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ORGANOSILICON COMPOUNDS OF THE FURAN SERIES. V*. FURYLORGANYLSILANES

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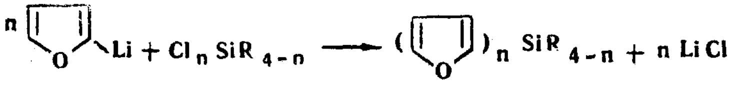
Twelve new furylorganylsilanes and furfurylorganylsilanes are synthesized by reacting 2-furyllithium, 5-methyl-2-furyllithium, and 5-trimethylsilyl-2-furyllithium with organylchlorosilanes, organylchlorohydrosilanes, chloromethyltriorganylsilanes, and silicon tetrachloride.

β-(2-furyl)ethyltrimethylsilane and 1-furyl-2-trimethylsilylethanol-1, which were previously unknown, are synthesized by reacting trimethylsilylmethyl magnesium chloride with furfuryl chloride and furfural, respectively.

The organosilicon derivatives of furan, with a silyl group attached to the furan ring either directly or through a carbon atom, have been little investigated. Only isolated representatives of compounds of this type are known, furyltrimethylsilane [2, 3], certain analogs, and 2-trimethylsilylethyl-3-carboethoxy-5-methylfuran [5]. Nor are there any convenient methods of synthesizing furylsilanes (reaction of chlorosilanes with furylmercurichloride [6] and hydrosilylation of furan with diphenylsilane [7] do not give positive results).

The present paper describes organolithium and organomagnesium synthesis of furylorganylsilanes, with 1-4 furyl groups joined to the central silicon atom, as well as furfurylsilanes, where the silyl group is separated from the heterocyclic ring by a methylene group, and β-(2-furyl)ethylsilanes with two methylene groups between the silicon atom and the furan ring.

2-Furyllithium reacts with organylchlorosilanes and $SiCl_4$ to give furylsilanes:

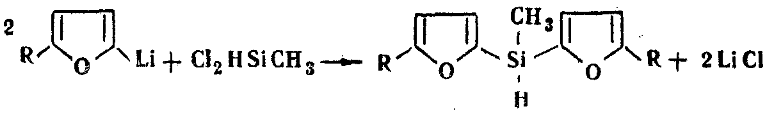


$R=CH_3$, C_2H_5, C_6H_5; $n=1-4$.

5-Methyl-2-furyllithium reacts similarly with chlorosilanes.

Reaction is readily brought about by adding a solution of the chlorosilane in tetrahydrofuran to a solution of furyllithium in the same solvent cooled to 0°. After separating the lithium chloride, the liquid furylsilanes are separated by vacuum distillation, and the solid ones by recrystallization from heptane. Reaction product yields are 40-85% of the theoretical.

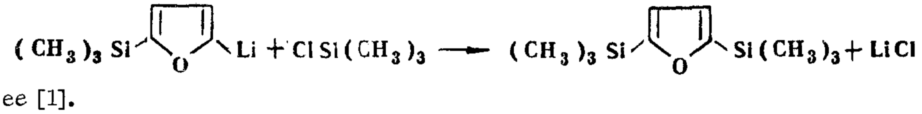
When organylhydrochlorosilanes are reacted with organolithium compounds, substitution by an organic radical usually takes place at the Si–H bond. However, a more than 40% yield of difurylmethylsilane can be obtained, along with trifurylmethylsilane, by adding a solution of furyllithium to methyldichlorosilane while cooling to –10° to –15°, the equation being



$R=H$, CH_3.

Bis-(5-methyl-2-furyl)methylsilane was also obtained in 41.8% yield in accordance with the above equation. This compound reduces mercuric chloride (in pyridine) to mercury, which is characteristic of hydrosilanes [8]. It also reacts with water in tetrahydrofuran or dioxan in the presence of chloroplatinic acid, being converted to the corresponding silanol [9, 10] with evolution of hydrogen. The IR spectrum, which has an intense band ν_{Si-H} at 2155 cm^{-1}, also confirms the presence of an Si–H bond.

