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Addition of nitrile oxides to 2,3-dihydrofurylsilanes. Crystal and molecular structure of tetrahydrofuro-[2,3-*d*]-isoxazolylsilanes

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Abstract

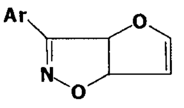
Silylsubstituted tetrahydrofuro-[2,3-*d*]-isoxazoles were prepared by the [2 + 3] cycloaddition of nitrile oxides to 5-(2,3-dihydrofuryl)silanes. Compounds with two condensed bicycles at the silicon atom: bis[6a-(3-methyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazolyl)]dimethylsilanes and bis[6a-(3-methyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazolyl)]diphenylsilanes were prepared by the addition of acetonitrile oxide to the corresponding bis[5-(2,3-dihydrofuryl)]silanes. X-ray analysis demonstrated that 3-methyl-6a-trimethylsilyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole exists as *RR*/*SS* enantiomers, while bis[6a-(3-methyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazolyl)]diphenylsilane-as *SSRR*/*RRSS* enantiomers. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cyclo-addition; Nitrile oxides; Dihydrofurylsilanes; Silanes

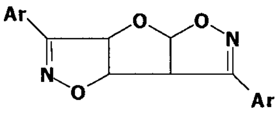
1. Introduction

Factors affecting the regio- and stereoselectivity of the [2 + 3] cycloaddition of nitrile oxides to the carbon–carbon double bond have been intensively studied [1–5]. It has been found that the direction of addition depends on the electronic and steric properties of the substituents in the unsaturated compound [6].

The cycloaddition of nitrile oxides to furan was investigated [7]. The dipolarophilic activity of these heteroaromatic compounds is strongly diminished relatively to the isocyclic system of cyclopentadiene because of the loss of aromaticity in the cycloaddition transition state. The α-carbon of the heteroaromatic compound binds to the carbon terminus of the moderately electrophilic nitrile oxides and cycloadduct **A** is formed with high regioselectivity.



A



B

Due to the presence of rather reactive enol ether moieties in the cycloadducts **A**, the further addition occurs readily and in the case of furan only the asymmetric bisadduct **B** is formed from the monoadduct **A**.

The high directing effect of the cyclic enol ether moiety in cycloaddition reaction with moderately electrophilic nitrile oxides is well documented [8–10]. The cycloaddition of nitrile oxides to 2,3-dihydrofuran completely confirms the expectations. The resonance interaction between the double bond and the oxygen electron pair places as negative charge at the β-carbon of the enol ether (^{13}C spectra) [11–13], thereby increasing the nucleophilic potential of the double bond and differentiating the vinylic carbons. The moderately electrophilic benzonitrile oxide [14] does indeed react 1.8 times faster with 2,3-dihydrofuran than with the isocyclic reference cyclopentene and a highly regioselective cycloaddition takes place [15].

If 2,3-dihydrofuran contains a silyl group in the position 5, two opposite electronic effects operate in its molecule: donation to the double bond from the unshared electron pair of the oxygen and withdrawal to the unoccupied 3d-orbitals of the silicon. The resulting polarization of the double bond as well as the steric effect of the silyl group will determine the direction of the addition of nitrile oxides to the 5-(2,3-dihydrofuryl)silanes.

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To examine the influence of the silyl substituents on the direction of [2 + 3] cycloaddition, we have investigated the addition of acetonitrile oxide and benzonitrile oxide to 5-(2,3-dihydrofuryl)silanes containing one and two dihydrofuryl groups.

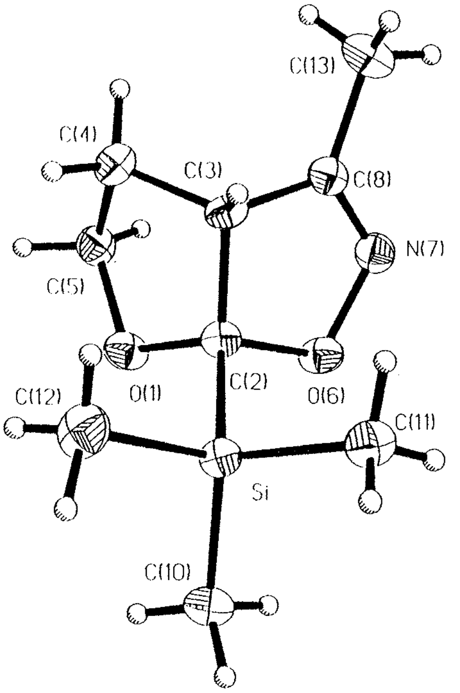


Fig. 1. The structure of **1** showing 30% probability displacement ellipsoids.

