂) ₄ CH ₂	113-13.5			C ₁₀ H ₂₁ NO ₄ Si	11.98	49.06	8.71	11.35	48.56	8.56	249	247	57
(CH ₂) ₂ CHCH ₂	99-100			C ₁₀ H ₂₁ NO ₄ Si	11.39	48.26	8.46	11.35	48.56	8.56	250	247	71
CH ₃ CH ₂ (CH ₂) ₃ CH	131-32			C ₁₀ H ₂₁ NO ₄ Si	11.55	48.11	8.42	11.35	48.56	8.56	245	247	62
(CH ₂) ₃ C	146.5-47.5	252, 247	247-37	C ₁₀ H ₂₁ NO ₄ Si	11.46	48.45	8.71	11.35	48.56	8.56	248	247	59
CH ₃ (CH ₂) ₂ CH ₂	102.5-103.5			C ₁₁ H ₂₃ NO ₄ Si	11.48	50.66	8.73	10.47	50.55	8.87	265	261	66
(CH ₂) ₂ CHCH ₂ CH ₂	134.5-136.0			C ₁₁ H ₂₃ NO ₄ Si	10.70	50.94	9.00	10.47	50.55	8.87	264	261	63
(CH ₂) ₃ CCH ₂	178-80			C ₁₁ H ₂₃ NO ₄ Si	10.43	50.03	8.77	10.47	50.55	8.87	261	261	69
CH ₃ (CH ₂) ₃ CH ₂	82-83			C ₁₂ H ₂₅ NO ₄ Si	10.63	52.64	9.19	10.20	52.33	9.15	276	275	87
CH ₃ (CH ₂) ₄ CH ₂	80-81	392, 386	387-64	C ₁₂ H ₂₅ NO ₄ Si	10.28	62.19	10.70	7.24	61.97	10.66	388	388	51
CH ₃ (CH ₂) ₁₁ CH ₂	193.5-95.5	271, 273	273-41	C ₁₃ H ₂₇ NO ₄ Si	7.39	52.10	8.36	10.27	52.72	8.48	277	273	58
C ₄ H ₁₁	190.5-92.0	277, 281	281-38	C ₁₃ H ₂₇ NO ₄ Si	10.48	54.86	7.08	9.98	55.49	6.81	285	281	32†
C ₄ H ₉ CH ₂					10.40								86
					9.27								79

† Without catalyst. ‡ Lit.¹⁶: m.p. 100-102°; b.p. 180° 0.6 mm.

Table 3. 1-Aroxysilatrane ROSi(OCH₂CH₂)₃N

R	m.p., t (°C)	Mol. formula	Found (%)			Calculated (%)			Yield of unrefined products (%)
			Si	C	H	N	Si	C	
C ₆ H ₆	228-29.5 (CHCl ₃ + CCl ₄)	C ₁₂ H ₁₁ NO ₄ Si	10-11 10-51	54-12	6-75	5-36	10-50	6-41	99 89†
2-CH ₃ C ₆ H ₄	218-19.5 (xylene)	C ₁₃ H ₁₃ NO ₄ Si	10-03 10-03	55-31	6-69	5-04	9-98	6-81	98 83†
3-CH ₃ C ₆ H ₄	162.5-63.5 (xylene)	C ₁₃ H ₁₃ NO ₄ Si	10-22 10-14	55-86	6-96	5-23	9-98	6-81	89 82†
4-CH ₃ C ₆ H ₄	188-89 (CHCl ₃ + n-heptane)	C ₁₃ H ₁₃ NO ₄ Si	9-73 9-97	55-30	7-05	5-15	9-98	6-81	98 56†
4-(CH ₃) ₂ CC ₆ H ₄	252-53 (CHCl ₃ + n-heptane)	C ₁₄ H ₁₃ NO ₄ Si	8-89 8-89	58-95	7-64	4-31	8-68	7-79	70 90
5-CH ₃ -2-(CH ₃) ₂ CHC ₆ H ₄	217.5-18.5 (CHCl ₃ + n-heptane)	C ₁₄ H ₁₃ NO ₄ Si	8-74 8-81	59-60	7-59	4-53	8-68	7-79	81† ~100
4-ClC ₆ H ₄	166-67 (xylene)	C ₁₃ H ₁₀ ClNO ₄ Si	9-51 9-49	47-61	5-60	4-59	9-31	5-34	~100†
2,4,6-Cl ₃ C ₆ H ₂	230-30.5 (xylene)	C ₁₂ H ₁₁ Cl ₃ NO ₄ Si†	7-48 7-47	38-69	3-88	4-06	7-58	3-81	28
2-O ₂ NC ₆ H ₄	233-34 (xylene)	C ₁₃ H ₁₀ N ₂ O ₆ Si	9-20 9-35	45-93	5-33	8-73	8-99	5-16	58
3-O ₂ NC ₆ H ₄	197.5-198.5 (xylene)	C ₁₃ H ₁₀ N ₂ O ₆ Si	9-16 9-10	46-50	5-13	8-69	8-99	5-16	87 91†
4-O ₂ NC ₆ H ₄	182.5-184 (toluene)	C ₁₃ H ₁₀ N ₂ O ₆ Si	8-67 8-97	46-42	5-22	9-17	8-99	5-16	75 ~100†
2-C ₁₀ H ₇	184.5-185.5 (ethanol)	C ₁₆ H ₁₅ NO ₄ Si	8-95 8-98	60-45	6-01	4-61	8-85	6-03	88

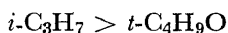
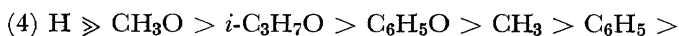
† The solvent (or mixture) used for crystallization is given in brackets.
28-90 per cent; calculated 28-68 per cent.

‡ Without a catalyst.

§ Found; Cl, 11-98 per cent; calculated 11-75 per cent.

¶ Cl, found:

SILATRANES



Exact quantitative data will be published elsewhere.

DIPOLE MOMENTS AND THE STRUCTURE OF SILATRANES

According to the classical tetrahedral theory of organic compounds the Si-substituted 2,2',2''-aminotriethoxysilanes can have two kinds of steric structures with a tetrahedral XSiO₃ group—one is a non-strained “bi-convex” (III) (Figure 1) and the other also a practically non-strained “concavo-convex” (IV) (Figure 2). It is obvious, that the existence of a donor-acceptor trans-annular bridge between the nitrogen and silicon atoms is possible only in structure (IV). A study of the Stuart-Briegleb atom model reveals that only one form of “concavo-convex” structure (IVa) (Figure 3) is possible, in which the distance between the silicon and nitrogen atoms is such as to allow the formation of a coordinated bond†. Nevertheless, to assume that silatranes have the structure (IV) is jumping to premature conclusions. We have to keep in mind that in the presence of a trans-annular donor-acceptor bond Si←N the covalency of the silicon atom raises to five. In this case, the hybridization of its valency orbitals is not more tetrahedral (*sp*³) as usual, but *sp*³*d*, which corresponds to penta-coordinated silicon atom with bonds directed towards the apexes of the trigonal bipyramid. Consequently, the molecular configuration of the silatranes should be expressed by structure (V) (Figure 4), which contains the SiO₃ planar group and a tetrahedral four-coordinated (onium) nitrogen atom.

The most decisive evidence for the existence of the silatrane configuration (V) must be the presence of a trans-annular donor-acceptor bond between the silicon and nitrogen atoms. This fact can be verified by measurements of the corresponding dipole moments.

In this laboratory we have measured the electric dipole moments of six 1-organyl- and 1-organoxy-silatranes (I; R = CH₃, (CH₃)₂CH, CH₂=CH, C₆H₅, C₂H₅O, C₆H₅O). As can be seen from the results presented in Table 4 these dipole moments are very high (of the order 5.7–7.1 D).

Calculated on bond moments the general dipole moment of the grouping Si(OCH₂CH₂)₃N, which does not contain the trans-annular donor-acceptor Si←N bond (III), equals 0.93 D, with the vector directed from the silicon toward the nitrogen atom‡. The dipole moments of organyl- and organoxy-silatranes (2,2',2''-aminotriethoxysilanes) have been calculated based on the value 0.93 D and the Si-R bond moments in structure (III). The

† On the contrary, the possibility of structural configurations for “bi-convex” as well as for “concavo-convex” forms exists in similar molecular models of boratranes B(OCH₂CH₂)₃N with a planar BO₃ grouping.

