HETEROORGANIC FURAN DERIVATIVES.

62.* THE MOLECULAR AND CRYSTAL STRUCTURE AND REACTIVITY OF 2-FURYLHYDROSILANES

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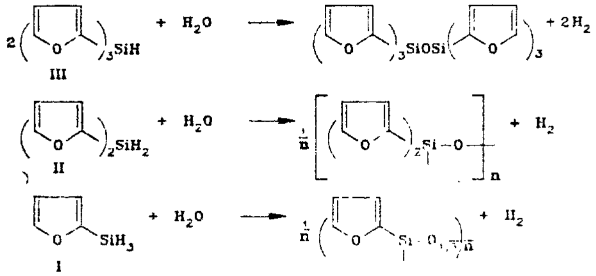
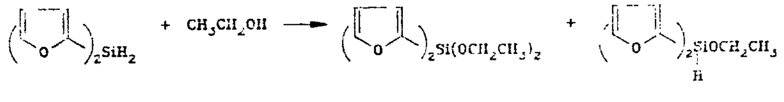
In contrast to reported hydrosilanes with alkyl and aromatic substituents at the silicon atom, 2-furyl-, di(2-furyl)- and tri(2-furyl)silanes undergo dehydrocondensation with water, while di(2-furyl)silane also undergoes this reaction with ethanol in the absence of catalyst. The structures of 2-furyl-, di(2-furyl)- and tri(2-furyl)silane were studied by electron diffraction.

Tri(2-furyl)silane (III) was the first of the 2-furylhydrosilanes with the general formula R_nSiH_{4-n} (R = 2-furyl) to be synthesized [2]. Its reactivity in hydrosilylation [2, 3] and dehydrocondensation [4] immediately attracted attention. Thus, for example, the hydrosilylation of 1-vinylsilatrane by tri(2-furyl)silane begins even at room temperature [2, 3], while the autocatalytic dehydrocondensation of this compound with aminoalcohols proceeds so rapidly that its rate cannot be measured [4]. While the autocatalytic dehydrocondensation of triorganylhydrosilanes with aminoalcohols and the hydrosilylation of unsaturated compounds catalyzed by chloroplatinic acid for other triorganylhydrosilanes occur at low rate or under more vigorous conditions, the noncatalytic dehydrocondensation with water has been found only for 2-furylhydrosilanes:



The intensity of the S—H stretching band for tri(2-furyl)silane relative to that of the ring $C=C$ stretching band in the IR spectra is reduced by a factor of approximately 2 over 24 h. In addition, tri(2-furyl)silane is quantitatively converted to hexa(2-furyl)disiloxane upon heating for 1 h with an equimolar amount of water in THF. Di(2-furyl)silane (II) is completely hydrolyzed by atmospheric moisture in a film over about 3 min. The hydrolysis of 2-furylsilane (I) also proceeds rather readily at room temperature but the hydrolysis product retains residual 2-furylsiloxane after 48 h as indicated by the Si—H stretching band which appears in the IR spectrum at 2209 cm^{-1}.

Di(2-furyl)silane also undergoes dehydrocondensation with ethanol in the absence of catalyst upon heating of the reagents at reflux in an argon atmosphere:



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*For Communication 61, see [1].

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR, Kazan 420083. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 25-30, January, 1987. Original article submitted July 11, 1986.

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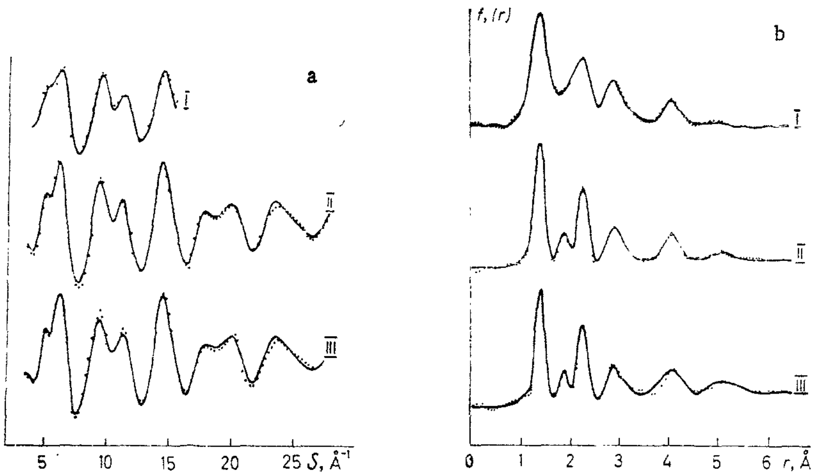

