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FURAN DERIVATIVES OF GROUP IV ELEMENTS (REVIEW)

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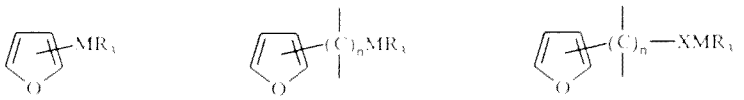
Published data and the results of personal investigations on the methods of synthesis, chemical and physical properties, and biological activity of the furan derivatives of silicon, germanium, tin, lead, titanium, and zirconium are summarized.

1. DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

The furan derivatives of group IVB elements represent a fairly widely studied class of compound, among which it is possible to single out several main types: Compounds in which the heteroorganic substituent is directly attached to the furan ring (I); compounds in which the heteroorganic substituent is separated from the ring by a hydrocarbon chain (II); compounds in which the element of group IVB is separated from the heterocycle by another heteroatom or carbofunctional group (III).

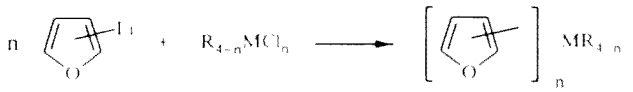


I II III

The physicochemical characteristics and the methods of preparation differ substantially, depending on the type of compound.

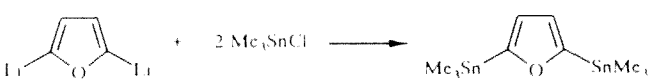
1.1. Synthesis of Compounds of Type I

1.1.1. Lithium Method. A general method for the synthesis of the furan derivatives of silicon, germanium, tin, and lead of type I is the reaction of 2- and 3-furyllithium and also their derivatives with halogenosilanes [1-25], halogenogermanes [3, 6-8, 15, 26-28], halogenostannanes [3, 6-8, 14, 15, 29, 30], and halogenoplumbanes [3, 6-8].



M = Si, Ge, Sn, Pb, R = Alk, Ar, n = 1–4

The reaction is usually carried out by adding the chlorine derivative of the group IVB element to a solution of lithiofuran in ether, hexane, or tetrahydrofuran at 0-25°C. The corresponding distannyl derivative was obtained from 2,5-dilithiofuran [31].



Latvian Institute of Organic Synthesis, Riga, Latvia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1587-1690, December, 1995. Original article submitted June 3, 1995.

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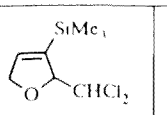
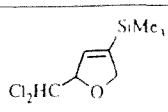
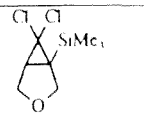
TABLE 1. Reaction of 3-Trimethylsilyl-2,5-dihydrofuran with Dichlorocarbene under the Conditions of Phase-Transfer Catalysis

Method of generation of $:CCl_2$*	Temperature °C	Reaction time, h	Product yields according to GLC		
					
A	25	1	23	17	44
B	25	5	20	23	32
C	40 45	8	21	31	32
D	63	55	16	26	16

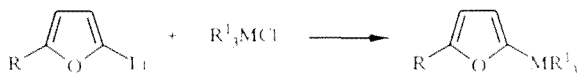
*A) The action of a 50% aqueous solution of sodium hydroxide on chloroform in the presence of $PhCH_2N^+Bu_3Cl^-$.

B) The action of solid powdered sodium hydroxide on chloroform in the presence of $(C_8H_{17})_3N^+MeCl$.

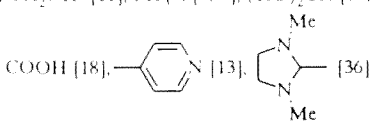
C) The conditions of method B without the catalyst but with ultrasonic treatment.

D) The thermal decomposition of sodium trichloroacetate in the presence of $PhCH_2N^+Bu_3Cl^-$.

By means of the lithium synthesis it is possible to obtain compounds containing the most varied groups in the heterocycle [5, 7, 11-23, 27, 32-36].

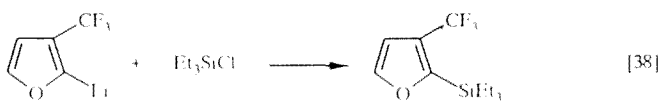


M = Si; R = Me [4], CH_2OR^2 [11], Me_3Si [4, 7], $(RO)_2CH$ [12, 34, 35], CH=NOH [14],

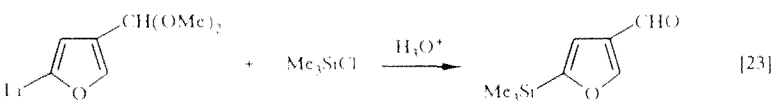


M = Ge; R = Me_3Si, Me_3Ge [7], $(EtO)_2CH$ [27]

M = Sn; R = Me [37], $PhCH_2CH_2$ [37], Me_3Si, Me_3Ge [7], $(RO)_2CH$ [37]



[38]



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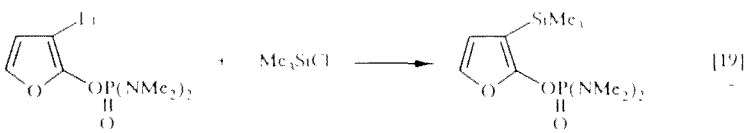

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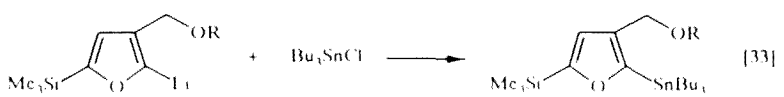
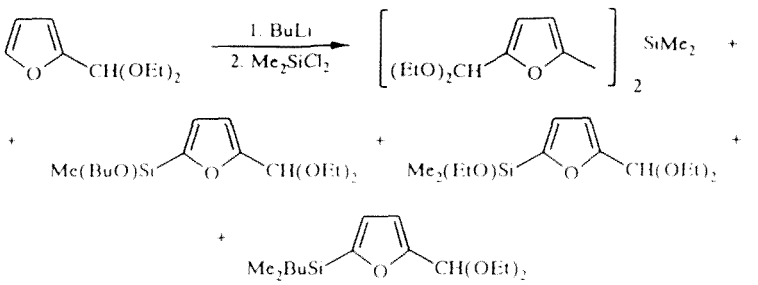
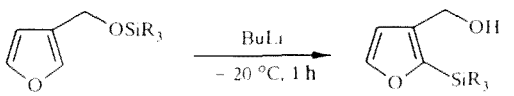


[33]

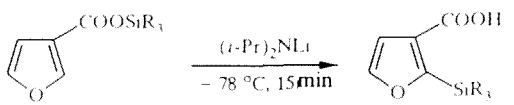
Whereas the silylation of the lithium derivative of furfural diethyl acetal [34, 35] with trialkylchlorosilanes takes place without complications at −25 to −30°C in ether and hexane, the reaction with dimethylchlorosilane under the same conditions leads to the formation of a whole series of silylation products [34].



The silylation of the furan ring in 3-(trialkylsilyloxymethyl)furans at −20°C in a mixture of hexamethylphosphorotriamide and dimethoxyethane or tetrahydrofuran by the action of butyllithium [25, 39] and of trialkylsilyl 3-furancarboxylates at −78°C in a mixture of hexamethylphosphorotriamide and tetrahydrofuran by the action of lithium diisopropylamide [40] takes place by an intramolecular mechanism of 1,4-O→C silyl migration.



R_3Si = t-$BuMe_2Si$ (87%), $(i\text{-}Pr)_3Si$ (86%), t-$BuPh_2Si$ (87%), t-$PrMe_2Si$ (24%)

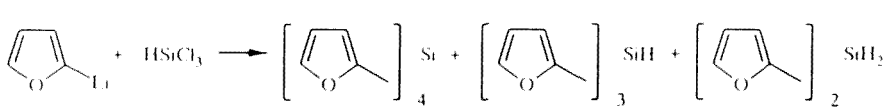


R_3Si = t-$BuMe_2Si$ (72%), $(i\text{-}Pr)_3Si$ (56%), Bu_3Si (51%), Et_3Si (57%), t-$BuPh_2Si$ (43%)

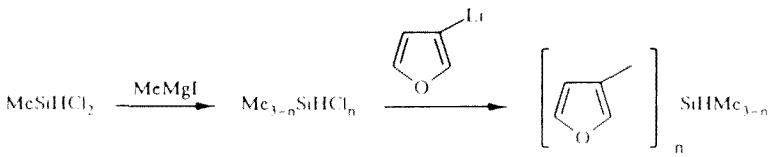
In the case of 3-[dimethyl(isopropyl)silyloxymethyl]furan 2,5-bis[dimethyl(isopropyl)silyl]-3-hydroxymethylfuran was isolated in addition to the monosilyl product, while only 3-hydroxymethylfuran was obtained from 3-(trimethylsilyloxymethyl)furan [25].

