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ORGANOSILICON COMPOUNDS OF THE FURAN SERIES

X. Hydrosilylation of 2-Vinylfuran*

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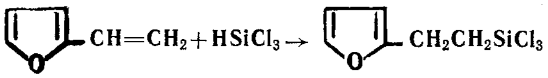
2-Vinylfuran is hydrosilylated by trichlorosilane, alkyldichlorosilanes, triethoxysilane, alkyldialkoxysilanes, trialkylsilanes, and tetraethyldisoloxane, in the presence of $H_2PtCl_6 \cdot 6H_2O$, 1% Pt/C, and 1% Pd/C. The structures of the products are shown by PMR, and IR spectra, and proved by reverse synthesis. It is shown that in the majority of cases hydrosilylation is in accordance with Farmer's rule. New views on the mechanism of hydrosilylation are put forward.

The present authors [2] previously prepared furylorganylsilanes by syntheses involving organolithium and organomagnesium compounds. It also appeared to be of interest to develop a synthesis of furylalkylsilanes by hydrosilylation of 2-vinylfuran in the presence of Group VIII metals and $H_2PtCl_6 \cdot 6H_2O$.

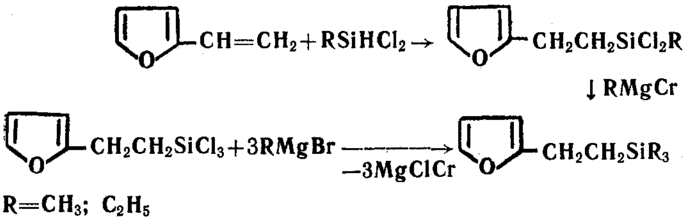
Trichlorosilane adds to 2-vinylfuran when they are heated together at 80-85° in a glass autoclave. Polymerization and resinification side reactions are hindered by carrying out the reaction in tetrahydrofuran or dioxane**. 18 hr heating gives a 60% yield of hydrosilylation product. There is no addition of trichlorosilane to 2-vinylfuran after 24 hr at 35° and atmospheric pressure.

The product of reaction of trichlorosilane with 2-vinylfuran has a PMR spectrum showing signals from protons of methylene groups only; there are none from methyl group protons***. This indicates that the reaction obeys the Farmer rule, and that β-(2-furyl)ethyltrichlorosilane**** is formed



The physical properties of the methylation product of the latter are completely identical with those of β-(2-furyl)ethyltrimethylsilane, which the present authors previously prepared from furfuryl chloride and trimethylsilylmethylmagnesium chloride [2]. This also confirms the structure of the hydrosilylation product given above. The product obtained by methylating the addition product from methyldichlorosilane and 2-vinylfuran has similar physical properties and IR spectrum. Therefore here, too, the silyl group adds at the end carbon atom of the vinyl group. This mode of addition is also confirmed by the PMR spectra.

Heating ethyldichlorosilane with 2-vinylfuran in tetrahydrofuran solution in the presence of $H_2PtCl_6 \cdot 6H_2O$ for 20 hr gives a 68% yield of hydrosilylation product, ethylated to a product whose physical properties are the same as those of β-(2-furyl)ethyltriethylsilane, prepared by ethylating β-(2-furyl)ethyltrichlorosilane. This indicates that ethyldichlorosilane adds in the same direction as trichlorosilane and methyldichlorosilane, i. e., that the silyl group goes to the least hydrogenated atom of the vinyl group



Triethylsilane adds to 2-vinylfuran in the presence of 1% Pd on carbon, 1% Pt on carbon, and $H_2PtCl_6 \cdot 6H_2O$. If the reaction is carried out at 100°, 1% Pt/C is more effective than 1% Pd/C. However, the hydrosilylation yield is low (28%). It is possible to raise the yield of hydrosilylation products to 40% by heating triethylsilane and 2-vinylfuran together with Pt/C in sealed tubes at 160°.

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*For Part IX see [1].

