Chemistry of Heterocyclic Compounds, Vol. 37, No. 11, 2001

NEW ORGANOSILICON DERIVATIVES OF NITROGEN-CONTAINING HETEROCYCLES*

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Results are summarized of investigations carried out by the authors on the synthesis and study of the reactivity of organosilicon derivatives of nitrogen-containing heterocycles YCH_2SiX_3*, where* $X = OMe$*, F, 1/3* $(OCH_2CH_2)_3N$*; Y = a heterocyclic substituent linked by a* CH_2 *group with an endocyclic nitrogen atom or an exocyclic sulfur atom.*

Keywords: nitrogen-containing heterocycles, organotrialkoxysilanes, organotrifluorosilanes, silatranes, silsesquioxanes.

In the second half of the last century organosilicon derivatives of nitrogen-containing heterocyclic compounds began to attract the attention of many investigators. Study of them made a valuable contribution to synthetic, theoretical, medicinal, and applied chemistry. Some of these compounds have already found practical application as synthons in organic synthesis, biologically active substances, sorbents, etc. (see for example [1-5]).

We have synthesized numerous organosilicon derivatives of nitrogen-containing heterocycles corresponding to the general formula YCH_2SiX_3, where $X = OMe$, F, 1/3 $(OCH_2CH_2)_3N$; Y is a heterocyclic substituent linked by a CH_2 group with an exocyclic sulfur atom or an endocyclic nitrogen atom. They are obtained by the interaction of S-sodium derivatives of 8-mercaptoquinoline, 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, and 2-mercaptobenzothiazole, and also the N-sodium derivatives of imidazole, 3,5-dimethylpyrazole, 1,2,4-triazole, indole, benzimidazole, phthalimide, 4-methyl-1-phenylpyrazolidin-3-one, with (chloromethyl)trimethoxy-, (chloropropyl)trimethoxy-, and methyl(chloromethyl)dimethoxysilanes in a polar aprotic solvent (DMSO, DMF) at 80-90°C in the presence of catalytic quantities of 18-crown-6 for 2-5 h [6-11] according to the following scheme.

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* The authors dedicate this paper to the glorious birthday of Academician E. Ya. Lukevics, who has made an enormous contribution to the chemistry of heteroorganic and heterocyclic compounds, and we wish him, with all our hearts, new scientific successes, with his previous exceptional efficiency and activity and, of course, good health.

This is particularly pleasant for the first author to greet the jubiland, with whom he worked closely, amicably, and fruitfully, for 10 years in the Institute of Organic Synthesis of the Latvian Academy of Sciences.

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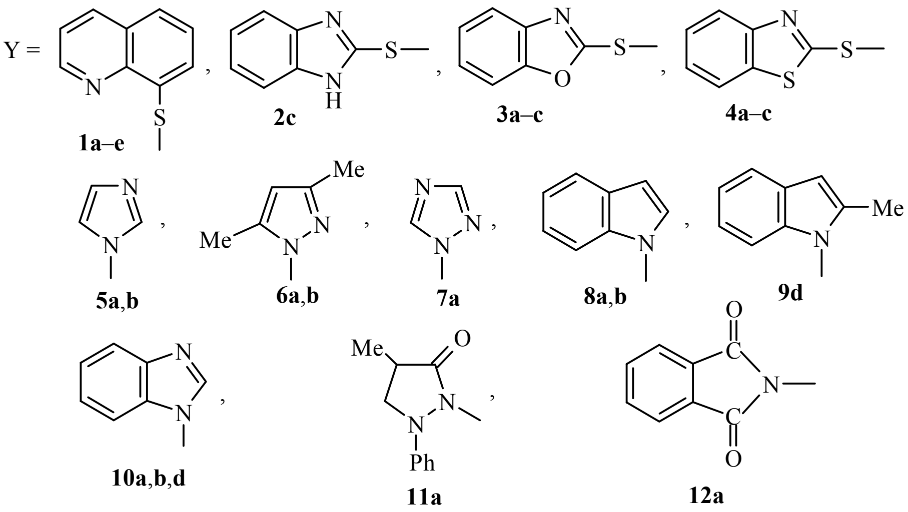
$$\mathrm{YNa + Cl(CH_2)_{\mathit{m}}\,Si(OMe)_{3\text{-}\mathit{n}}Me_{\mathit{n}} \longrightarrow Y(CH_2)_{\mathit{m}}\,Si(OMe)_{3\text{-}\mathit{n}}Me_{\mathit{n}} + NaCl}$$

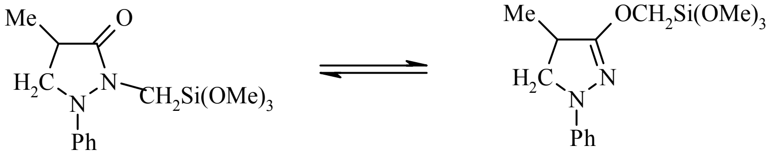
1–12



a *n* = 0, *m* = 1; **b** *n* = 1, *m* = 1; **c** *n* = 3, *m* = 1; **d** *n* = 0, *m* = 3

The (heterylthiomethyl)- and (N-heterylmethyl)trimethoxy- and methyl(dimethoxy)silanes obtained are colorless or slightly yellowish readily hydrolysable liquids. Compounds **3** and **4** are distilled in a vacuum of 1-3 mm Hg without decomposition, but **1**,**5-12** with partial decomposition. Characteristic absorption frequencies for the $Si(OMe)_3$ grouping are present in the IR spectra of silanes **1-12** with ν 815-825, 1056-1080, 2840 cm^{-1}, in addition to the frequencies of the appropriate heterocyclic fragments.