A whole series of silicofunctional furylsilanes were also synthesized by the lithium method. Furylhydrosilanes were obtained by this method [4, 5, 8, 41, 42]. On account of the high reactivity of the Si−H bond in furylhydrosilanes and the possible substitution of hydrogen by the organic radical during the action of organolithium reagents, the reaction is usually carried with cooling and with the addition of the furyllithium derivatives to the silane.

However, under these conditions only dimethylchloro- and methyldichlorosilane form the corresponding furylhydrosilanes with high yields [5], while in trichlorosilane further substitution of the hydrogen in the Si−H bond occurs even at −30°C [5, 43], and tetra(2-furyl)silane, tri(2-furyl)silane, and di(2-furyl)silane are formed in ratios of 11:9:1 [43].

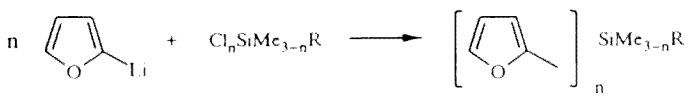


The formation of the di(2-furyl)silane is due to the reduction of the intermediate di(2-furyl)chlorosilane by the lithium hydride formed under the reaction conditions. Representatives of 3-furylhydrosilanes were obtained [8] by the successive addition of methylmagnesium iodide and 3-furyllithium to methylchlorosilane. Methyltri(3-furyl)silane is not formed under these conditions [8].



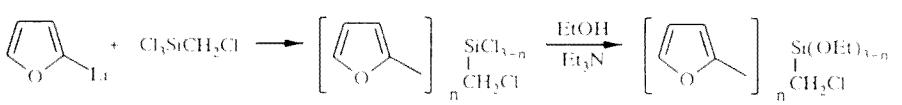
n = 1, 2

Furylchloromethylsilanes [43-45] and furylvinylsilanes [45,46] are formed with high yields from 2-furyllithium and the corresponding chlorosilanes.



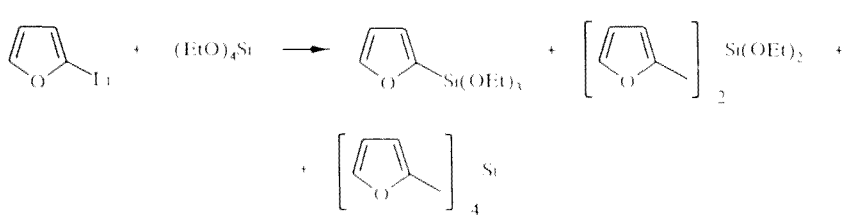
R = CH_2Cl, $CH{=}CH_2$; n = 1, 2

With the 2-furyllithium and chloromethyltrichlorosilane in a ratio of 2:1.17 a mixture of (2-furyl)chloromethylchlorosilanes was formed [43]. With ethanol in the presence of triethylamine they underwent alcoholysis.



n = 1...3

The main product from the reaction of 2-furyllithium with tetraethoxysilane at −30°C in tetrahydrofuran is 2-furyltriethoxysilane (9.8%). Small amounts of di(2-furyl)diethoxysilane and tetra(2-furyl)silane were found among the reaction products. It was not possible to synthesize tri(2-furyl)ethoxysilane by this method. It was also not isolated with furyllithium and tetraethoxysilane in ratios of 2:1 and 3:1. The yields of 2-furyltriethoxy- and tetra(2-furyl)silanes were only increased under these conditions [47].



Pentamethyl(2-furyl)disiloxane was obtained with an 82% yield by opening the ring in cyclotrisiloxane with 2-furyllithium followed by treatment of the intermediate lithium silanolate with trimethylchlorosilane [48].

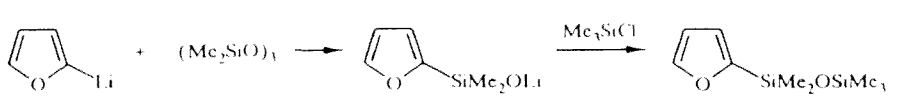
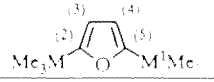


TABLE 2. Chemical Shifts δ in the ^{1}H, ^{13}C, ^{17}O, ^{29}Si, ^{73}Ge, ^{119}Sn, and ^{207}Pb NMR Spectra of Furan Derivatives R_nMMe_{4-n}

R	M	n	δ M, ppm	δ ^{17}O, ppm	δ ^{13}C, ppm					δ ^{1}H, ppm				
					$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	Me	$H_{(2)}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	Me
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2-Furyl	C	1	32,9	237,5	164,2	102,1	109,9	140,7	29,3	–	5,82	6,12	7,22	1,25
2-Furyl	Si	1	-11,5	252,7	160,2	120,0	109,7	146,7	-1,3	–	6,52	6,27	7,56	0,26
2-Furyl	Si	2	-24,7	253,2	157,1	121,8	109,9	147,4	-3,0	–	6,64	6,29	7,59	0,51
2-Furyl	Si	3	-39,2	252,7	154,3	123,8	110,2	148,2	-4,6	–	6,77	6,30	7,61	0,80
2-Furyl	Si	4	-56,0	253,2	151,4	125,5	110,4	149,1	–	–	6,89	6,36	7,67	–
2-Furyl	Ge	1	-22,1	252,3	160,4	117,8	109,5	146,1	-1,9	–	6,56	6,41	7,52	0,38
2-Furyl	Ge	2	-56,1		157,5	119,6	110,1	146,8	-2,9	–	6,54	6,28	7,55	0,64
2-Furyl	Ge	3	-79,5		154,4	121,2	110,2	147,4	-4,2	–	6,66	6,29	7,57	0,91
2-Furyl	Ge	4	-115,0		151,3	122,6	110,4	148,3	–	–	6,77	6,37	7,62	–
2-Furyl	Sn	1	-54,2	259,3	160,2	121,2	109,5	147,1	-9,2	–	6,47	6,29	7,60	0,32
2-Furyl	Sn	2	-115,8		157,9	122,5	109,9	147,8	-9,4	–	6,60	6,33	7,63	0,57
2-Furyl	Sn	3	-184,7		155,5	123,5	109,9	148,2	-9,7	–	6,71	6,35	7,65	0,84
2-Furyl	Sn	4	-260,1		153,1	124,7	110,2	149,0	–	–	6,83	6,42	7,72	–
2-Furyl	Pb	1			164,2	120,2	109,5	146,6	-1,4	–	6,34	6,25	7,52	1,00
Furfuryl	Si	1	1,2		154,5	104,0	110,7	140,2	-1,3	–	5,72	6,13	7,13	0,07
2-Furylethyl	Si	1	1,4		158,3	104,4	110,3	140,7	-1,5	–	5,89	6,19	7,31	0,10
3-Furyl	Si	1	-9,7		147,7	119,1	113,6	143,5	-0,3	7,38	–	6,41	7,52	0,24
3-Furyl	Si	2	-19,6		148,7	117,4	113,8	143,8	-1,1	7,39	–	6,41	7,52	0,44
3-Furyl	Si	3	-29,6		149,7	116,0	114,1	144,0	-1,6	7,42	–	6,45	7,54	0,64
3-Furyl	Si	4			150,5	114,3	114,3	144,3	–	7,44	–	6,49	7,57	–
3-Furyl	Ge	1			146,2	119,6	113,5	143,5	-0,9	7,31	–	6,38	7,52	0,36
3-Furyl	Ge	2			147,0	117,7	113,7	143,7	-1,5	7,35	–	6,41	7,54	0,57
3-Furyl	Ge	3			147,7	116,1	113,9	144,0	-1,9	7,39	–	6,44	7,57	0,78
3-Furyl	Ge	4			148,4	114,5	113,9	144,3	–	7,42	–	6,47	7,59	–
3-Furyl	Sn	1	-40,4		147,7	115,3	115,0	143,3	-9,1	7,34	–	6,46	7,63	0,28
3-Furyl	Sn	2	-80,1		148,3	114,0	115,2	143,6	-9,3	7,34	–	6,43	7,61	0,47
3-Furyl	Sn	3	-118,9		148,8	112,6	115,1	143,8	-9,2	7,39	–	6,46	7,62	0,65
3-Furyl	Sn	4	-157,4		149,3	111,4	115,1	144,2	–	7,44	–	6,50	7,65	–
3-Furyl	Pb	1	-76,7		147,9	120,5	116,1	143,2	-1,93	7,25	–	6,44	7,58	0,98
2-(4,5-Dihydro-furyl)	Si	1	-11,0	88,4	162,7	110,8	31,1	70,6	-1,8	–	5,20	2,59	4,28	0,16
2-(4,5-Dihydro-furyl)	Si	2	-23,2		159,6	113,3	31,2	70,9	-3,9	–	5,35	2,61	4,32	0,30
2-(4,5-Dihydro-furyl)	Si	3	-37,1		156,4	115,6	31,3	71,1	-6,0	–	5,53	2,65	4,35	0,45
2-(4,5-Dihydro-furyl)	Si	4	-51,9		153,8	118,0	31,3	71,3	–	–	5,71	2,66	4,38	–