‡ In calculation, the valency angles of C–N–C, Si–O–C and O–Si–O have been regarded as tetrahedrals, and the bond moments values of C–H, C–N, Si–O and C–O are 0.37; 0.45; 1.54 and 0.74 D respectively.

calculated values appear to be considerably lower than the experimental values (about 5 D less). The dipole moments of the similarly built organyl- and organoxytriethoxysilanes, $\text{RSi}(\text{OCH}_2\text{CH}_3)_3$, are also much lower than those of the corresponding silatranes (by 3.5–4.5 D).

Dipole moment studies reveal a strong polarity of the organyl- and organoxysilatranes. It also became apparent that structure (III) in its

Table 4. Dipole moments of 1-organyl- and 1-organoxysilatranes $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$

R	μ , D		$\text{RSi}(\text{OC}_2\text{H}_5)_3$ (ref. 84)	μ_{SiR}	$-\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$
	Found ($\pm 0.15\text{D}$)	Calc. for structure III			
CH_3	5.30	0.66	1.70	0.27	5.03
$(\text{CH}_3)_2\text{CH}$	5.55	0.66	—	0.27	5.28
$\text{CH}_2=\text{CH}$	5.88	0.5	—	0.4	5.5
C_6H_5	5.98	0.09	1.67	0.84	5.14
$\text{C}_2\text{H}_5\text{O}$	6.29	0.49	1.82	1.42	4.87
$\text{C}_6\text{H}_5\text{O}$	7.13	—	—	—	—
				Mean value	$5.2 \pm 0.2\text{D}$

“bi-convex” form cannot be applied to these compounds. The existence in these compounds of a trans-annular dipole bond $\overset{-}{\text{Si}} \leftarrow \overset{+}{\text{N}}$ with an onium nitrogen atom and a negatively charged penta-coordinated silicon atom has been substantiated. Experimental values of the dipole moment calculated for the group $-\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ are about 5.2 ± 0.2 D, with the vector directed from the nitrogen towards the silicon atom.

The dipole moment of the $\overset{-}{\text{Si}} \leftarrow \overset{+}{\text{N}}$ bond was evaluated as about 8.6 D (the transfer of an electron of the bond $\text{N} \rightarrow \text{Si}$ (sp^3d) over the interatomic distance about 1.8 Å). Therefore, the moment of the whole group $-\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ should amount to $8.6 - 1.1 = 7.5$ D (in case of structure V, however, but without the transannular bond $\text{Si} \leftarrow \text{N}$, the dipole moment will have a value of 1.06 D). A somewhat lower experimental value of the dipole moment of this group (5.2 D) is conditioned by reversed polarization induced by its own dipole moments as well as by a dipole moment induced in the R† substituent, bound to the silicon atom, and of course, because of the fact that the unshared electron of the nitrogen atom is not completely transferred to the 3d silicon orbital.

Similar high values of dipole moments are common for all molecules with dipolar bonds analogous to the $\text{Si} \leftarrow \text{N}$ bonds in silatranes (such as complexes of amines, ethers and sulphides with halogenides of boron, aluminium, titanium, tin, etc⁵²). The same high dipole moment values (8.8 D) are shown by boratranes¹⁶.

† It should be pointed out, that the experimental value of the moment for the grouping $-\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ (5.2 D) is based on the moments of $\text{R}-\text{Si}(sp^3)$ bonds shown in Table 4. Moment values of $\text{R}-\text{Si}(sp^3d)$ bonds will certainly differ from them.

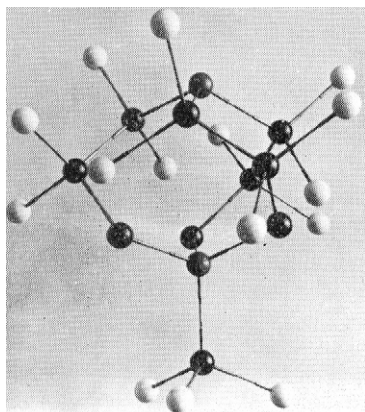


Figure 1. A “bi-convex” non-strained steric model of the l-methylsilatrane molecule (III)

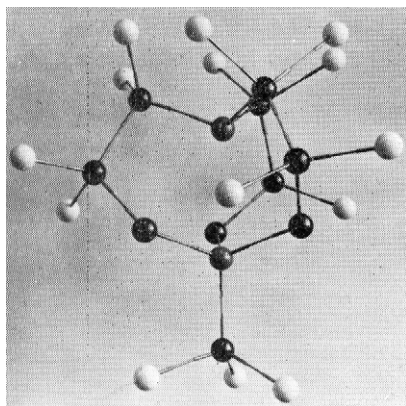


Figure 2. A “concavo-convex” almost non-strained steric model of the l-methylsilatrane molecule (IV)

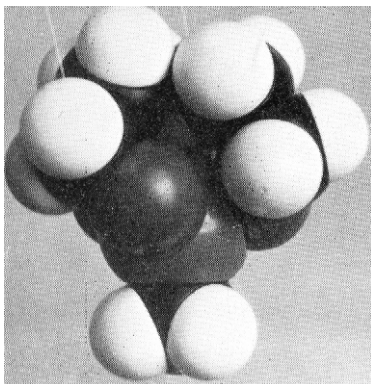


Figure 3. A "concavo-convex" steric Briggleb-Stuart model of the *l*-methylsilatrane (IVa)

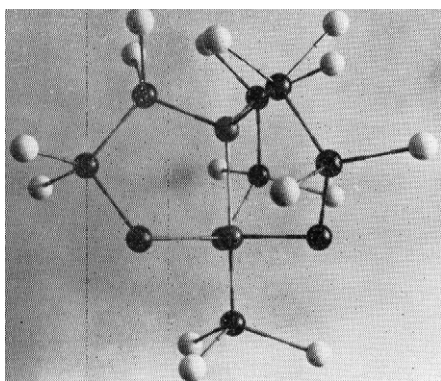


Figure 4. A steric structure of the *l*-methylsilatrane molecule (V)

INFRARED ABSORPTION SPECTRA

There have been no reports in the literature on the i.r. spectra of silatranes (I). It has been indicated only in a short note²⁶ that the frequency of the Si—H bond stretching vibrations in silatrane itself (I, R=H) is outside the region usually occupied by organosilicon compounds containing the HSi(O)₃ group (2190–2220 cm⁻¹†), and is shifted towards lower frequencies (to 2137 cm⁻¹ in a CHCl₃ solution, and to 2117 cm⁻¹ in a CH₃OH solution).

In this laboratory the i.r. spectra of ten organyl- and organoxysilatranes have been studied (I; X=H, CH₃, C₂H₅, (CH₃)₂CH, CH₂=CH, C₆H₅, C₂H₅O, *n*-C₁₄H₂₉O, C₆H₅O, *p*-CH₃C₆H₄O) in the region of 400–1700 cm⁻¹. The data are presented in Figure 5. For comparison purposes i.r. spectra

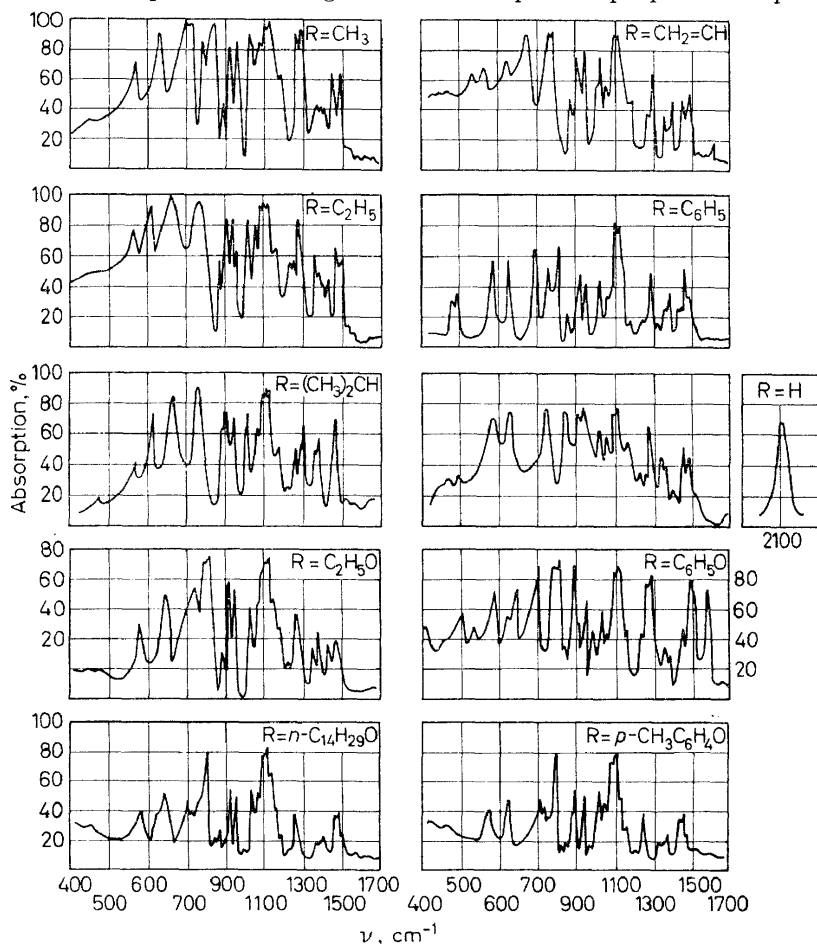


Figure 5. Infrared spectra of silatranes (I)

