Silyl isoxazolines-2: synthesis, structure and properties [1]

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Abstract

Silyl isoxazolines have been synthesized by [2 + 3] cycloaddition reaction of nitrile oxides and silylnitronates to vinyl- and allylsilanes. The direction of the cycloaddition reaction of nitrile oxides to trialkoxyvinylsilanes has been shown to depend on the nature of the substituents on silicon and on the method used to generate the nitrile oxides. The addition of silyl esters of aci-nitromethane to triethoxyvinylsilane gives both 5-silyl and 4-silyl isomers. The structures of silyl isoxazolines are discussed.

Keywords: Silicon; Isoxazolines; Vinylsilanes; Allylsilanes; Nitrile oxides; Silatrane

1. Introduction

Isoxazolines are widely used in the synthesis of functionally substituted compounds such as β-hydroxy-ketones and acids, γ-amino alcohols, α,β-cyanohydrins, amino sugars and complicated heterocycles [1-4]. Furthermore, many silicon-containing N-heterocycles possess biological activity [5]. Therefore, synthesis of silyl isoxazolines is important both for organic syntheses and for medicinal chemistry.

The method generally used for their preparation involves [2 + 3] cycloaddition of nitrile oxides [6,7] or silylnitronates [8,9] to alkenes. This method can be also used for the obtaining silicon-containing isoxazolines [10-15]. Thus, reaction with vinylsilanes of benzonitrile oxide generated from benzhydroxamic acid chloride in the presence of triethylamine, afforded 3-phenyl-5-trialkylsilylisoxazolines [10-12]. Reaction of trimethylallylsilane with benzhydroxamic acid chloride in the presence of hexabutyldistannoxane as a hydrogen chloride acceptor is of some interest [13]; it takes place without cleavage of the trimethylsilyl group. 3-Alkyl-5-trialkylsilyl-substituted isoxazolines were obtained by the treatment of vinylsilanes with nitrile oxides generated by the dehydration of the primary nitroalkanes with phenylisocyanate in the presence of the catalytic

amounts of triethylamine [15]. The reaction of trimethylsilylnitrile oxide with methylmetacrylate leads to the substituted isoxazoline having the silicon atom at 3 position [14].

To study the influence of the silyl substituent on the reactivity of C=C double bond in the cycloaddition reaction, we have investigated the reaction of vinyl- and allylsilanes with nitrile oxides and silylnitronates.

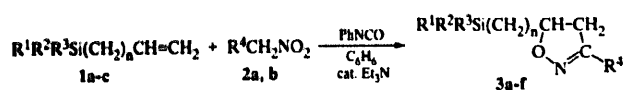## 2. Reaction of silylalkenes with nitrile oxides

We first studied the influence of the silyl substituent on the geometry of the isoxazoline ring and on the regioselectivity of the [2 + 3] cycloaddition reaction of alkenylsilanes and nitrile oxides. For this purpose we used two methods to generate the nitrile oxides: (1) dehydration of the primary nitroalkanes with phenylisocyanate in the presence of a catalytic amount of triethylamine (method A) [16]; (2) dehydrohalogenation of hydroxamic acid chlorides or dibromoformaldoxime with base (method B).

Vinyl- and allylsilanes 1a-c react with nitroethane (2a) or with 1-nitropropane (2b) in the presence of two equivalents of phenylisocyanate and of the catalytic amount of triethylamine in benzene to afford the corresponding 3-alkyl-5-trialkylsilylisoxazolines 3a-f.

The yields of 3a-f are from moderate to good (64-88%). The carbon analogue of trimethylvinylsilane, 3,3-dimethylbutene (4), reacts with acetonitrile and pro-

R¹R²R³Si(CH₂)ₙCH=CH₂ + R⁴CH₂NO₂ →(PhNCO, C₆H₆, cat. Et₃N)→ R¹R²R³Si(CH₂)ₙCH-CH₂ (3a-f)

1a-c   2a, b

R³₃SiCH=CH₂ →[R²C≡N→O]→ R³₃SiCH-CH₂ + R³₃SiCH-CH₂

12a-d   13a-g   14a-g

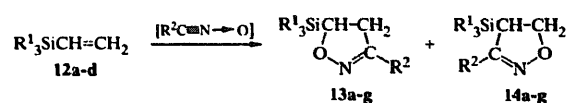| No.	R¹	R²	R³	R⁴	n
3a	Me	Me	Me	Me	0
3b	Me	Me	Me	Me	1
3c	Me	Me	Me	Et	0
3d	Me	Me	Me	Et	1
3e	Et	Et	Et	Me	0
3f	Et	Et	Et	Et	0

pionitrile oxides to give the corresponding 3-methyl-5-*t*-butylisoxazoline (5) and 3-ethyl-5-*t*-butylisoxazoline (6).

The corresponding nitrile oxides were also formed by dehydrohalogenation of benzhydroxamic acid chlorides (7a), chloroximinoethylacetate (7b) and dibromoformaldoxime (7c) with bases. The subsequent cycloaddition reaction with silylalkenes gave the silicon-containing isoxazolines 8a-f.

Compound 4 reacts with the benzonitrile oxide precursor 7a in the presence of triethylamine in ether to give the product of cycloaddition 3-phenyl-5-*t*-butylisoxazoline (9), while the reaction with the nitrile oxide precursor 7b under the same conditions gives the corresponding 3-ethoxycarbonyl-5-*t*-butylisoxazoline-2 (10).

It is known, that the reaction between dibromoformaldoxime with alkenes can be carried out under phase transfer catalysis conditions. This shortens the time of reaction and increases the yields [17,18]. The reaction of the bromonitrile oxide precursor 7c with trimethylvinyl- and trimethylallylsilanes or with the carbon analogue 4 was carried out in a two-phase liquid–liquid system (a mixture of aqueous potassium carbonate and ethylacetate) in the presence of a phase transfer (PT) catalyst (triethylbenzylammonium chloride) [19]. In this way, the silicon-containing isoxazolines-2 8e and 8f with the bromine atom at 3 position of the isoxazoline ring were obtained. Reaction of the carbon analogue 4 gave 3-bromo-5-*t*-butylisoxazoline-2 (11) [19].

The reaction with monosubstituted silylalkenes containing a trialkyl(aryl)silyl group proceeds regiospecifi-

cally, and always affords one isomer in which the oxygen atom is attached to the more-substituted carbon atom. The addition of nitrile oxides to triethoxyvinylsilane and to vinylsilatrane is somewhat different [20].

Along with the main product, 5-silylsubstituted isoxazoline-2 13, the second regioisomer, 4-silylsubstituted isoxazoline-2 14, is formed (see Table 1). The amount of the latter depends both on the nature of substituents on silicon and on the mode of generation of the nitrile oxide.

The introduction in 12b of the triethoxysilyl group in place of the trimethoxysilyl group in 12a increases the proportion of 4-isomer 14a (up to 20%), while the introduction of the tris(trimethylsiloxy)silyl group (12c) lowers the proportion of the regioisomer 14d to 9%. The mode of generation of the acetonitrile oxide also influences the ratio of products 13 and 14. Thus, the reaction of triethoxyvinylsilane (12b) with acetonitrile oxide generated by method A gives 13b and 14b in 6 : 1 ratio, but if the generation is by method B the ratio is only 2.3 : 1. Again, when acetonitrile oxide was generated by method A, vinylsilatrane (12d) gave predominantly isomer 13e, but generation by method B resulted in the other mode of addition to give 14e as the main product (13e : 14e = 1 : 2) [20].