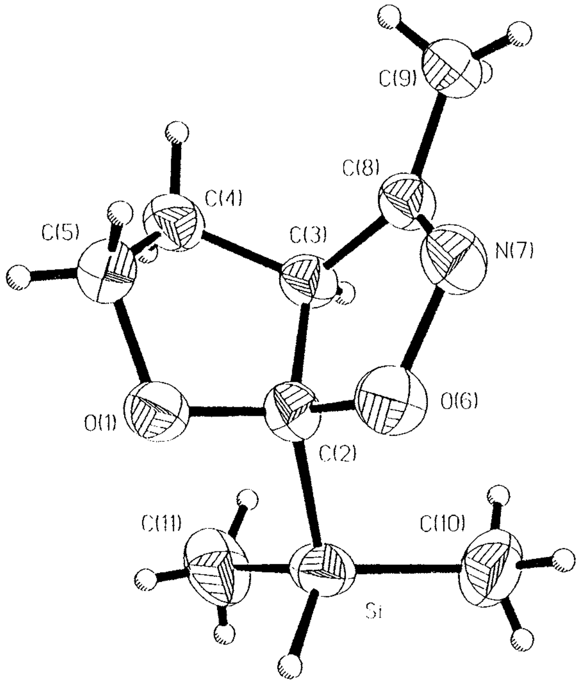
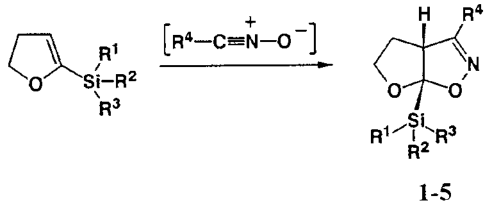


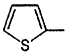
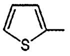
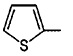
Fig. 2. The structure of **2** showing 30% probability displacement ellipsoids.

2. Results and discussion

[5-(2,3-Dihydrofuryl)]trimethylsilane adds acetonitrile oxide generated from nitroethane by the dehydration with phenylisocyanate in the presence of the catalytic amounts of triethylamine (Method A) [16], to give the corresponding condensed bicyclo-3-methyl-6a-trimethylsilyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]isoxazole (**1**):



1-5

No	R^1	R^2	R^3	R^4
1	CH_3	CH_3	CH_3	CH_3
2	CH_3	CH_3	H	CH_3
3	CH_3	CH_3	C_6H_5	CH_3
4	CH_3	CH_3	C_6H_5	C_6H_5
5				CH_3

The condensed bicycles **2**, **3**, **5** were synthesized under the similar conditions. 3-Phenyl-6a-phenyldimethylsilyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole (**4**) was obtained by the interaction of [5-(2,3-dihydrofuryl)]phenyldimethylsilane with benzonitrile oxide prepared from benzhydroxamic chloride in the presence of triethylamine (Method B).

The signal of the methyl group in 3 position of the dihydroisoxazole ring in bicycle **1** appears in ^{1}H-NMR spectra as a doublet with a long distance coupling $^4J = 0.8$ Hz, thus indicating that the carbon atom of acetonitrile oxide adds to 2,3-dihydrofurylsilane in 4 position.

In all cases the reaction proceeds regiospecifically giving one isomer in which the oxygen atom of nitrile oxide is bound with the mostly substituted carbon atom in dihydrofurylsilane.

Bicycle **1** consists of two heterocycles—tetrahydrofuran and dihydroisoxazole—with two common sp^3-hybridized carbon atoms which are asymmetric centres in this molecule. X-ray analysis has shown that the condensed bicycle **1** exists as an *RR*/*SS* enantiomer pair (Fig. 1). The angular hydrogen atoms in the condensed bicycles can be in *cis* or *trans* position towards each other. As the addition of acetonitrile oxide to [5-(2,3-dihydrofuryl)]trimethylsilane occurs stereospecifically, the trimethylsilyl group and the hydrogen atom of the product **1** are in the *cis*-position towards each other; this

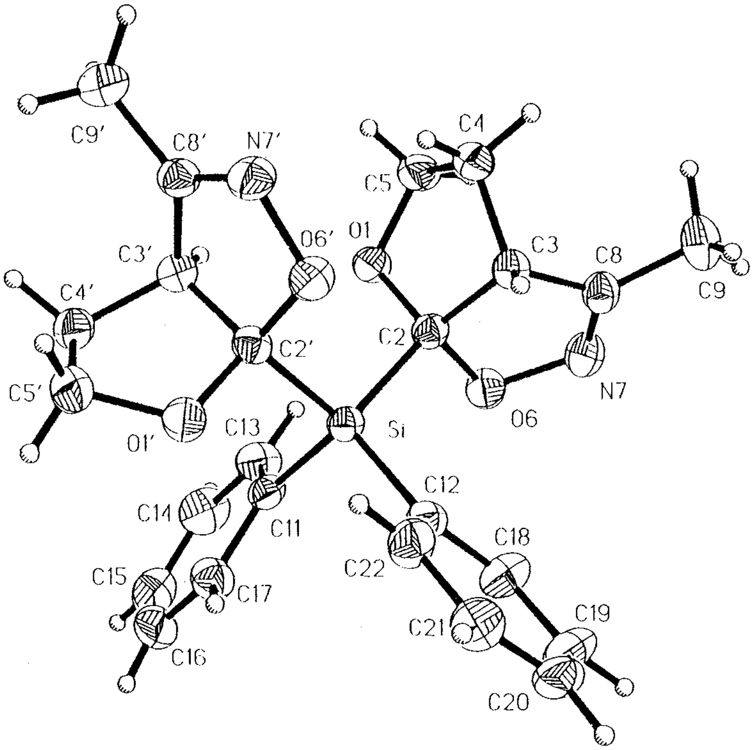


Fig. 3. The structure of **6** showing 30% probability displacement ellipsoids.