† As it is already known⁵⁸⁻⁵⁹, the vibration frequency of the bond Si—H in molecules of the type RR' R''SiH is linearly connected with the general inductive effect of the substituents R, R' and R'' and rises with the increase of their electron-acceptant ability (at the same time the polarity of the Si—H bond decreases).

of methyltriethoxysilane $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ (447, 645, 730, 780, 820, 855, 960, 1094, 1170, 1263, 1298, 1392, 1445, 1485 cm^{-1}) and of triethanolamine $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, (885, 910, 1040, 1075, 1155, 1250, 1285, 1360, 1410, 1450, 1485 cm^{-1}) have also been recorded (*Figure 6*).

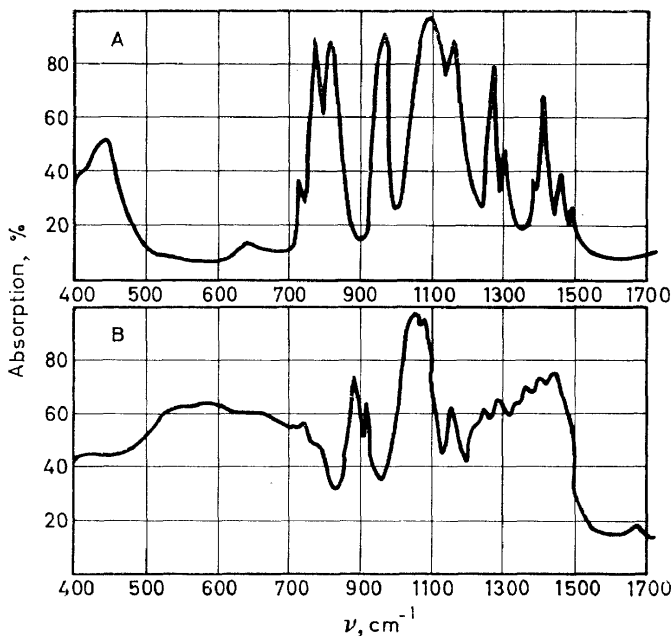


Figure 6. Infrared spectra of: (A) methyltriethoxysilane, $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$; and (B) triethanolamine, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$

Spectra were run on a Model UR-10 double-beam i.r. spectrophotometer with a KBr and NaCl prisms. Silatrane samples were used in tablet form with KBr, $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ and $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ in pure state.

The spectra of the molecules (structure I) can be discussed part by part. To the first part, common to all molecules, belongs the main cyclic silatrane skeleton (I) with an approximate symmetry of C_{3v} . In the second, the variable part, are the R substituents bound to the silicon atom ($\text{R} = \text{alkyl}$, alkenyl, aryl, alkoxy, and aryloxy). In noticing the spectral peculiarities of different organo-silicon compounds and in comparing the different frequencies it is possible to single out absorption bands corresponding to the cyclic system of all molecules (*Table 5*).

Absorption frequencies characteristic for R substituents (*Table 6*) have been identified on the basis of published data⁵⁷⁻⁶² as well as from our own observations.

Considering the structure-spectra correlation one can already anticipate a definite picture of silatrane vibration bands for bonds like Si-O, C-O, C-C, C-H, C-N and presumably also of the coordinate bond $\bar{\text{Si}} \leftarrow \overset{+}{\text{N}}$. It may also be expected that specific electron conditions of the silicon atom in structure (I) would bring about a change in the position and intensity of the bands $\nu(\text{Si-O})$ and $\nu(\text{Si-C})$.

SILATRANES

Table 5. Absorption frequencies, characteristic for silatrane structure (I), cm^{-1} .

R =	H	CH ₃	C ₂ H ₅	CH(CH ₃) ₂	CH=CH ₂	C ₆ H ₅	OC ₂ H ₅	OC ₄ H ₉ -z	OC ₆ H ₅	OC ₈ H ₁₇ CH ₃ - ρ	Vibration type
592 s	570	570	570	563	568	592	585	588	588	582	ν (Si-N) [or ν (Si-O)]
633 s	620 s	612 s	612 s	609 s	621	624	634	632	638	645	ν_2 (Si-O)
735 s	(675)	575	570 v.s.	661	675	787 v.s.	770 v.s.	832	792	765	ν_3 (Si-O)
865 s	772 s	768	880 m	788	767 v.s.	880 m	880 m	882 v.s.	875 v.s.	892 v.s.	ν_{as} (Si-O)
910 w	880 m	880 m	880 m	885 w	880 m	880 m	880 m	880 s	895 v.s.	892 v.s.	ν (C-N)
936 s	913 s	914 s	914 s	910 s	915 s	918 m	916 s	915 m	910 v.w	948 s	ν (C-C)
1020 m	946 s	942 s	942 s	942 s	946 s	950 m	941 s	941 m	945 s	1020 s	ν (Si-O)
1049 m	1020 s	1010 s	1010 s	1015 s	1021 s	1027 m	1021 s	1020 s	1023 s	1020 s	ν (C-O)
1085 v.s.	1055 m	1054 m	1054 m	1057 m	1052 m	1052 w	1052 w	1054 w	1048 m	1050 m	ν (C-C)
1110 v.s.	1095 s	1085 v.s.	1085 v.s.	1083 v.s.	1086 v.s.	1097 v.s.	1085 v.s.	1085 v.s.	1100 v.s.	1095 v.s.	ν (C-O)
1126 v.s.	1126 v.s.	1126 v.s.	1126 v.s.	1127 v.s.	1125 v.s.	1113 v.s.	1109 v.s.	1115 v.s.	1195 v.s.	1180 v.s.	} δ CH ₂
1168 w	1175 v.w	1175 v	1174 v.w	1174 w	1174 w	1170 w	1168 w	1168 w	1170 v.w	1170 v.w	
1270 s	1276 s	1282 s	1282 s	1282 s	1278 s	1274 s	1274 v.w	1272 w	1272 s	1272 v.s.	
1349 w	1360 m	1360 w	1360 w	1355 s	1360 m	1348 w	1360 w	1352 w	1352 w	1358 m	} δ CH ₂
1460 m	1456 s	1456 s	1456 s	1455 s	1464 m	1453 s	1455 w	1455 m	1456 m	1462 m	

Table 6. Absorption frequencies, characteristic for substituents R in (I), cm^{-1} .

R =	H	CH_3	C_2H_5	$\text{CH}(\text{CH}_3)_2$	$\text{CH}=\text{CH}_2$	C_6H_5	OC_2H_5	$\text{OC}_{1,4}\text{H}_{29-n}$	OC_6H_5	$\text{OC}_6\text{H}_4\text{CH}_3$
		720 v.s. 815 v.s. 855 v.w 1256 s 1410 m	962 m 1236 w 1418 m 1453 1010-1025	432 v.w 477 w 896 s	550 m 1005 v.w 945 s 1270-1280 1404 m 1592 w	488 m 498 m 695 s 709 m 750 s 1020 s 1113 v.s 1427 w	684 s 740 m 782 v.s 1145 v.w 1465 w	705 m 722 w 755 w 850 v.w 902 v.w 995 v.w 1142 v.w	500 m 545 w 700 v.s 788 s 809 v.s 835 v.w 888 v.w 1000 m 1155 v.w 1288 s 1598 v.s	450 m 462 m 482 w 538 s 645 m 675 v.s 845 v.s 1515 v.w 1550 v.w 1560 v.w 1582 v.w
	2100 s									

SILATRANES

A number of publications have appeared recently dealing with vibration spectra of organo-silicon compounds containing the Si-O-C group^{57-59, 63-73}. A study of these reports brings us to the conclusion that in i.r. absorption spectra of compounds with Si-O-C grouping, a very intense band is present at 1100 cm⁻¹ and bands of variable intensity in the interval of 620-840 cm⁻¹. In the majority of the above-indicated articles, the frequency ~ 1100 cm⁻¹ is assigned to the unsymmetric stretching vibration of the group Si-O-C with the stretched C-O bond prevailing; frequencies of the region 800-840 cm⁻¹ are attributed to symmetric stretching vibrations of Si-O. In passing from a single Si-O-C group to molecules containing several such groups, e.g. RSi(O-C)₃, three frequencies become apparent: one connected with the prevailing stretched Si-R bond, and two others assigned to the Si-O bond—one symmetric and the second degenerated.

