

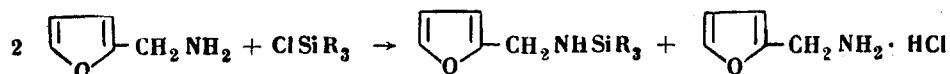
ORGANOSILICON COMPOUNDS OF THE FURAN SERIES. VI*. NITROGEN- AND SULFUR-CONTAINING ORGANOSILICON DERIVATIVES OF FURAN

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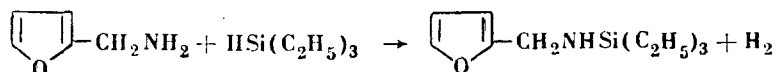
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Five new furfurylaminoorganosilanes and furfurylaminoalkyltriorganosilanes are synthesized by reacting furfurylamine with organylchlorosilanes, chloroalkyltriorganosilanes, and triorganylhydrosilanes. Furfuraldoxime readily reacts with triorganylchlorosilanes in the presence of triethylamine to give O-triorganylsilyl substituted oximes. It is shown for the first time that in the presence of H_2PtCl_6 aldoximes undergo dehydrocondensation with triorganosilanes, accompanied by reduction processes. Reaction of hexamethyldisilazane with pyromucamide gives the trimethylsilylamide. Pyromuconitrile and magnesium 3-(methyl-diethylsilyl)propyl chloride gives 1-furyl-4-(methyl-diethylsilyl)butanone-1. Reaction of organylchlorosilanes with furfurylmercaptan and sodium furfurylmercaptide permits synthesis of the first representatives of the sulfur-containing organosilicon derivatives of furan.

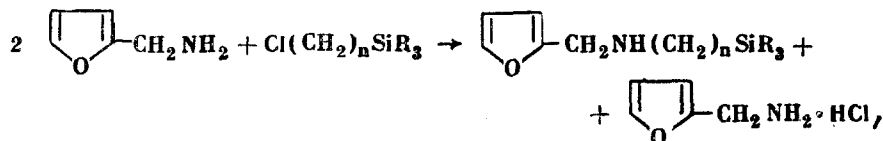
In the presence of chloroplatinic acid, alcohols and carboxylic acids of the furan series readily undergo dehydrocondensation with organylhydrosilanes [2, 3]. Generally speaking, there has so far not been any study made of the analogous reaction with compounds containing the amino and mercapto groups. The only paper mentioning the possibility of dehydrocondensation of triorganosilanes with amines in the presence of H_2PtCl_6 is wholly lacking in experimental data [4]. Furthermore, in all cases of hydrosilation of unsaturated amines, only addition of hydrosilane to the C=C bond takes place, and the N-H bond is unaffected [4-7]. No reaction of triethylsilane with furfurylamine was observed on boiling together for 6 hrs in the presence of chloroplatinic acid, either without a solvent or in tetrahydrofuran as solvent. Prior reduction of H_2PtCl_6 by triethylsilane without furfurylamine also gave no positive result. Consequently, furfurylaminosilanes were prepared by the reaction of furfurylamine with organochlorosilanes in ethereal solution according to the equation:



Trimethyl(α -furfurylamino)silane, dimethyl-bis-(α -furfurylamino)silane, and triethyl(α -furfurylamino)silane were synthesized in this way. The last-named was also prepared by dehydrocondensing furfurylamine with triethylsilane in the presence of potassium furfurylamide (cf. [8]).



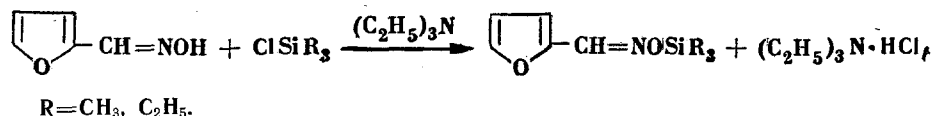
On boiling for 24 hrs in benzene with chloromethyltrimethylsilane and 3-chloropropyltriethylsilane, furfurylamine gives trimethyl(α -furfurylaminomethyl)silane and triethyl[3-(furfurylamino)propyl]silane, respectively.