is confirmed by the X-ray analysis. The torsion angles of the dihydroisoxazole fragment [C8–C3–C2–O6 4.6° (2) N7–C8–C3–C2 1.5° (3) C8–N7–O6–C2 5.7° (3)] show that this ring is close to the planar, but the torsion angles of the tetrahydrofuran fragment are larger [C3–C2–O1–C5 18.5° (2) C4–C5–O1–C2 36.3° (3) O1–C5–C4–C3 38.3° (3)].

In the condensed bicycle where instead of the tetrahydrofuran fragment there is isocyclic cyclopentane fragment, the isoxazole ring is almost planar and the angular hydrogen atoms are in *cis* position to each other [17,18].

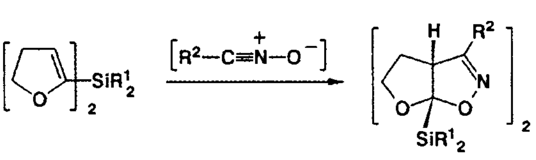
In the condensed bicycle **1** two oxygen atoms are attached to the carbon in α-position to the silicon atom. X-ray analysis has been undertaken to define if there is any extra interaction of the silicon atom with the unshared pair of electrons of the oxygen atom.

The distance between the silicon atom and every oxygen atom in α-position equals 2.74 Å. It is less than the sum of van der Vaals radius of the silicon and oxygen (3.4 Å) while the length of Si–C(2) bond [1.90 Å (2)] has the same order as the length between silicon and carbon in the methyl groups [1.86 Å (3)]. The angle C(10)–Si–C(2) [109.2°(11)] corresponds to the tetrahedral one and indicates that there is no additional coordination Si ← O.

Compound **2**, in which one of the methyl groups at the silicon atom is substituted for hydrogen, also exists in the form of enantiomer pair and the dimethylsilyl group is in the *cis* position towards hydrogen at C-3 (Fig. 2). The geometry of the dihydroisoxazole fragment is close to the planar [torsion angles: C8–C3–C2–O6 4.9° (5) N7–C8–C3–C2 1.5° (6) C8–N7–O6–C2 6.1° (5)]. The torsion angles of the tetrahydrofuran fragment are larger in this compound [C3–C2–O1–C5 17.8° (5) C4–C5–O1–C2 35.0° (5) O1–C5–C4–C3 37.5° (5)]. The hydrogen atoms at the silicon and at C-3 are in apical position to each other. The distance between the silicon atom and every oxygen atom in α-position equals 2.73 Å.

Compounds where there are two condensed bicycles with four asymmetric centres are obtained by the interaction of nitrile oxides with bis[5-(2,3-dihydrofuryl)]silanes.

Bis[5-(2,3-dihydrofuryl)]diphenylsilane adds acetonitrile oxide, generated by the dehydration of nitroethane with phenylisocyanate in the presence of the catalytical amount of triethylamine, to give the corresponding cyclic product-bis[6a-(3-methyl-3a,4,5,6a-tetrahydrofuro-[2,3-d)-isoxazolyl)]diphenylsilane (**6**). Compound **7**-bis[6a-(3-methyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazolyl)]dimethylsilane was prepared analogously.



6: R^1=Ph, R^2=Me

7: R^1=Me; R^2=Me

X-ray analysis of compound **6** (Fig. 3) demonstrates that it exists as enantiomer pair *SSRR*/*RRSS*. The hydrogen atoms in molecule at C-3 and C-3′ are in *cis*-position towards the silicon atom. It is also confirmed by the fact that the torsion angles C4–C3–C2–O1/C8–C3–C2–O6 and C4′–C3′–C2′–O1′/C8′–C3′–C2′–O6′ have the similar bending sign [19].

The dihydroisoxazole and tetrahydrofuran fragments of every condensed bicycle are bent differently in the molecule [the torsion angles: C8–C3–C2–O6 8.1°(3) C8′–C3′–C2′–O6′ 16.1°(3) N7–C8–C3–C2 3.7°(4) N7′–C8′–C3′–C2′ 10.2°(3) C8–N7–O6–C2 8.1°(3) C8′–N7′–O6′–C2′ 11.8°(3); C3–C2–O1–C5 14.1° (3) C3′–C2′–O1′–C5′ 3.4°(3) C4–C5–O1–C2 33.3°(4) C4′–C5′–O1′–C2′ 25.2°(4) O1–C5–C4–C3 37.6°(4) O1′–C5′–C4′–C3′ 35.8°(4)]. It is shown by the difference in distances between the silicon atom and the oxygen atoms in α-position (Si–O1 2.73 Å, Si–O6 2.70 Å and Si–O1′ 2.71 Å Si–O6′ 2.75 Å).