The reaction with nitrile oxides of vinylsilanes having bromine in α to the silicon atom proceeds by the splitting of hydrogen bromide from the intermediate 3-ethyl(phenyl)-5-trimethylsilyl-5-bromoisoxazoline-2, and the formation of the corresponding isoxazoles. Thus, we obtained 3-ethyl-5-trimethylsilylisoxazole (15), 3-phenyl-5-trimethylsilylisoxazole (16) and 3-methyl-5-triethoxysilylisoxazole (17).

The reaction of trimethyl(triethyl)(α-bromovinyl)silanes with dibromoformaldoxime was carried out in the two-phase liquid–liquid system (aqueous potassium carbonate and ethylacetate) in the presence of

R¹R²R³Si(CH₂)ₙCH=CH₂ + R⁴C=NOH(X) →(base)→ R¹R²R³Si(CH₂)ₙCH-CH₂ (8a-f)

7a-c
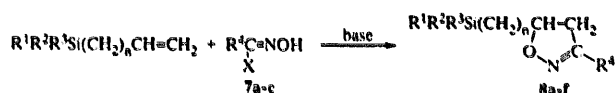
No.	R¹	R²	R³	R⁴	n	X
8a	Me	Me	Ph	Ph	0	Cl
8b	Me	Me	Ph	Ph	0	Cl
8c	Me	Me	Me	COOEt	0	Cl
8d	Me	Me	Me	COOEt	1	Cl
8e	Me	Me	Me	Br	0	Br
8f	Me	Me	Me	Br	1	Br

Table 1
Ratio of 5- and 4-silylisoxazolines-2

	R¹	R²	13	14	Conditions
a	MeO	CH₃	4	1	A[a]
b	EtO	CH₃	6	1	A[a]
b	EtO	CH₃	2.3	1	B[a]
c	EtO	C₂H₅	6	1	A[a]
d	Me₃SiO	CH₃	10	1	A[a]
e	N(CH₂CH₂O)	CH₃	2.3	1	A[b]
e	N(CH₂CH₂O)	CH₃	1	2	B[b]
f	EtO	C₆H₅	6	1	B[a]
g	N(CH₂CH₂O)	C₆H₅	3	1	B[b]

[a] GLC control. [b] ¹H NMR control.
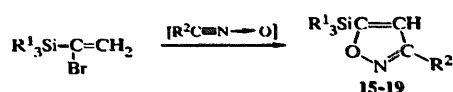
No.	R¹	R²
15	Me	Et
16	Me	Ph
17	EtO	Me
18	Me	Br
19	Et	Br
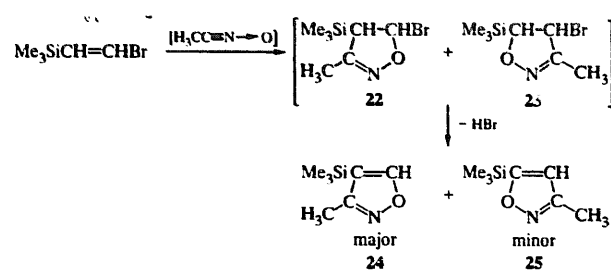
a PT catalyst (triethylbenzylammonium chloride) to afford the corresponding 3-bromo-5-trimethylsilylisoxazole (18) and 3-bromo-5-triethylsilylisoxazole (19). Isoxazole 18 was obtained by the counter synthesis from trimethylsilylacetylene and dibromoformaldoxime under the same conditions.

It is known that the trimethylsilyl group in silylacetylenes readily cleaved off in alkaline media [21], but the conditions of this PT reaction are evidently so mild that there is no such cleavage from the initial acetylene.

To study the regioselectivity and stereoselectivity in the reaction of [2 + 3] cycloaddition of acetonitrile oxide to 1,2-disubstituted ethylenes in which one of the substituents is the silyl group, we chose methyl (E-)-3-triethylsilylacrylate (20) as a model substrate.

The reaction proceeds regiospecifically to give only one adduct, 3-methyl-4-triethylsilyl-5-methoxycarbonylisoxazoline-2 (21) and stereospecifically with retention of the configuration of the initial silylalkene 20 in the silylisoxazoline 21 obtained (syn-addition).

The cycloaddition of acetonitrile oxide to trimethyl-(2-bromovinyl)silane proceeds differently.

It is known that 4- and 5-halogenoisoxazolines can only rarely be obtained owing to their thermal instability or to dehydrohalogenation by base [22]. We found that the products of cycloaddition, 3-methyl-4-trimethylsilyl-5-bromoisoxazoline (22) and 3-methyl-4-bromo-5-trimethylsilylisoxazoline (?3), also cannot be isolated because of dehydrobromination resulting from the presence of triethylamine. Instead, 3-methyl-4-trimethylsilylisoxazole (24) and 3-methyl-5-trimethylsilylisoxazole (25) were isolated, the former predominating.

The ability of organotriethoxysilanes to undergo condensation with triethanolamine was utilized in the synthesis of 1-substituted silatranes. The condensation reaction of triethanolamine with the mixture of 3-substituted-5-triethoxysilylisoxazolines-2 (26) and 3-sub-

stituted 4-triethoxysilylisoxazolines-2 (27) in boiling toluene in the presence of catalytic amounts of sodium hydroxide with simultaneous distillation of the formed ethanol gave a mixture of silatranes 28 and 29.
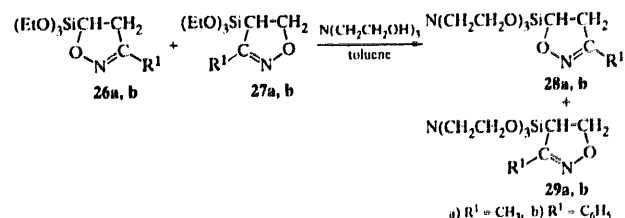
By crystallization we have isolated 5-silatranyl isomers 28a,b from the polar solutions, whereas 4-silatranyl isomers 29a,b separated first from chloroform. The corresponding 3-methyl-5-silatranylisoxazole (30) was obtained by the condensation of 3-methyl-5-triethoxysilylisoxazole (17) with triethanolamine.

3. Addition of silylnitronates to alkenylsilanes

Since the first silylnitronates were prepared [23], this series of compounds have been widely used in the synthesis of isoxazolines-2 [24]. The silyl esters of nitronic acid do not add to alkenes with a non-activated double bond [7]. As the double bond in vinylsilanes is polarized [25] an interaction with silylnitronates can be expected. We did, indeed, find that reaction of trialkylvinylsilanes with the primary nitroalkanes in the trimethylchlorosilane–triethylamine system in CCl₄ gives 5-trialkylsilylisoxazolines-2 (32a,b) [26].

The intermediate 1-trimethylsiloxy-5-trialkylsilylisoxazolidine (31a, b) could not be isolated because of spontaneous elimination of trimethylsilanol during work-up. Silylisoxazolines-2 32 (if R² = H) were prepared by the counter synthesis from the primary nitroalkanes 2a,b and vinylsilanes 1a–c in the presence of phenylisocyanate and a catalytic amount of triethylamine in benzene.

Trimethylvinylsilane (1a) interacts with 2-nitroethanol in the presence of two equivalents of trimethylchlorosilane and two equivalents of triethylamine as

an HCl acceptor to afford 3-trimethylsiloxymethyl-5-tri-methylsilylisoxazoline-2 (33). Methanolysis of 33 leads to 3-hydroxymethyl-5-trimethylsilylisoxazoline-2 (34).