**These solvents also prevent formation of alpha isomers. See [4, 5].

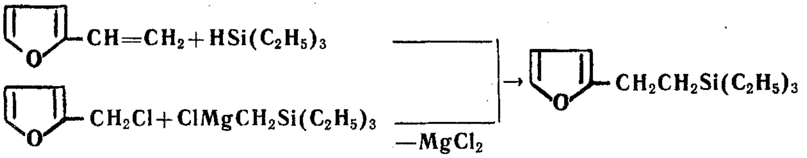
***The PMR spectra of the furylorganylsilanes will be dealt with in a separate paper.

****The IR spectra of the products from 2-vinylfuran and excess $HSiCl_3$ in the absence of the above solvents, indicate that two addition products (alpha and beta isomers) are formed.

In the presence of $H_2PtCl_6 \cdot 6H_2O$, triethylsilane adds slowly to 2-vinylfuran. After 45 hr, up to 45% of unchanged reactants can be distilled off from the reaction product; 70 hr heating cuts this figure to 25%, but the yield of 1-triethylsilyl-2-(furyl)ethane is not increased by increasing the reaction time to 100 hr, as the amount of high-boiling products gradually rises. Better results were secured by increasing the quantity of catalyst; after only 35 hr the yield was 40. 6%.

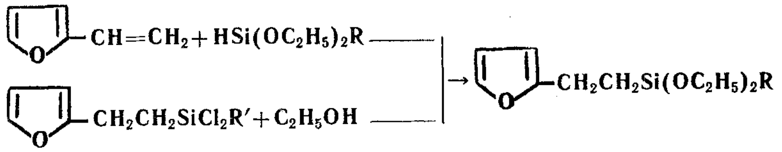
The UV spectra of the hydrosilylation product exhibit absorption maxima characteristic of the aromatic system of alkylfurans, viz., an intense maximum at 220 mμ (ε = 4000), and low intensity maximum at 275 mμ (ε = 72). At the same time there is none of the bathochromic shift due to the nonaromatic conjugated system of methylenedihydrofurans (λ_{max} 239 mμ; ε = 6300), thus excluding the possibility that a product with a dihydrofuran structure is present.

Comparison of physical properties and intensities of IR absorption spectrum maxima corresponding to antisymmetrical valence vibrations of methyl and methylene groups, proved that the addition product from triethylsilane and 2-vinylfuran was identical with β-(2-furyl)ethyltriethylsilane prepared from furfuryl chloride and triethylsilylmethylmagnesium chloride



Methyldiethylsilane adds more readily to 2-vinylfuran in the presence of $H_2PtCl_6 \cdot 6H_2O$ than does triethylsilane. The addition product proved to be identical with β-(2-furyl)ethylmethyldiethylsilane, prepared by ethylating β-(2-furyl) ethylmethyldichlorosilane.

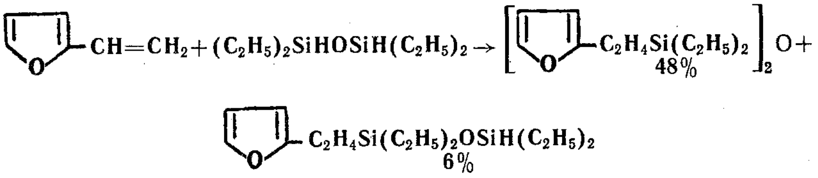
Ethyldiethoxysilane and triethoxysilane add more readily to 2-vinylfuran (yield 50-55%) than do trialkylsilanes. The structures of the products were proved by comparing their physical properties with those of the ethoxylation products prepared from β-(2-furyl)ethyltrichlorosilane and β-(2-furyl)ethylethyldichlorosilane. They can be ascribed the structures of β isomers, since they are identical with the products obtained by hydrosilylizing 2-vinylfuran with alkoxyhydrosilanes:



$R=C_2H_5$; C_2H_5O; $R'=Cl$; C_2H_5.

The structure of the product of hydrosilylizing 2-vinylfuran with ethyldiacetoxysilane*, which also proved to be a β isomer, was proved similarly.