Interpretation of the structure (I) reveals that the "lower" part of the silatrane skeleton is structurally similar to the molecules of RSi(OCH₃)₃ and RSi(OCH₂CH₃)₃ (where R=alkyl). In the most simple molecule of this group—CH₃Si(OCH₃)₃^{68, 72}—four frequencies are detected in the region lower than 900 cm⁻¹: 620- ν (Si-C), 668- ν_s (Si-O) and a doublet 728 and 790 cm⁻¹, the latter due to a band split in the second frequency ν_{as} (Si-O). In full accordance with this we have found in the CH₃Si(OCH₂CH₃)₃ spectrum frequencies of 645, 730 and 780 cm⁻¹. In silatrane spectra three vibration frequencies are constantly present at: 568-590, 620-675, and 770-795 cm⁻¹ (Table 7). In the spectrum (I) with R=CH₃ the frequency 675 cm⁻¹ is concealed on a wide band stretching from 790 to 635 cm⁻¹.

Table 7. Vibration frequencies of the oxygen-silicon silatrane skeleton, cm⁻¹

R	ν (Si←N)	ν (Si-O)		ν (Si-C)
H	592	633	755	—
CH ₃	570	(675)	772	620
CH ₂ CH ₃	570	675	770	615
CH(CH ₃) ₂	568	661	768	609
CH=CH ₂	568	675	767	621
C ₆ H ₅	592	624†	787	624†
OC ₂ H ₅	585	634	770	—
OC ₁₄ H _{29-n}	588	632	782	—
OC ₆ H ₅	588	638	775	—
OC ₆ H ₄ CH _{3-p}	582	645	795	—

† In case of phenylsilatrane frequencies ν (Si-O) and ν_A (Si-C) overlap.

In alkoxy and aroxysilatrane and also when R=H the first frequency is considerably higher than the one in alkylsilatrane. The same tendency can be observed in the third frequency. Contrary to this, the second frequency in this group of silatrane is usually lower. In alkylsilatrane still another frequency in the indicated region is observed, viz. 609-620 cm⁻¹, related to ν (Si-C) vibrations.

It has been indicated in the literature^{67, 69, 70} that frequencies higher than 700 cm⁻¹ are identified with the degenerate antisymmetrical vibrations of the Si-O bond in the silicon-oxygen skeleton, whereas frequencies lower than 700 cm⁻¹ are ascribed to symmetrical vibrations. In the first case, frequencies

of degenerate vibrations actually occupy a region near to the one expected (800 cm^{-1}); the symmetrical vibration frequencies, are probably in the region $620\text{--}675\text{ cm}^{-1}$.

If we assign the frequency in the region $568\text{--}590\text{ cm}^{-1}$ to vibrations of the coordinate bond $\nu(\text{Si} \leftarrow \text{N})$ we observe, for instance in the case of silatrane itself ($\text{R}=\text{H}$), an irregular shift in the frequencies discussed for the skeleton. This possibly could be explained by changing vibration forms affected by the small mass of the substituent ($\text{R}=\text{H}$).

These frequency assignments should be taken only as a presumption. Another possibility could be also considered, namely, the shift of the frequency $\nu_s(\text{Si}-\text{O})$ from the region $620\text{--}675$ toward $568\text{--}590\text{ cm}^{-1}$ as a result of $\text{Si}-\text{O}$ and $\text{Si} \leftarrow \text{N}$ bonds interrelation.

No indications concerning vibration frequencies of the coordinate bond $\text{Si} \leftarrow \text{N}$ are found in the literature. As it is known, stretching vibrations of the $\text{Si}-\text{N}$ bond are in the region of $920\text{--}980\text{ cm}^{-1}$ (in silazanes) and at $790\text{--}830\text{ cm}^{-1}$ (in aminosilanes)^{57, 74-76}. It appears from these data as well as from the force constants, that the $\text{Si}-\text{N}$ frequency is situated lower than the frequency $\text{C}-\text{N}$. The frequency of the coordinate bond $\text{Si} \leftarrow \text{N}$ should correspondingly be even lower than that of the ordinary bond $\text{Si}-\text{N}$. The tentative band assignments to higher regions are therefore fully acceptable.

Further attention is required by the region of KBr and the frequency of a full symmetrical stretching vibration of the $\text{Si}-\text{C}$ bond^{70, 77, 78}, for which $\text{R} = \text{CH}(\text{CH}_3)_2$, C_2H_5 , CH_3 , $\text{CH}=\text{CH}_2$ corresponds to 609 , 615 , 620 and 621 cm^{-1} respectively. The full symmetrical frequency $\nu_s(\text{Si}-\text{C})$ depends only slightly on the radical mass, but is strongly influenced by the very character of the substitution at the silicon atom.

The inter-dependence of the nature of the hydrocarbon radicals bound to the central silicon atom and the $\nu_A(\text{Si}-\text{C})$ frequency has been previously indicated⁷⁷. More precisely, a correlation exists between the state of the electron shell of the $\text{Si}-\text{C}$ bond and the $\nu_A(\text{Si}-\text{C})$ frequency which raises with the increase of the radical's R electronegativity. A markedly lower [as compared with $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$] frequency of $\nu_A(\text{Si}-\text{C})$ in the alkylsilatrane spectra (645 and $609\text{--}620\text{ cm}^{-1}$ respectively) corresponds to the frequencies of molecules such as $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$ or $(\text{CH}_3)_3\text{SiCH}=\text{CHCH}_3$ whereas the general $-\text{I}$ effect of $(\text{OCH}_2\text{CH}_2)_3\text{N}$ grouping (in the absence of the bond $\text{Si} \leftarrow \text{N}$) should be even greater, than in the grouping $(\text{OCH}_2\text{CH}_3)_3$. This fact, as well as the shift described in literature²⁶ of the absorption band $\nu(\text{Si}-\text{H})$ in silatrane itself (I , $\text{R}=\text{H}$) towards lower frequencies (corresponding to our data for (I) with $\text{R}=\text{H}$ the $\nu(\text{Si}-\text{H})$ is 2100 cm^{-1}) is an additional proof of the existence in (I) of an intramolecular coordinate bond $\text{Si} \leftarrow \text{N}$ the presence of which lowers the electronegativity of the central silicon atom and consequently raises the polarity of its bonds with C or H .

The structural fragment $\text{Si}-\text{O}-\text{C}-\text{C}$ is characterized by typical frequencies $940\text{--}950\text{ cm}^{-1}$, $1015\text{--}1020\text{ cm}^{-1}$ and the split band group in the region of $1080\text{--}1130\text{ cm}^{-1}$. Silatranes with $\text{R}=\text{C}_2\text{H}_5$, OC_2H_5 , $\text{CH}=\text{CH}_2$, $\text{CH}(\text{CH}_3)_2$ have in the region $1080\text{--}1130\text{ cm}^{-1}$ frequencies of 1085 , 1095 and 1125 cm^{-1} . In silatranes with $\text{R}=\text{CH}_3$, C_6H_5 , OC_6H_5 , $\text{OC}_{14}\text{H}_{29-n}$ and $\text{OC}_6\text{H}_4\text{CH}_3-p$ two frequencies have been observed— 1085 and 1125 cm^{-1} .