On distilling compound **11a** in vacuum two main fractions were isolated, a low-boiling and a high-boiling with bp 164 and 182°C at 4 mm Hg respectively. The presence of a reversible N–C=O ⇄ N=C–O rearrangement in the **11a** molecule was proved with the aid of IR and UV spectroscopy.



The existence of the N=C–O structure in compound **11a** is caused by an *n*,σ*-hyperconjugation effect in the $NCH_2Si(OMe)_3$ fragment leading to a reduced electron-donating ability for the nitrogen atom [11].

2-(Benzimidazolylthiomethyl)trimethoxy- (**2a**) and 2-(benzimidazolylthiomethyl)methyldimethoxysilane (**2b**) failed to be isolated in a pure state by distillation due to a polycondensation reaction involving NH and OCH_3 groups with elimination of methanol. However compound **2a** was successfully converted into the corresponding derivatives of silatrane and silsesquioxane without isolation from the reaction mixture.

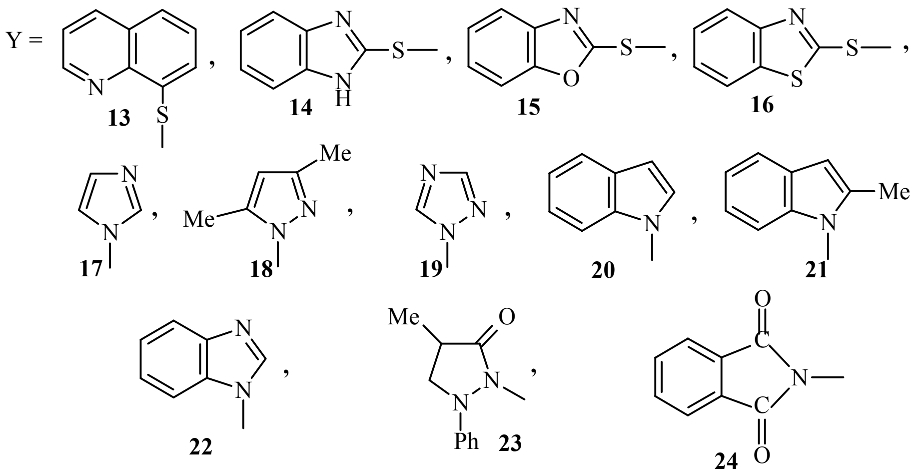
Transesterification of (heterylthiomethyl)- and (N-heterylmethyl)trimethoxysilanes with triethanolamine leads to the corresponding (heterylthiomethyl)- and (N-heterylmethyl)silatrane [6-11].

(Heterylthiomethyl)- and (N-heterylmethyl)silatranes **13-24** are colorless crystalline substances soluble in halogenated hydrocarbons, MeCN, DMSO, and DMF, with mp from 127°C (**22**) to 237°C (**14**).

In the IR spectra the absorption bands at 570-575, 775-785, 905-915, 935-940, 1075-1085, and 1105-1115 cm^{-1}, which do not depend on the nature of the heterocycle, correspond to the silatranyl group $Si(OCH_2CH_2)_3N$ (SA) [12-14].

The absorption bands in the UV spectra of YCH_2-SA **13**, **15**, and **16** are shifted bathochromically in comparison with the spectra of YCH_2SiMe_3 [15]. This shift amounts to 13, 2, and 5 nm in the spectra of compounds **13**, **15**, and **16** respectively. The significant bathochromic shift of this band in the UV spectrum of compound **13** is evidently caused by the super electron-donating effect of the CH_2-SA group which increases significantly the nucleophilicity of the sulfur atom conjugated with the quinoline heterocycle. Such a significant change in UV spectra under the influence of an inductive effect of a substituent unconjugated with the sulfur atom has not been observed until the present.

$$Y(CH_2)_m\,Si(OMe)_3 + (HOCH_2CH_2)_3N \longrightarrow \underset{\textbf{13–24}}{Y(CH_2)_m\,Si(OCH_2CH_2)_3N} + 3\,HOMe$$



m = 1; for **21**, **22** *m* = 1, 3

In silatranes **13**, **15**, and **16** containing the SCH_2-SA fragment, coordination interaction between the Si atom and the endocyclic heteroatom (N, O, S), i.e. with the closure of a six- or five-membered chelate ring, did not occur. The $YSCH_2Si$ fragment is planar (torsion angle SCSiO is 179°) [6,16] and a *n*,σ-hyperconjugation effect is impossible as a result of this.

The crystal and molecular structure of compounds **13**, **16**, and **19** have been established by X-ray structural analysis [6,10,16] (Figs. 1-3).

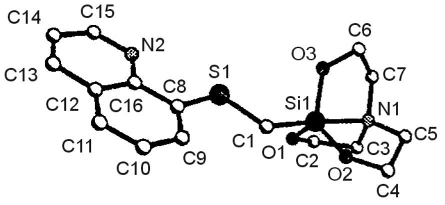


Fig. 1. 8-(Silatranylmethylthio)quinoline (**13**).

