UDC 547.72 + 546.287

FURAN ORGANOSILICON COMPOUNDS

XII. Furylorganylhydrosilanes*

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A series of 2-furyl- and 5-methyl-2-furylorganylhydrosilanes are synthesized by reacting 2-furyllithium and 5-methyl-2-furyllithium with organylchlorohydrosilanes. Furylorganylhydrosilanes reduce $HgCl_2$ in pyridine to free mercury; while in the presence of H_2PtCl_6 water converts them to the corresponding silanols, with alcohols they undergo dehydrocondensation, and with unsaturated compounds there is hydrosilanation.

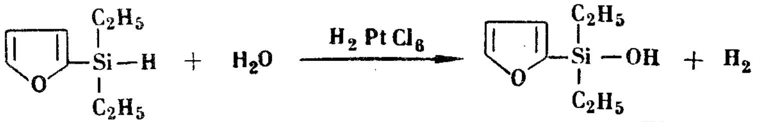
We previously prepared [2] the first representative of the furylorganylhydrosilanes in 40% yield by reacting 2-furyllithium with methyldichlorosilane at $-15°$ C in tetrahydrofuran.

The present work makes use of this method to synthesize dialkyl(2-furyl)- and dialkyl(5-methyl-2-furyl) hydrosilanes (in 40–50% yield), the equation being

$R = H, CH_3; \quad R' = CH_3, C_2H_5; \quad R'' = CH_3, C_2H_5, p\text{-}C_3H_7$

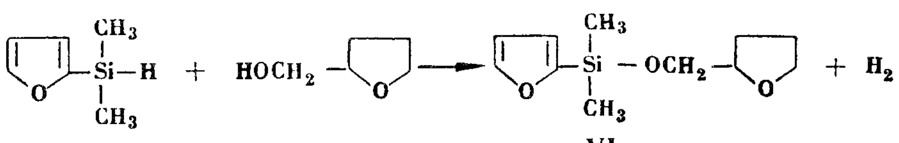
When 2-furyllithium reacts with trichlorosilane, the main reaction product is tetra(2-furyl) silane (I), and tri(2-furyl) silane (II) is formed in only insignificant yield. The yield of II could not be raised either by lowering the reaction temperature to $-45°$ C, or by substituting another solvent, such as diethyl ether, for the tetrahydrofuran.

2-Furylorganylhydrosilanes readily undergo reaction involving the Si–H bond; this is predominantly exothermic and fast. Thus 2-furyl- and 5-methyl-2-furylorganylhydrosilanes in pyridine immediately reduce mercuric chloride to mercury metal. In the presence of H_2PtCl_6 they undergo vigorous reaction with water dissolved in dioxane, and this reaction made it possible to synthesize the first of the 2-furylorganylsilanes, diethyl(2-furyl) silanol:-



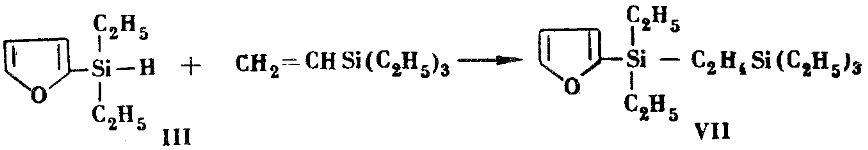
III IV

Dehydrocondensation of dimethyl(2-furyl) silane (V) with tetrahydrofurfuryl alcohol is rapidly catalyzed by H_2PtCl_6. The resultant dimethyl(2-furyl) tetrahydrofurfuryloxysilane (VI) is formed in 88.4% yield:-



V VI

Addition of III to triethylvinylsilane in the presence of H_2PtCl_6:-



III VII

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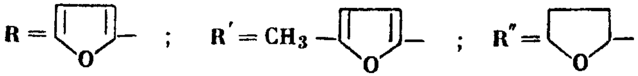
* For Part XI see [1].