When tetraethyldisiloxane reacts with 2-vinylfuran (mole ratio of reactants 1: 2) in the presence of $H_2PtCl_6 \cdot 6H_2O$, the main reaction product is a 1: 2 adduct, and the 1: 1 adduct can be isolated in small amounts only; in the latter, one Si—H link is preserved



The mechanism of hydrosilylation catalyzed by Group VIII metals and their derivatives is not fully known. Some authors consider it to be ionic, others adduce evidence in favor of a radical mechanism [3]. We have not been able to detect free radicals in the system $HSiCl_3$ and Et_3SiH plus Pt/C or $H_2PtCl_6 \cdot 6H_2O$ by EPR. In hydrosilylations in the presence of H_2PtCl_6 it must also be borne in mind that the extent of reduction of the latter can depend on the structure of the hydrosilane. Also it is impossible to exclude formation of complexes containing simultaneously unsaturated compound, hydrosilane, and catalyst. Consequently, in a particular case it is hardly possible to speak of a typical ionic or radical process.

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*The present authors were the first to effect addition of acetoxyhydrosilanes to a double bond.

Table 1

2-Vinylfuran Hydrosilylation Using 0.1 M H_2PtCl_6

Hydrosilane	Amounts of reactants					Reaction temperature, °C (solvent)	Reaction time, hr	Yield	
	Hydrosilane		Vinylfuran		Catalyst, ml				
	g	Mole	g	Mole				g	%
$HSiCl_3$	67.7	0.5	47.0	0.5	0.2	35 (dioxane)	24	—	—
$HSiCl_3$	40.7	0.3	28.2	0.3	0.4	80—85 (THF)*	18	41.2	60
CH_3SiHCl_2	23.0	0.2	18.8	0.2	0.3	50—60 (THF)	20	24.4	58.4
CH_3SiHCl_2	23.0	0.2	18.8	0.2	0.2	50—70 (dioxane)	20	24.9	62
CH_3SiHCl_2	57.5	0.5	47.0	0.5	0.5	50—70 (dioxane)	25	73.9	70.7
$C_2H_5SiHCl_2$	32.3	0.25	23.5	0.25	0.3	70—80 (THF)	20	37.8	67.8
$C_2H_5SiHCl_2$	51.6	0.4	37.6	0.4	0.2	70—90 (dioxane)	20	57.6	64.6
$C_2H_5SiH(OC_2H_5)_2$	19.2	0.13	12.2	0.13	0.3	100—120	25	16.1	51.3
$(C_2H_5O)_3SiH$	16.4	0.1	9.4	0.1	0.1	100—120	15	14.5	56.2
$CH_3(C_2H_5)_2SiH$	12.1	0.12	9.4	0.1	0.1	80—100	40	8.6	43.8
$CH_3(C_3H_7)_2SiH$	15.6	0.12	9.4	0.1	0.2	80—100	80	7.7	34.4
$C_2H_5(C_3H_7)_2SiH$	11.5	0.08	7.5	0.08	0.1	100—120	100	6.0	31.6
$(C_2H_5)_2SiHOOCCH_3$	7.3	0.05	4.7	0.05	0.1	100—120	20	6.5	54.2
$C_2H_5SiH(OOCCH_3)_2$	17.6	0.1	9.8	0.1	0.2	100—120	25	12.7	46.4
$[(C_2H_5)SiH]_2O$	19.0	0.1	18.8	0.2	0.3	100—120	30	18.0**	47.6**

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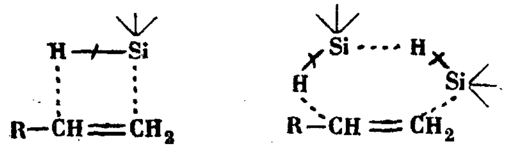
*THF = tetrahydrofuran.