The corresponding bicycle without a silyl substituent (3-methyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole (**8**), was obtained by the addition of acetonitrile oxide to 2,3-dihydrofuran.

Table 1
^{13}C-, ^{29}Si-NMR chemical shifts of tetrahydrofuroisoxazoles

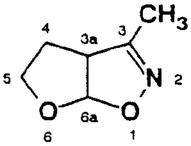
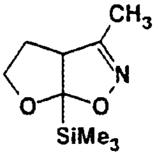
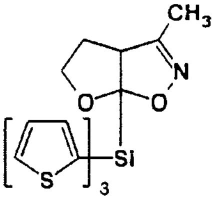
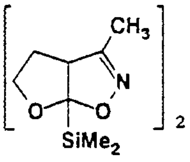
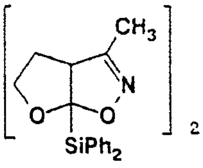
Formula	C_3	C_{3a}	C_{6a}	C_5	C_4	CH_3	RSi	^{29}Si
	156.58	55.61	108.61	66.76	29.62	12.43	–	–
	155.24	59.12	114.33	67.05	31.02	12.36	3.98	−0.16
	155.56	59.76	113.04	67.27	30.90	12.47	−6.56 −6.47	−15.83
	155.33	60.16	112.57	67.33	30.28	11.97	128.46(4’) 129.64(2’) 133.36(5’) 139.08(3’)	−32.28
	156.76 156.18	59.12 59.65	113.13 112.98	67.00 66.91	30.87 30.55	12.50	−8.05	−7.76 −7.06
	156.62 156.13	60.85 61.21	113.43 113.30	67.35 67.03	29.69 30.08	11.92	128.72 129.51 129.74 130.72 136.79	−22.47 −21.84

Table 2
Crystal data and measurement conditions for **1**,**2**, and **6**

Empirical formula	$C_9H_{17}NO_2Si$	$C_8H_{15}NO_2Si$	$C_{24}H_{26}N_2O_4Si$
Formula weight	199.33	185.30	434.56
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Radiation (Å)	Mo–K_α graphite monochromated $\lambda = 0.71069$		
Space group	*Pbca*	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	11.356(3)	5.225(2)	13.827(4)
b (Å)	10.843(3)	8.539(5)	13.761(4)
c (Å)	18.385(4)	23.678(8)	11.846(3)
α (°)	90	90	90
β (°)	90	90.28(4)	93.78(2)
γ (°)	90	90	90
Volume (Å^3)	2263.8(10)	1056.4(8)	2249.1(11)
Molecular multiplicity *Z*	8	4	4
Density (calculated) (g/cm^3)	1.170	1.165	1.283
Number of electrons *F*(000)	864	400	920
Theta range for data collection (°)	2.22–25.04	1.72–24.98	2.09–22.55
Scan mode	$\theta/2\theta$	θ/θ	$\theta/2\theta$
Index ranges	$0 \leq h \leq 13$	$0 \leq h \leq 6$	$0 \leq h \leq 13$
	$0 \leq k \leq 12$	$0 \leq k \leq 10$	$0 \leq k \leq 14$
	$0 \leq l \leq 21$	$-27 \leq l \leq 28$	$-12 \leq l \leq 12$
Reflections collected	1715	1453	2565
Data/restraints/parameters	1715/0/186	1453/0/169	2565/0/384
Completeness to 2θ (%)	82.8	73.0	82.5
Goodness-of-fit on $\hat{F}2$	1.008	1.099	1.068
Final *R* indices $[I > 2\sigma(I)]$	0.0387	0.0757	0.0377
R indices (all data)	0.0442	0.0830	0.0410
Largest diff. peak and hole (e Å^{-3})	0.390 and −0.146	0.385 and −0.291	0.275 and −0.168

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1** and **2** [a]

	Compound **1**					Compound **2**			
	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Si	8934(1)	2042(1)	3249(1)	33(1)	Si	1151(2)	3148(2)	4322(1)	75(1)
O(1)	6905(1)	3152(1)	3722(1)	42(1)	O(1)	−1164(5)	503(3)	3942(1)	71(1)
O(6)	8447(1)	3059(1)	4574(1)	41(1)	O(6)	−944(6)	2554(4)	3292(1)	76(1)
N(7)	8158(2)	2534(2)	5270(1)	41(1)	N(7)	137(8)	2176(4)	2752(1)	78(1)
C(2)	7828(2)	2398(2)	3997(1)	33(1)	C(2)	413(7)	1722(4)	3734(2)	60(1)
C(3)	7233(2)	1306(2)	4389(1)	33(1)	C(3)	2645(8)	920(4)	3431(1)	58(1)
C(4)	5919(2)	1467(2)	4222(2)	43(1)	C(4)	2294(10)	−806(5)	3565(2)	73(1)
C(5)	5832(2)	2844(2)	4102(1)	42(1)	C(5)	−529(10)	−912(5)	3649(2)	76(1)
C(8)	7527(2)	1576(2)	5167(1)	37(1)	C(8)	2092(8)	1327(5)	2827(2)	62(1)
C(10)	9479(3)	3515(2)	2851(2)	48(1)	C(9)	3635(12)	773(7)	2346(2)	81(1)
C(11)	10156(2)	1165(2)	3686(2)	47(1)	C(10)	2934(17)	4816(8)	4013(3)	106(2)
C(12)	8177(3)	1094(3)	2552(2)	56(1)	C(11)	3059(18)	2101(10)	4866(3)	109(2)
C(13)	7103(3)	823(3)	5794(2)	57(1)					