R=CH₃, C₂H₅; n=1,3.

The reaction of furfurylamine with triorganyl(chloroalkyl)silanes can also be effected by using a 1:1 molar ratio of reactants in the presence of triethylamine, but it is necessary to heat the reaction mixture for much longer (up to 60 hrs).

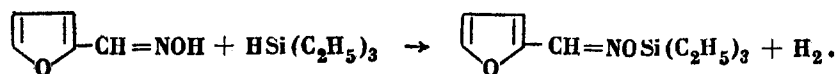
Furfuraldoxime reacts with triorganylchlorosilanes in the presence of triethylamine to give O-(triorganylsilyl)furfuraldoxime in 75-78% yield**:



*Part V, see [1].

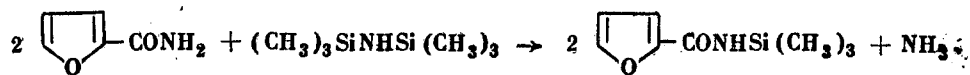
**An analogous reaction with oximes of aliphatic and aromatic aldehydes is known [9-13].

O-(triethylsilyl)furfuraldoxime is also formed by heating together triethylsilane and furfuraldoxime dissolved in tetrahydrofuran for 24 hrs in the presence of H_2PtCl_6 :

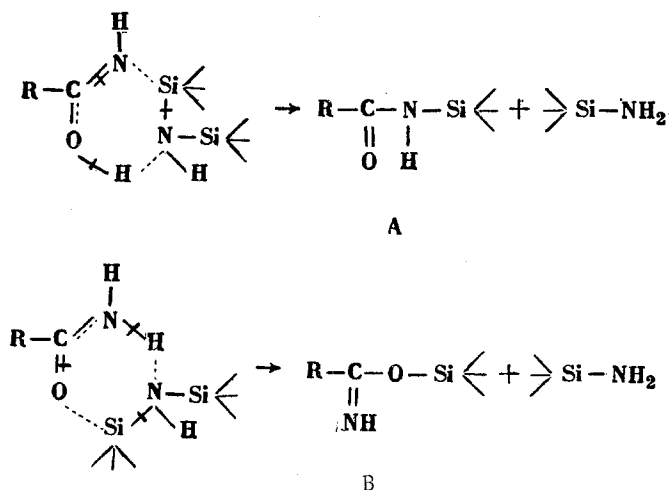


Here the yield of final reaction product is considerably less (about 34%) than in the synthesis from triethylchlorosilane. This is due to reduction side reactions, since triethylsilane and H_2PtCl_6 give a very active hydrogenation catalyst [14]. In the presence of such a catalyst the hydrogen evolved on reaction of triethylsilane with furfuraldoxime reduces the triethylsilylfurfuraldoxime formed. Accordingly, the reaction product is found to contain amines and triethylsilanol, indicating that reduction proceeds with splitting of the N-O bond.

Pyromucamide reacts readily with hexamethyldisilazane with separation of ammonia according to the equation:

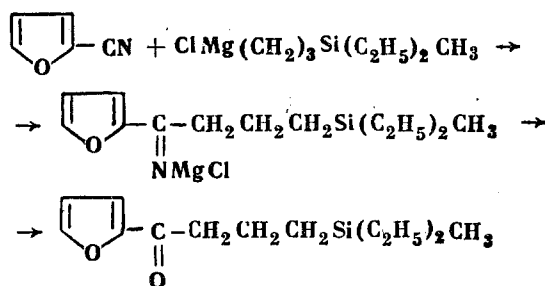


The monosilyl derivative is also obtained using excess hexamethyldisilane, so that in the first stage of the reaction a silyl-substituted amide and trimethylaminosilane are formed, after which condensation to disilazane and separation of ammonia occurs. The reaction can proceed through 6-membered activated complexes, with simultaneous attack on the silicon atoms and the nitrogen of the Si-N linkage in the hexamethyldisilazane:

