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Synthesis and Stereochemistry of Substituted 1,3-Dioxa-2-silacyclohexanes:
VII.[1] Synthesis and Stereochemistry of Substituted 2-Vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes

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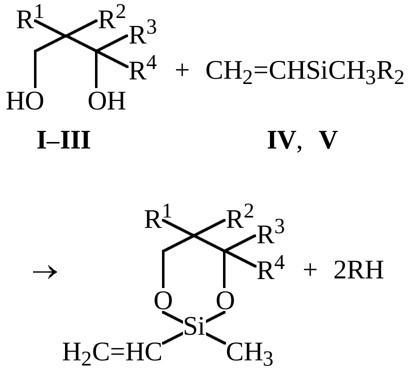
Abstract—The stereochemistry of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes was studied by ^{1}H and ^{13}C NMR spectroscopy. The configurational and conformational assignment of a mixture of 2-vinyl-2,4-dimethyl-1,3-dioxa-2-silacyclohexane diastereomers with various ratios of the *cis* and *trans* forms was made. The molecules of both conformers occur chiefly in the *chair* conformartion with equatorial location of the methyl group at the C^4 atom. The experimental data were confirmed by AM1 and MM+ optimization of the molecular geometry.

The synthesis procedures and conformational features of 2,2-disubstituted 1,3-dioxa-2-silacyclohexanes are described in sufficient detail in [1–4]. Proceeding with these studies, we have developed the synthesis procedures and examined the stereochemistry of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes. Condensation of 1,3-diols **I**–**III** with a 10% excess of vinylmethyldichlorosilane **IV** or vinylmethyldiacetoxysilane **V** in hexane at 50–60°C for 3–4 h gives target compounds **VI**–**VIII** in a 45–75% yield.



I–**III** **IV**, **V**

VIa, **VIb**, **VII**, **VIII**

R^1 = R^2 = R^3 = H, R^4 = CH$_3$ (**I**, **VIa**, **VIb**); R^1 = R^2 = H, R^3 = R^4 = CH$_3$ (**II**, **VII**); R^1 = R^2 = CH$_3$, R^3 = R^4 = H (**III**, **VIII**); R = Cl (**IV**), OAc (**V**).

Condensation of diols **I**–**III** with vinylmethyldiacetoxysilane **V** occurs with a high selectivity in the absence of a solvent.

Compounds **VI**–**VIII** prepared by condensation of diols **I**–**III** with vinylmethyldiacetoxysilane **V** are stable in 3-month storage in the dark without moisture access. The same compounds prepared from vinylmethyldichlorosilane **IV** contain a minor amount of hydrogen chloride which is difficult to remove. Therefore, compounds **VI**–**VIII** prepared by this method are unstable and polymerize to give cyclic polysiloxanes (about 20% from GC–MS data).

Thus, condensation of diols **I**–**III** with vinylmethyldiacetoxysilane **V** is a convenient route to compounds **VI**–**VIII**, which are prepared in the purer state and in a higher yield than by the similar reaction with vinylmethyldichlorosilane **IV**.

The structure of compounds **VI**–**VIII** was determined by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

Leaning upon our previous data [1, 5] on the stereochemistry of six-membered organosilicon ethers, we studied the conformational features of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes by ^{1}H and ^{13}C NMR spectroscopy and also by AM1 and MM+ calculations.

The ^{1}H NMR data for a mixture of isomers of **VI** are listed in Table 1. The shape of the signals of C^6

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[1] For communication VI, see [1].

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Table 1. Chemical shifts (δ, ppm) of axial (H_a) and equatorial (H_e) protons in the ^1H NMR spectra of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes **VI–VIII**

Comp. no.	H^4_a	H^4_e	H^5_a	H^5_e	H^6_e	H^6_a	$SiCH_2=CH$	$Si–CH_3$	$CH_3–C^4$	$CH_3–C^5$
VIa (*cis*)	4.16	–	1.73	1.58	4.00	3.99	6.05–5.81	0.15	1.20	–
VIb (*trans*)	4.13	–	1.62	1.54	3.96	3.93	6.05–5.81	0.14	1.18	–
VII	–	–	1.77	1.74	4.07	4.01	6.05–5.81	0.14	1.26, 1.25	–
VIII	3.67	3.52	–	–	3.52	3.67	6.05–5.81	0.25	–	1.08, 0.85

Table 2. Proton coupling constants (*J*, Hz) in the ^1H NMR spectra of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes **VI–VIII**