TABLE 3. Chemical Shifts δ in the ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR Spectra of 2,5-Disubstituted Furans [7, 434]

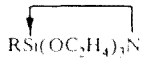
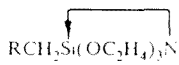
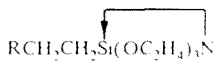


M	M^1	δ_{M}, ppm	δ_{M^1}, ppm	δ ^{13}C, ppm						δ ^{1}H, ppm			
				$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	Me_3M	Me_3M^1	$H_{(3)}$	$H_{(4)}$	Me_3M	Me_3M^1
Si	Si	−11,4		164,4	119,8			−1,3		6,48	6,48	0,27	
Si	Ge	−11,7		164,6	119,9	117,9	165,0	−1,3	−1,5	6,37	6,48	0,27	0,42
Si	Sn	−11,5	−55,2	165,0	119,6	120,5	164,5	−1,3	−9,4	6,53	6,62	0,27	0,34
Ge	Ge			164,2	117,9			−1,5		6,38	6,38	0,42	
Ge	Sn		−55,3	165,2	117,5	120,7	163,6	−1,9	−9,7	6,45	6,45	0,24	0,42
Sn	Sn									6,43	6,43	0,34	

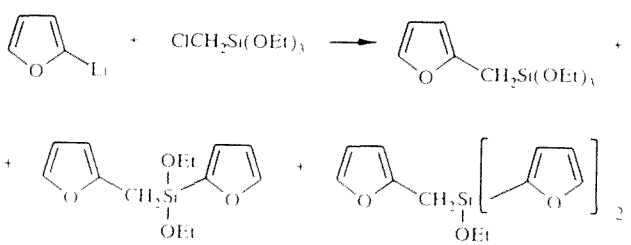
TABLE 4. Chemical Shifts $\delta\ ^1H_{Si}$, $\delta\ ^{17}O$, and $\delta\ ^{29}Si$ and the Spin—Spin Coupling Constants (Si—H) of Furylhydrosilanes (R = 2-furyl, R^1 = 3-furyl)

Compound	$\delta\ ^1H_{Si}$, ppm	$\delta\ ^{29}Si$, ppm	$^1J_{Si-H}$, ppm	$\delta\ ^{17}O$, ppm
$RSiHMe_2$	4,41	-28,49	195,0	253,0
R_2SiHMe	4,94	-42,23	208,9	253,2
R_2SiHEt	4,86	-37,25	206,0	253,6
R_2SiHBu	4,88	-39,39	205,7	254,2
$R^1{}_2SiHMe$	4,84	-36,80	198,6	250,2
R_3SiH	5,45	-57,60	224,0	252,7

TABLE 5. Chemical Shifts δ^1H, ^{13}C, and ^{29}Si of Furylethoxysilanes and Furylaminoalkoxysilanes (R = 2-furyl) [344]

Compound	$\delta\ ^{29}Si$, ppm	$\delta\ ^{13}C$, ppm				$\delta\ ^1H$, ppm		
		$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$
$RC(OEt)_3$	—	158,8	117,9	112,0	146,4	7,19	6,52	7,59
$RSi(OEt)_3$	-67,2	151,9	123,4	109,6	147,5	7,02	6,42	7,69
$R_2Si(OEt)_2$	-50,6	153,0	124,0	109,8	147,9	6,94	6,44	7,72
R_3SiOEt	-43,9	153,5	125,3	110,4	148,8	7,00	6,47	7,77
$RCH_2Si(OEt)_3$	-53,0	151,5	105,4	110,7	140,4	—	—	—
$RCH_2CH_2Si(OEt)_3$	—	158,1	104,2	110,3	140,8	6,00	6,27	7,30
	-89,3	163,0	117,9	109,1	144,6	6,64	6,30	7,56
	-73,4	157,4	103,8	110,4	139,3	5,92	6,24	7,24
	-68,0	161,5	103,6	110,6	140,6	5,96	6,25	7,27
$R(EtO)Si(OC_2H_4)_2NMe$	-80,5	158,1	119,3	109,3	145,4	6,65	6,30	7,55
$R_2Si(OC_2H_4)_2NMe$	-69,4	159,2	120,1	109,8	146,1	—	—	—
$RSi(OC_2H_4NMe_2)_3$	-66,4	151,6	124,1	110,0	148,0	6,89	6,38	7,66

The reaction of 2-furyllithium with chloromethyltriethoxysilane takes place both at the C—Cl bond and at the Si—O bond [47].



3-Furyltriethoxysilane was obtained with a 25% yield from 3-furyllithium and tetrachlorosilane followed by alcoholysis with ethanol in the presence of pyridine [47].

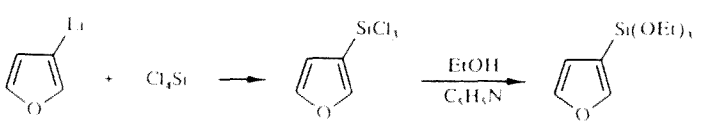
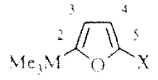


TABLE 6. $\delta^{1}H$, ^{17}O, ^{13}C, and ^{29}Si Chemical Shifts of 5-Substituted 2-Trimethylsilyl- and 2-Trimethylgermylfurans [401]



X	M	$\delta^{29}Si$, ppm	$\delta^{17}O$, ppm	$\delta^{13}C$, ppm					$\delta^{1}H$, ppm		
				$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	MMe_3	$H_{(3)}$	$H_{(4)}$	MMe_3
H	Si	−11,5	252,7	160,2	120,0	109,7	146,7	−1,3	6,52	6,27	0,26
Me	Si	−11,7		158,9	120,9	106,3	156,9	−0,7	6,73	6,13	0,26
CH_2NH_2	Si	−11,8	252,7	163,4	121,9	106,1	158,7	−0,6	6,67	6,22	0,25
$CH(OEt)_2$	Si	−11,1		160,3	121,2	108,7	157,6	−0,9	6,70	6,40	0,27
CHO	Si	−8,7	249,0	168,7	123,2	123,2	157,2	−1,2	7,06	7,55	0,34
COOH	Si	−9,7	241,5	166,2	122,7	118,4	150,3	−0,9	6,92	7,22	0,32
CN	Si	−8,4	258,3	169,7	122,2	123,7	129,6	−1,3	7,05	7,61	0,31
NO_2	Si	−7,5		167,4	122,0	111,7	156,7	−1,8	6,85	7,36	0,41
CH=NOH (*Z*)	Si	−10,5		162,2	123,1	117,3	150,4	−0,9	7,23	6,96	0,31
CH=NOH (*E*)	Si			161,1	122,6	112,1	153,2	−1,0	6,84	6,71	0,30
$CH=NNHC(O)NH_2$	Si	−10,7		162,3	123,0	111,5	153,3	−0,8	6,84	6,85	0,30
$CH=NNHC(S)NH_2$	Si	−10,4		163,4	123,2	113,0	154,8	−0,7	6,85	6,97	0,26
CH=CHCHO	Si	−10,1		164,3	123,4	116,2	155,5	−0,9	6,98	7,13	0,34
H	Ge		252,3	160,4	117,8	109,5	146,1	−1,9	6,66	6,48	0,42
Me	Ge			159,4	119,2	106,2	156,3	−1,5	6,43	5,97	0,39
$CH(OEt)_2$	Ge			165,9	115,6	120,6	151,7	−1,5	6,49	6,41	0,41
CHO	Ge			171,1	120,8	121,8	157,5	−1,5	6,71	7,25	0,49
COOH	Ge			161,4	108,4	118,8	156,6	−1,5	6,67	7,34	0,49
CN	Ge			170,4	119,4	122,1	126,2	−1,7	6,61	7,08	0,46
CH=NOH (*Z*)	Ge			163,4	121,3	117,4	150,2	−1,2	7,28	6,63	0,50
CH=NOH (*E*)	Ge			162,5	120,8	112,1	152,6	−1,1	6,57	6,57	0,44