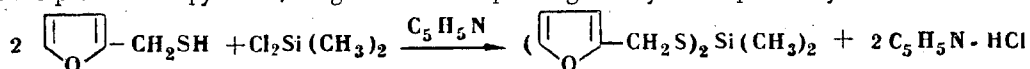


On the basis of the IR spectra of the products of a similar reaction, structure A, with a silyl group on the nitrogen atom [15], has been assigned to them. The IR spectrum of the trimethylsilylamide of pyromucic acid does not afford an unequivocal choice between structures A and B, since the amide band II, $\nu_{\text{Si-N}}$ and $\nu_{\text{Si-O(C)}}$, cannot be completely differentiated from the corresponding absorption bands of monosubstituted furans. The 1645 cm^{-1} absorption band observed in the spectrum of the compound prepared, may correspond to the amide band in compound A, and also to $\nu_{\text{C=N}}$ in compound B. The 3246 cm^{-1} absorption band can also be related to $\nu_{\text{N-H}}$ in both A and B.

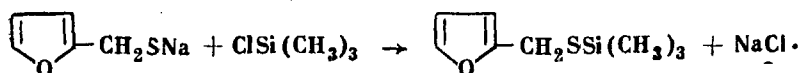
Pyromuconitrile reacts with magnesium 3-(methyldiethylsilyl)propyl chloride to give the amine of 1-furyl-4-(methyldiethylsilyl)butanone-1, which on hydrolysis is transformed into the corresponding ketone:



Furfurylmercaptan or furfurylamine and triethylsilane do not react when boiled together for 12 hrs in the presence of chloroplatinic acid. However, there is a slow reaction with trimethylchlorosilane and dimethyldichlorosilane in diethyl ether in the presence of pyridine, to give the corresponding furfurylmercaptomethylsilanes:



Somewhat better results are obtained by reacting trimethylchlorosilane with sodium furfurylmercaptide in benzene:



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

EXPERIMENTAL

Trimethyl(α -furfurylamino)silane. In a 3-necked flask fitted with a gastight mechanical stirrer, dropping funnel, and reflux condenser with calcium chloride tube, we place a solution of 19.4 g (0.2 mole) furfurylamine in 20 ml absolute ether. The flask is cooled in ice water, and 10.8 g (0.1 mole) trimethylchlorosilane in 15 ml ether are added dropwise while stirring. After all the triethylchlorosilane has been added, the reaction mixture is heated for 8 hrs on a steam bath. The precipitate of furfurylamine hydrochloride is filtered off and washed with ether. The ether is distilled off, and the residue distilled in a vacuum. Yield 10.7 g (63.2%) b.p. 85-86° (31 mm).

Triethyl(α -furfurylamino)silane and dimethyl-bis-(α -furfurylamino)silane are prepared in a similar way.

Triethyl(α -furfurylamino)silane. 0.05 g (0.00125 g-at) metallic potassium is dissolved in 9.8 g (0.101 mole) furfurylamine. 11.6 g (0.1 mole) triethylsilane are added to the resultant brown solution, and the whole refluxed for 6 hrs. The liquid is separated from the dark brown precipitate and distilled in a vacuum. Yield 16.4 g (77.5%), b.p. 89° (2 mm).

No reaction was observed in a similar experiment where 0.1 ml 0.1 M H_2PtCl_6 in isopropanol was used as catalyst instead of potassium. In another series addition of 20 ml tetrahydrofuran did not lead to positive results.

Triethyl[3-(α -furfurylamino)propyl]silane. A solution of 19.4 g (0.2 mole) furfurylamine and 19.2 g (0.1 mole) 3-chloropropyltriethylsilane in 40 ml dry benzene is refluxed 24 hrs, and then decomposed with 20% KOH solution. The benzene layer is separated and dried over potash. The solvent is distilled off, and the residue distilled in a vacuum. Yield 12 g (47.6%), b.p. 131° (1.5 mm).