The frequency 1055 cm^{-1} in the i.r. spectra of (I) is placed at the edge

of a very strong band 1095 cm^{-1} . Considering previously reported data⁷¹ this band can possibly be identified with stretching vibrations of the C–C bond in the silatrane skeleton. Comparison of i.r. spectra (I) with the $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ spectrum revealed the frequency 911 cm^{-1} common to both. Similarly, this frequency could be identified with vibrations of the C–N bond. The band 944 cm^{-1} is situated in the region of stretching vibrations C–C. However, its greater intensity suggests an overlapping by other frequencies of the Si–O–C–C grouping. It is interesting to notice that the frequency $880\text{--}895\text{ cm}^{-1}$ is present in all the spectra of organyl- and alkoxy-silatrane and also in the spectrum of $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$. In the spectra of the indicated silatrane this frequency is of medium intensity, in the spectrum of triethanolamine the intensity raises considerably. In aroxysilatrane spectra this absorption band is shifted to 895 cm^{-1} and is extremely intensive. Consequently, frequencies of $880\text{--}895\text{ cm}^{-1}$ and 910 cm^{-1} should be considered as characteristic to the C–N bond.

For the cyclic skeleton structure (I) also specific are the frequencies 1360 and 1440 cm^{-1} attributed to deformation modes of the group CH_2 . In favour of this speaks the fact that frequencies 1360 and 1462 cm^{-1} are also present in the spectrum of $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$. Band assigned to R substituents in (I) are easily identified (*Table 6*) as considerable work has been already done in this field.

It has been observed that frequencies of the R substituents are seldom perturbed or considerably shifted in spite of the fact that they are associated with a nitrogen coordinated silicon atom. Even vibration frequencies of the vinyl group, which is very sensible to inductive effects, have the usual size (945 and 1010 cm^{-1}).

In a number of spectra, overlapping occurs between the R substituents and the frequencies reflected in the variable intensity of the absorption bands. Thus, according to previous work⁷⁶, the C_2H_5 group is identified by frequencies 1012 , 1380 and 1460 cm^{-1} . In structure (I; $\text{R}=\text{C}_2\text{H}_5$) these absorption bands overlap the skeleton frequencies (1016 , 1366 and 1460 cm^{-1} respectively). Frequency assignments for the vinyl group⁶⁰, 955 and $1270\text{--}1280\text{ cm}^{-1}$, coincide with absorption band pattern of the skeleton (I) (945 and 1283 cm^{-1}). Frequency assignments for the C_6H_5 group^{78, 79} are at 1435 , 1190 , 1125 and 1032 cm^{-1} . In the spectrum of the structure (I; $\text{R}=\text{C}_6\text{H}_5$) we have bands of 1427 , 1170 , 1113 and 1027 cm^{-1} . Bands of 1113 and 1027 cm^{-1} overlap the absorption bands of the skeleton (I). Frequency 740 cm^{-1} is also referred to the C_6H_5 group⁷⁸. Almost the same absorption band (750 cm^{-1}) is observed in structure (I; $\text{R}=\text{C}_6\text{H}_5$).

For the cyclic structure (I) frequencies of 1360 and 1460 cm^{-1} are specific; they correspond to deformation vibrations of $\text{R}=\text{CH}_3$ with bands at 815 and 1259 cm^{-1} , whereby the first represents the pendulum vibrations of the group CH_3 and the second, the deformation vibrations of Si– CH_3 .

For the structure (I; $\text{R}=\text{C}_2\text{H}_5$) the frequencies 963 and 1016 cm^{-1} stretching C–C of the ethyl groups at the silicon atom⁶¹ are specific. Frequency 1412 cm^{-1} corresponds to the deformation vibrations of CH_2 ; 1370 cm^{-1} to the symmetric deformation vibrations of CH_3 ; 1453 cm^{-1} to the asymmetric deformation vibrations of CH_3 in the C_2H_5 group.

It is necessary to mention that substantial changes in stretching vibrations

of the C—H bond occur depending on different solvents used in i.r. spectral analyses of (I). Further investigations will be required to arrive at more exact definitions.

PROTON MAGNETIC RESONANCE SPECTRA

Studies on the p.m.r. spectra of 1-organyl- and 1-organoxy-silatrane (I) (Figure 7) support the validity of the previously suggested structure of these compounds and give valuable information concerning the electron density distribution in the molecule.

The p.m.r. spectrum of the O—CH₂—CH₂— fragment in the silatrane molecules reflects the A₂X₂ system expressed in small constant values of the spin-spin interaction between OCH₂ and CH₂ protons (5–6 Hz) as compared

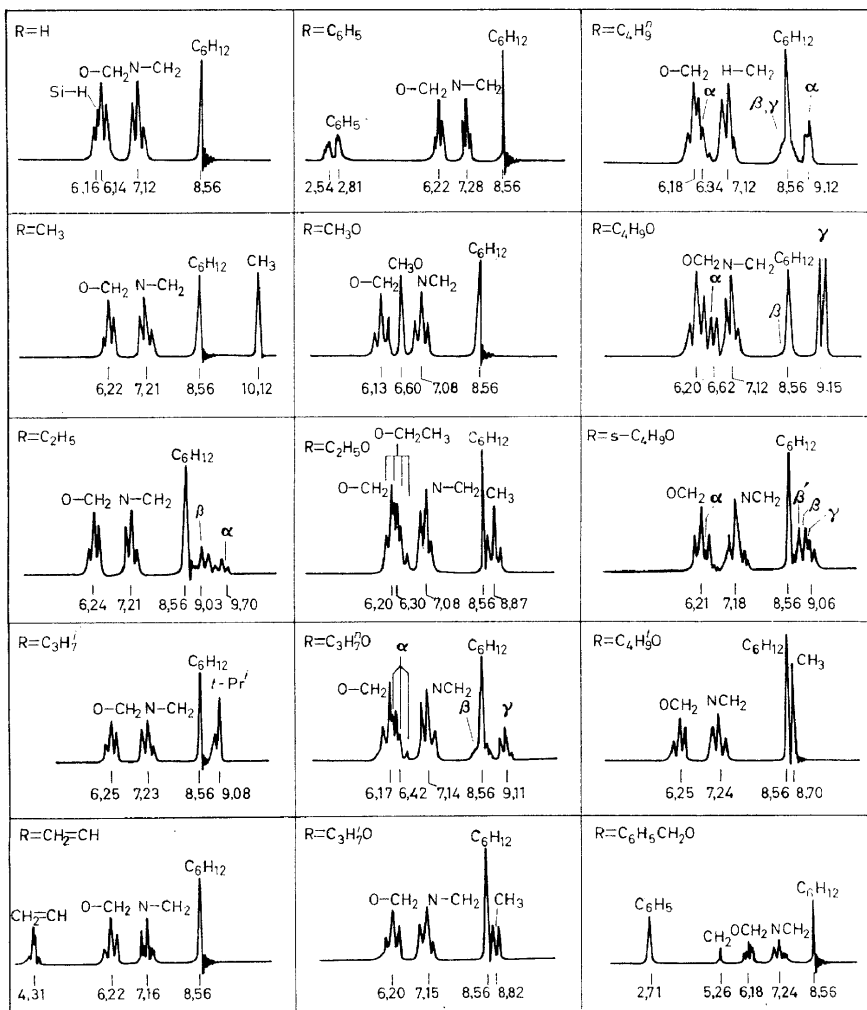


Figure 7. The H¹ n.m.r. spectra of silatrane (I)

SILATRANES

with their chemical shifts. A certain asymmetry of the two triplets is due to the fact that the A_2X_2 system is not clearly expressed and tends toward A_2B_2 . The appearance in a silatrane skeleton of a simple p.m.r. of this kind instead of an A_6B_6 spectrum reveals an interaction of the second order between its three half-rings. The half-rings $Si-O-CH_2-CH_2-N$ themselves remain independent but are identical. Assignments of the other signals in the p.m.r. spectra do not present any difficulties.