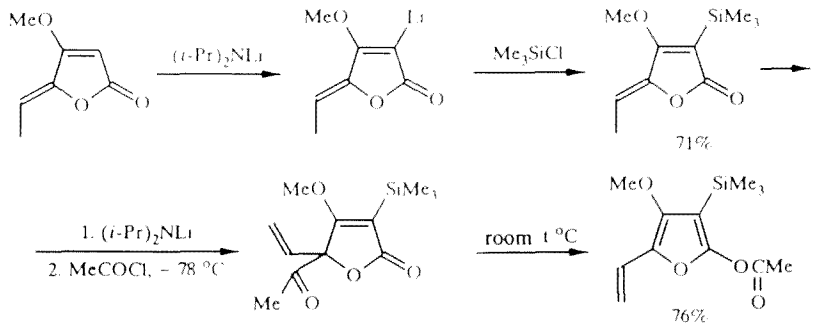
TABLE 7. δ ^{17}O Chemical Shifts of the Carbonyl Group of 5-R-Substituted Furfurals in CD_3CN

R	δ ^{17}O (C=O), ppm	R	δ ^{17}O (C=O), ppm
t-Bu	523.2	Me_3Ge	533.0
Me	521.7	Me_3Si	537.1
H	537.8	NO_2	574.8

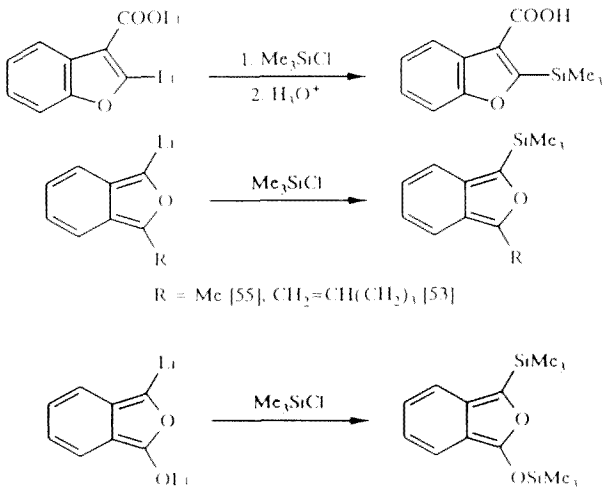
The furylchlorosilanes were not isolated on account of their instability and were only used in the synthesis as intermediate products [43, 47]. At the same time, furylbromogermanes [28] were more stable and were isolated in the pure form. Thus, the reaction of an ether solution of tetrabromogermane with 2-furyllithium in a ratio of 5:1 at −35°C gave a mixture of 2-furyltribromogermane, di(2-furyl)bromogermane, and tetra(2-furyl)germane. The use of an equimolar ratio of the initial substances also led to the indicated mixture of products, but the fraction of the tribromo and dibromo products was greatly reduced [28].

n = 1...4

In addition to the lithium derivatives of furan, the lithium compounds of butenolides [49, 50], obtained during metallation with lithium diisopropylamide at low temperatures, were also used for the synthesis of silylfurans.



The organolithium method of synthesis is extremely useful for the production of the organosilicon derivatives of benzofuran [51, 52], isobenzofuran [53-56], naphtho[1,2-c]furan [57], and 2,3-dihydrofuran [58-61], and also the organotin derivatives of 2,3-dihydrofuran [61, 62].

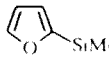
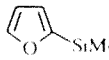
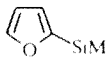
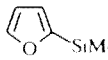
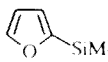
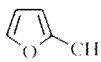
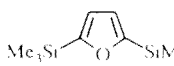
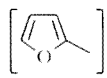
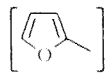
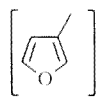
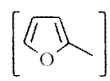
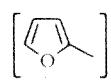


[51, 52]

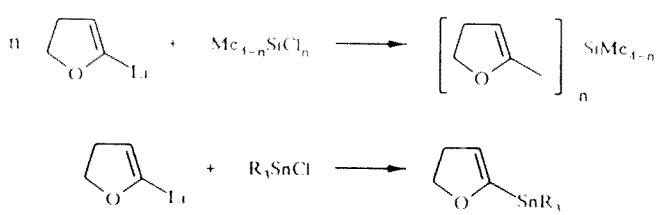
R = Me [55], CH_2=$CH(CH_2)_3$ [53]

[56]

TABLE 8. Ionization Potentials (eV) of Furylsilanes

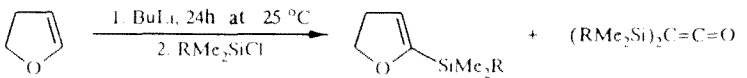
Compound	IP_1	IP_2	Reference
	8,37	10,14	[443]
	8,92	10,40	[443]
	8,62	10,22	[443]
	8,53	10,14	[443]
	8,62	10,13	[443]
	8,38	10,08	[443]
	8,44	9,94	[445]
	8,48	10,01	[444]
	8,53	10,07	[443]
	8,15	10,00	[444]
	8,16	9,67	[445]
	8,79	10,31	[443]
	8,71	10,20	[443]
	8,84	10,07	[443]
	8,60	10,18	[443]
	8,75	10,33	[443]
	9,23	10,07	[443]
	8,66	10,20	[443]
	8,33	9,96	[444]

5-(2,3-Dihydrofuryl)silanes and stannanes were obtained with 65-80% yields by the treatment of 5-(2,3-dihydrofuryl)lithium with methylchlorosilanes [58] and stannanes [61] in tetrahydrofuran at −20°C.



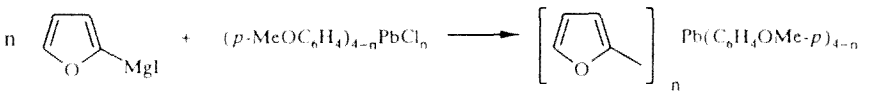
A similar reaction in tetrahydrofuran [58] or in a mixture of ether and hexane [59, 63, 64] gave hydrosilanes containing the 5-(2,3-dihydrofuryl) group at the silicon atom. Under these conditions, however, not only the chlorine atoms but also the hydrogen of the Si–H bond is substituted. Thus, 6% of dimethylbis[5-(2,3-dihydrofuryl)]silane was also isolated during the synthesis of dimethyl[5-(2,3-dihydrofuryl)]silane, obtained with a yield of 50%. The yield of the hydrosilane with two dihydrofuryl groups amounted to 22% with an 18% yield of methyltris[5-(2,3-dihydrofuryl)]silane. By conducting the reaction with trichlorosilane even at −70°C it was possible to obtain a small yield (13%) of tris[5-(2,3-dihydrofuryl)]silane, while the main product was tetra[5-(2,3-dihydrofuryl)]silane (45%) [63].

If the lithium derivative is kept at 25°C for 24 h before the addition of the chlorosilane, disilylketenes are formed in addition to the dihydrofurylsilanes on account of degradation of the 5-(2,3-dihydrofuryl)lithium [60].



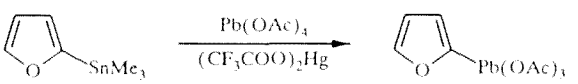
R = H, Me

2-Furylmagnesium iodide was also used for the introduction of a 2-furyl group [65], but 2-furylmercury chloride did not enter into reaction with chlorosilanes [66] and chlorostannanes [67].