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

3. Experimental

^{1}H-, ^{13}C-, ^{29}Si-NMR spectra were measured on a WH-360/DS (Bruker) instrument at 360.1, 90.56 and 71.50 MHz, respectively (Table 1).

The melting points were determined on a 'Digital melting point analyzer' (Fisher), the results are given without correction.

3.1. Synthesis of compounds **1–3**, **5–8**

3.1.1. Method A

Nitroethane (0.01 mol) and triethylamine (2 drops) in dry benzene (20 ml) are added dropwise for 4 h to the reaction mixture of 2,3-dihydrofurylsilane (0.01 mol), phenylisocyanate (0.02 mol) and triethylamine (1 ml) in dry benzene at room temperature (r.t.). After some minutes, CO_2 begins to evolve and diphenylurea precipitates. The mixture is heated for 4 h at 70–80°C. After cooling to r.t. diphenylurea is filtered off and the solvent removed using a rotary evaporator. The solid residue was recrystallized from the corresponding solvent.

3-Methyl-6a-trimethylsilyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole (**1**), m.p. 71.5°C (from petrolether). Yield 60%. ^{1}H-NMR (360 MHz, $CDCl_3$/TMS) δ (ppm): 0.12 (s, 9H, Me_3Si), 1.9–2.1 (m, 2H, CH_2), 1.96 (d, 3H, $^4J = 0.8$ Hz, CH_3), 3.4–3.6 (m, 2H, CH_2), 3.98 (m, 1H, $J = 0.8$ Hz, $J = 5.9$ Hz, $J = 6.0$ Hz, CH). Anal. Calc. for $C_9H_{17}NO_2Si$: C, 54.27; H, 8.58; N, 7.0. Found: C, 54.50; H, 8.60; N, 6.91.

3-Methyl-6a-dimethylsilyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole (**2**), m.p. 50°C (from hexane). Yield 40%. ^{1}H-NMR (90.1 MHz, $CDCl_3$/TMS) δ (ppm): 0.22 (d, 6H, $J = 4$ Hz, $(CH_3)_2Si$), 1.9–2.2 (m, 2H, CH_2), 2.02 (d, 3H, $^4J = 0.8$ Hz, CH_3), 3.4–3.7 (m, 2H, CH_2), 3.9–4.2 (m, 2H, CH and SiH).

3-Methyl-6a-phenyldimethylsilyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole (**3**), m.p. 56.5°C (from petrolether) Yield 25%. ^{1}H-NMR (90.1 MHz, $CDCl_3$/TMS) δ (ppm): 0.44 (d, 6H, $(CH_3)_2Si$), 1.7–2.1 (m, 2H, CH_2), 1.93 (s, 3H, CH_3), 3.4–3.7 (m, 2H, CH_2), 3.9–4.2 (m, 1H, CH), 7.36 (m, 3H, H_{arom}), 7.60 (m, 2H, H_{arom}). Anal. Calc. for $C_{14}H_{19}NO_2Si$: C, 64.32; H, 7.34; N, 5.35. Found: C, 64.13; H, 7.42; N, 5.35.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **6** [a]

	x	*y*	*z*	U_{eq}
Si	7475(1)	9266(1)	2365(1)	39(1)
O(1)	6663(1)	7812(1)	1051(1)	49(1)
O(6)	5584(1)	8785(1)	2009(1)	52(1)
O(1′)	9436(1)	9373(1)	2617(1)	52(1)
O(6′)	8787(1)	7879(1)	3151(1)	53(1)
N(7)	4892(2)	8232(2)	2600(2)	59(1)
N(7′)	9370(2)	7110(2)	2717(2)	57(1)
C(2)	6510(2)	8292(2)	2091(2)	42(1)
C(3)	6390(2)	7481(2)	2967(2)	44(1)
C(4)	6682(3)	6553(2)	2370(2)	58(1)
C(5)	6410(3)	6803(2)	1147(2)	61(1)
C(8)	5335(2)	7545(2)	3134(2)	50(1)
C(9)	4799(3)	6841(3)	3824(3)	74(1)
C(2′)	8709(2)	8654(2)	2334(2)	42(1)
C(3′)	8996(2)	8198(2)	1229(2)	43(1)
C(4′)	9674(2)	8931(2)	744(2)	54(1)
C(5′)	10171(2)	9353(3)	1807(3)	63(1)
C(8′)	9476(2)	7284(2)	1674(2)	48(1)
C(9′)	10061(3)	6640(2)	982(3)	68(1)
C(11)	7415(2)	10200(2)	1218(2)	44(1)
C(12)	7318(2)	9841(2)	3775(2)	44(1)
C(13)	6887(2)	10082(2)	179(2)	60(1)
C(14)	6872(3)	10799(3)	−638(3)	77(1)
C(15)	7387(3)	11637(3)	−453(3)	78(1)
C(16)	7919(3)	11768(2)	556(3)	73(1)
C(17)	7928 (2)	11062(2)	1376(3)	58(1)
C(18)	6436(2)	10239(2)	4029(2)	63(1)
C(19)	6310(3)	10667(2)	5062(3)	73(1)
C(20)	7070(3)	10731(2)	5860(2)	69(1)
C(21)	7944(3)	10350(2)	5634(2)	70(1)
C(22)	8075(2)	9909(2)	4601(2)	58(1)