**Also isolated was 1.7 g (6%) of the product of addition of 1 molecule of disiloxane to 1 molecule of 2-vinylfuran.

Hydrosilylation can proceed via intermediate 4- or 6-membered cyclic complexes formed by molecules of unsaturated compound and hydrosilane:



There at least, one of the molecules going to make up the complex is chemisorbed by the catalyst. Undoubtedly further special research is needed to establish the actual mechanism of hydrosilylation in the presence of Group VIII metals and their derivatives.

Experimental

Diethylacetoxysilane. 19.6 g (0.16 mole) diethylchlorosilane was added to a vigorously stirred suspension of 82 g (1 mole) anhydrous sodium acetate in 200 ml dry benzene, and the whole then refluxed for 6 hr, cooled and filtered, the precipitate being washed with benzene. The solvent was distilled off, and the residue distilled in a vacuum. Yield of diethylacetoxysilane 14.1 g, or 57.9%. Bp 29-30° (8 mm); n_D^{20} 1.4080; d_4^{20} 0.8924. Found: Si 19.20, 19.21%; MR_D 40.36. Calculated for $C_6H_{14}O_2Si$: Si 19.18%; MR_D 40.32.

β-(2-Furyl)ethyltriethylsilane. 17.5 g (0.15 mole) furfuryl chloride in 25 ml dry ether was added to a vigorously stirred ether solution of triethylsilylmethylmagnesium chloride, prepared from 4.8 g (0.2 gram atom) magnesium and 33 g (0.2 mole) chloromethyltriethylsilane, and cooled with ice. Next day the products were refluxed for 2 hr, and then decomposed with ammonium chloride solution, the ether layer separated and dried over magnesium sulfate. The solvent was distilled off under reduced pressure (water pump) and the residue distilled in a vacuum to give 11.3 g (35.8%) β-(2-furyl)ethyltriethylsilane, bp 84° (2 mm).

Hydrosilylating 2-vinylfuran. The appropriate hydrosilane and catalyst were placed in a flask fitted with a reflux condenser, and the 2-vinylfuran added. With trichlorosilane, methyldichlorosilane, and ethyldichlorosilane, the 2-vinylfuran was introduced dissolved in tetrahydrofuran or dioxane, the solvent comprising 80% by weight of the total reactants. After heating, the unreacted reactants were distilled, the Pd/C or Pd/C catalyst, when used, being first filtered off. The hydrosilylation product was isolated by distillation under vacuum. The reaction with trichlorosilane at 80-85° was carried out in a 250 ml glass pressure bottle. Hydrosilylation conditions and product yields are given in Tables 1 and 2.

Table 2

Hydrosilylation of 2-Vinylfuran with Triethylsilane*

Reactants				Catalyst	Amount of catalyst	Reaction time, hr	Yield	
Triethylsilane		Vinylfuran						
g	Mole	g	Mole				g	%
5.8	0.05	4.7	0.05	$H_2PtCl_6 \cdot 6H_2O$	0.04 ml	14	—	—
17.4	0.15	14.1	0.15	"	0.6 "	35	12.8	40.6
11.6	0.1	9.4	0.1	"	0.1 "	45	6.1	29.0
58.0	0.5	47.0	0.5	"	0.3 "	70	36.9	35.1
58.0	0.5	47.0	0.5	"	0.3 "	105	34.3	32.7
11.6	0.1	9.4	0.1	1% Pd/C	0.5 g	100	2.1	10.0
11.6	0.1	9.4	0.1	1% Pt/C	0.4 "	100	5.9	28.1
5.8	0.05	4.7	0.05	1% Pt/C	0.2 "	15**	4.2	40.0
11.6	0.1	9.4	0.1	Pyridine	7.9 "	75	—	—

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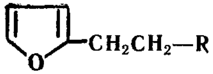
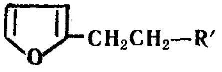
*Reaction temperature 100-110°.