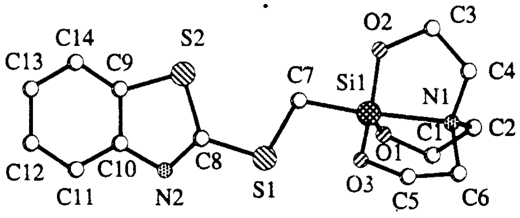


Fig. 2. 2-(Silatranylmethylthio)benzothiazole (**16**).

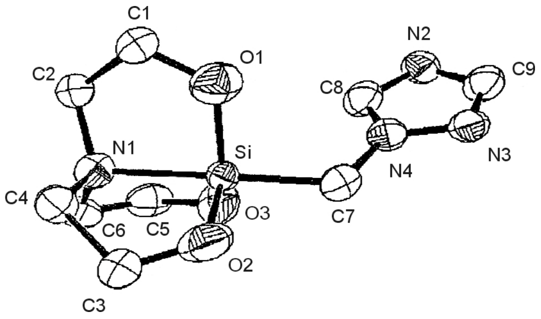


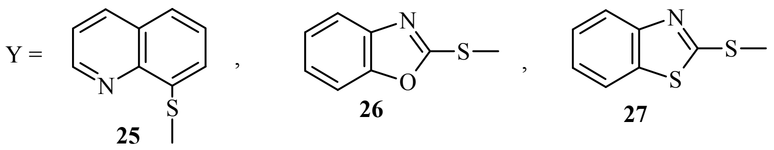
Fig. 3. 1-(Silatranylmethyl)-1,2,3-triazole (**19**).

The geometry of the silatrane system in 8-(silatranylmethylthio)quinoline (**13**), 2-(silatranylmethylthio)benzothiazole (**16**), and 1-(silatranylmethyl)-1,2,4-triazole (**19**) was close to standard. The N→Si bond lengths in them were 2.111(3) for **13**, 2.100(2) for **16**, and 2.095(5) Å for **19** respectively. These values indicate that the YCH_2 group in these compounds displays a weak –I-effect. The significant linear correlation between the values of $l_{N\rightarrow Si}$ and $\sigma_{I(YCH2)}$ in silatranes indicates that the values of σ_I for these substituents were 0.22 for **13**, 0.26 for **16**, and 0.28 for **19** [17].

The presence on the silicon atom of two and particularly of three highly electronegative fluorine atoms significantly increases its electrophilicity. In favorable steric conditions this leads to a donor–acceptor interaction of the exocyclic silicon atom and the endocyclic nitrogen atom of the heterocycle.

The reactions of trimethoxy- and methyldimethoxysilylmethyl derivatives of 8-mercaptoquinoline, 2-mercaptobenzoxazole, and 2-mercaptobenzothiazole with boron trifluoride etherate lead to the corresponding (heterylthiomethyl)trifluoro- and methyldifluorosilanes **25-27**.

$$YCH_2Si(OMe)_{3-n}\,Me_n + \frac{3-n}{3}\,Et_2O\,BF_3 \longrightarrow \underset{\mathbf{25–27}}{YCH_2SiF_{3-n}\,Me_n} + \frac{3-n}{3}\,B(OMe)_3 + \frac{3-n}{3}\,Et_2O$$



25 **26** **27**

n = 0; for **25** n = 0, 1

Compound **25** (n = 0) was an oily, difficult to crystallize substance with a sharp odor, **25** (n = 1) a yellow amorphous powder, and **26**, **27** were colorless crystals without odor, stable in the air.

In the IR spectra of compound **25** (n = 1) the absorption bands at 870 and 940 cm^{-1} correspond to the SiF_2Me group. The addition of phenol or $HClO_4$ to a solution of **25** (n = 1) in acetonitrile with the aim of protonating the nitrogen atom and breaking the proposed N→Si bond did not lead to a shift in the ν (Si–F) in the spectrum [6]. The position of these bands is also retained in the spectra of solutions of **25** (n = 1) in trifluoroacetic acid. The ν (Si–F) bands remained unchanged in position and intensity also on reducing the temperature of a solution of compound **25** (n = 1) in CS_2 to close to freezing.

The spectroscopic data therefore indicate the absence of a N→Si coordinated bond in the **25** (n = 1) molecule.

In the UV spectrum of compound **25** (n = 1) a significant (18 nm) hypsochromic shift of the long wave band (λ_1 317 nm) was observed in comparison with 8-ethylthioquinoline (λ_1 335 nm). Since the silicon atom in **25** (n = 1) is tetracoordinated, such a large shift may be caused by the overall –I-effect of the CH_2SiF_2Me group and the n,σ*-hyperconjugation in the $SCH_2Si(F)$ group reducing the electron density on the sulfur atom.

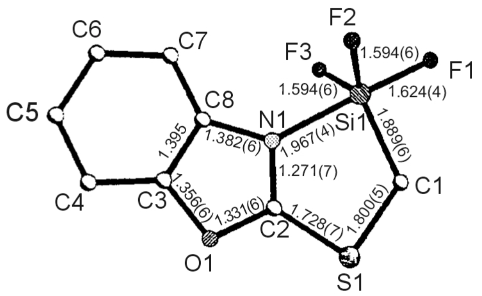


Fig. 4. 2-(Trifluorosilylmethylthio)benzoxazole (**26**).