Chloromethyltrimethylsilane and furfurylamine, when reacted, likewise give trimethyl(α -furfurylaminomethyl)silane (54.2%). A 39.7% yield of the same compound is obtained by refluxing for 60 hrs a solution of 9.7 g (0.1 mole) chloromethyltrimethylsilane, and 10.1 g (0.1 mole) triethylamine in 25 ml benzene.

O-triethylsilylfurfuraldoxime. A solution of 7.5 g (0.05 mole) triethylchlorosilane in 10 ml benzene is added, with stirring and ice cooling, to a mixture of 5.5 g (0.05 mole) furfuraldoxime, 5.2 g (~0.05 mole) triethylamine, and 10 ml dry benzene; then the reaction mixture is refluxed for 8 hrs. The precipitated triethylamine hydrochloride is filtered off and washed with benzene. The solvent is taken off under a water pump. Yield 8.8 g (78.2%) b.p. 92° (3 mm). IR spectrum ν cm^{-1} : 1503(21); 1540(17); 1565(21); 1610(36); 1645(20).

O-trimethylsilylfurfuraldoxime is obtained in a similar way.

Refluxing for 24 hrs a solution of 5.5 g (~0.05 mole) furfuraldoxime, 5.8 g (0.05 mole) triethylsilane, and 0.1 ml 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (in isopropanol) in 10 ml tetrahydrofuran gives 3.8 g (33.8%)

Nitrogen- and sulfur-containing organosilicon derivatives of furan

Compound*	B. p., °C (pressure, mm)	n_D^{20}	d_4^{20}	MR _D		Empirical formula	N, %		Si, %		Yield %
				Found	Calculated		Found	Calculated	Found	Calculated	
$\text{FuCH}_2\text{NHHSi(CH}_3)_3$	85-86 (31)	1.4570	0.9246	49.87	50.35	$\text{C}_8\text{H}_{15}\text{NOSi}$	8.00	8.27	16.32	16.43	63.2
$\text{FuCH}_2\text{NHSi(CH}_2\text{H}_5)_3$	89 (2)	1.4656	0.9218	63.46	63.88	$\text{C}_{11}\text{H}_{21}\text{NOSi}$	6.57	6.63	13.21	13.24	64.8**
$(\text{FuCH}_2\text{NH})_2\text{Si(CH}_3)_2$	120-121 (2)	1.4971	1.0593	69.18	70.42	$\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2\text{Si}$	10.95	11.19	10.85	10.92	57.1
$\text{FuCH}_2\text{NHCH}_2\text{Si(CH}_3)_3$	86-87 (12)	1.4671	0.9252	54.99	55.77	$\text{C}_9\text{H}_{17}\text{NOSi}$	7.39	7.64	15.02	15.11	54.2
$\text{FuCH}_2\text{NHCH}_2\text{CH}_2\text{Si(CH}_3)_3$	131 (1.5)	1.4807	0.9263	77.83	78.56	$\text{C}_{14}\text{H}_{27}\text{NOSi}$	5.41	5.53	10.91	11.01	47.6
$\text{FuCH=NOSi(CH}_3)_3$	74 (10)	1.4849	0.9976	52.65	51.39	$\text{C}_8\text{H}_{13}\text{NO}_2\text{Si}$	7.54	7.64	15.00	15.13	76.9
$\text{FuCH=NOSi(CH}_2\text{H}_5)_3$	91-92 (3)	1.4920	0.9881	66.17	64.92	$\text{C}_{11}\text{H}_{19}\text{NO}_2\text{Si}$	6.06	6.22	12.17	12.28	78.2
$\text{FuCONHSi(CH}_3)_3$	m. p. 86-88					$\text{C}_8\text{H}_{15}\text{NO}_2\text{Si}$	7.81	7.64	15.24	15.28	92.4
$\text{FuCOCH}_2\text{CH}_2\text{CH}_2\text{Si(CH}_3)_2$	122-123 (2)	1.4805	0.9404	72.08	70.41	$\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si}$			11.32	11.43	21
$\text{FuCH}_2\text{SSi(CH}_3)_3$	94-95 (11)	1.5020	0.9937	55.37	55.80	$\text{C}_8\text{H}_{13}\text{OSSi}$			14.73	14.87	35
$(\text{FuCH}_2\text{S})_2\text{Si(CH}_3)_2$	130-135 (2)	1.5050	1.0321	81.75	81.32	$\text{C}_{12}\text{H}_{16}\text{O}_2\text{S}_2\text{Si}$			9.46	9.57	30.7