Table 3

Furylorganylhydrosilanes and their Derivatives



Compound	Bp, °C (pressure mm)	n_D^{20}	d_4^{20}	MR_D		Formula	Si, %		Yield, %
				Found	Calcu-lated		Found	Calcu-lated	
R(CH$_3$)$_2$SiH **(V)**	114.5—115(770)	1.4390	0,8684	38,26	38.50	$C_6H_{10}OSi$	22,09; 22.16	22.25	40.4
R(CH$_3$)C$_2$H$_5$SiH	139 —140(768)	1.4550	0.8902	42.75	43.01	$C_7H_{12}OSi$	19.83; 19.90	20.02	42.1
R(CH$_3$)C$_3$H$_7$SiH	49 — 51 (10)	1.4460	0,8668	47,47	47.76	$C_8H_{14}OSi$	18,07; 18.11	18.20	52.5
R(C$_2$H$_5$)$_2$SiH **(III)**	50 (10)	1.4528	0.8809	47,32	47.52	$C_8H_{14}OSi$	18.16; 18.25	18.20	55.1
R′(CH$_3$)$_2$SiH	130 —131(750)	1.4376	0,8607	42.74	43.13	$C_7H_{12}OSi$	19.80; 19.89	20.02	34.2
R′(C$_2$H$_5$)$_2$SiH	68 — 69 (13)	1.4468	0.8645	52.00	52.15	$C_9H_{16}OSi$	16.72; 16.74	16.69	41.0
R′Si(CH$_3$)$_3$	142 —143(765)	1.4444	0.8635	47.50	47.50	$C_8H_{14}OSi$	18.14; 18.18	18.20	54.5
R(C$_2$H$_5$)$_2$SiOH **(IV)**	88 (5)	1,4751	1.0147	47.26	47.80	$C_8H_{14}O_2Si$	16.09; 16.19	16,49	82.2
R(CH$_3$)$_2$SiOCH$_2$R″ **(VI)**	101 —102 (3)	1.4560	1.0036	61.31	61.79	$C_{11}H_{18}O_3Si$	12,18; 12.27	12.41	88.4
R(C$_2$H$_5$)$_2$SiC$_2$H$_4$Si(C$_2$H$_5$)$_3$ **(VII)**	135 —137 (4)	1.4760	0.8999	92.96	93.57	$C_{16}H_{32}OSi_2$	18,70; 18.81	18.94	72.3

proceeds just as readily as does addition of methyldiethylsilane [3].

The table gives physical constants, yields, and analytical data for all the hitherto unknown furylorganylsilanes which have now been synthesized.

Experimental

Diethyl(2-furyl) silan (III). A solution of 24.3 g (0.2 mole) diethylchlorosilane in 15 ml tetrahydrofuran was cooled to −15° C, stirred vigorously, and a 1.2 M solution of 2-furyllithium in furan added slowly to neutral reaction, the temperature being held at −15° to −20° C. The reaction mixture was then decomposed with water, the tetrahydrofuran layer separated off, and dried over $MgSO_4$. The solvent was distilled off, and the residue vacuum-distilled. Yield of III bp 50° C (10 mm), 17.0 g (55.1%). Other dialkyl(2-furyl)- and dialkyl(5-methyl-2-furyl) silanes were prepared similarly.

Preparation of tri-(2-furyl) silane (II). When 2-furyllithium and trichlorosilane were reacted together under various conditions, the residue left after distilling off the solvent crystallized.

To isolate II, the crystals of I were washed with cold hexane, in which I was only slightly soluble. The solution was evaporated and the oil which remained, in amount always too small for distillation, was sucked off from the crystals of tetra(2-furyl) silane (I) which separated. The oily material thus obtained reduced $HgCl_2$ in pyridine, and was hydrolyzed by alkali with the evolution of H_2. The IR absorption spectrum showed an intense band at 2181 cm^{-1}, corresponding to the value of ν(Si−H) calculated for II.

Diethyl(2-furyl) silanol (IV). 0.015 ml 0.1 M $P_2PtCl_6 \cdot 6H_2O$ in dry iso-PrOH was added to 4.63 g (0.03 mole) III, and then 0.54 g (0.03 mole) water in 10 ml dioxane added dropwise, when there was a vigorous evolution of H_2, and the temperature of the reactants spontaneously rose to 65° C. When evolution of H_2 was complete, the dioxane was distilled under reduced pressure at a water pump. The residue was vacuum-distilled, yield, 4.20 g (82.2%) IV, bp 88° C (5 mm).

Dimethyl(2-furyl) tetrahydrofuryloxysilane (VI). 0.015 ml 0.1 M H_2PtCl_6 solution in iso-prOH and 4.1 g (0.04 mole) tetrahydrofuryl alcohol were added to 5 g (0.04 mole) V. At the end of the exothermic period, the reaction mixture was heated for 3 hr on a boiling water bath. Vacuum-distillation yielded 8.0 g (88.4%) VI, bp 101°–102° C (3 mm).

(Triethylsilylethyl) diethyl(2-furyl)silane (VII). 6.2 g (0.04 mole) III, 5.7 g (0.04 mole) triethylvinylsilane and 0.015 ml 0.1 M solution $H_2PtCl_6 \cdot 6H_2O$ in iso-PrOH were heated for 4 hr at 140°–150° C. Vacuum-distillation yielded 8.6 g (72.3%) VII, bp 135°–137° C (4 mm).

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