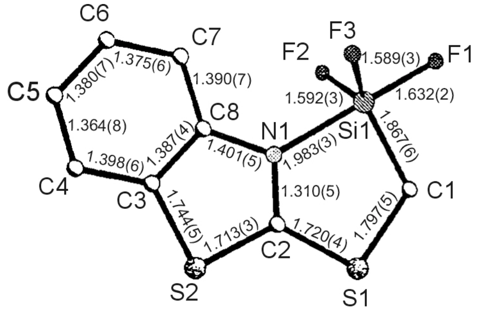


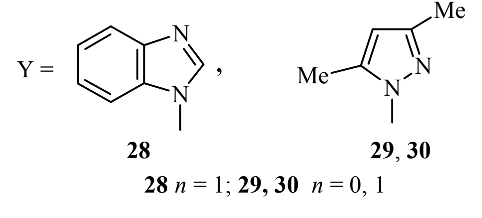
Fig. 5. 2-(Trifluorosilylmethylthio)benzothiazole (**27**).

In the IR spectra of compounds **26** and **27** the absorption bands of the SiF_3 grouping (465-470, 730, 750-755, 840-845, 890 cm^{-1}) confirm the trigonal bipyramid environment of the silicon atom [15]. As a result of the donor–acceptor interaction of N→Si the bands of the skeletal vibrations of the oxazole and thiazole heterocycles were displaced towards high frequency in the range 1000-1400 cm^{-1}. The presence in these compounds of the donor–acceptor N→Si bond was confirmed by data of X-ray structural analysis. The length of this coordinate bond in **26** and **27** was 1.967(4) and 1.988(3) Å respectively (Figs. 4,5) [18}.

The similarity of the chemical structures of compounds **26** and **27** causes the near identity of their corresponding geometric parameters. The coordination polyhedron of the pentacoordinate Si atom in their molecules is a distorted trigonal bipyramid. The interatomic distance N→Si in the **26** molecule is 0.02 Å shorter than in **27**, which corresponds with the greater electronegativity of the O atom compared with S. The length of the axial Si–F(1) bond in **26** is 1.624(4) and in **27** is 1.632(2). The length of the equatorial Si–F(2) and Si–F(3) bonds are 1.594(6), 1.594(6) in **26**, and 1.592(3) and 1.589(3) Å in **27** respectively.

2-(Trifluorosilylmethylthio)benzoxazole **26** exists in benzene solution as a mixture of cyclic and acyclic forms (μ = 4.4 and 3.9 D respectively).

On interacting the N-(trimethoxysilylmethyl) and the N-methyl(dimethoxy)silylmethyl derivatives of 3,5-dimethylpyrazole (**6a,b**) and benzimidazole (**10b**) with an excess of boron trifluoride etherate $Et_2O{\cdot}BF_3$ not only does substitution of a methoxy group by a fluorine atom occur but also coordination of the nitrogen atom with a molecule of BF_3 (formation of a B-trifluoroborazane derivative).



$$YCH_2Si(OMe)_{3-n}Me_n + \frac{3-n}{3}Et_2O{\cdot}BF_3 \longrightarrow F_3B[YCH_2SiF_{3-n}Me_n] \xrightarrow{+KF} YCH_2SiF_{3-n}Me_n + KBF_4$$

28, **29** **30**

28 **29**, **30**

28 *n* = 1; **29, 30** *n* = 0, 1

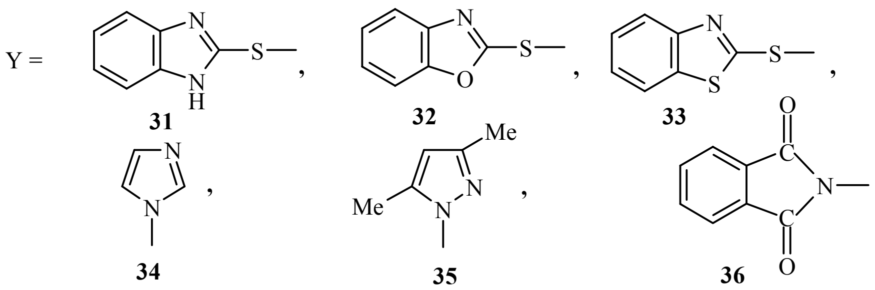
Potassium fluoride and urea were used for the first time to split off BF_3 from adducts **29** (n = 0,1). Complexes **28** and **29** were colorless powders of mp up to 109°C, **30** (n = 0,1) were colorless readily hydrolyzable liquids.

Hydrolysis of 2-(heterylthiomethyl)- and (N-heterylmethyl)trimethoxysilanes leads to the corresponding poly-2-(heterylthiomethyl)- (**31-33**) and poly-(N-heterylmethyl)silsesquioxanes (**34-36**) [7,9,19].

The polysilsesquioxanes **31-33** are finely dispersed yellow powders, and **34-36** are colorless powdery substances. Their structures were confirmed by the presence in the IR spectra of intense absorption bands at 1020-1100 cm^{-1} (Si–O–Si) and the absence of absorption bands for silanol groups at 3690 cm^{-1} (Si–OH).

$$\mathrm{YCH_2Si(OMe)_3} + 1.5\ \mathrm{H_2O} \longrightarrow 1/n\ [\mathrm{YCH_2SiO)_{1.5}]_n} + 3\ \mathrm{HOMe}$$

31–36



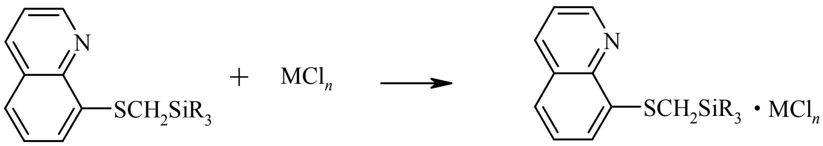
The adsorption of compounds of noble metals at a high oxidation level, Au(III), Pd(II), and Pt(IV) by silsesquioxanes **31-33** has been investigated. Poly-2-(benzimidazolylthiomethyl)silsesquioxane **31** possessed the best adsorption characteristics in relation to gold(III) (70-95%). For the quantitative (to 99%) removal of micro amounts of palladium(II) from hydrochloric acid solutions, poly-2-(benzothiazolylthiomethyl)silsesquioxane **33** proved to be more promising. The same sorbent is preferred for the group removal of Au(III), Pd(II), and Pt(IV) (95-100%) from concentrated HCl solutions.