**77.5% on synthesis from $(\text{C}_2\text{H}_5)_3\text{SiH}$

*Fu 2-furyl

O-triethylsilylfurfuraldoxime, triethylsilanol, and an unidentified mixture of amines.

Trimethylsilylpyromucamide. 3.33 g (0.03 mole) pyromucamide is suspended in 9.68 g (0.06 mole) hexadimethyldisilazane, and the mixture boiled until evolution of ammonia ceases. The crystals formed are filtered off from excess hexamethyldisilazane, and recrystallized from hexane. Yield 5.08 g (92.4%) b.p. 86-88°.

IR spectrum (in Nujol) ν cm⁻¹: 857, 890, 938, 1015, 1022, 1034, 1083, 1102, 1129, 1405, 1435, 1455, 1475, 1485, 1562, 1580, 1625, 1642, 3106, 3135, 3246, 3360.

1-Furyl-4-(methyldiethylsilyl)butanone-1. 4.8 g (0.2 g-at) magnesium and 50 ml dry ether are placed in a 3-necked round bottomed flask fitted with a gastight mechanical stirrer, dropping funnel, and reflux condenser with a calcium chloride tube. A crystal of iodine is added to start the reaction; this is followed by a mixture of 0.5 ml ethyl bromide plus 4.5 ml of a solution of 35.8 g (0.2 mole) methyldiethyl(3-chloropropyl)silane in 40 ml ether. The rest of this ethereal solution is added fast enough to keep the ether boiling steadily, after which the mixture is heated on a steam bath until all the magnesium has dissolved. 14.3 g (0.16 mole) pyromuconitrile in 15 ml ether is added to the resultant solution of magnesium 3-(methyldiethylsilyl)propyl chloride. The reaction mixture is heated on a steam bath for 6 hrs, and decomposed next day with 20% acetic acid. The ether layer is separated, neutralized with soda solution, and dried over magnesium sulfate. The ether is distilled off, and the residue thrice vacuum-fractionated, to give 8.0 g (21%) b.p. 122-123° (2 mm). In the IR spectrum we have $\nu_{C=O}$ 1673 (79) cm⁻¹.

Trimethyl(furfurylmercapto)silane. 2.3 g (0.1 g-at) sodium are dissolved in 11.4 g (0.1 mole) furfurylmercaptan diluted with 50 ml benzene. 10.8 g (0.1 mole) trimethylchlorosilane are added to the resultant suspension of sodium furfurylmercaptide, and the mixture refluxed for 8 hrs with vigorous stirring. The precipitate is filtered off and washed with benzene, the solvent distilled off, and the residue distilled in a vacuum to give 6.5 g (35%) b.p. 94-95° (11 mm).

Dimethyl-bis-(furfurylmercapto)silane was similarly prepared (yield 30.7%). 20 hrs refluxing of 11.4 g (0.1 mole) furfurylmercaptan, 6.5 g (0.05 mole) dimethyldichlorosilane, and 9.5 g (0.12 mole) pyridine in 30 ml ether gives a 16.2% yield of the same compound.

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