Comp. no.	$H^4_a–H^4_e$	$H^4_a–H^5_e$	$H^4_a–H^5_a$	$H^5_a–H^5_e$	$H^5_e–H^6_a$	$H^5_e–H^6_e$	$H^5_a–H^6_a$	$H^5_a–H^6_e$	$H^6_e–H^6_a$
VIa (*cis*)	6.28	2.89	10.05	–13.98	2.15	1.54	11.66	3.61	–12.2
VIb (*trans*)	6.12	2.76	9.42	–13.73	2.29	1.46	11.48	4.02	–12.0
VII	–	–	–	–14.4	6.1	4.7	4.4	6.3	–12.5
VIII	–10.9	–	–	–	–	–	–	–	–10.9

Table 3. Chemical shifts (δ_C, ppm) of the carbon atoms of the ring and substituents in the ^{13}C NMR spectra of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes **VI–VIII**

Comp. no.	C^4	C^5	C^6	$Si–CH_3$	$Si–\mathit{C}H_2=CH$	$Si–CH_2=\mathit{C}H$	$5-CH_3$	$4-CH_3$
VIa (*cis*)	69.74	38.37	62.71	–4.88	135.21	134.72	–	24.09
VIb (*trans*)	69.74	38.02	63.12	–2.14	134.96	133.83	–	24.21
VII	73.04	41.50	60.16	–1.45	134.16	136.01	–	30.34, 29.57
VIII	71.38	32.48	71.38	–2.16	135.18	134.65	19.50, 19.83	–

methylene protons in the ring of the minor isomer and the coupling constants $^3J_{6a5a}$ and $^3J_{6e5a}$ (Table 2) are close to those observed in the previously studied spectra of 2,4-dimethyl-2-phenyl-1,3-dioxa-2-silacyclohexane [1]. The value of $^3J_{4a5a}$ suggests axial location of the proton at C^4 and correspondingly the equatorial location of the methyl substituent at the C^4 atom. Hence, the molecules of the minor isomer are characterized by the *trans* configuration of the methyl groups at C^4 and Si and chiefly occur in the *chair* conformation.

The signal of the proton at the C^4 atom of the major isomer is shifted downfield relative to the minor isomer; hence, the methyl group at the silicon atom and the methyl group in the ring have the *syn* arrangement. We term this compound as the *cis* isomer. The coupling constants of the *cis* isomer suggest that this compound also occurs chiefly in the *chair* conformation.

The ^{13}C NMR spectra (Table 3) show no upfield shift of the C^4 signal in the *cis* isomer relative to the *trans* isomer. This fact suggests that the orientation of the methyl substituent does not change. Hence, the methyl group at C^4 in both isomers occupies the equatorial position. This assumption is confirmed by experimental determination of the direct C–H coupling constant. For both diastereomers of **VI** the coupling constants determined from the spectra that were taken without proton decoupling are approximately equal ($^1J_{^{13}C–H}$ 140.3, $^1J_{^{13}C–H}$ 140.9 Hz). This fact confirms the assumption that both diastereomers have the conformation with the similar location of the proton and substituent at C^4.

The molecular geometry was optimized by a program realizing the atom–atom potential in the MM+ parametrization [6, 7] using the standard parameters and by the AM1 quantum-chemical method [8].

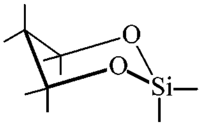
For substantiated conformational assignment of the molecules of **VI**–**VIII**, we optimized their geometry by the MM+ molecular-mechanics method and AM1 quantum-chemical method. On the potential energy surface of these molecules we found a number of

Table 4. Relative energis of the conformers of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes **VI**–**VIII** (kcal mol^{-1})

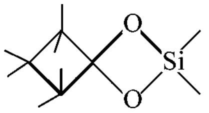
Comp. no.	Con-former[b]	MM+		AM1		Comp. no.	Con-former[b]	MM+		AM1	
		E_{min}	ΔE	$-E_{min}$	ΔE			E_{min}	ΔE	$-E_{min}$	ΔE
VIa	C_a	3.8	0.1	2297.1	0.0	**VII**	C_a	5.4	0.0	2572.7	0.5
(*cis*)	C_e	3.7	0.0	2296.8	0.3		C_e	5.9	0.5	2572.5	0.7
	1,4-*Twist*	7.1	3.4	–	–		1,4-*Twist*	7.9	2.5	2573.2	0.0
	2,5-*Twist*	–	–	2295.7	1.4		2,5-*Twist*	–	–	–	–
VIb	C_a	4.9	0.0	2595.6	0.8	**VIII**	C_a	4.7	0.0	2575.2	0.0
(*trans*)	C_e	5.4	0.5	2595.5	0.9		C_e	4.8	0.1	2574.4	0.8
	1,4-*Twist*	7.7	2.8	2596.4	0.0		1,4-*Twist*	–	–	–	–
	Boat	–	–	2595.8	0.6		2,5-*Twist*	–	–	2574.8	0.4
							Boat	9.2	4.4	–	–