Fig. 1. Curves for the reduced molecular intensity component SM(S) (a) and radial scattering f(r) (b) for furylsilanes I-III. The theoretical curves are given by solid lines and the experimental curves are given by dotted lines.

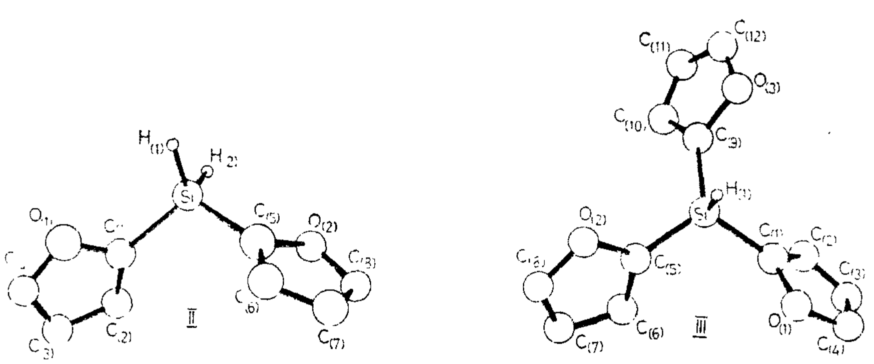

Fig. 2. Molecular models for furylsilanes II and III.

Tri(2-furyl)silane and 2-furylsilane do not react with ethanol under analogous conditions.

The molecular structure of 2-furylhydrosilanes held interest in light of their high reactivity. Furthermore, the molecular structure of hydrosilanes with heterocyclis substituents at the silicon atom has not yet been studied.

2-Furylsilane (I). The experimental and theoretical scattering curves are shown in Fig. 1. The structural analysis was carried out assuming that the furan ring is planar and has C_3V symmetry, while the silyl group has C_3V symmetry. One of the hydrogen atoms of the silyl group lies in the plane of the furan ring. The molecular structure in this case may be given by 10 independent parameters: the SiCC, CCC, CCH, and CSiH bond angles and Si—C, C—O, C=C, C—C, C—H, and Si—H bond lengths. The initial parameters were selected on the basis of literature data for furan and alkylsilanes. The geometric parameters were refined by the method of least squares. The C—H and Si—H bond lengths and CCH and CSiH bond angles were not refined. The C—O and C=C bond lengths and the vibrational amplitudes were refined by the group method. The parameters of the furan ring were not varied in the general cycle due to their strong correlation. Mean values for all three silanes were taken in the final minimization step. The results obtained are given in Table 1.

Di(2-furyl)silane (II). The molecular model and numbering of the atoms are given in Fig. 2. The curves for the reduced molecular intensity component and radial scattering are given in Fig. 1. In order to determine the molecular structure, the parameters listed for monofurylsilane as well as the CSiC bond angle and rotation angle of the furan ring (φ) are required. We considered C_s symmetry models ($\varphi_1' = \varphi_2$) with φ = 0, 45, 60, 90, 120, 150, and 180° and C_2 symmetry models ($\varphi_1' = -\varphi_2$) with the same angles (φ = 0° corresponds to the