Trimethylallylsilane reacts readily with nitrile oxides (yield ca. 42–77%), but in the subsequent reaction with the O-silyl ester of aci-nitromethane the outcome is similar to that for an alkene with a nonactivated double bond, and 5-trimethylsilylmethylisoxazoline-2 (35) was obtained in very low yield (ca. 10%).

The cycloaddition reaction with trialkylvinylsilanes proceeds regiospecifically and always affords 5-trial-kylsilylisoxazoline, while the addition of silyl ether of nitromethane to triethoxyvinylsilane proceeds differently.

Along with the expected product, 5-triethoxysily-lisoxazoline-2 (38), there is its isomer, 4-triethoxysily-lisoxazoline-2 (39). The intermediate isoxazolidines 36 and 37 could not be isolated because of the ease of elimination of trimethylsilanol.

GLC analysis showed that the reaction of vinyltri-ethoxysilane with nitromethane in the trimethylchlorosi-lane=triethylamine system in CCl$_4$ at room temperature for 2 days gave two products in 3.7 : 1 ratio. The ratio of the 5-silyl to 4-silyl isomers is indicated by the respec-tive integrals in the ^{1}H NMR spectrum agreed with that indicated by GLC.

The protons at C-4 and C-5 in the obtained isoxazo-lines 38 and 39 were analyzed as ABM spectra. The group of signals of isoxazoline 38 in the ^{1}H NMR spectrum corresponding to the methylene protons at C-4 appears at higher field than the double doublet of the methine proton at C-5. The methylene protons at C-4 also show spin–spin coupling with the proton at the 3 position of the isoxazoline ring ($^3J = 1.8$ Hz). The triplet multiplicity of the proton on the C-3-triplet addi-tionally indicates the proximity of the methylene group.

In the ^{1}H-coupled ^{13}C spectrum of isomer 38 the signal from the C-4 atom in the isoxazoline ring (37.78 ppm) appears to be a double double triplet (tdd, $J = 133.8$ Hz, $J = 11.7$ Hz, $J = 4.1$ Hz) but the signal from the carbon in the 5 position (65.76 ppm) is a doublet ($J = 136.3$ Hz). The signal of the silicon atom appears at -59.6 ppm in the ^{29}Si NMR spectrum. Analysis of all NMR data demonstrates that the triethoxysilyl group is on the carbon atom at the 5 position in the isoxazo-line ring in isomer 38.

The group of signals of isomer 39 in the ^{1}H NMR spectrum corresponding to the methylene protons at C-5 (4.20 ppm and 4.42 ppm) lies at lower field than the methine proton at C-4 (2.71 ppm). The latter has the form of double double doublet ($^3J = 1.8$ Hz) due to interaction with the proton at C-3 of the isoxazoline ring. The appearance of a doublet for proton at C-3 also indicates the proximity of the methine proton. The methylene protons in isomer 39 at C-5 have $J_{gem} = 10$ Hz, confirming that the substituent is on C-4 position of the isoxazoline ring [27].

In the ^{13}C NMR spectrum of isomer 39, owing to the anisotropic effect of the silyl group, the C-4 signal is shifted to higher field (34.24 ppm), while deshielding by the nearby oxygen atom shifts the C-5 signal towards lower field (67.70 ppm) compared with that for isomer 38. The silicon signal appears at -58.58 ppm in the ^{29}Si NMR spectrum. The analysis of all the NMR data reveals that the triethoxysilyl group is on C-4 of the isoxazoline ring.

To study the regio- and stereoselectivity of the addi-tion of silylnitronate to 1,2-disubstituted ethylenes, in which one of the substituents is a silyl group, we have chosen methyl 3-(E)-triethylsilylacrylate as a model compound.

The [2 + 3] cycloaddition of the silyl ester of aci-nitromethane to silylacrylate 20 occurs regio- and stere-ospecifically to afford one isomer, 4-(E)-triethylsilyl-5-methoxycarbonylisoxazoline-2, in which the positions

R₃Si—CH-CH₂
    O   CH
     N
      OH

32a, b   →   R₃SiCH-CH₂CN
                    OH
                    41a, b

of the substituents of the initial silylalkene **20** are unchanged. Desilylation of 4,5-substituted isoxazoline **40** in weakly acidic media gives 5-methoxycarbonylisoxazoline-2, which was also obtained by the counter synthesis from methyl acrylate and the silyl ether of aci-nitromethane. Its ^{1}H NMR data agree with those previously reported [8].

It is known, that 3-unsubstituted isoxazoline-2 having the methoxycarbonyl group in the 5-position undergoes ring opening to generate the corresponding cyanohydrins [28]. 5-Trimethyl(triethyl)silylisoxazoline-2 (**32a** and **32b**) in acetonitrile in the presence of triethylamine at 80°C are converted within 4 h into the silylcyanohydrins **41a** and **41b**.

The reaction of isoxazoline **32a** in the two-phase liquid–solid system (hexane–NaOH) proceeds differently. After 15 min the reaction is complete, but instead of the expected cyanohydrin **41a**, 3-(E)-trimethylsilylacrylonitrile (**42**) is formed, along with a small amount of the Z-isomer (**43**) (ca. 5%). Under the same condi-

tions, 5-triethylsilylisoxazoline-2 is almost quantitatively converted into triethylsilylcyanohydrin **41b**, accompanied by 3-(E)-triethylsilylacrylonitrile in 3% yield.

5-Silatranylisoxazoline-2 and 4-silatranylisoxazoline-2 were prepared by treatment of a mixture of 5-triethoxysilylisoxazoline-2 (**38**) and 4-triethoxysilylisoxazoline-2 (**39**) with triethanolamine.

4. Structures of the silicon-containing isoxazolines

The reactions of monosubstituted trialkylsilylalkenes with nitrile oxides proceed regiospecifically. This is confirmed by the ^{1}H NMR spectra of the silicon-containing isoxazolines (Table 2), in which the chemical shifts H_A (3.6–4.7 ppm) are below those for the methylene protons H_B and H_C. This means that the silyl substituent is on the carbon atom at the 5-position in the isoxazoline ring.

The range of geminal coupling constants for the spin–spin interaction in the sterically unhindered methylene groups is from -12 Hz to $+2.5$ Hz [29], the J_{BC} constant thus being negative. Comparison of $^2J_{BC}$ values for the isoxazoline derivatives shows that the substituent R^1 has a significant influence in the order:

Table 2
^{1}H NMR chemical shifts and spin–spin coupling constants of isoxazoline

$$H_A\text{--}C\text{--}C\text{--}H_B$$
$$R^1\text{--}C \quad H_C$$
$$O\text{--}N\text{--}C\text{--}R^2$$