A characteristic factor of the chemical shifts in the p.m.r. spectra of the silatranes (Table 8) is a well expressed inductive influence of the substituents

Table 8. Chemical shifts τ in p.m.r. spectra of silatranes (I)

<i>R</i>	$\tau_{Si-O-CH_2}$	$\tau_{Si\leftarrow N-CH_2}$	τ_R
H	6.14	7.12	6.06
CH ₃	6.22	7.21	10.12
CH ₃ ^{β} CH ₂ ^{α}	6.24	7.21	9.70 (α); 9.03 (β)
CH ₃ ^{β'} (CH ₃ ^{β})CH ^{α}	6.25	7.23	9.08
CH ₂ =CH	6.22	7.16	4.31
C ₆ H ₅	6.22	7.28	2.81; 2.54
CH ₃ O	6.19	7.08	6.60
CH ₃ ^{β} CH ₂ ^{α} O	6.20	7.08	8.87 (β); 6.30 (α)
CH ₃ ^{γ} CH ₂ ^{β} CH ₂ ^{α} O	6.17	7.14	9.11 (γ); 8.58 (β); 6.42 (α)
CH ₃ ^{δ} CH ₂ ^{γ} CH ₂ ^{β} CH ₂ ^{α} O	6.18	7.12	9.12 (δ); 8.56-8.58 (β, γ); 6.34 (α)
(CH ₃) ₂ ^{γ} CH ^{β} CH ₂ ^{α} O	6.20	7.12	9.15 (γ); 8.55 (β); 6.62 (α)
CH ₃ ^{γ} CH ₂ ^{β} (CH ₃ ^{β'})CH ^{α} O	6.21	7.18	9.06 (γ); 8.85 (β'); 8.78 (β); 6.18 (α)
(CH ₃) ₃ CO	6.25	7.24	8.70
C ₆ H ₅ CH ₂ O	6.18	7.29	5.26(CH ₂); 2.71(C ₆ H ₅)

R on the electronic screening of the methylene protons in the fragment $-O-CH_2-CH_2-$ but only when the R represents some alkyl radicals. This effect would be expected considering that all the other substituents R have the capacity of $d_\pi - p_\pi$ -conjugation with the silicon atom, acting in the direction opposite to the inductive $-I$ effect of the substituents. For 1-phenyl- and 1-benzoxysilatrane, besides the already mentioned two effects (the inductive and the $d_\pi - p_\pi$ -interaction), there is still another effect influencing the chemical proton shifts of the methylene groups, namely, the magnetic anisotropy resulting from π -electron circulation of the aromatic ring. In addition, the $d_\pi - p_\pi$ -conjugation between the O and Si atoms in the very skeleton of the silatrane plays seemingly a considerable part in the relative stability of the chemical shifts of OCH_2 -protons following changes in the character of the substituents at the central silicon atom.

A distinguishing characteristic of the silatrane structure is the participation of the unshared nitrogen electron pair in the formation of a trans-annular dipole coordinate bond with the silicon atom, achieved through its vacant $3d$ -orbitals³⁰⁻³³. This peculiar trait of the electronic structure of the silatrane molecules, already confirmed by high values of their dipole moments³¹ (5-7D) as well as by i.r. spectroscopic data⁸⁵, can also be observed in their p.m.r. spectra.

In fact, if one should compare the chemical shifts of the corresponding

protons in the Si-substituted triethoxysilane $\text{RSi}(\text{OCH}_2\text{CH}_3)_3$ and in 1-substituted silatranes a considerable shift of substituent protons toward higher fields in the silatrane molecules will be noticed, which proves that the electron density at the silicon atom of the silatrane molecules is considerably higher:

	R=H	CH ₃	CH ₃ CH ₂	CH ₂ =CH	CH ₂ O
τ_{R} in (I)	6.06	10.12	9.70(α);9.03(β)	4.31	8.87(β)6.30(α)
τ_{R} in $\text{RSi}(\text{OCH}_2\text{CH}_3)_3$	5.74	9.96	9.30(α);9.00(β)	4.02	8.77(β)6.20(α)

A comparison of the chemical shifts of the CH_2 -protons in the silatrane fragment $\text{Si} \leftarrow \text{N} - \text{CH}_2$ with those of the $\text{N} - \text{CH}_2 -$ protons in triethanolamine and N-dimethylethanolamine ($\tau = 7.39$ and 7.55 p.p.m. on grounds of published and our own data⁸¹) reveals that the nitrogen atom in silatrane molecules is screened less distinctly than in β -oxyethylamine. Similar decrease in electron density at the nitrogen atom can be observed in the case of substitution of one hydrogen atom in the NH_2 group of the β -amino-ethoxytrimethylsilane by a trimethylsilyl group: the chemical shifts of $\text{N} - \text{CH}_2$ -protons in $(\text{CH}_3)_3\text{SiOCH}_2\text{CH}_2\text{NH}_2$ and in $(\text{CH}_3)_3\text{SiOCH}_2\text{CH}_2\text{NHSi}(\text{CH}_3)_3$ are 7.37 and 7.16 p.p.m. respectively. The shift of the signal from the methylene protons in the second compound towards a less distinctive field is ascribed to $d_\pi - p_\pi$ -conjugation of the silicon atom with the unshared electron nitrogen pair, and the value of this chemical shift is comparable to the chemical shift of the methylene protons in the $\text{Si} \leftarrow \text{N} - \text{CH}_2$ fragment of the silatranes.

The p.m.r. spectra of all compounds were obtained in CHCl_3 solutions. Cyclohexane was used as an internal standard and chemical shifts were measured in p.p.m. on the τ -scale ($\tau\text{Si}(\text{CH}_3)_4 = 10.00$).

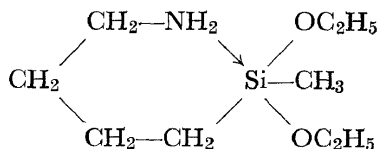
PHYSIOLOGICAL ACTIVITY

In the light of the now available literature⁸² the outlook for a possible discovery among organosilicon compounds of substances with specific biological and pharmacological activity seemed to be rather dim. Polyorganosiloxanes and silicohydrocarbons (not containing the Si-H bond) are, as a rule, physiologically inert. The biological effect of monomers of the type $\text{R}_{4-n}\text{SiX}_n$ (where R = organic radical, X = a hydrolysable functional group or atom, and $n = 1-4$) is chiefly due to the products of their hydrolysis (HX)†. Organosilicon compounds with a carbon-functional group do not differ much in physiological activity from their purely organic analogues. The only relatively toxic compound of this group described is methyl(4-aminobutyl)diethoxysilane⁸³ $\text{NH}_2(\text{CH}_2)_4\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$ (on rabbit skin absorption $\text{LD}_{50} = 0.045$ ml/kg). The high physiological activity of this

† It is interesting to note that physiologically the most active compounds are with $n = 1$ (R_3SiX).

SILATRANES

compound should be ascribed, in our opinion, to the probability of an intramolecular coordination of the δ -amino group with the central silicon atom



This has been substantiated by research work in our laboratory which brought us to the discovery of a number of new physiologically active organo-silicon compounds containing a nitrogen atom in the γ and δ position to the central silicon atom.

It thus seemed justified to expect that silatranes might also be physiologically active because of a stable intramolecular donor-acceptor bond $\text{Si} \leftarrow \text{N}$ in their structure. This assumption has been substantiated by pharmacological tests of thirteen 1-substituted silatranes (I; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, (\text{CH}_3)_2\text{CH}, \text{CH}_2 = \text{CH}, \text{C}_6\text{H}_5, 3\text{-ClC}_6\text{H}_4, \text{CH}_3\text{O}, \text{C}_2\text{H}_5\text{O}, \text{C}_6\text{H}_5\text{O}, 4\text{-CH}_3\text{C}_6\text{H}_4\text{O}, 5\text{-CH}_3\text{-2-}(\text{CH}_3)_2\text{CHC}_6\text{H}_3\text{O}, 4\text{-ClC}_6\text{H}_4\text{O}, 4\text{-O}_2\text{NC}_6\text{H}_4\text{O}$ as well as of 3,7-dimethyl-1-phenylsilatrane.

During the preliminary pharmacological testing a well expressed physiological activity has been demonstrated by 1-phenylsilatrane



which is the compound most sparingly soluble in water. Its toxicity was experimentally studied on white mice. Already doses of 0.20–0.25 mg/kg injected intraperitoneally cause motor excitation followed sometimes by a change in the position of the tail, typical to the action of morphine (test of Straub). At the same time heavy breathing was observed. At slightly higher doses (~ 0.35 mg/kg) 1-phenylsilatrane causes alternating clonic and tonic convulsions. At a dosage of around 0.4 mg/kg this convulsive effect might cause death. The mean lethal dose of 1-phenylsilatrane, calculated by the method of Litchfield and Wilcoxon, is 0.43 (0.36–0.50) mg/kg ($P = 0.05$).

The toxic effect of 1-phenylsilatrane on unanaesthetized cats is similar to the one described. Injected intraperitoneally 0.30 mg/kg of the compound cause first twitch, like muscle contractions of the ears and lids, followed shortly thereafter by severe tonic and clonic convulsions. The animal dies in about 8 min after the injection. The toxic effect of 1-phenylsilatrane is much weaker, however, in cats anaesthetized with uretan (1 g/kg) or with chloralose (30 mg/kg). Even an intravenous administration of a tenfold lethal dose does not kill the animal. Dosages of 0.30–0.40 mg/kg cause only convulsive contractions of the skeletal muscles followed by intensive breathing.