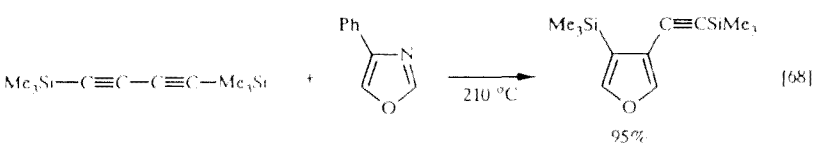


n = 1, 2

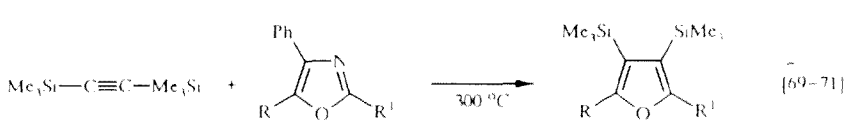
Trimethyl- and tributyl(2-furyl)stannanes react readily with lead tetraacetate (ratio 1:1) in the presence of a catalytic amount of mercury(II) trifluoroacetate in deuterochloroform with the formation of triacetyl(2-furyl)plumbane [499].



1.1.2. Cyclization. Various types of cyclization reaction have been used for the synthesis of organosilicon furan compounds of type I. Of great practical interest is the unusual Diels–Alder retro-reaction between phenyloxazoles and silyl- or stannylacetylene compounds [68-72], which takes place in sealed tubes at elevated temperature and leads to 3,4-disubstituted furans.

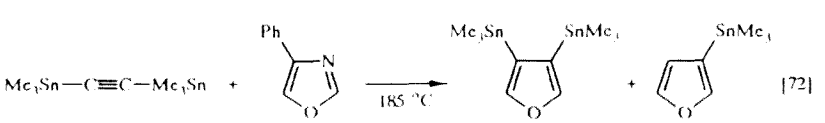


[68]



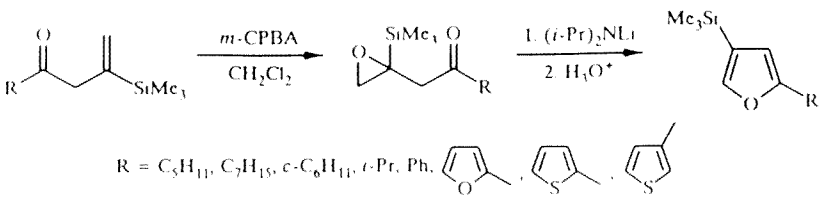
[69–71]

R = R¹ = H; R = Me, R¹ = H; R = Me, R¹ = D

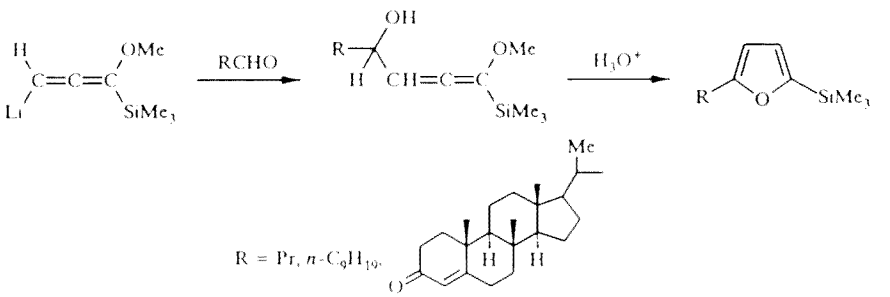


[72]

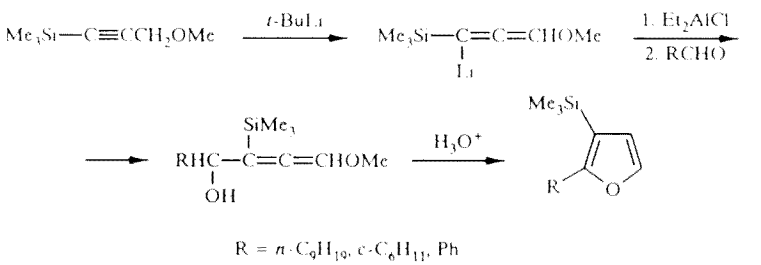
2-Substituted 4-trimethylsilylfurans can be obtained from silylenones by a two-stage synthesis [73, 74]: initially the double bond is epoxidized by m-chloroperbenzoic acid, and the furan derivatives are then formed with 60-80% yields in reaction with lithium diisopropylamide [73, 74] or *tert*-butyllithium [74].



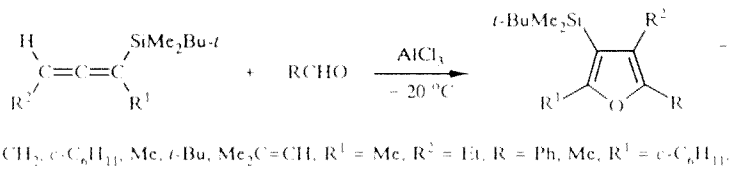
Various furylsilanes were obtained by the cyclization of allene systems. Thus, it was established that the lithium derivative of 1-trimethylsilyl-1-methoxyallene is transformed into 2-trimethylsilyl-5-alkylfurans in the presence of aliphatic aldehydes [75].



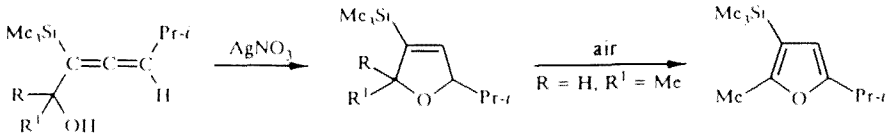
It was possible to increase the yield of 3-trimethylsilylfurans by substituting the lithium atom in 1-trimethylsilyl-1-lithio-3-methoxyallene by a diethylaluminum group by the action of diethylaluminum chloride on the lithium derivative at −78°C [76]. Without the aluminum reagent the yield of 2-cyclohexyl-3-trimethylsilylfuran amounts to 30%, while in the presence of diethylaluminum chloride the yield is increased by more than twice (67%).



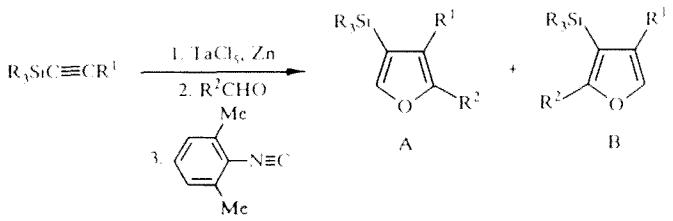
A furan ring is also formed in the reaction of silylallenes with acyl ions, which are generated in the reaction of the acid chlorides with aluminum chloride in methylene chloride. Various tetrasubstituted furans were obtained with high yields by this method [77].



Under the influence of silver nitrate in an inert atmosphere α-silylallene alcohols undergo cyclization to 3-trimethylsilyl-2,5-dihydrofurans with yields of 42-72%. In air the compounds with R = H undergo autooxidation to the corresponding 3-trimethylsilylfurans [78].



2,3,4-Trisubstituted furans were obtained by treating the silylalkyne complex of low-valent tantalum, synthesized from the silylalkyne, tantalum pentachloride, and zinc in a mixture of dimethoxyethane and benzene at 25°C, with aldehydes, followed by the addition of an isocyanide [79,80].

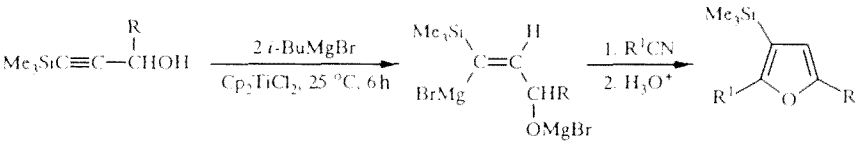


R_3Si = Me_3Si; R^1 = n-$C_{10}H_{21}$, Ph; R^2 = Pr

R_3Si = t-$BuMe_2Si$; R^1 = n-$C_{10}H_{21}$, Ph; R^2 = Pr

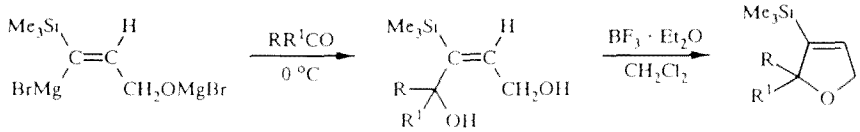
The reaction with trialkylsilylacetylenes is highly regioselective, and the isomer A is mostly formed (94-98%) [79].

The hydromagnesiation of 3-trimethylsilylprop-2-yn-1-ol with isobutylmagnesium in the presence of a catalytic amount of dicyclopentadienyldichlorotitanium followed by treatment of the intermediate (Z)-vinyl Grignard reagent with nitriles gives 3-trimethylsilylfurans with yields of up to 88% [81,82].