Data on the elemental analysis of sorbents "saturated" with the appropriate metal show that the poly-2-(heterylthiomethyl)silsesquioxanes **31** and **33** displace two atoms of chlorine from the coordination sphere of the metal chloride. This indicates that they are bidentate. However on removing metals with sorbent **32** the process of complex formation is accompanied by the displacement of only one chlorine atom from the coordination sphere of the metal which indicates it is a monodentate complex-forming group, i.e. it indicates the absence of coordination of the metal with an oxygen atom, characteristic of the noble metals. The low values of the sorption capacity (64, 48, 34 mg/g for Au(III), Pd(II), and Pt(IV) respectively), and of the distribution coefficient D, which is 800 for Au(III), 650 for Pd(II), and 610 cm^2/g for Pt(IV), for sorbent **32** are a consequence of this.

In the IR spectra of sorbents **31-33** "saturated" with metal, bands are present at 300-400 cm^{-1} indicating the presence of a metal–nitrogen bond. The spectroscopic data and the bidentate nature of the complex-forming groups of sorbents **31** and **33,** but not of **32**, indicate that the coordination centers in **31** and **33** are the pyridine nitrogen atom and the endocyclic NH fragment or S respectively. In sorbent **32** only the nitrogen atom is a coordination center. The sulfide sulfur atom of the exocyclic $SCH_2SiO_{1.5}$ grouping does not participate in the process of complex formation. This is evidently caused by its steric unavailability.

The coordinating ability of the organosilicon derivatives of the widely known complexone 8-mercaptoquinoline containing $SiMe_3$, $Si(OMe)_3$, and $Si(OCH_2CH_2)_3N$ is of particular interest. The formation of complexes by these compounds is provided by the presence of favorably disposed S and N atoms, and also by the character of the substituent at the Si atom and the nature of the metal being absorbed. Compounds **1a,c** and **13** form complexes of 1:1 composition with $CuCl_2$, $ZnCl_2$, $PtCl_2$, and $SnCl_2$ [20].

The complexes **37-46** obtained were variously colored powders, insoluble in water.

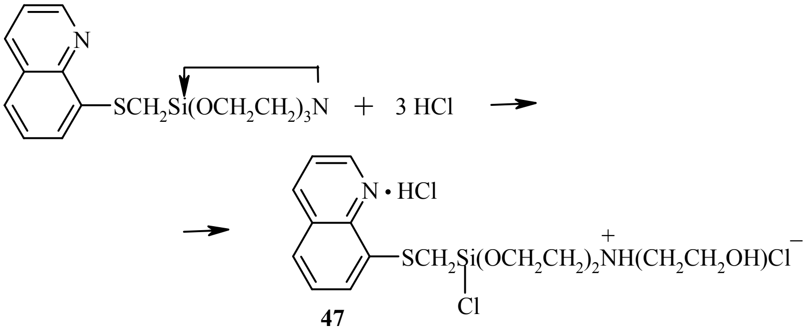


1a,c, **13**

37–46

1a R = OMe; **37** MCl_n = $CuCl_2$, **38** $ZnCl_2$, **39** $SnCl_2$, **40** HCl; **13** R = 1/3 $(OCH_2CH_2)_3N$,
41 MCl_n = $CuCl_2$, **42** $ZnCl_2$, **43** $SnCl_2$, **44** HCl; **1c** R = Me, **45** MCl_n = $PtCl_2$, **46** $CuCl_2$

8-(Silatranylmethylthio)quinoline **13** forms a hydrochloride of composition 1:1 on interaction with an equimolar quantity of HCl in diethyl ether. Breakdown of the silatrane framework was observed with an excess of HCl (1:3).



47

The structure of compound **47** was confirmed by the presence in the IR spectrum of a broad absorption band with a maximum at 3300 cm^{-1} (ν (OH)) and by the disappearance of the absorption band at 570 cm^{-1} (skeletal vibration of the silatrane framework).

The UV spectra of solutions in CH_3CN of the compounds **37-46** obtained may be divided into 3 types. The spectra of complexes **38**, **42**, and **45** belong to the first type. The presence in these spectra of absorption bands for the initial ligands **1a,c** and **13**, the intensity of which depended on the concentration of the complex in solution, is caused by partial dissociation. Complexes of this type are characterized by a hypsochromic shift of the short wave absorption band (λ_{max} 250-260 nm) to 235-240 nm. The long wave band (λ_{max} = 335-350 nm) was also displaced towards the blue region (310-320 nm). It was split into two closely located components.

The UV spectra of complexes **39** and **43** belong to the second type, and are similar to the spectra of **1a,c** and **13**. The hydrochlorides of complexes **39** and **43** were also partially dissociated in solution into the initial components. A distinguishing special feature of spectra of the second type was the presence of absorption bands at 360-410 nm and splitting of the short wave absorption band into two with maxima at 260-275 and 230-245 nm.