[a] The dash denotes unstable structure (transforms into other structures at optimization). [b] C_a is the *chair* with the axial vinyl substituent at C^2 and equatorial methyl substituent at C^4; C_e is the *chair* with the equatorial vinyl substituent at C^2 and equatorial methyl substituent at C^4.

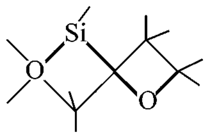
minima corresponding to the *chair*, 1,4-*twist*, and 2,5-*twist* conformers. The total and relative electron energies of these conformers are listed in Table 4.



chair



2,5-*twist*



1,4-*twist*

As seen from Table 4, both calculation methods give the *chair* conformation as the most preferable (except **VII** in AM1 calculations). It should be noted that the numerical values of the relative energies (ΔE) are low and suggest that the conformers coexist in the dynamic equilibrium.

It should be noted that the most of bond lengths and bond and torsion angles in specific conformers of **VI**–**VIII** (Table 5) are practically independent of the calculation procedure (AM1 or MM+) and mainly agree with the experimental data [9, 10]. However, there is a significant disagreement for the Si–O bond lengths (for the other bond lengths, the difference does not exceed 0.02 Å). The MM+ calculation gives for the Si–O bond lengths in **VI**–**VIII** the average value of 1.630 ± 0.001 Å, and the AM1 calculation, 1.780 ± 0.006 Å (the experimental value [9, 10], determined by X-ray diffraction, is 1.64 ± 0.02 Å). Therefore, for calculation and interpretation of the spectral data we chose the MM+ method of molecular mechanics.

To estimate the conformational composition of **VIa**, **VIb**, **VII**, and **VIII**, we compared the experimental (this work) and calculated vicinal proton–proton coupling constants. The coupling constants in separate conformers were determined by the Karplus equation [9] from the corresponding torsion angles τ. The results (Table 6) show that both diastereomers of **VI** chiefly occur in the *chair* conformation with equatorial methyl group at the C^4 atom.

The coupling constants in **VII** (Table 2) considerably differ from those of the *chair* conformers, i.e., it is a flexible form. Probably, there is an equilibrium between the 2,5-*twist* and 1,4-*twist* forms. The chemical shifts of the methyl groups in **VII** in the ^1H (1.25 and 1.26 ppm) and ^{13}C (30.34 and 29.57 ppm) NMR spectra differ. For the 1,4-*twist* form, the chemical shifts in the spectra should be equivalent, and therefore we believe that the 2,5-*twist* form is the major conformer.

In the ^1H NMR spectrum of **VIII**, the signal of the axial methyl protons at C^5 is shifted downfield relative to the equatorial substituent. Such inversion of chemical shifts is typical of 1,3-heterocycles in the *chair* conformation and is due to anisotropy of the diamagnetic susceptibility of the C–O bonds [10].

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were taken on a Tesla BS-587A spectrometer at a working frequency of 80 (^1H) and 20 MHz (^{13}C) and on a Bruker AM-300 spectrometer at a working frequency of 300 (^1H) and 75 MHz (^{13}C). To attain the maximal resolution, we recorded the ^1H NMR spectra of dilute solutions (<1% in $CDCl_3$), taking the chloroform signal at

Table 5. Optimized molecular geometry of the most stable conformers of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes **VI–VIII**, calculated by the MM+ method

Comp. no.	Conformer	Bond length, Å				Bond angle, deg		
		1–2	2–3	6–1	3–4	1–2–3	6–1–2	2–3–4
VIa (*cis*)	C_a	1.631	1.631	1.409	1.411	107.3	117.8	117.9
	C_e	1.631	1.631	1.408	1.411	107.6	117.4	118.0
	1,4-*Twist*	1.629	1.631	1.408	1.411	107.5	120.5	118.1
VIb (*trans*)	C_a	1.631	1.631	1.408	1.410	107.9	117.9	119.6
	C_e	1.630	1.629	1.407	1.410	108.7	117.6	120.7
	1,4-*Twist*	1.631	1.629	1.408	1.411	108.0	117.3	121.6
VII	C_a	1.630	1.630	1.407	1.413	107.9	117.8	120.5
	C_e	1.629	1.629	1.407	1.413	108.8	117.5	121.7
	1,4-*Twist*	1.629	1.628	1.408	1.412	109.1	117.4	122.6
VIII	C_a	1.631	1.631	1.409	1.408	106.6	117.9	117.5
	C_e	1.631	1.631	1.408	1.408	106.8	117.6	117.6
	Boat	1.630	1.631	1.407	1.409	105.5	118.1	115.4