**In a sealed glass tube, at 160 ± 5°.

Reactions of β-(2-furyl)ethylchlorosilanes. β-(2-Furyl)ethylchlorosilanes were methylated and ethylated, with, respectively, excess of MeMgI and EtMgBr in ether. After adding the β-(2-furyl)ethylchlorosilanes to the Grignard reagent, the reaction mixture was allowed to stand overnight, refluxed on a steam bath, and then decomposed with 10% acetic acid. After neutralizing with soda, drying over magnesium sulfate, and distilling off the ether, the reaction products were separated by distilling in a vacuum. Ethoxylation was effected by adding a 50% ether solution of chlorosilane to a solution of ethanol plus pyridine in an equal volume of ether at 0°. After refluxing on a steam bath, the precipitate was filtered off, washed with ether, the ether distilled off, and the ethoxylation product isolated by vacuum distillation. Table 3 gives the reaction conditions and yield of ethoxylation products. Table 4 gives the physical constants and analytical data of the furylethylsilanes synthesized.

The IR spectrum of β-(2-furyl)ethyltrimethylsilane, made by methylating β-(2-furyl)ethylmethyldichlorosilane showed the following bands in the C—H valence vibration region (% absorption in brackets): 2860 (37); 2908

Table 3

Reactions of β-(2-Furyl)ethylchlorosilanes  and Their Products 

Starting Compound	Amount of chlorosilane		Reactant	Amount		Reaction time, hr**	Reaction product	Yield	
	g	Mole		g*	Mole			g	%
$SiCl_3$	11.5	0.05	CH_3MgJ	6.1	0.25	5	$Si(CH_3)_3$	6.9	82
$SiCl_3$	11.5	0.05	C_2H_5MgBr	6.1	0.25	6	$Si(C_2H_5)_3$	8.5	80.9
$SiCl_3$	11.5	0.05	C_2H_5OH	7.8	0.17	4	$Si(OC_2H_5)_3$	10.4	80.6
			Pyridine	13.4	0.17				
$SiCl_2CH_3$	20.9	0.1	CH_3MgJ	7.3	0.3	5	$Si(CH_3)_3$	13.3	79.2
$SiCl_2CH_3$	16.7	0.08	C_2H_5MgBr	4.9	0.2	5	$SiCH_3(C_2H_5)_2$	11.4	72.6
$SiCl_2CH_3$	8.4	0.04	C_2H_5OH	4.6	0.1	6	$SiCH_3(OC_2H_5)_2$	6.4	70.1
			Pyridine	8.8	0.11				
$SiCl_2C_2H_5$	22.3	0.1	C_2H_5MgBr	7.3	0.3	7	$Si(C_2H_5)_3$	17.7	84.1
$SiCl_2C_2H_5$	8.9	0.04	CH_3COONa	9.8	0.12	15***	$SiC_2H_5(OOCCH_3)_3$	3.5	32.6
$SiCl_2C_2H_5$	8.9	0.04	C_2H_5OH	4.6	0.1	6	$SiC_2H_5(OC_2H_5)_2$	7.5	77.3
			Pyridine	8.8	0.11				

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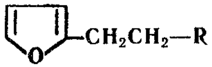
*In the syntheses with RMgX the amount of Mg is given in g (gram-atoms).