The third type comprises the spectra of complexes **37** and **41**. They, together with the extremely weak absorption bands of **1a,c** and **13** are superpositions of the spectra of the first two types, a chelate structure and with a N→Cu bond.

An X-ray analysis of 8-(trimethylsilylmethylthio)quinoline with $PtCl_2$ (**45**) has been carried out to establish unequivocally the structure of the resulting complexes [21] (Fig. 6).

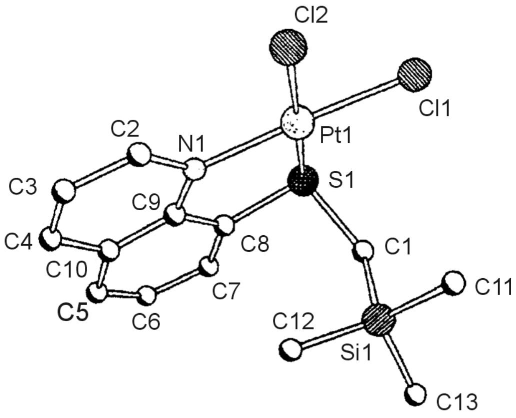


Fig. 6. The complex of 8-(trimethylsilylmethylthio)quinoline with $PtCl_2$ (**45**).

The Pt atom in complex **45** is coordinated with the N and S atoms with the formation of a chelate ring. There are two symmetrically independent molecules of the complex in the unit cell. The main differences of their conformation are the orientation of the trimethylsilyl group relative to the mean plane of the molecule, i.e. a so-called contact conformation takes place, when two conformational isomers co-exist in the structure (Fig. 7). The bond lengths of Pt-N and Pt-S were 2.017(9) and 2.225(3) Å respectively.

The biological activity of the compounds synthesized is caused both by the presence of the heterocyclic system and by the presence of the silicon atom in the appropriate framework.

The fungicidal (*in vitro*) and pesticidal activity of (heterylthiomethyl)- and (N-heterylmethyl)triorganylsilanes, silatranes and their complexes with metal chlorides have been studied (Tables 1, 2).

The data of Tables 1 and 2 indicate that 1-(2-heterylthiomethyl)silatranes **14-16**, and the complexes of 8-(trimethoxysilylmethylthio)quinoline with $ZnCl_2$ **38** and $SnCl_4$ **39** at the discriminating concentration show an effective insecticidal action on house flies and rice weevils. However on reducing the concentration to 0.05% the loss of insects did not exceed 35%. 2-(Silatranylmethylthio)benzimidazole **14**, the complexes of 8-(trimethoxysilylmethylthio)quinoline with $SnCl_4$ **39** and 8-(silatranylmethylthio)quinoline with HCl **44** at a dose of 80 mg/kg possess high nematocidal activity, causing a loss of nematodes of 65-100%. On the whole the compounds studied did not possess high fungicidal and bactericidal activity at low concentrations.

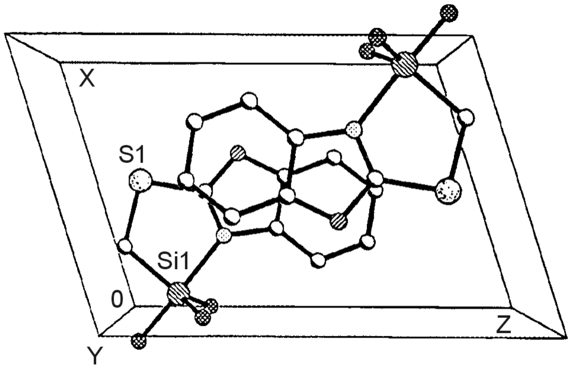


Fig. 7. Orientation of the trimethylsilyl group relative to the mean plane of the molecule.

TABLE 1. Insectoacaricidal and Nematode Activity of YCH_2SiX_3 and Their Complexes with Metal Chlorides (MCl_n)*

Compound	Y	X	MCl_n	Loss of insects, % (action of 0.5% aq. soln.)		Reduction of gall formation on cucumber roots, %
				house flies	rice weevils	
14	2-Benzimidazolylthio-	1/3 $(OCH_2CH_2)_3N$	—	35	100	65
15	2-Benzoxazolylthio-	1/3 $(OCH_2CH_2)_3N$	—	32	100	Herbicidal effect
16	2-Benzothiazolylthio-	1/3 $(OCH_2CH_2)_3N$	—	45	100	0
18	3,5-Dimethylpyrazolyl-	1/3 $(OCH_2CH_2)_3N$	—	88	59	0
22	1-Benzimidazolyl-	1/3 $(OCH_2CH_2)_3N$	—	42	100	65
38	8-Quinolylthio-	OMe	$ZnCl_2$	100	100	41
39	8-Quinolylthio-	OMe	$SnCl_4$	82	100	100
41	8-Quinolylthio-	$(OCH_2CH_2)_3N$	$CuCl_2$	2	24	6
44	8-Quinolylthio-	$(OCH_2CH_2)_3N$	HCl	0	0	88

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* Jointly with O. K. Grib, E. A. Prokhorchuk, and A. G. Emlina (Dnepropetrovsk Institute of Chemical Technology).