No.	R^1	R^2	Chemical shifts, δ (ppm)					Coupling constants J (Hz)			
			H_A	H_B	H_C	H_{R^1}	H_{R^2}	AC	AB	BC	Long range
3e	Et₃Si	Me	3.87	3.00	2.75	0.69(CH₂) 1.03(CH₂)	2.05	10.9	16.0	−15.4	
3a	Me₃Si	Me	3.88	3.00	2.71	0.18	2.07	10.7	15.2	−15.5	
29a	(NCH₂CH₂O)₃Si	Mc	3.68	2.94	2.84	2.90(CH₂N) 3.86(CH₂O)	1.98	10.9	16.6	−15.6	
13b	(EtO)₃Si	Me	3.85	3.07	2.91	1.29(CH₃) 3.93(OCH₂)	2.03	11.3	15.0	−15.9	
3b	Me₃SiCH₂	Me	4.68	2.93	2.44	0.07(CH₃) 0.88, 1.20 (CH₂Si)	1.96	8.9	9.2	−16.0	6.0;8.0 (SiCH₂·H_A) 14.0(^2JSiCH₂)
5	(CH₃)₃C	Me	4.22	2.84	2.62	0.91	1.93	9.0	10.4	−17.2	
3f	Et₃Si	Et	3.86	2.95	2.73	1.13(CH₃) 2.45(CH₂)	0.62(CH₂) 0.95(CH₃)	10.8	15.9	−15.5	0.2(CH₂·H_B) 0.5(CH₂-H_C) 14.8(^2JSiCH₂)
3c	Me₃Si	Et	3.67	2.81	2.53	0.07	1.00(CH₃) 2.21(CH₂)	10.5	15.0	−15.7	0.6(CH₂·H_B) 1.1(CH₂·H_C)
13c	(EtO)₃Si	Et	3.87	3.05	2.99	1.23(CH₃) 3.91(OCH₂)	1.17(CH₃) 2.92(CH₂)	11.4	15.0	−16.0	0.5(CH₂·H_B) 0.9(CH₂·H_C)
3d	Me₃SiCH₂	Et	4.63	2.95	2.48	0.07(CH₃) 0.96; 1.20 (CH₂Si)	1.17(CH₃) 2.35(CH₂)	9.0	9.3	−16.2	0.4(CH₂·H_B) 0.5(CH₂·H_C) 6.0; 8.3 Si(CH₂-H_A) 14.0(^2JSiCH₂)
6	(CH₃)₃C	Et	4.24	2.80	2.68	0.91	1.15(CH₃) 2.34(CH₂)	8.9	10.5	−17.3	0.6(CH₂·H_B) 0.6(CH₂-H)

Scheme 1.

Fig. 2. Molecular structure of 28a.
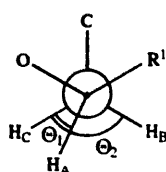
Et_3Si > Me_3Si > $N(CH_2CH_2O)_3Si$ > $(EtO)_3Si$ > Me_3SiCH_2 > Me_3C. This agrees with MO model for the influence of β-substituents [30]. An increase in the electronegativity of the substituent group leads to a shift of ^2J towards the more negative values.

Compared with J_{gem}, interpretation of the vicinal constants of the spin–spin interaction is more complicated, as four nuclei participate in the interaction and the values are influenced by a greater number of parameters (three lengths of bond, two interbond angles and a dihedral angle).

Comparison of the influence of R^1 and R^2 on ^3J reveals that the coupling constant value is determined mainly by R^1, the influence of R^2 being insignificant. $^3J_{AC}$ falls from 11.3 Hz to 8.9 Hz in the order $(EtO)_3Si$ > $N(CH_2CH_2O)_3Si$ ~ Et_3Si > Me_3Si > Me_3C > Me_3-$SiCH_2$. The value of ^3J can be expected to be lowered by an electronegative substituent in the α-position [31]. It is found that owing to the lower electronegativity of the silicon atom the vicinal constant for the silicon-containing isoxazolines is always higher than that of the derivatives with tert-butyl or trimethylsilylmethyl substituents.

The vicinal constants for the spin–spin interaction J_{AB} and J_{AC} vary over the ranges 9.3–16.6 Hz and 8.9–11.3 Hz respectively. In terms of the Karplus equation [32], the dihedral angles for protons H_A and H_C (Θ_1) should be ca. 0° and the angles H_A and H_B (Θ_2) should be ca. 120°. Going from the silyl-substituted isoxazolines to the carbon analogues leads to a decrease in both $^3J_{AB}$ and $^3J_{AC}$, and thus a decrease in Θ_1 and increase in Θ_2.

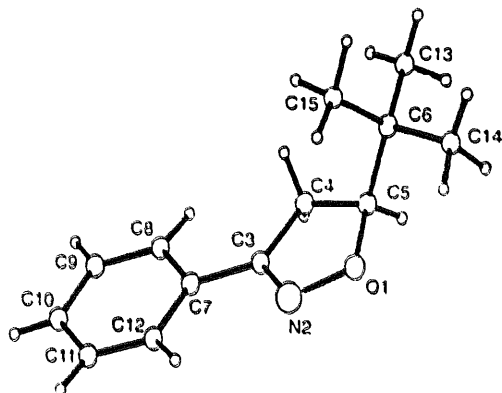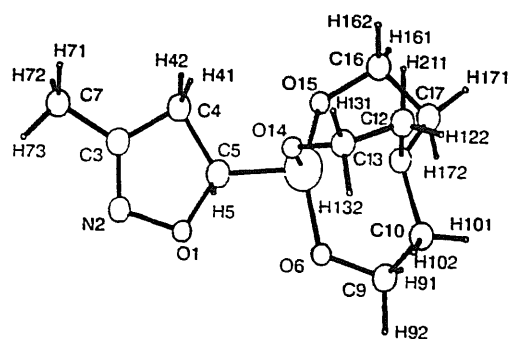To establish the dependence of the geometry of the isoxazoline ring on the nature of the substituent in the 5-position (the silyl or tert-butyl group) an X-ray diffraction study of 3-phenyl-5-tert-butylisoxazoline-2 (9) was carried out. The results can be compared with the data for the 3-methyl-5-silatranylisoxazoline-2 (28a) [20]. In compound 9, the isoxazoline ring has an almost planar structure and the bond angles in the tert-butyl substituent are: C6–C5–O1 109.65° and C6–C5–C4 118.08° (Fig. 1). The C6–O1 distance is 2.437 Å and the C6–C4 distance is 2.601 Å. The five-membered ring in 3-methyl-5-silatranylisoxazoline (28a) has an envelope form; the C5–C4–O1 plane deviates from the O1–N2–C3–C4 plane by 25.6° (Fig. 2). The angles of Si-C5-O1 and Si-C5-C4 bonds are 114° and 117°, respectively.

On the basis of the X-ray data for compounds 9 and 28a, values of Θ_1 and Θ_2 were also calculated for tert-butyl and silatranyl substituents in the 5-position of the isoxazoline ring. The results confirm the assumption that changing from the silyl group to the tert-butyl group should result in a decrease of Θ_1 and an increase in Θ_2. Values of Θ_1 = 8.0° and Θ_2 = 113.4° are found for 3-methyl-5-silatranylisoxazoline-2; Θ_1 = 1.8° and Θ_2 = 122.7° for 3-phenyl-5-tert-butylisoxazoline (9).

5. Experimental

^1H, ^{13}C, ^{29}Si NMR spectra were recorded on a WH-360/DS (Bruker) instrument at 360.1 MHz, 90.56 MHz and 71.50 MHz respectively. Mass spectra were recorded on a Kratos MS-25 apparatus (70 eV).

X-ray reflections from compound 9 were measured on the Syntex P2₁ single-crystal diffractometer. The detailed crystal data and the conditions used are shown in Table 3. The structure was determined by the direct method (program SHELX-86) [33] and refined by full-matrix least squares using SHELXL-93 [34] with the unit weight scheme. The nonhydrogen atoms were refined anisotropically and the hydrogen isotropically. The fractional coordinates and the equivalent isotropic displace-

Fig. 1. Molecular structure of 9.