R = H, Pr; R^1 = Me, Et, i-Pr, Ph

If ketones are used instead of nitriles in a similar reaction [83], (E)-but-2-ene-1,4-diols are formed with high yields as intermediate products and are quickly dehydrated to 3-trimethylsilyl-2,5-dihydrofurans by the action of boron trifluoride etherate.



3-Tributylstannylfuran was obtained by the addition of the stannyl cuprate reagent ($Bu_3SnCu \cdot Me_2S \cdot LiBr$) to the triple bond of but-2-yne-1,4-diol in tetrahydrofuran, followed by the oxidation of 2-tributylstannylbut-2-ene-1,4-diol with pyridinium chlorochromate in methylene chloride at 0°C [84].

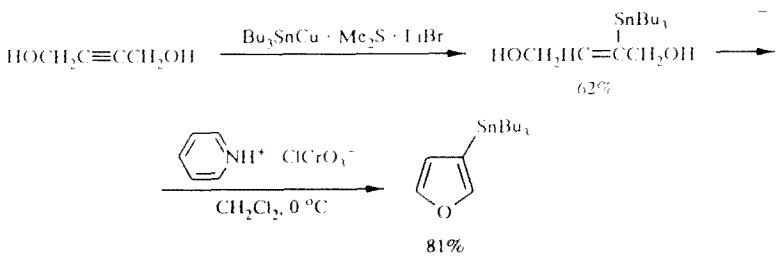
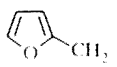
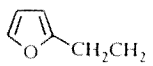
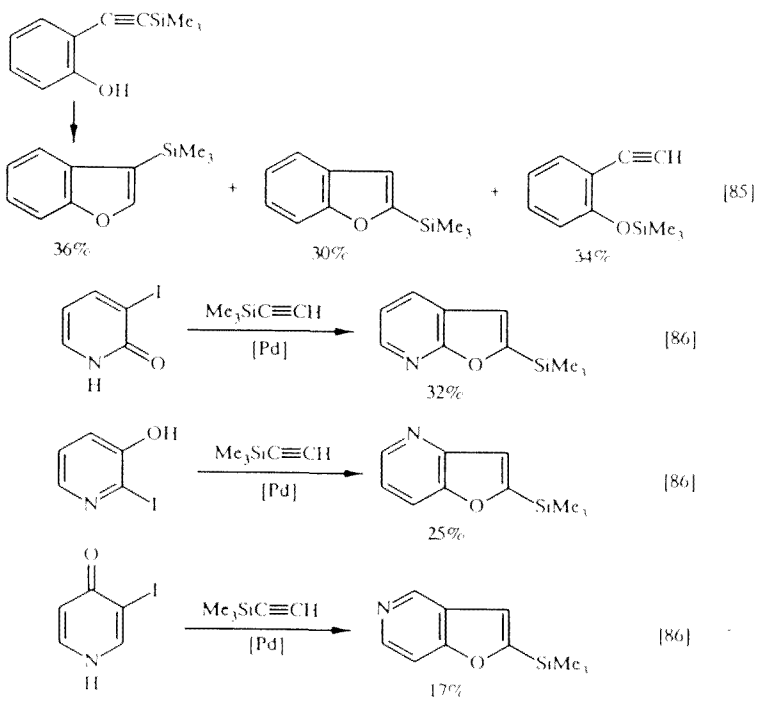


TABLE 9. Charge Transfer Frequencies in the Spectra of the Charge Transfer Complexes of Furan Derivatives R_nMMe_{4-n} with TCE (R = 2-furyl [448], 3-furyl [450])

R	n	ν_{ct}, cm^{-1}				
		M - C	M - Si	M - Ge	M - Sn	M - Pb
2-Furyl	1	19150	20400	20000	—	—
2-Furyl	2	—	20900	20700	19750	—
2-Furyl	3	—	22000	21600	19700	—
2-Furyl	4	—	22750	22200	21750	—
	1	—	18200	—	—	—
	1	—	19400	—	—	—
3-Furyl	1	20400	21200	20800	20400	20000
3-Furyl	2	—	21400	21100	20800	—
3-Furyl	3	—	21800	21300	21000	—
3-Furyl	4	—	22100	21400	21200	—

A mixture of isomeric 2- and 3-trimethylsilylbenzofurans [85] can be obtained by vacuum flash photolysis of o-trimethylsilylethynylphenol at 750°C. Furopyridines are formed with low yields from 3-iodo-2-pyridone, 2-iodo-3-hydroxypyridine, and 3-iodo-4-pyridone by heating in a sealed tube with trimethylethynylsilane in triethylamine under the influence of the palladium catalyst $(Ph_3P)_2PdCl_2$ and CuI [86].

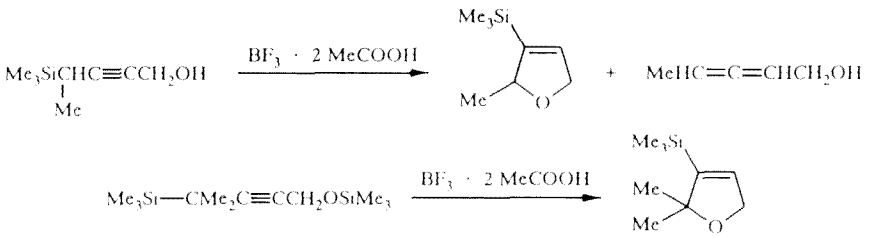


The formation of 3-trimethylsilyl-2,5-dihydrofurans during the cyclization of silylallenes [78] and the derivatives of 2-trimethylsilylbut-2-ene-1,4-diols [83] has already been discussed above. The cyclization of the silyl derivatives of propargyl alcohol in the presence of Lewis acids [87, 88] and the dehydration of silyl- and germylbut-2-ene-1,4-diols [89-93] have become convenient methods for the synthesis of 3-silyl-2,5-dihydrofurans.

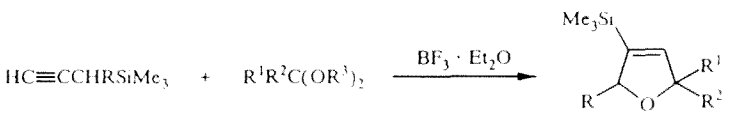
TABLE 10. Experimental and Calculated Parameters of the Stretching Vibrations of the Si—H Bond in the IR Spectra of Furylhydrosilanes (R = 2-furyl)

Compound	ν_{expt}, cm^{-1}	$\Delta\nu = \nu_{calc} - \nu_{expt}$, cm^{-1}	Compound	ν_{expt}, cm^{-1}	$\Delta\nu = \nu_{calc} - \nu_{expt}$, cm^{-1}
$RSiH_3$	2177	12	R_2SiH_2	2174	28
$RSiHMe_2$	2141	6	R_2SiHMe	2158	25
RSiHMeEt	2137	7	R_2SiHEt	2152	27
$RSiHEt_2$	2130	12	R_2SiHBu	2152	26
$RSiHBu_2$	2131	10	$R_2SiH(CH_2Cl)$	2184	22
RSiHMePh	2145	15	R_3SiH	2173	43

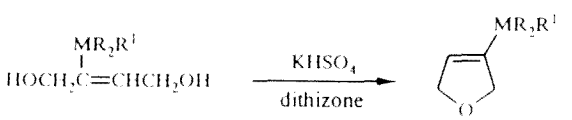
In the presence of $BF_3 \cdot 2CH_3COOH$ in methylene chloride at $-5°C$ the silyl derivatives of propargyl alcohol give a mixture of the allene formed as a result of protodesilylation and the cyclization product 3-trimethylsilyl-2,5-dihydrofuran. The ratio of these products depends on the ratio of the propargyl compound and the complex of boron trifluoride with acetic acid. If the ratio of $Me_3SiCHMeC \equiv CCH_2OH$ and $BF_3 \cdot 2CH_3COOH$ is changed from 1:1 to 1:2, the yield of the allene is reduced from 27% to <5%, while the yield of 3-silyl-2,5-dihydrofuran is increased from 67% to 78%. Only the cyclic product is formed from 4-methyl-4-trimethylsilyl-1-trimethylsilyloxypent-2-yne under the influence of $BF_3 \cdot 2CH_3COOH$ (1:1) with a yield of 82% [87].



