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Abstract

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SYNTHESIS AND STABILITY OF SOME FURYLSILANES

The dual character of the behavior of the furan ring as a diene and as an aromatic system makes furan and its derivatives interesting objects for the study of many chemical reactions. It seemed of interest to us to synthesize and study some properties of furan derivatives in which the α-carbon atom of the ring is directly bonded to a silicon atom.

Furylsilanes have scarcely been described in the literature. Benkeser and Kerry (^1), studying the acylation reaction of various organosilicon compounds, were the first to synthesize trimethylfurylsilane, obtained its acyl derivative, and 5-trimethylsilyl-2-furylcarboxylic acid. The latter was obtained by oxidation of trimethylfurylsilane with selenium dioxide (^2). Ibori and Sperry studied the cleavage of trimethylsilylfuran by hydrochloric acid (^3). This exhausts all the data on furylsilanes that we were able to find in the literature. The present work gives the results of the synthesis and study of the chemical stability of some furylsilanes.

Furylsilanes cannot be obtained using organomercury derivatives of furan, which, as is known, are more accessible and stable than the corresponding sodium-, lithium-, and magnesium-organic compounds. Experiments carried out by us showed that furylmercury chloride does not react in ether with silicon tetrachloride or with diethyldichlorosilane. Heating the same reagents for 10 h in benzene likewise did not lead to the desired results. As was shown by Lukevics and Giller (^4), furylmercury chloride is reduced by triethylsilane and does not react with silicon tetrachloride, silicon tetrafluoride, or with trimethyl- and triethylchlorosilanes upon more prolonged heating in various solvents.

The furylsilanes whose properties are given in Table 1 were synthesized according to the scheme:

$$\text{(furyl)Li} + \mathrm{R}_{\mathrm{nSiCl}_{4-\mathrm{n}}} \longrightarrow \mathrm{R}_{\mathrm{nSi}}\text{(furyl)}_{4-n}$$

Furan was metalated with n-butyllithium or phenyllithium. Furyl lithium reacts with alkyl-(phenyl)-chlorosilanes in good yields (about 50–60%). After distillation, the reaction products were subjected to adsorption purification on silica gel.

The structures of the furylsilanes listed in Table 1 were confirmed by absorption spectra in the infrared region.

For some furylsilanes, heating curves were recorded by the method of differential thermal analysis. As the thermograms showed, furylsilanes undergo no changes upon heating in air up to the boiling temperature. Thus, phenylfurylsilanes do not decompose upon heating to temperatures of about 400–450°.

To assess the chemical stability of the furylsilanes, they were heated at 30° in glacial acetic acid containing 12.5% HCl. This procedure seems to us more suitable than the method of passing HCl through the acid, since it makes it possible to avoid certain difficulties and inaccuracies.

Table 1

Structural formula	Empirical formula	B.p., °C/mm	M.p., °C	d_4^{20}	n_D^{20}	Mol. wt., found	Yield, %	Found, % C	Found, % H	Found, % Si	Calculated, % C	Calculated, % H	Calculated, % Si
tetra(2-furyl)silane	$C_{16}H_{12}O_4Si$		92	–	–	296,31	38,4	64,83	3,97	9,24	64,85	4,08	9,47
methyltri(2-furyl)silane	$C_{13}H_{12}O_3Si$	128/5	–	1,1380	1,5450	244,28	45,0	63,99	5,06	11,50	63,92	4,95	11,49
ethyltri(2-furyl)silane	$C_{14}H_{14}O_3Si$	174/2	–	1,1401	1,5500	258,31	39,6	–	–	10,67	65,09	5,46	10,87
phenyltri(2-furyl)silane	$C_{18}H_{14}O_3Si$		90	–	–	306,35	38,2	70,62	4,37	8,94	70,56	4,62	9,16
dimethyldi(2-furyl)silane	$C_{10}H_{12}O_2Si$	54/2	–	1,0151	1,5035	192,26	71,0	63,00	6,65	14,47	62,47	6,29	14,60
diethyldi(2-furyl)silane	$C_{12}H_{16}O_2Si$	82/1,8	–	1,0256	1,5115	220,31	65,0	66,10	7,81	12,50	65,42	7,32	12,74
diphenyldi(2-furyl)silane	$C_{20}H_{16}O_2Si$		164–165	–	–	316,39	50,2	76,37	5,40	8,94	75,92	5,10	8,87
triethyl(2-furyl)silane	$C_{10}H_{18}OSi$	36/6,5	–	0,9001	1,4697	182,30	66,5	65,45	10,07	15,40	65,88	9,95	15,39
triphenyl(2-furyl)silane	$C_{22}H_{18}OSi$		178–180	–	–	326,42	45,7	81,26	5,27	9,11	80,94	5,56	8,60
methyldiphenyl(2-furyl)silane	$C_{17}H_{16}OSi$	160/3	–	0,0842	1,5840	264,36	50,8	77,28	6,44	10,72	77,23	6,11	10,61

During the reaction the concentration of HCl does not change, which facilitates certain kinetic measurements.