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

Table 5
Bond lengths (Å) and angles (°) for **1** and **2**

Compound **1**		Compound **2**	
Bond lengths (Å)			
Si–C(12)	1.854(3)	Si–C(10)	1.854(6)
Si–C(10)	1.862(3)	Si–C(11)	1.854(7)
Si–C(11)	1.864(3)	Si–C(2)	1.888(4)
Si–C(2)	1.902(2)	O(1)–C(2)	1.417(5)
O(1)–C(2)	1.421(2)	O(1)–C(5)	1.432(5)
O(1)–C(5)	1.443(3)	O(6)–N(7)	1.438(5)
O(6)–N(7)	1.438(2)	O(6)–C(2)	1.447(4)
O(6)–C(2)	1.461(2)	N(7)–C(8)	1.265(6)
N(7)–C(8)	1.276(3)	C(2)–C(3)	1.533(5)
C(2)–C(3)	1.542(3)	C(3)–C(8)	1.497(5)
C(3)–C(8)	1.497(3)	C(3)–C(4)	1.519(6)
C(3)–C(4)	1.534(3)	C(4)–C(5)	1.493(7)
C(4)–C(5)	1.513(3)	C(8)–C(9)	1.476(6)
C(8)–C(13)	1.492(3)		
Bond angles (°)			
C(12)–Si–C(10)	111.0(1)	C(10)–Si–C(11)	112.0(4)
C(12)–Si–C(11)	111.2(2)	C(10)–Si–C(2)	107.8(3)
C(10)–Si–C(11)	111.06(13)	C(11)–Si–C(2)	108.0(3)
C(12)–Si–C(2)	107.80(12)	C(2)–O(1)–C(5)	108.3(3)
C(10)–Si–C(2)	109.20(11)	N(7)–O(6)–C(2)	109.8(3)
C(11)–Si–C(2)	106.45(11)	C(8)–N(7)–O(6)	108.9(3)
C(2)–O(1)–C(5)	108.5(2)	O(1)–C(2)–O(6)	109.1(3)
N(7)–O(6)–C(2)	110.0(2)	O(1)–C(2)–C(3)	106.2(3)
C(8)–N(7)–O(6)	108.6(2)	O(6)–C(2)–C(3)	104.6(3)
O(1)–C(2)–O(6)	109.3(2)	O(1)–C(2)–Si	109.6(2)
O(1)–C(2)–C(3)	106.6(2)	O(6)–C(2)–Si	108.3(3)
O(6)–C(2)–C(3)	104.3(2)	C(3)–C(2)–Si	118.7(3)
O(1)–C(2)–Si	110.29(13)	C(8)–C(3)–C(4)	113.7(3)
O(6)–C(2)–Si	107.88(12)	C(8)–C(3)–C(2)	101.5(3)
C(3)–C(2)–Si	118.13(14)	C(4)–C(3)–C(2)	104.0(3)
C(8)–C(3)–C(4)	112.7(2)	C(5)–C(4)–C(3)	102.0(4)
C(8)–C(3)–C(2)	101.5(2)	O(1)–C(5)–C(4)	104.2(4)
C(4)–C(3)–C(2)	104.2(2)	N(7)–C(8)–C(9)	121.2(4)
C(5)–C(4)–C(3)	101.8(2)	N(7)–C(8)–C(3)	114.8(3)
O(1)–C(5)–C(4)	104.2(2)	C(9)–C(8)–C(3)	124.0(4)
N(7)–C(8)–C(13)	120.8(2)		
N(7)–C(8)–C(3)	115.2(2)		
C(13)–C(8)–C(3)	124.0(2)		

3-Methyl-6a-tris(2-thienyl)silyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole (**5**), m.p. 152°C (from acetonitrile). Yield 83%. ^{1}H-NMR (360.1 MHz, $CDCl_3$/TMS) δ (ppm): 1.6–1.8 (m, 1H, CH), 1.93 (bs, 3H, CH_3), 1.9–2.1 (m, 1H, CH), 3.5–3.8 (m, 2H, CH_2) 4.05 (m, 1H, CH), 7.25 (dd, 1H, $J = 0.5$ Hz, $J = 5.0$ Hz, H_{thien}), 7.6 (dd, 1H, $J = 0.5$ Hz, $J = 3.0$ Hz, H_{thien}), 7.75 (dd, 1H, $J = 0.5$ Hz, $J = 5.0$ Hz, H_{thien}). Anal. Calc. for $C_{18}H_{17}NO_2S_3Si$: C, 53.57; H, 4.24; N, 3.47. Found: C, 53.48; H, 4.21; N, 3.39.