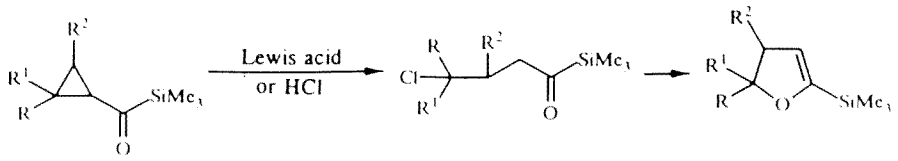
Under the influence of boron trifluoride etherate propargyltrimethylsilanes $HC \equiv CCHRSiMe_3$ enter into reaction with various acetals $R^1R^2C(OR^3)_2$, and as a result 3-trimethylsilyl-2,5-dihydrofurans are formed in addition to the ethers containing an allene group [88]. The yield can be increased by using silane $-BF_3 \cdot Et_2O-$acetal ratios of 1:2:1, and in the case of R = Me, R^1 = H, and R^2 = i-Bu, it amounts to 80%.



The dehydration of silylbut-2-ene-1,4-diols, obtained during the hydrosilylation of but-2-yne-1,4-diols, in the presence of $KHSO_4$ and dithizone gives yields of 68-80%. In contrast to this the yield of 3-trimethylgermyl-2,5-dihydrofuran does not exceed 10% on account of cleavage of the C—Ge bond. A milder dehydrating agent (a mixture of triphenylphosphine and diethyl diazodicarboxylate) was therefore used to increase the yield to 50% [90].

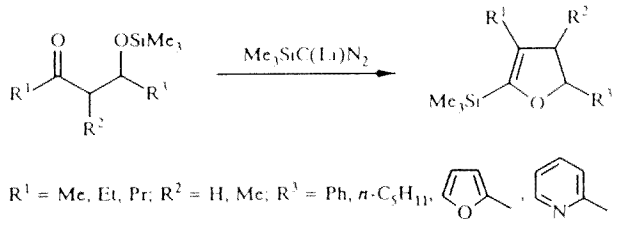


During opening of the ring in cyclopropyl trimethylsilyl ketones by Lewis acids ($SnCl_4$, $BF_3 \cdot Et_2O$, $TiCl_4$, HCl) under mild conditions at $-70°C$ either linear products (3-chloropropyl trimethylsilyl ketones) or cyclic 2-trimethylsilyl-4,5-dihydrofurans are formed, depending on the substituents R, R^1, and R^2. Cyclization with ring enlargement does not occur for cyclopropyl trimethylsilyl ketones with R = R^1 = R^2 = H; R = H and R^1 = R^2 = Me; and R = R^2 = Me and R^1 = H [94, 95].



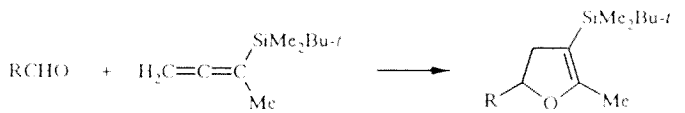
R = R¹ = Me, R² = H (74% $SnCl_4$, 71% $BF_3 \cdot Et_2O$)
R = R² = H, R¹ = Ph (56% $TiCl_4$; 70% HCl)

β-Trimethylsilyloxy ketones react with lithium derivatives of trimethylsilyldiazomethane and form 2-trimethylsilyl-4,5-dihydrofurans (yields 23-90%) [96].

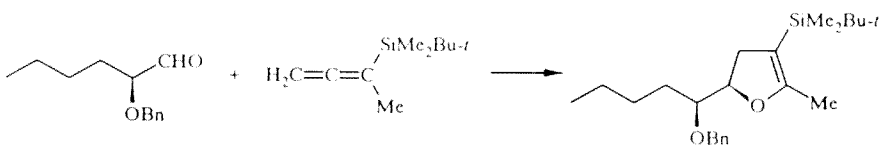


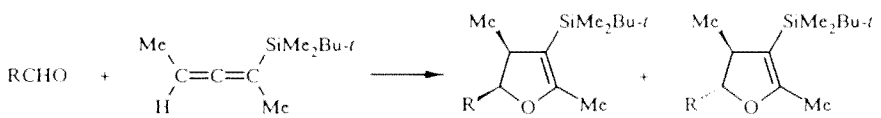
R^1 = Me, Et, Pr; R^2 = H, Me; R^3 = Ph, *n*-C_5H_{11},

In methylene chloride at −78°C under the influence of titanium tetrachloride silylallenes undergo cyclization with aldehydes to 3-silyl-4,5-dihydrofurans. In many cases the reaction is stereoselective. For example, only one isomer was obtained from chiral α-benzyloxyhexanal and 1-methyl-1-dimethyl(*tert*-butyl)silylallene. 1,3-Dimethyl-1-dimethyl(*tert*-butyl)silylallene reacts with achiral aldehydes with the preferential formation of the *cis*-substituted dihydrofurans [97].



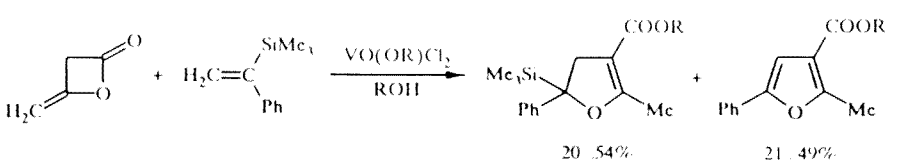
R = *c*-C_6H_{11} (76%), $PhCH_2CH_2$ (70%)



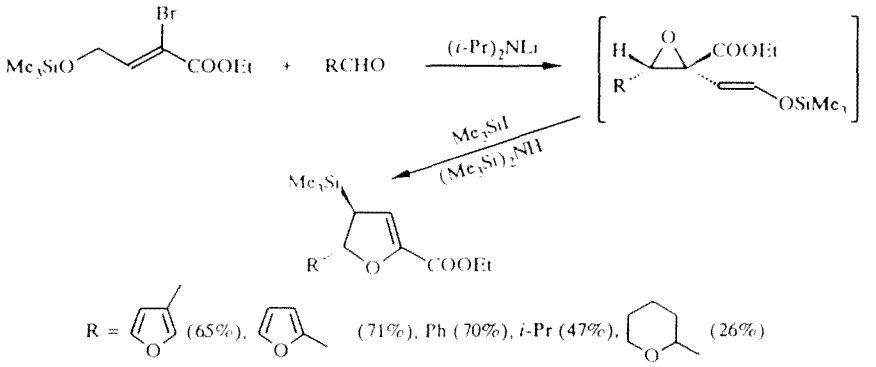


R = Me (78%, *cis*:*trans* = 1.4 : 1)
R = *c*-C_6H_{11} (97%, *cis*:*trans* = 7 : 1)
R = *t*-Bu (92%, *cis*)

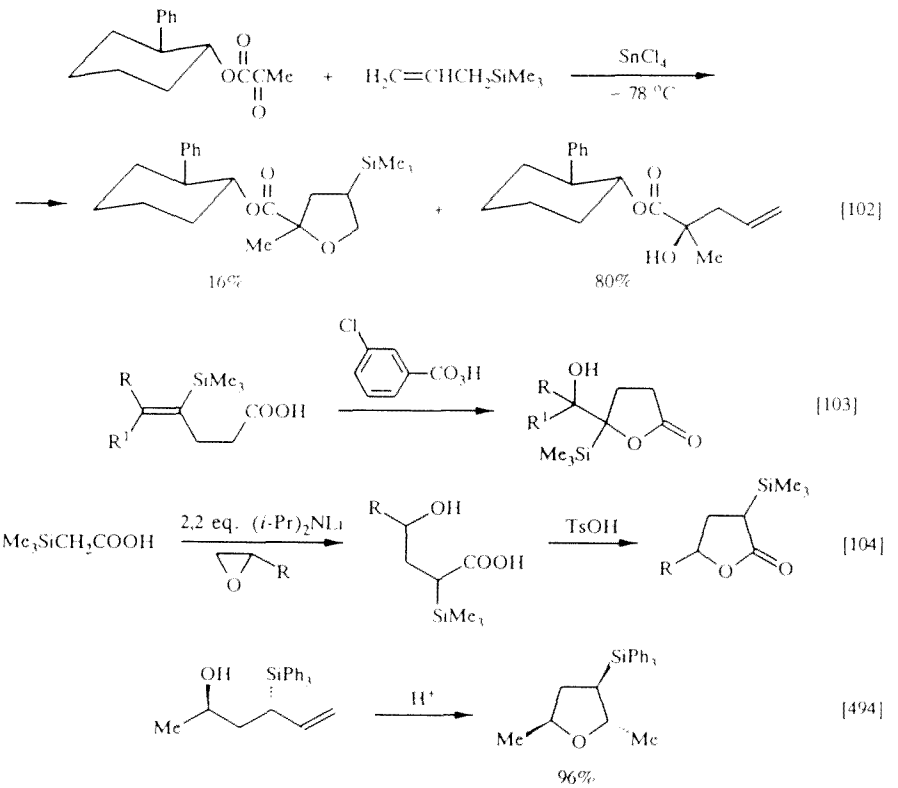
Diketene enters into cyclization with α-silylstyrene under the influence of vanadium complexes $VO(OR)Cl_2$ at −75°C. As a result, their aromatization products are formed together with the 2-trimethylsilyl-2-phenyl-5-methyl-3-alkoxycarbonyl-2,3-dihydrofuran [98]. The yield of the furan compounds is increased if the reaction mixture is heated and also in the presence of oxygen.