TABLE 1. Geometric Parameters* of 2-Furylsilanes

Parameter	Bond lengths, Å			Parameter	Angles, deg			Parameter	Amplitudes, Å			Parameter	Dihedral angles, deg		
	I	II	III		I	II	III		I	II	III		I	II	III
Si—C	1,871 (15)	1,869 (11)	1,857 (11)	C—Si—C	—	108,3 (3,6)	113,7 (2,2)	Si—C	0,055 (—)	0,055 (—)	0,055 (—)	$\mathrm{H_1{-}Si{-}C_1{-}O_1}$	0,0	0,0	38,6
C—O	1,378 (—)	1,378 (—)	1,378 (—)	Si—C—C	127,8 (3,4)	130,2 (1,8)	129,1 (2,2)	C—O	0,055 (—)	0,055 (—)	0,055 (—)	$\mathrm{H_1{-}Si{-}C_1{-}C_2}$	180,0	−180,0	−141,4
C=C	1,378 (—)	1,378 (—)	1,378 (—)	C—C—C	106,0 (—)	106,0 (—)	106,0 (—)	C=C	0,055 (—)	0,055 (—)	0,055 (—)	$\mathrm{H_2{-}Si{-}C_1{-}O_1}$	—	−121,7	—
C—C	1,440 (—)	1,440 (—)	1,440 (—)	[C—O—C]	105,9 (—)	105,9 (—)	105,9 (—)	C—C	0,055 (—)	0,055 (—)	0,055 (—)	$\mathrm{H_2{-}Si{-}C_1{-}C_2}$	—	58,3	—
C—H	1,080	1,080	1,080	[C—C—O]	111,1 (—)	111,1 (—)	111,1 (—)	$\mathrm{C_1 \ldots C_3}$	0,060 (—)	0,060 (—)	0,060 (—)	$\mathrm{C_1{-}Si{-}C_5{-}C_6}$	—	−60,8	−27,5
Si—H	1,490	1,490	1,490	[Si—C—O]	121,2 (3,4)	118,8 (1,8)	119,9 (2,2)	$\mathrm{C_1 \ldots C_4}$	0,060 (—)	0,060 (—)	0,060 (—)	$\mathrm{C_1{-}Si{-}C_5{-}O_2}$	—	119,2	152,5
				$\mathrm{C_3{-}C_2{-}H}$	130,0	130,0	130,0	$\mathrm{C_2 \ldots O_1}$	0,060 (—)	0,060 (—)	0,060 (—)	$\mathrm{C_1{-}Si{-}C_9{-}C_{10}}$	—	—	104,7
				$\mathrm{C_3{-}C_4{-}H}$	124,0	124,0	124,0	Si . . . O	0,092 (22)	0,105 (25)	0,106 (22)	$\mathrm{C_1{-}Si{-}C_9{-}O_3}$	—	—	−75,3
				C—Si—H	111,0	[109,4]	[104,8]	$\mathrm{Si \ldots C_2}$	0,092 (22)	0,105 (25)	0,106 (22)				
				φ	—	60,8 (6,0)	38,6 (5,7)	$\mathrm{Si \ldots C_3}$	0,102(37)	0,106 (35)	0,112 (36)				
								$\mathrm{Si \ldots C_4}$	0,102(37)	0,106 (35)	0,112 (36)				

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*The standard deviations ($3\sigma_{mls}$) are given in parentheses. (—) indicates that the value was not refined in the general cycle. The dependent angles are given in brackets. The braces indicate group variation. The R factor for the experimental and theoretical curves are 0.089 for I, 0.115 for II, and 0.119 for III.

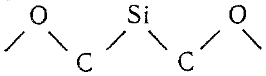
TABLE 2. Si-C Bond Lengths in Hydrosilanes

Compound	$r_{(Si-C)}$, Å	Method*	Reference
I	1,871(15)	ED	This work
II	1,869(11)	ED	This work
III	1,857(11)	ED	This work
$MeSiH_3$	1,867(1)	MW	[8]
Me_2SiH_2	1,867(2)	MW	[9]
Me_3SiH	1,868(2)	MW	[10]
$MeSiH_2NMe_2$	1,867(6)	ED	[11]
$Me_2SiHNMe_2$	1,869(3)	ED	[11]
$(Me_2SiH)_2NH$	1,867(3)	ED	[12]
$H_3SiCH_2SiH_3$	1,874(12)	MW	[13]
$CH_2{=}CH{-}SiH_3$	1,853	MW	[14]
$CH_2{=}CH{-}CH_2{-}SiH_3$	1,875(4)	ED	[15]
Cyclobutylsilane	1,873(3)	ED	[16]
Cyclopentadienylsilane	1,881(10)	ED	[17]
$C_6H_5SiH_3$	1,812	ED	[14]
Et_3SiH	1,887(4)	ED	[18]
t-Bu_3SiH	1,934(6)	ED	[19]

*Here and in Table 3: ED — electron diffraction, MW — microwave spectroscopy, X — X-ray diffraction analysis.