2-Furyltrialkylsilanes are metalized by butyllithium in tetrahydrofuran. Reaction of the lithium derivative of 2-furyl-trimethylsilane with trimethylchlorosilane gives the first organosilicon furan derivative, with two silyl groups in the furan ring:



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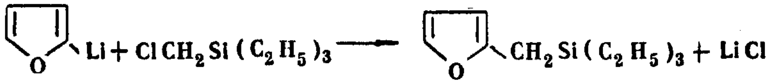
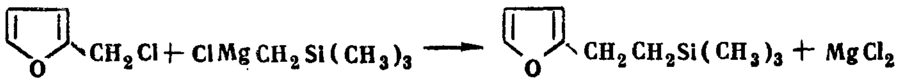
*For Part IV see [1].

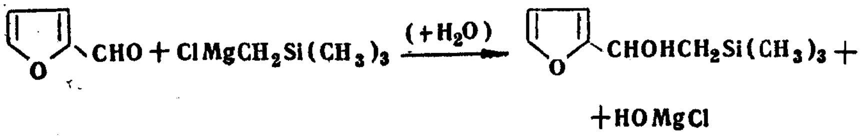
Furfuryltriethylsilane is obtained by reacting furyllithium with chloromethyltriethylsilane:



Reaction is slow, and prolonged heating is necessary.

β-(2-Furyl)ethylsilane is prepared by a Grignard reaction. Furfuryl chloride and furfural react energetically with trimethylsilylmethylmagnesium chloride to give β-(2-furyl)ethyltrimethylsilane and 1-furyl-2-trimethylsilylethanol-1, respectively:





1-Furyl-2-trimethylsilylethanol-1 smoothly forms a phenylurethane, but on dehydration with oxalic acid it suffers β-decomposition:

Physical constants, yields, and analytical data for all furylorganylsilanes synthesized are given in the table.

EXPERIMENTAL

2-Furyltriphenylsilane. A one-liter 4-necked round bottomed flask is fitted with a mechanical stirrer (gastight seal), a dropping funnel, a reflux condenser (protected against atmospheric moisture), a gas inlet tube for passing nitrogen, and a thermometer. 7.0 g (1 g-at) of finely cut lithium and 150 ml dry tetrahydrofuran are introduced. The reaction mixture is cooled to about –30°, and about 10 ml of a solution of 46.3 g (0.5 mole) n-butyl chloride in 50 ml tetrahydrofuran is added. The rest of the n-butyl chloride is added dropwise with vigorous stirring and reaction begins, the temperature being held at –20° to –25°. After all the butyl chloride has been added, the reaction mixture is gradually heated to 10°, and stirring continued until all the lithium has completely dissolved. 37.4 g (0.55 mole) furan are added to the resultant solution of n-butyllithium, which is held at about –20°. The temperature is slowly raised to 15°, and stirring continued until a negative test for butyllithium is obtained [12]. The resultant solution of furyllithium is cooled with ice water, and 94.3 g (0.32 mole) triphenylchlorosilane in 180 ml tetrahydrofuran are added. The mixture is left overnight at room temperature, and then decomposed with 120 ml water. The organic layer is separated off, and the aqueous layer extracted with a small amount of ether. The tetrahydrofuran solution is united with the ether extract, and the whole dried with magnesium sulfate. The solvent is distilled off, and the residue recrystallized from heptane. Yield 88.8 g (85%). White needles m.p. 158-158.5°.

Tetrafurylsilane is similarly synthesized from 2-furyllithium and $SiCl_4$.

Di(2-furyl)dimethylsilane. A solution of 12.9 g (0.1 mole) dimethyldichlorosilane in 20 ml tetrahydrofuran is slowly added, with stirring, to a solution of 0.21 mole 2-furyllithium in 100 ml tetrahydrofuran cooled to 0°. Next day the reaction mixture is decomposed with water, the tetrahydrofuran layer separated off, and dried with magnesium sulfate. The residue after distilling off the solvent is distilled in a vacuum. Yield 8.6 g (44.7%) b.p. 69-70° (2 mm).

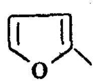
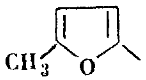
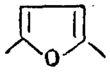
2-Furyltrimethylsilane, 2-furyltriethylsilane, tri(2-furyl)methylsilane, 5-methyl-2-furyltriethylsilane, and 2,5-bis-(trimethylsilyl)furan are prepared similarly. In reacting furyllithium with chloromethyltriethylsilane, the reaction mixture is boiled for 48 hrs.