**Reaction carried out in boiling ether.

***Reaction carried out in boiling benzene.

Table 4

β-(2-Furyl)ethylsilanes 

R	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Formula	Si, %	
				Found	Calc.		Found	Calc.
$SiCl_3$	65 (3)	1.4752	1.2700	50.91	51.02	$C_6H_7Cl_3OSi$	12.39: 12.43^{a}	12.23
$SiCl_2CH_3$	95 (14)	1.4810	1.1681	50.95	51.39	$C_7H_{10}Cl_2OSi$	13.51: 13,69^{б}	13.43
$SiCl_2C_2H_5$	75,5 (2)	1.4834	1.1454	55.69	55.90	$C_8H_{12}Cl_2OSi$	12.69: 12.79^{в}	12.58
$Si(OC_2H_5)_3$	95,5—96 (2)	1.4388	1.0000	67.94	68.30	$C_{12}H_{22}O_4Si$	10.98: 11.09	10.87
$Si(OC_2H_5)_2CH_3$	75 (2)	1.4464	0.9729	62.64	62.91	$C_{11}H_{20}O_3Si$	12.21: 12.32	12.30
$Si(OC_2H_5)_2C_2H_5$	99 (2)	1.4510	0.9697	67.20	67.42	$C_{12}H_{22}O_3Si$	11,54: 11.63	11.59
$Si(CH_3)_3$*	40 (2)	1.4582	0.8825	52.06	52.13	$C_9H_{16}OSi$	16.49: 16.60	16.69
$SiCH_3(C_2H_5)_2$	78—79 (5)	1.4689	0.8960	61.01	61.15	$C_{11}H_{20}OSi$	14.23: 14.26	14.30
$SiCH_3(C_3H_7)_2$**	89—90 (3)	1.4650	0.8790	70.58	70.65	$C_{13}H_{24}OSi$	12.38: 12.43	12.51
$Si(C_2H_5)_3$	84 (2)	1.4710	0.8970	65.56	65.66	$C_{12}H_{22}OSi$	13.43: 13.47	13.35
$SiC_2H_5(C_3H_7)_2$**	103—105 (3)	1.4750	0.8862	75.75	75.65	$C_{14}H_{26}OSi$	11.86: 11.88	11.78
$SiOOCCH_3(C_2H_5)_2$**	111—113 (4)	1.4599	1.0002	65.81	66.54	$C_{12}H_{20}O_3Si$	11.83: 11.95	11.68
$Si(OOCCH_3)_2C_2H_5$	136—138 (6)	1.4651	1.1036	67.48	67.42	$C_{12}H_{17}O_5Si$	10.12: 10.20	10.43
$Si(C_2H_5)_2OSiH(C_2H_5)_2$**	97—99 (1)	1.4714	0.9445	84.27	84.44	$C_{14}H_{28}O_2Si_2$	19.32: 19.43	19.74
$Si(C_2H_5)_2OSi(C_2H_5)_2C_2H_4C_4H_3O$**	165—168 (1)	1.4835	0.9801	110.40	110.66	$C_{20}H_{34}O_3Si_2$	14.98: 15.08	14.83

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*The literature [2] gives bp 80° (26 mm); n_D^{20} 1. 4590; d_4^{20} 0. 8821.

**Position of the silyl group not ascertained. a) Found: Cl 46. 36, 46. 44%. Calculated: Cl 46. 33%. b) Found: Cl 33. 98, 34. 04%. Calculated: Cl 33. 91%. c) Found: Cl 31. 88, 31. 91%. Calculated: Cl 31. 78%.

(60), 2935 (51), 2962 (77) cm^{-1}. The IR spectrum of the product of methylating β-(2-furyl)ethyltrichlorosilane had 2860 (42), 2906 (60), 2930 (56), 2962 (80) cm^{-1}. The IR spectrum of the product from furfuryl chloride and trimethylsilylmethylmagnesium chloride had 2856 (30), 2905 (49), 2931 (41), 2961 (71) cm^{-1}. The spectra were measured with a UR-10 instrument.

The IR spectrum of β (2-furyl)ethyltriethylsilane (in CCl_4) prepared by adding triethylsilane to 2-vinylfuran, had the following absorption maxima (ε in brackets): 2909 (235); 2954 (330) cm^{-1}. The IR spectrum of the reaction product from furfuryl chloride and triethylsilylmethylmagnesium chloride had 2909 (240), 2953 (335) cm^{-1}. The spectra were measured on an IKS-12 instrument.

With solutions of triethylsilane and trichlorosilane containing $4 \cdot 10^{-5}$ to $1.6 \cdot 10^{-4}$ mole $H_2PtCl_6 \cdot 6H_2O$ per 1 mole hydrosilane, or suspensions containing $4 \cdot 10^{-2}$ to $2 \cdot 10^{-2}$ g platinum, as 1% Pt/C, per 1 mole hydrosilane, no signals were obtained on a RE-1301 instrument in the interval g = 1.95-2.05.

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