In the experiments on unanaesthetized rabbits 0.20 mg/kg of 1-phenylsilatrane injected intravenously cause agitation and convulsive contractions of the skeletal muscles. The same compound injected in a dose of 0.30 mg/kg results in pronounced clonico-tonic convulsions lasting several minutes. There is no lethal effect.

Frogs are extremely resistant to 1-phenylsilatrane. Even doses of 30–40 mg/kg have no effect at all. Administration of higher doses is made difficult due to a low water solubility of the compound.

As we see, 1-phenylsilatrane is characterized by a great variability in its physiological action depending on the sensitiveness of the species. It is extremely toxic to mammals (about twice as toxic as strychnine) and obviously non-toxic or almost non-toxic to frogs, microbes and fungi.

The mechanism of muscle twitching and convulsions under the influence of 1-phenylsilatrane has been studied on an isolated m.rectus abdominis of the frog. At a concentration of 10^{-1} no contractions occur. Similarly, this compound acting in concentration 10^{-1} for 2 min does not change markedly the reaction of muscle on acetylcholine in concentrations of 10^{-1} .

Immersion of frog isolated hind leg muscles in Ringer solution with 0.01 per cent of 1-phenylsilatrane and also a perfusion with this solution of the frog's hind legs (method of Trendelenburg) does not cause any contractions.

As we see, these results excluded the direct influence of 1-phenylsilatrane on the peripheral neuro-muscular mechanism.

In experiments on decerebrated cats convulsions and accelerated breathing appear already after a dose of 0.10–0.20 mg/kg of 1-phenylsilatrane injected intravenously. A previous pharmacological denervation (with 5 ml of a 5 per cent novocain) of the sinocarotid regions does not significantly influence the stimulation of breath. In experiments on spinal cats spasmodic twitching of the muscles is caused only by higher dosages of 1-phenylsilatrane. Cats with completely destroyed nervous system do not react even to intravenous injections of 1.5 mg/kg of the compound.

These experimental data confirm the assumption that convulsive reactions occur under the influence of 1-phenylsilatrane on the central nervous system. No doubt, its action on the spinal cord is of great importance. It is therefore a worthwhile observation that contrary to other known substances which influence the spinal cord, 1-phenylsilatrane is not active in frogs. It may be assumed that it acts on a certain enzyme system, very important to the normal function of the nervous apparatus of mammals and absent or unimportant to the normal activity of the frog nervous system. Cholinesterase of horse blood serum and acetylcholinesterase of rat erythrocyte stroma and of the brain are not inhibited by 1-phenylsilatrane.

1-(*m*-Chlorophenyl)- and 3,7-dimethyl-1-phenylsilatrane are much less active. The latter in experiments on white mice is active only when given intraperitoneally in doses as high as 5 mg/kg, which cause a change in the position of the tail; 10 mg/kg increase the motor excitation of the animals and cause clonic-tonic convulsions (already 3–5 min after injection) with a possible lethal effect. The mean lethal dose of this compound calculated by the method of Litchfield and Wilcoxon is 14.7 mg/kg ($P=0.05$). LD_{50} of 1-(*m*-chlorophenyl)silatrane is 4.4 mg/kg. As we can see, introduction of a chlorine atom in the phenyl group and of methyl groups into the heterocycle of phenylsilatrane decreases the toxicity of the compound considerably. It is interesting to note that a substitution in 1-phenylsilatrane of the silicon atom by a germanium atom reduces considerably the toxicity of the compound (1-phenylgermatrane is about 100 times less toxic than its silicon analogue).

SILATRANES

All the other investigated silatranes are physiologically inactive or produce an insignificant biological effect. Thus, for instance, 1-phenoxyilatranes in experiments on white mice are active only at dosages starting with 100 mg/kg. This causes a decrease in motor activity of the animal. At 150 mg/kg twitching occurs, sometimes followed by tonic convulsions; 200 mg/kg can be fatal. In experiments on cats under urethane anaesthesia, 1-phenoxyilatrane in doses of 10 mg/kg and higher causes a short lasting (for about 1 min) drop in blood pressure. All the 1-aryloxyilatranes are even less active.

The mean lethal dose of 1-methoxyilatrane administered by intraperitoneal injection for white mice is 2100 mg/kg, and 1-ethoxyilatrane dose not seem to act even at 1600 mg/kg. In experiments on anaesthetized cats 1-ethoxyilatrane in doses of 10 mg/kg does not exert an appreciable influence on blood pressure or on the effects of acetylcholine, histamine and adrenaline.

In all the other silatranes investigated no pharmacological activity could be observed. LD₅₀ for the studied silatranes administered intraperitoneally to white mice are given in *Table 9* (order of decreasing activity).

Table 9. LD₅₀ of silatranes (I) for white mice

<i>R</i>	LD ₅₀ (mg/kg)	<i>R</i>	LD ₅₀ (mg/kg)
C ₆ H ₅	0.43	CH ₃ O	2100
<i>m</i> -ClC ₆ H ₄	4.4	5-CH ₃ -2-(CH ₃) ₂ - CHC ₆ H ₃ O	4000
3,7-Dimethyl-1- phenylsilatrane	14.7	C ₂ H ₅ O	non-toxic
C ₆ H ₅ O	200	CH ₃	non-toxic
<i>p</i> -O ₂ NC ₆ H ₄ O	700	C ₂ H ₅	non-toxic
<i>p</i> -ClC ₆ H ₄ O	1050	(CH ₃) ₂ CH	non-toxic
<i>p</i> -CH ₃ C ₆ H ₄ O	1270	CH ₂ =CH	non-toxic

On the basis of the newly acquired data it is not unreasonable to assume that continued research on physiologically active substances among compounds with a coordinated nitrogen bound silicon atom might result in interesting findings suitable for practical purposes.

References

- ¹ C. A. Rojahn. *D. R. Pat.* 582149 (1933); *Chem. Zbl.* **11**, 2704 (1933).
- ² Y. Hirata, K. Inukai, and T. Tsujiuchi. *J. chem. Soc. Japan, Pure chem. sect.* **69**, 58 (1948).
- ³ H. C. Brown and E. A. Fletcher. *J. Am. chem. Soc.* **73**, 2808 (1951).
- ⁴ Fr. Hein and R. Burkhardt. *Z. anorg. allg. Chem.* **268**, 159 (1952).
- ⁵ C. A. Lucchesi. *Dissertation Abstr.* **15**, 2007 (1955).
- ⁶ S. H. Langer and I. N. Elbling. *Industr. Engng. Chem.* **49**, 1113 (1957).
- ⁷ I. N. Elbling and S. H. Langer. *U.S. Pat.* 2785192 (1957); *Chem. Abstr.* **51**, 11377 (1957).
- ⁸ H. Steinberg and D. L. Hunter. *Industr. Engng. Chem.* **49**, 174 (1957).
- ⁹ H. Weidmann and H. K. Zimmerman. *Liebigs Ann.* **619**, 28 (1958).
- ¹⁰ H. Weidmann and H. K. Zimmerman. *Liebigs Ann.* **620**, 4 (1959).
- ¹¹ H. K. Zimmerman and H. Weidmann. *Liebigs. Ann.* **628**, 37 (1959).
- ¹² H. Steinberg and D. L. Hunter. *J. Am. chem. Soc.* **82**, 853 (1960).
- ¹³ W. H. Sweet, A. H. Soloway, and G. L. Brownell. *Acta Unio Intern. Contra Cancrum*, **16**, 1216 (1960).
- ¹⁴ A. A. Schleppek and C. D. Gutsche. *J. org. Chem.* **25**, 1378 (1960).
- ¹⁵ R. Neu. *Arch. Pharm.* **294/66**, 721 (1961).
- ¹⁶ H. C. Fu, T. Psarras, H. Weidmann, and H. K. Zimmerman. *Liebigs. Ann.*, **641**, 116 (1961).