Reaction of 2-furyllithium with methyldichlorosilane. A solution of 23.0 g (0.2 mole) methyldichlorosilane in 30 ml tetrahydrofuran is cooled to about –15°, and a 1.2 M solution of furyllithium in tetrahydrofuran is slowly added until the reaction is neutral. After decomposing with water, the solvent is distilled off, and the residue distilled in a vacuum. Yield 15.4 g (43.2%) di(2-furyl)methylsilane b.p. 67°(4 mm) and 9.7 g tri(2-furyl)methylsilane b.p. 128° (4 mm).

Bis-(5-methyl-2-furyl)methylsilane is obtained in a similar way.

β-(2-Furyl)ethyltrimethylsilane. A solution of 17.5 g (0.15 mole) furfuryl chloride in 25 ml dry ether is added to an ethereal solution of trimethylsilylmethyl magnesium chloride prepared from 4.8 g (0.2 g-at) magnesium and 25.0 g (~0.2 mole) chloromethyltrimethylsilane, cooled in ice and vigorously stirred. Next day the reaction mixture is de-

Furylorganylsilanes

R =  ; R′ =  ; R″ = 

Compound	B. p., °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Empirical formula	Si, %		Yield %
				Found	Calculated		Found	Calculated	
$RSi(CH_3)_3$*	125—126 (760)	1.4458	0.8764	42.66	42.87	$C_7H_{12}OSi$	19.95; 19.99	20.02	57.6
R_2SiHCH_3	67 (4)	1.5041	1.0385	50.84	51.09	$C_9H_{10}O_2Si$	15.55; 15.63	15.76	43.2
$R_2Si(CH_3)_2$	69—70 (2)	1.5020	1.0316	55.02	55.46	$C_{10}H_{12}O_2Si$	14.52; 14.59	14.60	44.7
R_3SiCH_3	128 (4)	1.5342	1.1251	67.52	68.05	$C_{13}H_{12}O_3Si$	11.08; 11.19	11.49	33.4
R_4Si	m. p. 92.5—93.5					$C_{16}H_{12}O_4Si$	9.58; 9.64	9.48	30
$RSi(C_2H_5)_3$	55 (2.5)	1.4668	0.8988	56.27	56.40	$C_{10}H_{18}OSi$	15.36; 15.30	15.41	58.1
$RSi(C_6H_5)_3$	m. p. 158—158.5					$C_{22}H_{18}OSi$	8.71; 8.83	8.60	85
$RCH_2Si(C_2H_5)_3$	58—60 (2)	1.4618	0.8948	60.32	61.03	$C_{11}H_{20}OSi$	13.92; 13.98	14.30	26.4
$RCH_2CH_2Si(CH_3)_3$	80 (26)	1.4590	0.8821	52.16	52.13	$C_9H_{16}OSi$	16.60; 16.64	16.69	37.2
$RCHOHCH_2Si(CH_3)_3$	75—76 (1)	1.4740	0.9792	52.90	53.68	$C_9H_{16}O_2Si$	15.01; 15.12	15.24	53.3
$R'Si(C_2H_5)_3$	68 (3)	1.4647	0.8924	60.80	61.03	$C_{11}H_{20}OSi$	14.09; 14.17	14.30	52
R'_2SiHCH_3	84.5 (3)	1.5010	1.0203	59.58	60.35	$C_{11}H_{14}O_2Si$	12.94; 13.03	13.22	41.8
$(CH_3)_3SiR''Si(CH_3)_3$	64 (7)	1.4474	0.8558	66.38	66.39	$C_{10}H_{20}OSi_2$	26.32; 26.39	26.44	31.1

*Literature data [2]: b. p. 124-125(750); n_D^{20} 1.4470; d_D^{20} 0.880.

composed with a solution of ammonium chloride. The ether layer is separated off, dried over magnesium sulfate, the solvent distilled off, and the residue distilled in a vacuum to give 9.4 g (37.2%) β-(2-furyl)ethyltrimethylsilane, b.p. 80° (26 mm).

1-Furyl-2-trimethylsilylethanol-1. An ether solution of trimethylsilylmethyl magnesium chloride, prepared from 8 g (0.33 g-at) magnesium, and 40.8 g (0.33 mole) of chloromethyltrimethylsilane is cooled to 0°, and a solution of 32.0 g (0.33 mole) freshly distilled furfural in 50 ml dry ether is added dropwise. Next day the reaction mixture is decomposed with water. The ether layer plus ethereal extracts is washed with 50 ml 20% sodium bisulfite and dried over potash. The solvent is distilled off, and the residue distilled in a vacuum. Yield 32.4 g (53.3%), b.p. 75-76° (1 mm).

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