As can be seen from Table 2, which gives the results of this study, furylsilanes are readily destroyed by hydrogen chloride. Trimethylfuryl-, trifurylmethyl-, and dimethyldifurylsilanes are almost completely destroyed after half an hour. This conclusion does not contradict the results of the kinetic study by Eaborn and Sperry (^{3}), but to us it seems that in this case the reaction proceeds in a different direction. Eaborn believes that in the case of trimethylfurylsilane (apparently by analogy with other trimethylsilyl-substituted aromatic compounds) cleavage of the silicon-furyl radical bond takes place. In work (5) no data confirming this are given, and the course of the reaction is judged only from the change in the intensity of the absorption band at 231 mμ. In this region only trimethylfurylsilane has an absorption maximum. Of the proposed reaction products, trimethylchlorosilane is transparent, and furan has no maximum in the absorption spectrum at this wavelength.

Table 2

Compound	Time, min	Amount of unconverted furylsilane, %	Compound	Time, min	Amount of unconverted furylsilane, %
[structural formula: trimethylfurylsilane]	25	3.97	[structural formula: dimethyldifurylsilane]	16	1.25
[structural formula: trimethylfurylsilane]	48	1.93	[structural formula: dimethyldifurylsilane]	30	0.78
[structural formula: trimethylfurylsilane]	120	0.99	[structural formula: dimethyldifurylsilane]	90	0.67
[structural formula: diphenylmethylfurylsilane]	9	94.0	[structural formula: methyltrifurylsilane]	17	2.58
[structural formula: diphenylmethylfurylsilane]	18	91.8	[structural formula: methyltrifurylsilane]	48	2.14

Compound	Time, min	Amount of unconverted furylsilane, %	Compound	Time, min	Amount of unconverted furylsilane, %
[structural formula: diphenylmethylfurylsilane]	26	50.3	[structural formula: methyltrifurylsilane]	130	1.81
[structural formula: diphenylmethylfurylsilane]	90	46.6 (40.0)			
[structural formula: diphenylmethylfurylsilane]	120	34.2 (30.0)			

Usually, in an aqueous or alcoholic medium, the action of acids on furan and its homologues begins with attack by a proton on the ring, which leads to the formation of a very reactive ion

$$\left[\ \text{furan ring bearing } R \text{ substituents and } H\ \right]^+$$

and then ring opening occurs with formation of 1,4-dicarbonyl compounds. Thus, under the conditions in which Eaborn and Sperry carried out the reaction (aqueous methanolic hydrochloric acid solution), opening of the furan ring is quite possible.

We reproduced Eaborn' s experiments with trimethylfurylsilane; however, in traps cooled to $-70°$, neither furan nor trimethylchlorosilane was detected. On this basis we believe that, in the case of furylsilanes under the action of hydrogen chloride, opening of the furan ring occurs first.

To some extent this conclusion is also confirmed by the slower destruction of diphenylmethylfurylsilane. As can be seen from Table 2, during the time in which the other furylsilanes were almost completely destroyed, diphenylmethylfurylsilane was destroyed by only 8-9%. Triphenylfurylsilane is also destroyed considerably more slowly.

Experimental Part

Preparation of furylsilanes. As the metallating reagent in our syntheses we used *n*-butyl- or phenyllithium, which were prepared by a known method (5), starting from 2.4 g of lithium and 1 g-mol of bromide, respectively. To an ethereal solution of the organolithium compound, 1 g-mol of furan was added dropwise, and then the mixture was heated for 3–4 h. After removal of unreacted lithium from the reaction medium, ···

the alkyl-(phenyl)-chlorosilane (in the case of trialkyl-(phenyl)-chlorosilane, in an amount of 0.45 g-mole) was added dropwise, and the reaction mixture was then heated for 6–8 h.

The ethereal solution of the furylsilanes obtained was washed with water and dried over calcium chloride. After the first distillation or recrystallization, the product was subjected to adsorption purification on silica gel.

Recording of heating curves. To record the heating curves, a 0.15 g sample of furylsilane was taken and heated in air in an apparatus for differential thermal analysis. Temperature measurements were carried out with a Kurnakov pyrometer with automatic recording of thermograms.

Study of chemical stability. Glacial acetic acid containing 12.5% HCl was poured into a three-necked flask equipped with a condenser and a dropping funnel. The flask was placed in a water bath, in which the temperature was maintained by a thermostat at $30 \pm 0.05°$. Stirring was carried out with an electromagnetic stirrer. After 0.5 h, a 50% solution of furylsilane in heptane was added to the reaction vessel.

Samples were periodically withdrawn from the reaction mixture; these were neutralized with sodium carbonate solution and then analyzed by gas–liquid chromatography.

In experiments with trimethylfurylsilane, the reaction vessel was connected to a trap cooled to $-70°$.

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Note: Figure translations are in progress. See original paper for figures.

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