TABLE 3. Furan Ring Parameters in Different Compounds

Compound	$r_{(C-O)}$, Å	$r_{(C=C)}$, Å	$r_{(C-C)}$, Å	Bond angles, deg		
				∠COC	∠CCC	∠CCO
Furan (MW) [20]	1,362(1)	1,361(1)	1,431(2)	106,5(0,1)	106,1(0,1)	110,7(0,1)
Furan (X) [21]	1,368(6)	1,322(6)	1,428(7)	106,2(0.6)	106,8(0,2)	110,1(0,4)
2-Bromofuran (ED) [22]	1,350(9)	1,386(11)	1,420(20)	—	105.9(0,2)	111,1(1,0)
3-Bromofuran (ED)[23]	1,363(12)	1,345(15)	1,428(18)	—	107,3(1,3)	109,1(2,5)
2-Chlorofuran (ED) [22]	1,362(20)	1,379(24)	1,377(35)	—	106,7(1,0)	110,3(1,5)
Furylsilane	1,378	1,378	1,440	105,9	106,0	111,1

planar conformation with trans orientation of the O—C bonds relative to the Si—C bonds: ). Preliminary analysis showed that the C_s symmetry conformation with the furan rings twisted by 60° is most probable. This model was found to give the best agreement with the experimental data. Both the C—O bonds in the conformation found are eclipsed by Si—H bonds (Table 1).

Tri(2-furyl)silane (III). Only C_s symmetry models were analyzed with φ = 0, 30, 60, 90, 120, 150 and 180°. In the conformation with φ = 0°, each of the C—O bonds is eclipsed by an Si—H bond (the $H{-}Si(CO)_3$ molecular fragment has cis-C_{3v} symmetry). The best accord of the curves was achieved with φ = 38.6 (5.7)°. Then the tri(2-furyl)silane molecule has propeller form, in which each ring makes an angle of 38.6° with the H—Si—C plane. This angle is 56° in acetyltriphenylsilane [5] and 44° [6] and 51° [7] in tetraphenylsilane.

The r(Si—C) values obtained in this work are compared with literature data for organylhydrosilanes in Table 2. The parameters obtained for the furan ring are compared with the literature data for furan and its simplest derivatives in Table 3. The 4π-electrons of the double bonds form an electron sextet with the unshared electron pair of the oxygen atom characteristic for aromatic systems. Structural evidence for this hypothesis is found in the bond variation. The mean length for these bonds (1.39 Å) virtually corresponds to the C—C bond length in the benzene molecule. The Si—C bond length is equal to 1.87-1.86 Å. This may indicate a trend toward a decrease in the Si—C bond length as in the methylphosphine series [24] but we cannot draw a definite conclusion since the differences in these values are within experimental error. Furthermore, such a trend was not observed for methylsilanes. The CSiC bond angle in tri(2-furyl)silane is expanded to 113.7 (2.2)°, which may be attributed to steric interactions. The CSiC bond angle in di(2-furyl)silane is close to the tetrahedral value (108.3 (3.6)°).

Thus, since nucleophilic substitution at the silicon atom proceeds through a pentacoordinated state [25, 26], the expansion of the CSiC bond angle in tri(2-furyl)silane markedly facilitates the attack of a nucleophile on the silicon atom. There is no steric hindrance for di(2-furyl)- and 2-furylhydrosilanes. Thus, nucleophilic substitution is accomplished even more readily for the same intramolecular electronic interactions in these molecules [27, 28].

EXPERIMENTAL

The electron diffraction patterns were obtained on an ÉG-100A electron diffractometer with 40 kV accelerating voltage using a cubic sector. The electron wavelength was determined relative to ammonium chloride. The photometric tracings were treated in the usual manner [29]. The IR spectra were obtained on a Perkin-Elmer 500B spectrometer in Vaseline mull, while the spectra of the liquid samples were taken neat. The PMR spectra were taken on a Bruker WH-90/DS spectrometer in $CDCl_3$ with TMS as the internal standard.