Table 3
Crystal data and intensity collection parameters for **9**

Empirical formula	$C_{13}H_{17}NO$
Formula weight	203.28
Temperature	293(2)°K
Wavelength (Å)	0.71069
Crystal system	orthorhombic
Space group	Pbca (no. 61)
Unit cell dimensions (Å)	
a	10.484(3)
b	19.723(8)
c	11.590(4)
Volume (Å³)	2396.5(14)
Z	8
Density (calculated) (g cm⁻³)	1.127
Absorption coefficient (mm⁻¹)	0.071
$F(000)$	880
Theta range for data collection (deg)	2.07 to 21.02
Index ranges	$0 \leqslant h \leqslant 10, 0 \leqslant k \leqslant 19,$ $0 \leqslant l \leqslant 11$
Reflections collected	975
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	975/0/205
Goodness-of-fit on F^2	0.975
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0475, wR2 = 0.1204$ (for 833 refl.)
R indices (all data)	$R1 = 0.0591, wR2 = 0.1304$
Extinction coefficient	0.007(2)
Largest diff. peak and hole (eff⁻³)	0.132 and −0.140

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for **9**

	x	y	z	U_{eq}
O(1)	2849(3)	5796(2)	1832(2)	84(1)
N(2)	2034(3)	6249(2)	1256(3)	70(1)
C(3)	1805(3)	6752(2)	1898(3)	54(1)
C(4)	2445(5)	6719(2)	3042(4)	70(1)
C(5)	3099(5)	6039(2)	2993(4)	66(1)
C(6)	2705(4)	5504(2)	3863(3)	64(1)
C(7)	965(4)	7299(2)	1493(3)	55(1)
C(8)	745(5)	7863(2)	2177(4)	73(1)
C(9)	−78(5)	3867(3)	1808(5)	86(2)
C(10)	−689(5)	8319(3)	761(5)	83(1)
C(11)	−457(4)	7768(3)	77(4)	76(1)
C(12)	358(4)	7262(2)	436(4)	66(1)
C(13)	3058(8)	5758(4)	5058(5)	102(2)
C(14)	3449(7)	4850(3)	3611(6)	94(2)
C(15)	1288(5)	5353(4)	3785(7)	99(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

instrument equipped with a flame-ionization detector and a capillary column 5m × 0.53mm, df = 2.65 μ, HP-1, nitrogen, as with carrier gas.

Melting points were determined on a digital melting point analyzer (Fisher).

Vinylsilanes, nitroalkanes, nitroethanol were from Fluka. The syntheses of (1-bromovinyl)triethoxysilane [35], and the precursors of nitrile oxides **7a** [36], **7b** [37], **7c** [38], the vinylsilatrane [39], **8e**, **f**, **11** [19], **9** [10], **13a**, **14a** [20], **13e**, **14e** [20] were carried out using published methods.

5.1. Synthesis of silylisoxazolines

5.1.1. Method A

A solution of the nitroalkane (0.02 mol) and triethylamine (2 drops) in dry benzene (30 ml) was added

ment parameters for **9** are listed in Table 4. Selected intramolecular distances and angles are listed in Table 5. (Hydrogen atom coordinates, anisotropic thermal parameters, and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.) Figs. 1 and 2 show perspective views of molecules **9** and **28a**.

GLC analysis was performed with a Varian 3700

Table 5
Selected bond lengths (Å) and angles (deg) for **9**

O(1)–N(2)	1.405(4)	C(6)–C(15)	1.518(7)
O(1)–C(5)	1.452(5)	C(6)–C(14)	1.536(7)
N(2)–C(3)	1.264(5)	C(7)–C(8)	1.384(6)
C(3)–C(7)	1.469(5)	C(7)–C(12)	1.383(5)
C(3)–C(4)	1.488(5)	C(8)–C(9)	1.384(6)
C(4)–C(5)	1.507(6)	C(9)–C(10)	1.376(7)
C(5)–C(6)	1.517(6)	C(10)–C(11)	1.367(6)
C(6)–C(13)	1.519(7)	C(11)–C(12)	1.378(6)
N(2)–O(1)–C(5)	109.9(3)	C(5)–C(6)–C(14)	108.7(4)
C(3)–N(2)–O(1)	109.6(3)	C(13)–C(6)–C(14)	109.1(5)
N(2)–C(3)–C(7)	120.2(3)	C(15)–C(6)–C(14)	108.7(5)
N(2)–C(3)–C(4)	113.9(4)	C(8)–C(7)–C(12)	118.2(4)
C(7)–C(3)–C(4)	125.9(4)	C(8)–C(7)–C(3)	120.5(4)
C(3)–C(4)–C(5)	102.2(4)	C(12)–C(7)–C(3)	121.3(4)
O(1)–C(5)–C(4)	104.3(3)	C(7)–C(8)–C(9)	120.3(5)
O(1)–C(5)–C(6)	109.7(3)	C(10)–C(9)–C(8)	120.9(5)
C(4)–C(5)–C(6)	118.1(4)	C(11)–C(10)–C(9)	119.0(5)
C(5)–C(6)–C(13)	108.1(4)	C(10)–C(11)–C(12)	120.6(5)
C(5)–C(6)–C(15)	111.3(4)	C(7)–C(12)–C(11)	121.0(5)
C(13)–C(6)–C(15)	110.9(5)		

dropwise over 4 h to a mixture of the vinylsilane (0.02 mol), phenylisocyanate (0.04 mol) and triethylamine (1 ml) in dry benzene (20 ml) at room temperature. After some minutes, evolution of CO_2 began and diphenylurea separated out. The mixture was heated for 4 h at 70–80°C, then allowed to cool to room temperature. The diphenylurea was filtered off the solvent removed by rotating evaporation, and the residue distilled in vacuum.

3a, b.p. = 47°C/2.5 mm (yield 88%). ^{1}H NMR (see Table 2). MS (70 eV, m/z) 158([M]$^+$ + 1)(0.1), 157([M]$^+$)(0.5), 156([M]$^+$ − 1)(0.2), 116(8), 101(63), 75(14), 74(10), 73(100), 59(56), 45(37), 43(32), 42(10), 41(12).

3b, b.p. = 61–62°C/3 mm (yield 42%). ^{1}H NMR (see Table 2). MS (70 eV, m/z) 171([M]$^+$)(16), 156([M]$^+$ − 15)(21), 115(12), 85(19), 82(59), 75(58), 74(20), 73(100), 61(11), 59(68), 55(20), 45(43), 44(11), 43(59), 42(20), 41(91).

3c, b.p. = 68–69°C/3 mm (yield 50%). ^{1}H NMR (see Table 2). ^{13}C NMR (90.56 MHz, CDCl$_3$) δ ppm: − 3.93 (CH$_3$–Si), 11.03 (CH$_3$CH$_2$), 21.17 (CH$_3$CH$_2$), 39.77 (C-4), 72.88 (C-5), 159.71 (C-3). ^{29}Si NMR (71.50 MHz, CDCl$_3$) δ ppm: − 0.41. MS (70 eV, m/z) 171([M]$^+$)(0.5), 170([+]$^+$ − 1)(0.3), 101(69), 75(12), 73(100), 59(40), 45(21), 43(20).