Bis[6a-(3-methyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazolyl)]diphenylsilane (**6**), m.p. 180°C (from ethyl acetate). Yield 25%. ^{1}H-NMR (90.1 MHz, $CDCl_3$/TMS) δ (ppm): 1.3–2.0 (m, 2H, CH_2), 1.91 (d, 6H, $J = 4.8$ Hz, CH_3), 3.4–3.7 (m, 1H, CH), 3.8–4.2 (m, 2H, CH_2), 7.39 (m, 6H, H_{arom}), 7.88 (m, 4H, H_{arom}). Anal. Calc. for $C_{24}H_{26}N_2O_4Si$: C, 66.34; H, 6.03; N, 6.44. Found: C, 66.18; H, 6.06; N, 6.34.

Bis[6a-(3-methyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazolyl)]dimethylsilane (**7**), m.p. 140°C (from ethyl acetate). Yield 32%. ^{1}H-NMR (90.1 MHz, $CDCl_3$/TMS) δ (ppm): 0.29 (s, 6H, $(CH_3)_2Si$), 1.8–2.2 (m, 4H, CH_2), 1.98 (s, 6H, CH_3), 3.4–3.7 (m, 2H, CH_2), 3.9–4.2 (m, 4H, CH_2 and CH_2). Anal. Calc. for $C_{14}H_{22}N_2O_4Si$: C, 54.17; H, 7.15; N, 9.02. Found: C, 54.09; H, 7.12; N, 8.88.

Table 6
Bond lengths (Å) and angles (°) for **6**

Bond lengths (Å)			
Si–C(11)	1.868(2)	C(8)–C(9)	1.495(4)
Si–C(12)	1.874(2)	C(2′)–C(3′)	1.528(3)
Si–C(2)	1.904(2)	C(3′)–C(8′)	1.501(3)
Si–C(2′)	1.906(2)	C(3′)–C(4′)	1.515(4)
O(1)–C(2)	1.426(3)	C(4′)–C(5′)	1.510(4)
O(1)–C(5)	1.438(3)	C(8′)–C(9′)	1.483(4)
O(6)–N(7)	1.439(3)	C(11)–C(17)	1.389(4)
O(6)–C(2)	1.448(3)	C(11)–C(13)	1.398(4)
O(1′)–C(2′)	1.434(3)	C(12)–C(18)	1.388(4)
O(1′)–C(5′)	1.443(3)	C(12)–C(22)	1.388(4)
O(6′)–C(2′)	1.440(3)	C(13)–C(14)	1.381(4)
O(6′)–N(7′)	1.445(3)	C(14)–C(15)	1.367(5)
N(7)–C(8)	1.272(3)	C(15)–C(16)	1.373(5)
N(7′)–C(8′)	1.277(3)	C(16)–C(17)	1.373(4)
C(2)–C(3)	1.540(3)	C(18)–C(19)	1.379(4)
C(3)–C(8)	1.488(4)	C(19)–C(20)	1.369(5)
C(3)–C(4)	1.528(4)	C(20)–C(21)	1.361(5)
C(4)–C(5)	1.512(4)	C(21)–C(22)	1.388(4)
Bond angles (°)			
C(11)– Si–C(12)	110.86(10)	O(6′)–C(2′)–C(3′)	105.0(2)
C(11)– Si–C(2)	111.31(11)	O(1′)–C(2′)–Si	107.8(2)
C(12)– Si–C(2)	109.15(11)	O(6′)–C(2′)–Si	110.0(2)
C(11)– Si–C(2′)	106.71(10)	C(3′)–C(2′)–Si	118.8(2)
C(12)– Si–C(2′)	111.09(11)	C(8′)–C(3′)–C(4′)	114.9(2)
C(2)–Si–C(2′)	107.66(10)	C(8′)–C(3′)–C(2′)	100.2(2)
C(2)–O(1)–C(5)	109.1(2)	C(4′)–C(3′)–C(2′)	104.7(2)
N(7)–O(6)–C(2)	109.4(2)	C(5′)–C(4′)–C(3′)	101.5(2)
C(2′)–O(1′)–C(5′)	110.2(2)	O(1′)–C(5′)–C(4′)	105.0(2)
C(2′)–O(6′)–N(7′)	108.8(2)	N(7′)–C(8′)–C(9′)	121.6(2)
C(8)–N(7)–O(6)	108.8(2)	N(7′)–C(8′)–C(3′)	114.9(2)
C(8′)–N(7′)–O(6′)	108.0(2)	C(9′)–C(8′)–C(3′)	123.5(2)
O(1)–C(2)–O(6)	109.9(2)	C(17)–C(11)–C(13)	116.8(2)
O(1)–C(2)–C(3)	106.0(2)	C(17)–C(11)–Si	119.4(2)
O(6)–C(2)–C(3)	104.5(2)	C(13)–C(11)–Si	123.8(2)
O(1)–C(2)–Si	109.3(2)	C(18)–C(12)–C(22)	117.0(2)
O(6)–C(2)–Si	106.7(2)	C(18)–C(12)–Si	120.9(2)
C(3)–C(2)–Si	120.0(2)	C(22)–C(12)–Si	122.1(2)
C(8)–C(3)–C(4)	113.7(2)	C(14)–C(13)–C(11)	121.2(3)
C(8)–C(3)–C(2)	101.4(2)	C(15)–C(14)–C(13)	120.4(3)
C(4)–C(3)–C(2)	104.5(2)	C(14)–C(15)–C(16)	119.6(3)
C(5)–C(4)–C(3)	101.3(2)	C(15)–C(16)–C(17)	120.2(3)
O(1)–C(5)–C(4)	104.5(2)	C(16)–C(17)–C(11)	121.8(3)
N(7)–C(8)–C(3)	115.0(2)	C(19)–C(18)–C(12)	121.6(3)
N(7)–C(8)–C(9)	120.9(3)	C(20)–C(19)–C(18)	120.3(3)
C(3)–C(8)–C(9)	124.1(3)	C(21)–C(20)–C(19)	119.4(3)
O(1′)–C(2′)–O(6′)	109.5(2)	C(20)–C(21)–C(22)	120.7(3)
O(1′)–C(2′)–C(3′)	105.4(2)	C(21)–C(22)–C(12)	121.0(3)
		C(20)–C(21)–C(22)	120.8(3)
		C(12)–C(22)–C(21)	121.0(3)