TABLE 2. Fungicidal Activity of YCH_2SiX_3 and Their Complexes with Metal Chlorides (MCl_n)

Compound	Y	X	MCl_n	Percent inhibition of growth and development*					
				colonies of bacteria and molds (conc. 0.003%)				diseases on green plants (0.1%)	
				1	2	3	4	5	6
14	2-Benzimidazolylthio-	1/3 $(OCH_2CH_2)_3N$	—	20	20	27	0	25	41
15	2-Benzoxazolylthio-	1/3 $(OCH_2CH_2)_3N$	—	26	14	26	20	0	53
16	2-Benzothiazolylthio-	1/3 $(OCH_2CH_2)_3N$	—	26	11	8	0	0	0
18	3,5-Dimethylpyrazolyl-	1/3 $(OCH_2CH_2)_3N$	—	20	28	18	0	0	0
22	Benzimidazolyl-	1/3 $(OCH_2CH_2)_3N$	—	7	14	0	0	12	0
38	8-Quinolylthio-	OMe	$ZnCl_2$	20	40	0	26	12	0
39	8-Quinolylthio-	OMe	$SnCl_4$	20	11	20	13	31	0
41	8-Quinolylthio-	1/3 $(OCH_2CH_2)_3N$	$CuCl_2$	45	14	36	17	18	0
44	8-Quinolylthio-	1/3 $(OCH_2CH_2)_3N$	HCl	33	2	34	4	18	0
46	8-Quinolylthio-	Me	$CuCl_2$	20	25	26	20	12	55

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* 1 – *Xanthomonas malvacearum*; 2 – *Fusarium moniliforme*; 3 – *Penicillium cyclopium*; 4 – *Venturia inaegualis*; 5 – *Aspergillus niger*; 6 – *Botrytis cinerea.*

The toxicity of (heterylthiomethyl)silatranes depended markedly on the nature of the endocyclic heteroatom. The LD_{50} of 8-(silatranylmethylthio)quinoline, 2-(silatranylmethylthio)benzimidazole, -benzoxazole, -benzothiazole, and 1-(N-silatranylmethyl)benzimidazole were 5, 205, 1349, 3000, and 603 mg/kg respectively. No anticorazole effect was displayed by these compounds at 10 mg/kg 30 min after injection of corazole. On administering substances **15** and **16** an hour before injection of corazole an anticonvulsant effect was observed.

EXPERIMENTAL

2-Methyl-1-[3-(trimethoxysilyl)propyl]indole (9d). Sodium (3.01 g, 0.131 mol) in methanol (50 ml) was added to 2-methylindole (17.25 g, 0.131 mol). The methanol was distilled off on a rotary evaporator. Dimethyl formamide (DMF) (100 ml), 18-crown-6 (0.003 g), and (3-chloropropyl)trimethoxysilane (26.03 g, 0.131 mol) were added. The mixture was stirred for 2 h at 80-90°C. The precipitated solid was filtered off. Compound **9d** (27.68 g, 72%) was isolated by distillation; bp 168-172°C/2 mm Hg. Found, %: C 59.99; H 8.05; N 4.72; Si 9.22. $C_{15}H_{23}NO_3Si$. Calculated, %: C 61.40; H 7.90; N 4.77; Si 9.57.

1-[3-(Trimethoxysilyl)propyl]benzimidazole (10d) was obtained analogously; bp 158-160°C/2 mm Hg (65%). Found, %: C 56.23; H 7.53; N 10.75; Si 9.73. $C_{13}H_{20}N_2O_3Si$. Calculated, %: C 55.69; H 7.19; N 9.99; Si 10.02.

2-Methyl-1-(3-silatranylpropyl)indole (21). Triethanolamine (0.34 g, 0.002 mol) was added to **9d** (0.67 g, 0.002 mol). The reaction product crystallized from the reaction mixture after several hours. Compound **21** (0.6 g, 88%) was isolated on recrystallization from a mixture of chloroform–hexane (1:1); mp 141-142°C. Found, %: C 61.74; H 8.37; N 7.86; Si 8.22. $C_{18}H_{26}N_2O_3Si$. Calculated, %: C 62.39; H 7.56; N 8.08; Si 8.11.

1-(3-Silatranylpropyl)benzimidazole (22) was prepared analogously (85%); mp 172-173°C. Found, %: C 56.11; H 7.81; N 12.26; Si 8.09. $C_{16}H_{23}N_3O_3Si$. Calculated, %: C 57.63; H 6.95; N 12.60; Si 8.42.

[2,5-Dimethyl-1-(trifluorosilylmethyl)pyrazole]trifluoroboron (29). Boron trifluoride etherate (14.05 g, 0.099 mol) was added dropwise to 2,5-dimethyl-1-(trimethoxysilylmethyl)pyrazole (**6a**) (7.65 g, 0.033 mol). The mixture was stirred on a magnetic stirrer at 34°C for 1 h. The low boiling fraction was distilled off. Complex **29** (7.35 g, 85%) was isolated by distillation and had mp 50-53°C. Found, %: C 27.22; H 3.48; F 42.23; N 10.69; Si 10.04. $C_6H_9BF_6N_2Si$. Calculated, %: C 27.50; H 3.46; F 43.50; N 10.69; Si 10.72.

[1-(Methyldifluorosilylmethyl)benzimidazole]trifluoroboron (28) was obtained analogously; mp 109°C (92% yield). Found, %: C 38.50; H 3.70; F 32.79; N 10.34; Si 9.23. $C_9H_{10}BF_5N_2Si$. Calculated, %: C 38.60; H 3.60; F 33.92; N 10.00; Si 10.03.