3d, b.p. = 78°C/2.5 mm (yield 78%). ^{1}H NMR (see Table 2). ^{13}C NMR (90.56 MHz, CDCl$_3$) δ, ppm: − 1.16 (CH$_3$–Si), 10.76 (CH$_3$CH$_2$), 21.47 (CH$_3$CH$_2$), 24.06 (CH$_2$Si), 44.20 (C-4), 78.66 (C-5), 160.02 (C-3). ^{29}Si NMR (71.50 MHz, CDCl$_3$) δ, ppm: − 0.45. MS (70 eV, m/z)185([M]$^+$)(16), 170([M]$^+$ − 15)(10), 115(12), 101(13), 96(28), 85(10), 75(49), 74(14), 73(100), 68(65), 67(27), 59(54), 43(22), 42(13), 41(70).

3e, b.p. = 78–79°C/3 mm (yield 54%). ^{1}H NMR (see Table 2). MS (70 eV, m/z) 199([M]$^+$)(0.5), 130(10), 129(100), 115(10), 103(12), 101(79), 87(67), 73(32), 71(14), 59(60), 58(10), 57(18), 47(10), 45(30), 43(10), 41(28).

3f, b.p. = 109–110°C/3 mm (yield 70%). ^{1}H NMR (see Table 2). ^{13}C NMR (90.56 MHz, CDCl$_3$) δ, ppm: 1.75 (CH$_3$CH$_2$Si), 7.04 (CH$_3$CH$_2$Si), 10.84 (CH$_3$CH$_2$), 21.00 (CH$_3$CH$_2$), 40.06 (C-4), 71.10 (C-5), 159.44 (C-3). ^{29}Si NMR (71.50 MHz, CDCl$_3$) δ, ppm: − 4.27.

5, b.p. = 93°C/20 mm (yield 71%). ^{1}H NMR (see Table 2). MS (70 eV, m/z) 142([M]$^+$ + 1)(2), 141([M]$^+$)(9), 84(12), 58(10), 57(100), 56(32), 55(10), 43(37), 42(20), 41(59).

6, b.p. = 66–67°C/2 mm (yield 52%). ^{1}H NMR (see Table 2). ^{13}C NMR (90.56 MHz, CDCl$_3$) δ, ppm: 10.87 (CH$_3$CH$_2$), 21.25 (CH$_3$CH$_2$), 24.99 ((CH$_3$)$_3$C), 33.86 (−C−), 37.39 (C-4), 87.95 (C-5), 159.31 (C-3).

5.1.2. Method B

A solution of triethylamine (0.03 mol) in dry ether (50 ml) was dropped into a solution of vinylsilane (0.03

mol) and precursor of nitrile oxide **7a–c** in dry ether (100 ml) over 4 h. Then the triethylamine hydrochloride formed was filtered off. The ether layer was washed with water and dried over Na$_2$SO$_4$. After distillation of the solvent the residue was distilled or recrystallized.

8a, m.p. = 71°C (yield 72%). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.44 (s, 3H, CH$_3$Si), 0.46 (s, 3H, CH$_3$Si), 3.07 (dd, 1H, J = 15.6 Hz, J = 15.8 Hz, CH), 3.41 (dd, 1H, J = 11.0 Hz, J = 15.8 Hz, CH), 4.3 (dd, 1H, J = 11.0 Hz, J = 15.6 Hz, SiCH), 7.31–7.74 (m, 10H, H$_{arom}$).

8b, m.p. = 83°C (from hexane) (yield 40%). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.78 (s, 3H, CH$_3$Si), 3.22 (dd, 1H, J = 16.0 Hz, J = 16.2 Hz, CH), 3.60 (dd, 1H, J = 11.9 Hz, J = 16.0 Hz, CH), 4.73 (dd, 1H, J = 11.9 Hz, J = 16.2 Hz, SiCH), 7.24–7.89 (m, 15H, H$_{arom}$). ^{13}C NMR (90.56 MHz, CDCl$_3$) δ, ppm: − 6.35 (CH$_3$Si), 38.59 (C-4), 73.30 (C-5), 126.89 (C$_{arom}^m$ C-3), 128.08 (C$_{arom}^m$ Si), 128.11 (C$_{arom}^m$ Si), 128.59 (C$_{arom}^o$ C-3), 129.60 (C$_{arom}^i$ C-3), 129.89 (C$_{arom}^p$ C-3), 129.91 (C$_{arom}^o$ Si), 133.63 (C$_{arom}^i$ Si), 133.87 (C$_{arom}^i$ Si), 134.96 (C$_{arom}^p$ Si), 135.04 (C$_{arom}^p$ Si), 156.67 (C-3). ^{29}Si NMR (71.50 MHz, CDCl$_3$), δ, ppm: − 10.69.

8c, b.p. = 112°C/4 mm (yield 30%). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.13 (s, 9H, (CH$_3$)$_3$Si), 1.38 (t, 3H, J = 6.8 Hz, CH$_3$CH$_2$O), 3.00 (dd, 1H, J = 15.6 Hz, J = 16.5 Hz, CH), 3.42 (dd, 1H, J = 11.9 Hz, J = 16.5 Hz, CH), 4.29 (dd, 1H, J = 11.9 Hz, J = 15.6 Hz, SiCH), 4.47 (q, 2H, J = 6.8 Hz, CH$_3$CH$_2$O).

8d, b.p. = 123°C/4 mm (yield 50%). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.1 (s, 9H, (CH$_3$)$_3$Si), 1.02 (dd, 1H, J = 8.9 Hz, J = 12.7 Hz, CH$_3$Si), 1.32 (dd, 1H, J = 6 Hz, J = 12.7 Hz, CH$_3$Si), 1.33 (t, 3H, J = 6.9 Hz, CH$_3$CH$_2$O), 2.80 (dd, 1H, J = 9.6 Hz, J = 16.9 Hz, CH), 3.36 (dd, 1H, J = 10.1 Hz, J = 16.9 Hz, CH), 4.44 (q, 2H, J = 6.9 Hz, CH$_3$CH$_2$O), 5.00 (m, 1H, CH–O).

10, b.p. = 116°C/8 mm (yield 43%). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.96 (s, 9H, (CH$_3$)$_3$C), 1.38 (t, 3H, J = 6.5 Hz, CH$_3$CH$_2$O), 2.89 (dd, 1H, J = 9.6 Hz, J = 17.5 Hz, CH), 3.11 (dd, 1H, J = 9.6 Hz, J = 17.5 Hz, CH), 4.33 (q, 2H, J = 6.5 Hz, CH$_3$CH$_2$O), 4.51 (dd, 1H, J = 9.6 Hz, J = 9.6 Hz, CH).

13a,14a, b.p. = 85°C/1.5 mm (yield 33%) (13a : 14a = 4 : 1).

3-Methyl-5-trimethoxysilylisoxazoline-2 (**13a**). ^{1}H NMR (360.1 MHz, CDCl$_3$/TMS) δ, ppm: 2.01 (s, 3H, CH$_3$), 2.97 (ddq, 1H, J = 0.9 Hz, J = 14.3 Hz, J = 16.5 Hz, CH), 3.00 (ddq, 1H, J = 0.9 Hz, J = 11.7 Hz, J = 16.5 Hz, CH), 3.61 (d, 9H, J = 0.4 Hz, CH$_3$O), 3.88 (dd, 1H, J = 11.7 Hz, J = 14.3 Hz, SiCH). MS (70 eV, m/z) 205([M]$^+$)(0.1), 149(48), 122(11), 121(100), 91(74), 90(14), 61(20), 59(18).