The starting 2-furylhydrosilanes were synthesized according to our previous procedures [27]. The hydrolysis of high-boiling di(2-furyl)- and tri(2-furyl)silanes were studied in a neat film, while volatile 2-furylsilane was studied in a closed system in bulk. The reaction was monitored relative to the change in the relative intensity of the hydroxyl group stretching band in the IR spectra at 2188 cm^{-1} for 2-furylsilane, 2183 cm^{-1} for di(2-furyl)silane, and 2185 cm^{-1} for tri(2-furyl)silane.

Hexa(2-furyl)disiloxane. A sample of 1.15 g (5 mmoles) tri(2-furyl)silane in 2 ml THF was placed in a round-bottomed flask with a reflux condenser and azotometer. A sample of 0.09 ml (5 mmole) water was added and the mixture was heated at reflux until no further hydrogen was liberated (1 h). The solvent was distilled off and the residue was crystallized from ether to give a quantitative yield (1.2 g) of hexa(2-furyl)disiloxane, mp 74-75°C. PMR spectrum: 6.33 (4-H), 6.85 (3-H), 7.60 ppm (5-H). Found, %: C 60.4, H 3.7. Calculated, %, for $C_{24}H_{18}O_7Si_2$: C 60.7, H 3.8.

Alcoholysis of Di(2-furyl)silane by Ethanol. A mixture of 0.164 g (1 mmole) di(2-furyl)silane and 0.092 g (2 mmoles) ethanol was heated at reflux for 2 h in an argon atmosphere. Gas—liquid chromatographic analysis and PMR spectroscopy indicated that di(2-furyl)ethoxyhydrosilane [1.26 (CH_3), 3.92 (CH_2O), 5.34 (SiH), 6.47 (4-H), 6.98 (3-H), 7.47 ppm (5-H)] and di(2-furyl)diethoxysilane [1.28 (CH_3), 3.96 (OCH_2), 6.45 (4-H), 6.96 (3-H), 7.72 ppm (5-H)] are formed in 1:10 ratio.

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HYDROSILYLATION OF HETEROCYCLIC ALDEHYDES

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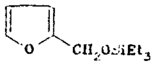
The hydrosilylation of O-, S-, and N-heterocyclic aldehydes with triethylsilane has been studied in the presence of different metal complex catalysts and the corresponding silyl ethers of hetarylcarbinols obtained. The rhodium complexes $Rh(PPh_3)_3Cl$ and $[Et_3PhCH_2N]RhCl_4$ have been found to be the most efficient catalysts for these reactions.

Hydrosilylation is a method for the preparation of organosilicon compounds. Besides this, this reaction is used in organic synthesis as an intermediate reaction, for instance, for the preparation of alcohols by the hydrosilylation of aldehydes and ketones, followed by hydrolysis [1].

So far, the hydrosilylation of heterocyclic aldehydes has not been sufficiently studied. In earlier work [2] prolonged refluxing (48-78 h) of aldehydes with triethylsilane (one of the most easily accessible hydrosilanes) in the presence of Spyer's catalyst (solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol) gave triethyl(furfuryloxy)silane (I), triethyl(5-methylfurfuryloxy)silane (II), and triethyl(2-thienylmethoxy)silane (III) with yields of 39, 27, and 41% respectively. The low yields demonstrate the low effeciency of the platinum catalyst in the addition of the silane to the C=O bond; besides this, as a strong acid H_2PtCl_6 enhances tar formation from the initial aldehydes.



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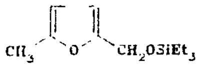

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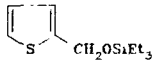

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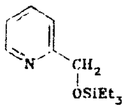

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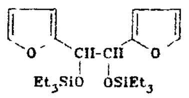

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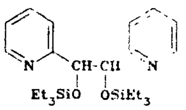

VI

The hydrosilylation of furfural and pyridine-2-aldehyde with triethylsilane in the presence of nickel chloride catalysts was carried out at 100-110° for 2-3 h [3, 4]; besides

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