- 17 A. A. Schlepplik and C. D. Gutsche. *J. Org. Chem.* **27**, 3684 (1961).
- 18 R. C. Mehrotra and G. Srivastava. *J. Indian chem. Soc.* **39**, 521 (1962).
- 19 H. K. Zimmermann. *Advan. Chem. Ser.* **42**, 23 (1964).
- 20 J. M. Pugh and R. H. Stokes. *Aust. J. Chem.* **16**, 204 (1964).
- 21 J. M. Pugh and R. H. Stokes. *Aust. J. Chem.* **16**, 211 (1964).
- 22 Fr. Hein and P. W. Albert. *Z. Anorg. Allg. Chem.* **269**, 67 (1952).
- 23 S. G. Kemp and V. G. Bashford. *Brit. Pat.* 810323 (1959); *Chem. Abstr.* **53**, 12741 (1959).
- 24 J. M. Icken and E. J. Jahren (to International Latex Corporation). *Belg. Pat.* 619940 (1963); *Chem. Abstr.* **60**, 2768 (1964).
- 25 A. B. Finestone. *U.S. Pat.* 2953545 (1960); *Chem. Abstr.* **55**, 4045 (1961); *D.R. Pat.* 1131681 (1962); *Chem. Abstr.* **58**, 4598 (1963).
- 26 C. L. Frye, G. E. Vogel, and J. A. Hall. *J. Am. chem. Soc.* **83**, 996 (1961).
- 27 C. M. Samours. *U.S. Pat.* 3118921 (1964); *Chem. Abstr.* **60**, 10715 (1964).
- 28 M. G. Voronkov and G. I. Zelčans. *U.S.S.R. Pat.* 162139 (1964).
- 29 M. G. Voronkov and G. I. Zelčans. *U.S.S.R. Pat.* 165722 (1964).
- 30 M. G. Voronkov and G. I. Zelčans. *Khim. Geteroc. Soed.* **50** (1965).
- 31 M. G. Voronkov, I. B. Mažeika, and G. I. Zelčans. *Khim. Geteroc. Soed.* **58** (1965).
- 32 J. J. Baltkajs, M. G. Voronkov, and G. I. Zelčans. *Latv. PSR Zinat. Akad. Vest. Riga.* **102** (1964).
- 33 M. G. Voronkov and G. I. Zelčans. *Khim. Geteroc. Soed.* **210** (1965); **511** (1966).
- 34 A. N. Jegorochkin, V. A. Pestunovich, M. G. Voronkov, and G. I. Zelčans. *Khim. Geteroc. Soed.* **300** (1965).
- 35 R. Müller and Ch. Date. *J. prakt. Chem.* **22**, 222 (1963).
- 36 T. E. Graham and J. M. C. Thompson. Unpublished data. V. Bažant, V. Chvalkovský, and J. Rathouský, *Organosilicon compounds*. Publishing House of the Czechoslovak Academy of Sciences (1965).
- 37 L. J. Dumoulin (to Société des usines chimiques Rhône-Poulenc), *Fr. Pat.* 1087874 (1955); *Chem. Abstr.* **53**, 6077 (1959).
- 38 National Lead Corp. *Brit. Pat.* 755728 (1956); *Chem. Abstr.* **51**, 8128 (1957).
- 39 Titangesellschaft m.b.h. (H. H. Beacham, I. M. Panik, C. A. Russel), *D.R. Pat.* 964319 (1957); *Chem. Abstr.* **54**, 16857 (1960).
- 40 N. V. Titaan. *Dutch Pat.* 85336 (1957); *Chem. Abstr.* **53**, 7993 (1959).
- 41 C. O. Bostwick. *U.S. Pat.* 2824114 (1958); *Chem. Abstr.* **52**, 7743 (1958).
- 42 C. M. Samours. *U.S. Pat.* 2935522 (1960); *Chem. Abstr.* **54**, 19491 (1960).
- 43 G. M. Omietanski. *U.S. Pat.* 2991299 (1961), Ref. *Ž. Chem.*, **1963**, 7H7611.
- 44 D. M. Puri and R. C. Mehrotra. *Res. J. Hindi Sci. Acad.* **5**, 187 (1962).
- 45 Wm. T. Miller. *J. Am. chem. Soc.* **62**, 2707 (1940).
- 46 M. G. Voronkov, A. F. Lapsin', *Khim. Geteroc. Soed.* **357** (1966).
- 47 K. Starke. *J. inorg. nucl. Chem.* **6**, 130 (1958).
- 48 F. C. Burns and K. Starke. *Trans. Kentucky Acad. Sci.* **19**, 45 (1958).
- 49 K. Starke. *J. inorg. nucl. Chem.* **11**, 37 (1959).
- 50 K. Starke. *Trans. Kentucky Acad. Sci.* **20**, 41 (1959).
- 51 C. K. Ingold. Structure and Mechanism in organic Chemistry, London, 95-98 (1953).
- 52 O. A. Osipov, V. I. Minkin, Yu. B. Kletenik, *Spravochnik po dopol'nym momentam* (Handbook of Dipole Moments), Izdatel. Rostov. Univ., 1961, Rostov na Donu, 1961, 34-40.
- 53 A. L. Smith and N. L. Angelotti. *Spectrochim. Acta* **15**, 412 (1959).
- 54 H. W. Thompson. *Spectrochim. Acta.* **16**, 238 (1960).
- 55 V. A. Ponomarenko and Yu. P. Yegorov. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1134** (1960).
- 56 H. Kriegsmann, G. Kessler, and P. Reich. *Z. Chem.* **1**, 346 (1961).
- 57 A. L. Smith. *Spectrochim. Acta* **16**, 87 (1960).
- 58 N. A. Chumaevskii. *Usp. Khim.* **32**, 1152 (1963).
- 59 L. J. Bellamy. The infrared spectra of complex molecules, London (1958).
- 60 M. C. Henry and J. G. Noltes. *J. Am. chem. Soc.* **82**, 555 (1960).
- 61 M. O. Bulanin, B. N. Dolgov, T. A. Speranskaya, and N. P. Kharitonov. *Zh. Fizich. Khim.*, **31**, 1321 (1957).
- 62 N. A. Chumaevskii. *Optika i spektroskopija.* **10**, 69 (1961).
- 63 I. Simon and M. McMahon. *J. chem. Phys.* **20**, 905 (1952).
- 64 H. Murata. *J. chem. Phys.* **20**, 347, 1184 (1952).
- 65 H. Joubean and H. Behr. *Z. anorg. allg. Chem.* **272**, 2 (1953).
- 66 A. N. Lazarev and M. G. Voronkov. *Optika un Spektroskopija.* **4**, 180 (1958).
- 67 H. Kriegsmann and K. Licht. *Z. Electrochem.* **62**, 1163 (1958).
- 68 R. Forneris and E. Funk. *Z. Electrochem.* **62**, 1130 (1958).
- 69 R. Okawara. *Bull. chem. Soc. Japan.* **31**, 154 (1958).
- 70 A. N. Lazarev, *Optika i spektroskopija*, **8**, 511 (1960).
- 71 A. N. Lazarev, M. G. Voronkov, *Optika i spektroskopija*, **8**, 614 (1960).
- 72 T. Tanaka. *Bull. chem. Soc. Japan* **33**, 446 (1960).

SILATRANES

- ⁷³ R. E. Richards and H. W. Thompson. *J. chem. Soc.* 124 (1949).
- ⁷⁴ R. Fessenden. *J. org. Chem.* **25**, 598, 2191 (1960).
- ⁷⁵ H. Kriegsmann and G. Engelhardt. *Z. anorg. allg. Chem.* **310**, 320 (1961).
- ⁷⁶ Ya. I. Ryskin and M. G. Voronkov, Coll., **24**, 3816 (1959).
- ⁷⁷ Yu. P. Egorov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1553 (1960).
- ⁷⁸ S. G. Durgar'yan and Yu. P. Egorov. *Zh. obshch. Khim.* **30**, 2600 (1960).
- ⁷⁹ C. W. Young, P. C. Servais, C. C. Curric, and M. J. Hunter. *J. Am. chem. Soc.* **70**, 3758 (1948).
- ⁸⁰ H. Kriegsmann. *Advance in Molecular Spectroscopy*. 1000 (1962).
- ⁸¹ *NMR Spectra Catalogue*, Varian Associates, New York (1962).
- ⁸² R. Levin. *The Pharmacy of Silicones and their Uses in Medicine*, London 1958.
- ⁸³ C. Eaborn. *Organosilicon Compounds*, London, 1960, 473-474.
- ⁸⁴ E. Larsson. *Trans. Chalm. Univ.* **25**, No. 115, 15 (1951).
- ⁸⁵ Yu. P. Egorov, M. G. Voronkov, T. B. Loucenko, G. I. Zelčans. *Khim. Geteroc. Soed.* 24 (1966).