3-Methyl-4-trimethoxysilylisoxazoline-2 (**14a**). ^{1}H

NMR (360.1 MHz, CDCl₃/TMS) δ, ppm: 2.02 (S, 3H, CH₃), 2.6 (ddq, $J = 0.9$ Hz, $J = 9.2$ Hz, $J = 11.7$ Hz, SiCH), 3.58 (s, 9H, CH₃O), 4.32 (dd, 1H, $J = 7.5$ Hz, $J = 9.2$ Hz, CH), 4.42 (dd, $J = 7.5$ Hz, $J = 11.7$ Hz, CH). MS (70 eV, m/z) 205 ([M]⁺)(12), 204 ([M⁺ − 1](32), 149(18), 122(10), 121(100), 107(32), 91(87), 90(12), 77(20), 68(12), 61(25), 59(31), 45(10), 41(10).

13d, 14d, b.p. = 122°C/1 mm (yield 35%) (**13d : 14d** = 10 : 1).

3-Methyl-5-tris(trimethylsiloxy)silylisoxazoline-2 (**13d**). ¹H NMR (360.1 MHz, CDCl₃/TMS) δ, ppm: 0.1 (s, 27H, Me₃Si), 1.98 (t, 3H, $J = 0.7$ Hz, CH₃), 2.77 (ddq, 1H, $J = 0.7$ Hz, $J = 15.0$ Hz, $J = 15.9$ Hz, CH), 2.86 (ddq, 1H, $J = 0.7$ Hz, $J = 12.7$ Hz, $J = 15.9$ Hz, CH), 3.68 (dd, 1H, $J = 11.3$ Hz, $J = 15.0$ Hz, SiCH). MS (70 eV, m/z) 364 ([M]⁺ − 15)(0.1), 323(8), 208(10), 207(53), 73(100).

3-Methyl-4-tris(trimethylsiloxy)silylisoxazoline-2 (**14d**). ¹H NMR (360.1 MHz, CDCl₃/TMS) δ, ppm: 0.08 (s, 27H, Me₃Si), 1.95 (d, 3H, $J = 0.7$ Hz, CH₃), 2.43 (ddq, 1H, $J = 0.7$ Hz, $J = 10.4$ Hz, $J = 11.9$ Hz, SiCH), 4.16 (dd, 1H, $J = 7.3$ Hz, $J = 10.4$ Hz, CH), 4.42 (dd, 1H, $J = 7.3$ Hz, $J = 11.9$ Hz, CH). MS (70 eV, m/z) 379 ([M⁺](16), 208(10), 207(46), 193(11), 191(10), 74(10), 73(100), 69(84) 55(10), 45(13), 41(11).

13g, m.p. = 204°C (from abs. ethanol) (yield 60%). ¹H NMR (360.1 MHz, DMSO-d_6/TMS) δ, ppm: 2.87 (t, 6H, $J = 5.6$ Hz, CH₂N), 3.29 (dd, 1H, $J = 15.6$ Hz, $J = 15.9$ Hz, CH), 3.35 (dd, 1H, $J = 11.1$ Hz, $J = 15.6$ Hz, CH), 3.80 (t, 6H, $J = 5.6$ Hz, CH₂O), 3.89 (dd, 1H, $J = 11.1$ Hz, $J = 15.9$ Hz, SiCH), 7.3 (m, 3H, H$_{arom}$), 7.8 (m, 2H, H$_{arom}$).

14g, m.p. = 230°C (from chloroform). ¹H NMR (36.1 MHz, DMSO-d_6/TMS) δ, ppm: 2.73 (t, 6H, $J = 5.6$ Hz, CH₂N), 2.91 (dd, 1H, $J = 7.5$ Hz, $J = 11.8$ Hz, SiCH), 3.65 (t, 6H, $J = 5.6$ Hz, CH₂O), 4.55 (dd, 1H, $J = 7.0$ Hz, $J = 11.8$ Hz, CH), 4.70 (dd, 1H, $J = 7.0$ Hz, $J = 7.5$ Hz, CH), 7.30 (m, 3H, H$_{arom}$), 7.7 (m, 2H, H$_{arom}$).

15, b.p. = 43°C/2 mm (yield 60%). ¹H NMR (90.1 MHz, CdCl₃/TMS) δ, ppm: 0.35 (S, 9H, Me₃Si), 1.31 (t, 3H, $J = 6.8$ Hz, CH₃CH₂), 2.73 (q, 2H, $J = 6.8$ Hz, CH₃CH₂), 6.28 (S, 1H, =CH).

16: b.p. = 116–117°C/2 mm (yield 51%). ¹H NMR (90.1 MHz, CdCl₃/TMS) δ, ppm: 0.4 (s, 9H, (CH₃)₃Si), 6.73 (S, 1H, =CH), 7.37–7.50 (m, 3H, H$_{arom}$), 7.72–7.90 (m, 2H, H$_{arom}$). MS (70 eV, m/z) 217 ([M]⁺)(36), 216(18), 174(51), 99(31), 77(18), 74(10), 73(100), 51(10), 45(20), 43(18).

17, b.p. = 83–84°C/1.5 mm (yield 25%). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 1.13 (t, 9H, $J = 6.8$ Hz, CH₃CH₂O), 2.6 (s, 3H, CH₃), 4.00 (q, 6H, $J = 6.8$ Hz, CH₃CH₂O), 6.6 (s, 1H, =CH).

18, b.p. = 38°C/1 mm (yield 60%). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 0.2 (s, 9H, CH₃Si), 6.46 (s, 1H, =CH). ¹³C NMR (90.56 MHz, CDCl₃) δ, ppm:

−1.74 (CH₃Si), 116.54 (C-4), 139.61 (C-3), 181.73 (C-5). ²⁹Si NMR (71.50 MHz, CdCl₃) δ, ppm: −0.70.

19, b.p. = 82°C/1 mm (yield 55%). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 0.46–1.04 (m, 15H, Et₃Si), 6.46 (s, 1H, =CH). ¹³C NMR (90.56 MHz, CDCl₃) δ, ppm: 3.33 (CH₃CH₂), 7.36 (CH₃CH₂), 117.32 (C-4), 139.55 (C-3), 180.10 (C-5). ²⁹Si NMR (71.50 MHz, CDCl₃) δ, ppm: −7.64.

3-Methyl-4-triethylsilyl-5-methoxycarbonylisoxazoline-2 (**21**), b.p. = 110°C/2 mm (SiO₂ hexane–2-propanol $R_f = 0.3$) (yield 25%). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 0.69–1.00 (m, 15H, Et₃Si), 1.99 (s, 3H, CH₃), 2.89 (ddq, 1H, $J = 0.8$ Hz, $J = 4.4$ Hz, SiCH), 3.73 (s, 3H, OCH₃), 4.82 (d, 1H, $J = 4.4$ Hz, CH).

24, 25 b.p. = 1.22°C/10 mm (yield 30%) (**24 : 25** = 9 : 1).

3-Methyl-4-trimethylsilylisoxazole (**24**). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 0.19 (s, 9H, Me₃Si), 2.24 (s, 3H, CH₃), 7.98 (s, 1H, =CH). MS (70 ev, m/z) 155 ([M]⁺)(7), 141(11), 140(100), 83(12), 73(10), 66(96), 59(13), 45(17), 43(35).

3-Methyl-5-trimethylsilylisoxazole (**25**). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 0.26 (s, 9H, Me₃Si), 2.23 (s, 3H, CH₃), 6.19 (s, 1H, =CH). MS (70 eV, m/z) 155 ([M]⁺)(10), 140(30), 112(42), 99(45), 74(10), 73(100), 55(10), 53(10), 45(39), 44(10), 43(50).