2,5-Dimethyl-1-(trifluorosilylmethyl)pyrazole (30) (*n* = 0). Boron trifluoride etherate (5.83 g, 0.03 mol) was added dropwise to **6a** (7.00 g, 0.03 mol). The mixture was stirred on a magnetic stirrer at 34°C for 1 h. The low boiling fraction was distilled off. Potassium fluoride (1.01 g, 0.0174 mol) or urea (1.04 g, 0.0174 mol) was added. Compound **30** (*n* = 0) (4.43 g, 76%) was isolated by distillation in vacuum; bp 63°C/5 mm Hg. Found, %: C 36.48; H 5.12; F 27.20; N 13.72. $C_6H_9F_3N_2Si$. Calculated, %: C 37.10; H 4.67; F 29.34; N 14.46.

2,5-Dimethyl-1-(methyldifluorosilylmethyl)pyrazole (30) (*n* = 1) was obtained analogously; bp 62°C/6 mm Hg (83% yield). Found, %: C 44.58; H 6.62; F 18.07; N 14.57; Si 13.99. $C_7H_{12}F_2N_2Si$. Calculated, %: C 44.19; H 6.39; F 19.97; N 14.72; Si 14.76.

Compounds **1-8**, **10a,b-20**, and **31-47** were obtained by the procedures described previously in [6,7,9-11,18-21].

REFERENCES

1. E. Ya. Lukevics and A. E. Pestunovich, *Usp. Khim.*, **41**, 1994 (1972).
2. E. Ya. Lukevics and I. D. Segal, *Pyridine and Quinoline Derivatives of Group IVB Elements*, Prepr., Riga (1986), Chap. 1, 64 pp., Chap. 2, 71 pp.
3. E. Lukevics and I. D. Segal, *Organomet. Chem. Rev.*, 69 (1988).
4. V. A. Lopyrev, L. I. Larina, and M. G. Voronkov, *Zh. Org. Khim.*, in the press.
5. M. G. Voronkov, V. A. Pestunovich, and Yu. I. Baukov, *Metallorg. Khim.*, **4**, 1210 (1991).
6. M. G. Voronkov, N. F. Chernov, O. M. Trofimova, Yu. E. Ovchinnikov, Yu. T. Struchkov, and G. A. Gavrilova, *Izv. Akad. Nauk, Ser. Khim.*, 758 (1993).
7. M. G. Voronkov, N. F. Chernov, O. M. Trofimova, and T. N. Aksamentova, *Izv. Akad. Nauk, Ser. Khim.*, 1965 (1993).
8. O. M. Trofimova, N. F. Chernov, and M. G. Voronkov, *Usp. Khim.*, **68**, 318 (1999).
9. N. F. Chernov, Yu. I. Bolgova, O. M. Trofimova, and M. G. Voronkov, *Zh. Obshch. Khim.*, **69**, 1453 (1999).
10. M. G. Voronkov, E. A. Zel'bst, A. A. Kashaev, O. M. Trofimova, Yu. I. Bolgova, V. S. Fundamenskii, and N. F. Chernov, *Dokl. Akad. Nauk*, **376**, 5 (2001).
11. E. I. Brodskaya, Yu. I. Bolgova, O. M. Trofimova, N. F. Chernov, and M. G. Voronkov*, Zh. Obshch. Khim.*, in the press.
12. M. G. Voronkov, V. M. Dyakov, and S. V. Kirpichenko, *J. Organomet. Chem.*, **233**, 1 (1982).
13. V. Pestunovich, S. Kirpichenko, and M. Voronkov, in Z. Rappoport and Y. Apeloig (editors), *The Chemistry of Organic Silicon Compounds*, Vol. 2, New York (1998), p. 1447.
14. M. G. Voronkov, S. G. Shevchenko, E. I. Brodskaya, V. P. Baryshok, V. M. Dyakov, Yu. L. Frolov, P. Raikh, and I. L. Anisimova, in V. A. Koptyug (editor*), Atlas of Spectra of Organic Compounds*, Novosibirsk (1985), Pt. 31, p. 175.
15. E. I. Brodskaya, V. V. Belyaeva, O. M. Trofimova, N. F. Chernov, V. B. Pukhnarevich, and M. G. Voronkov, *Zh. Obshch. Khim.*, **70**, 1139 (2000).
16. Yu. E. Ovchinnikov, Yu. T. Struchkov, N. F. Chernov, O. M. Trofimova, and M. G. Voronkov, *Dokl. Akad. Nauk*, **328**, 330 (1993).
17. M. G. Voronkov and V. V. Belyaeva, *Zh. Obshch. Khim.*, in the press.
18. Yu. E. Ovchinnikov, Yu. T. Struchkov, N. F. Chernov, O. M. Trofimova, and M. G. Voronkov, *J. Organomet. Chem.*, **461**, 27 (1993).
19. M. G. Voronkov, Yu. N. Pozhidaev, N. F. Chernov, and O. M. Trofimova, *Dokl. Akad. Nauk*, **326**, 827 (1992).
20. N. N. Chipanina, L. V. Sherstyannikova, O. M. Trofimova, H. F. Chernov, V. K. Turchaninov, and M. G. Voronkov, *Zh. Obshch. Khim.*, **70**, 1147 (2000).
21. N. K. Skvortsov, N. F. Chernov, O. M. Trofimova, V. K. Bel'skii, V. M. Svetlichnaya, and M. G. Voronkov, *Zh. Obshch. Khim.*, **64**, 54 (1994).