3-Methyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole (**8**), m.p. 83°C (from hexane/ethyl acetate). Yield 50%. ^{1}H-NMR (90.1 MHz, $CDCl_3$/TMS) δ (ppm): 2.02 (s, 3H, $J = 0.8$ Hz, CH_3), 1.9–2.4 (m, 2H, CH_2), 3.5–3.9 (m, 2H, CH_2), 3.9–4.3 (m, 1H, CH), 6.06 (d, 1H, $J = 6.1$ Hz, OCHO).

3.2. Synthesis of compound 4

3.2.1. Method B

The solution of triethylamine (0.02 mol) in dry ether (30 ml) at r.t. is dropped for 4 h into a solution of 2,3-dihydrofurylsilane (0.04 mol) and of benzhydroxamic chloride in dry ether (50 ml). After the addition of base the precipitated triethylamine hydrochloride is filtered off. The ether layer is washed with water and dried over sodium sulfate. After removal of a solvent in the rotary evaporator the dry residue was recrystallized (see Ref. [20]).

3-Phenyl-6a-phenyldimethylsilyl-3a,4,5,6a-tetrahydrofuro-[2,3-*d*]-isoxazole (**4**), m.p. 79°C (from ethyl acetate). Yield 25%. ^{1}H-NMR (90.1 MHz, $CDCl_3$/TMS) δ (ppm): 0.5 (d, 6H, $(CH_3)_2Si$), 1.80–1.90 (m, 1H, CH), 2.0–2.1 (m, 1H, CH), 3.5–3.6 (m, 1H, CH), 3.9–4.0 (m, 2H, CH_2), 7.40 (m, 6H, H_{arom}), 7.65 (m, 4H, H_{arom}). Anal. Calc. for $C_{19}H_{21}NO_2Si$: C, 70.54; H, 6.55; N, 4.33; C, 70.46; H, 6.62; N, 4.30.

3.3. X-ray Analysis of Condensed Bicycles 1, 2, 6

Compound **1** crystals were grown from petrolether, **2** crystals from hexane and **6** from ethyl acetate. Colourless crystals of these compounds were studied on the Syntex-P2 single-crystal diffractometer, the detailed crystal data and the measurement conditions are presented in Table 2.

Both structures were determined by direct methods (SHELXS-86 [21]) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97 [22]) employing unit weights. The nonhydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms-isotropically. The fractional coordinates and the equivalent isotropic displacement parameters for the nonhydrogen atoms for compounds **1**, **2** are listed in Table 3 and for compound **6**, in Table 4. Intramolecular distances and angles for both structures are reported in Table 5 for **1**, **2** and in Table 6 for compound **6**. Figs. 1–3 show a perspective view of molecules **1**, **2**, **6**.

4. Supplementary material

All crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the following deposition numbers: compound **1**, CCDC-118013; compound **2**, CCDC-118014; compound **6**, CCDC-118015. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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