3-Methyl-5-silatranylisoxazole (**30**), m.p. = 198°C (from ethylacetate) (yield 70%). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 2.26 (s, 3H, CH₃), 2.99 (t, 6H, $J = 6$ Hz, CH₂N), 3.93 (t, 6H, $J = 6$ Hz, CH₂O), 6.24 (s, 1H, =CH). ¹³C NMR (90.56 MHz, CDCl₃) δ, ppm: 11.26 (CH₃), 51.65 (CN), 57.92 (CO), 112.74 (C-4), 157.52 (C-3), 181.40 (C-5). ²⁹Si NMR (71.50 MHz, CDCl₃) δ, ppm: −74.35.

3-Trimethylsiloxymethyl-5-trimethylsilylisoxazoline-2 (**33**), b.p.-80°C/1mm (yield 25%). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 0.09 (s, 9H, Me₃Si), 0.18 (s, 9H, Me₃SiO), 2.73 (dd, 1H, $J = 14.9$ Hz, $J = 16.0$ Hz, CH), 3.13 (dd, 1H, $J = 10.5$ Hz, $J = 16.0$ Hz, CH), 3.89 (dd, 1H, $J = 10.5$ Hz, $J = 14.9$ Hz, SiCH), 4.51 (s, 2H, CH₂O).

3-Hydroxymethyl-5-trimethylsilylisoxazoline-2 (**34**) m.p. = 69°C (from ethylacetate) (yield 87%). ¹H NMR (90.1 MHz, CDCl₃/TMS) δ, ppm: 0.1 (s, 9H, Me₃Si), 2.3 (bs, 1H, OH), 2.83 (dd, 1H, $J = 15.6$ Hz, $J = 16.1$ Hz, CH), 3.19 (dd, 1H, $J = 11.2$ Hz, $J = 16.1$ Hz, CH), 3.99 (dd, 1H, $J = 11.2$ Hz, $J = 15.6$ Hz, SiCH), 4.34 (s, 2H, CH₂O).

38, 39d, b.p. = 94°C/3 mm (yield 29%) (**38 : 39** = 3.7 : 1).

5-Triethoxysilylisoxazoline-2 (**38**).
¹H NMR (360.1 MHz, CDCl₃/TMS) δ, ppm: 1.23 (t, 9H, $J = 6.6$ Hz, CH₃CH₂O), 2.95 (ddd, 1H, $J = 1.8$ Hz, $J = 15.4$ Hz, $J = 16.4$ Hz, CH), 3.17 (ddd, 1H, $J = 1.8$ Hz, $J = 11.4$ Hz, $J = 16.4$ Hz, CH), 3.69 (dd,

1H, $J = 11.4$ Hz, $J = 15.4$ Hz, CHSi), 3.88 (g, 6H, $J = 6.6$ Hz, CH$_3$CH$_2$O), 7.21 (t, 1H, $J = 1.8$ Hz, =CH). ^{13}C NMR (90.56 MHz, CDCl$_3$, ^{1}H-coupled ^{13}C spectrum) δ, ppm: 17.38 (q, $J = 125.6$ Hz, CH$_3$) 37.78 (tdd, $J = 41.1$ Hz, $J = 11.7$ Hz, $J = 133.8$ Hz, C-4), 52.27 (tm, $J = 3.6$ Hz, $J = 143.4$ Hz, CO), 65.76 (d, $J = 136.3$ Hz, C-5), 144.75 (dt, $J = 6.1$ Hz, $J = 7.12$ Hz, $J = 188.7$ Hz, C-3). ^{29}Si NMR (71.50 MHz, CDCl$_3$) δ, ppm: -58.58.

4-Triethoxysilyloxazoline-2 (**39**). ^{1}H NMR (360.1 MHz, CDCl$_3$/TMS) δ, ppm: 1.23 (t, 9H, $J = 6.6$ Hz, CH$_3$CH$_2$O), 2.71 (ddd, 1H, $J = 1.8$ Hz, $J = 10.3$ Hz, $J = 12.3$ Hz, SiCH), 3.85 (q, 6H, $J = 6.6$ Hz, CH$_3$CH$_2$O), 4.20 (dd, 1H, $J = 6.9$ Hz, $J = 10.3$ Hz, CH), 4.42 (dd, 1H, $J = 6.9$ Hz, $J = 12.3$ Hz, CH), 7.07 (d, 1H, $J = 1.8$ Hz, =CH). ^{13}C NMR (90.56 MHz, CDCl$_3$, ^{1}H-coupled ^{13}C spectrum) δ, ppm: 17.25 (q, $J = 125.6$ Hz, CH$_3$), 34.24 (dd, $J = 15.3$ Hz, $J = 125.1$ Hz, C-4), 58.15 (tm, $J = 3.6$ Hz, $J = 143.4$ Hz, CO), 67.70 (t, $J = 151.6$ Hz, C-5), 145.8 (dd, $J = 8.7$ Hz, $J = 189.7$ Hz, C-3). ^{29}Si NMR (71.50 MHz, CDCl$_3$) δ, ppm: -56.77.

4-Triethylsilyl-5-methoxycarbonylisoxazoline-2 (**40**) (SiO$_2$, hexane–ethylacetate $= 19:1$ $R_f = 0.15$). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.69–1.00 (m, 15H, ET$_3$Si), 3.02 (dd, 1H, $J = 1.6$ Hz, $J = 5.2$ Hz, SiCH), 3.71 (s, 3H, OCH$_3$), 4.84 (d, 1H, $J = 5.2$ Hz, CH). 7.04 (d, 1H, $J = 1.6$ Hz, =CH).

3-Trimethylsilyl-3-hydroxypropionitrile (**41a**), b.p. $= 85°C/3$ mm (yield 85%). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.02 (s, 9H, Me$_3$Si), 1.75 (bs, 1H, OH), 2.44 (dd, 2H, $J = 5.4$ Hz, $J = 7.4$ Hz, CH$_2$), 3.55 (dd, ^{1}H, $J = 5.4$ Hz, $J = 7.4$ Hz, SiCH). IR 3460 cm^{-1} (γ_{OH}), 2258 cm^{-1} ($\gamma_{C=N}$).

3-Triethylsilyl-3-hydroxypropionitrile (**41b**), b.p. $= 118°C/3$ mm (yield 83%). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.62–0.99 (m, 15H, Et$_3$Si), 2.11 (bs, 1H, OH), 2.56 (d, 2H, $J = 6.7$ Hz, CH$_2$), 3.76 (t, 1H, $J = 6.7$ Hz, CH).

(*E*)-3-Trimethylsilylacrylonitrile (**42**). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.01 (s, 9H, Me$_3$Si), 5.55 (d, 1H, $J = 19.8$ Hz, SiCH=), 6.93 (d, 1H, $J = 19.8$ Hz, =CH). MS (70 eV, m/z) 125([M]$^+$)(218), 111(12), 110(100), 84(17), 73(16), 59(49), 59(19), 43(16).

(*Z*)-3-Trimethylsilylacrylonitrile (**43**). ^{1}H NMR (90.1 MHz, CDCl$_3$/TMS) δ, ppm: 0.01 (s, 9H, Me$_3$Si), 5.90 (d, 1H, $J = 14.4$ Hz, SiCH=), 6.75 (d, 1H, $J = 14.4$ Hz, CH=). MS (70 eV, m/z) 125([M]$^+$)(30), 111(10), 110(80), 85(10), 84(100), 73(20), 59(10), 58(10), 43(10).

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