Comp. no.	Conformer	Torsion angle, deg					
		1–2–3–4	2–3–4–5	3–4–5–6	4–5–6–1	5–6–1–2	6–1–2–3
VIa (*cis*)	C_a	–40.1	51.7	–60.3	60.2	–50.9	39.5
	C_e	–39.5	50.6	–59.7	60.5	–51.5	39.7
	1,4-*Twist*	–9.2	–39.4	65.7	–34.7	–19.0	41.7
VIb (*trans*)	C_a	–36.1	46.2	–56.6	59.3	–50.8	38.2
	C_e	–31.4	41.4	–55.0	60.8	–51.7	6.4
	1,4-*Twist*	–38.2	19.0	33.0	–66.8	44.2	3.2
VII	C_a	–35.4	44.7	–55.5	59.5	–50.8	37.9
	C_e	–30.0	39.5	–53.9	61.1	–51.6	35.7
	1,4-*Twist*	32.9	–13.3	–36.2	67.0	–43.8	–1.3
VIII	C_a	–41.0	53.2	–60.0	59.2	–51.5	40.3
	C_e	–40.7	52.3	–59.4	59.4	–52.3	40.7
	Boat	12.3	–58.6	54.6	–0.5	–48.7	43.8

Table 6. Torsion angles τ and vicinal coupling constants for the most stable conformers of substituted 2-vinyl-2-methyl-1,3-dioxa-2-silacyclohexanes **VI** and **VII**, calculated by the MM+ method

Comp. no.	Conformer	τ, deg			$^3J_{HH}$, Hz[a]		
		H^6_a–H^5_a	H^6_e–H^5_a	H^4_a–H^5_a	H^6_a–H^5_a	H^6_e–H^5_a	H^4_a–H^5_a
VIa (*cis*)	C_a	176.9	55.8	178.8	11.0	2.5	11.0
	C_e	177.3	56.3	179.1	11.0	2.5	11.0
VIb (*trans*)	C_a	178.4	62.2	49.5	11.0	1.7	3.4
	C_e	177.3	56.2	48.0	11.0	2.5	3.6
	1,4-*Twist*	176.2	62.1	30.8	11.0	1.8	5.9
VII	C_a	175.5	54.8	–	10.9	2.7	–
	C_e	177.0	56.1	–	11.0	2.5	–
	1,4-*Twist*	176.8	61.1	–	11.0	1.8	–

[a] For the corresponding experimental values of $^3J_{HH}$, see Table 2.

Table 7. Physicochemical properties and elemental analysis of **VI**–**VIII**

Comp. no.	bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	MR_D		Found, %			Formula	Calculated, %			M_{calc}
				found	calculated	C	H	Si		C	H	Si	
VI	30–33 (2)	0.9197	1.4243	43.68	43.92	53.7	8.5	17.7	$C_7H_{13}SiO_2$	53.5	8.3	17.9	146.2
VII	50–52 (5)	0.9447	1.4345	47.73	47.56	56.5	8.7	16.3	$C_8H_{15}SiO_2$	56.1	8.8	16.4	172.1
VIII	37–39 (2)	0.9870	1.4585	47.73	47.56	56.5	8.7	16.3	$C_8H_{15}SiO_2$	56.1	8.8	16.4	172.1

7.27 ppm as reference. The ^{13}C NMR spectra were taken in the same solvent (5% solution) in the mode of total proton decoupling; the direct C–H coupling constants were determined from the spectra taken without proton decoupling and with the Overhauser effect.

Vinylmethyldiacetoxysilane **V** was prepared by acylation of vinylmethyldichlorosilane with acetic anhydride by the known procedure [11]. Condensation of vinylmethyldichlorosilane **IV** and vinylmethyldiacetoxysilane **V** with 1,3-diols **I**–**III** was performed by the published procedure [4]. The physicochemical constants and elemental analyses of the products are listed in Table 7.

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