The rearrangement of the silyl ethers of enols containing an oxirane ring (formed in turn in the reaction of the lithium derivative of ethyl 2-bromo-4-silyloxycrotonate with aldehydes) at the double bond was used for the synthesis of 3-trimethylsilyl-2,3-dihydrofurans. The rearrangement takes place at −78°C under the influence of Me_3SiI and $(Me_3Si)_2NH$ [99].



Compounds of the silyltetrahydrofuran series were also obtained by the cyclization method [100-104, 494].



1.1.3. Other Methods of Synthesis. A convenient method for the production of 3-silyl-substituted furans is the reaction of silylbutenolide, synthesized from silylcyclobutenone and m-chlorobenzoic acid, with diisobutylaluminum hydride in tetrahydrofuran at −20°C [105].

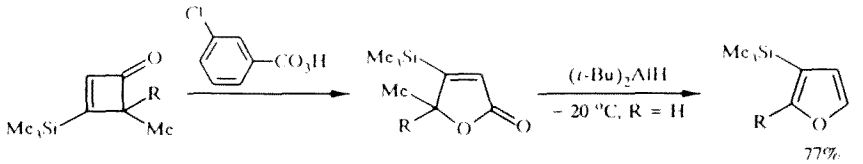


TABLE 11. Isomer Shifts of Furylstannanes in the Mössbauer Spectra

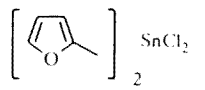
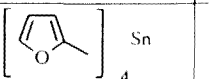
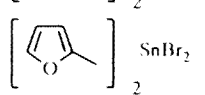
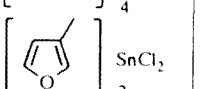
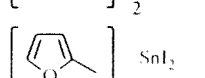
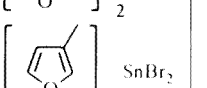
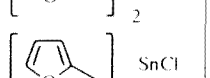
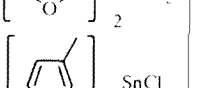
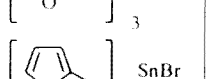
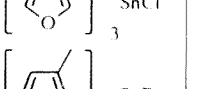
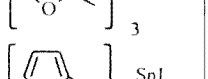
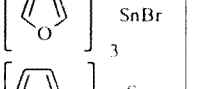
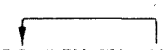
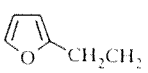
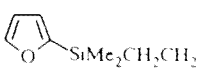
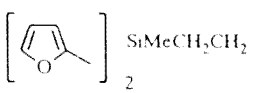
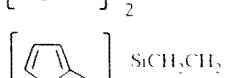
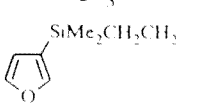
Compound	δ, mm/sec	Reference	Compound	δ, mm/sec	Reference
	1,10	[111,112]		1,06	[458]
	1,17	[111,112]		1,14	[112]
	1,34	[111]		1,23	[112]
	1,14	[111,112]		1,12	[112]
	1,17	[111,112]		1,18	[112]
	1,23	[111]		1,09	[112]

TABLE 12. Retention Parameters of Silatranes [460] 

R	I		ΔI	$\delta I = I_{expt} - I_{calc}$	
	Apiezon	OV-225		Apiezon	OV-225
	1996	3317	1324	530	1190
	1980	3029	1139	420	910
	1963	3097	1134	390	870
	2020	2953	933	350	620
	2132	2988	856	660	510
	2473	3537	1064	150	350
	2778	4068	1290	60	270
	2032	3002	970	110	420

The silylation of furan with the trimethylsilyl cation Me_3Si^+, obtained by γ-radiolysis of CH_4/Me_4Si mixtures in the gas phase, in the presence of triethylamine takes place selectively at position 2 of the furan ring, but the yield of 2-trimethylsilylfuran by this method is very small and does not exceed 3% [106].

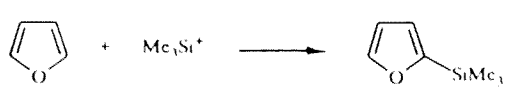
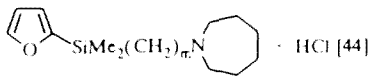
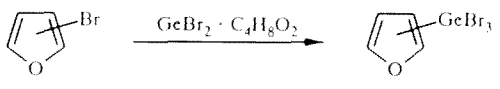


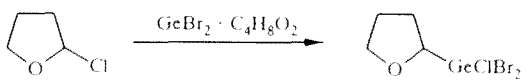
TABLE 13. Physiological Activity of the Hydrochlorides of Perhydroazepinoalkylsilanes



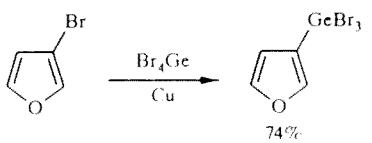
m	LD_{50}, mg/kg	ED_{50}, mg/kg		
		"Rotating rod"	"Tube"	Hypothermia
1	78 (58...105)	9 (6...15)	9 (6...15)	26 (11...35)
2	72 (38...137)	6 (4...8)	6 (4...8)	—
3	70 (64...77)	14 (7...28)	13 (8...19)	23 (14...39)

As already mentioned above [28], furylbromogermanes can be obtained by means of the lithium synthesis, but the reaction is not selective and a mixture of mono-, di-, and trifurylbromogermanes and also tetrafurylgermane is formed. It is possible to obtain 2- and 3-furyltribromogermanes [107, 108] and 2-tetrahydrofurylchlorodibromogermane [107] by the insertion of germanium dibromide, generated from germanium dibromide dioxanate, at the C–Br and C–Cl bonds of the halogen derivatives of furan. The insertion product from 2-chlorotetrahydrofuran is formed even when the mixture of reagents is boiled in benzene. In the case of bromofurans the reaction was conducted in a sealed tube at 130°C.

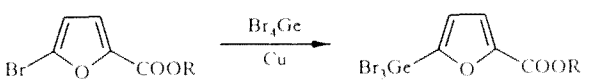




3-Furyltribromogermane [109] and 2-furyltribromogermanes with an ester group in the heterocycle [110] can be synthesized from the corresponding bromofurans and tetrabromogermane in the presence of copper powder. In the case of 3-bromofuran the reaction was conducted at 200°C in a sealed tube, while the esters of 5-bromo-2-furoic acids react in the boiling mixture. 2-Bromofuran, 2-bromo-5-nitrofuran, and 5-bromo-2-furancarboxylic acid do not enter into this reaction [110].

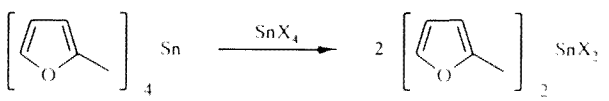


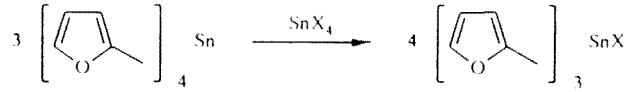
74%



R = Me, Et

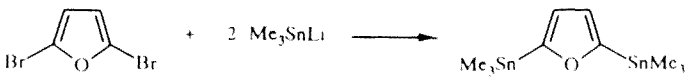
Furylhalogenostannanes [111, 112] can be obtained very easily by the disproportionation of tetrafurylstannanes and tetrahalogenostannanes. The difuryl and trifuryl derivatives can be obtained depending on their ratio.



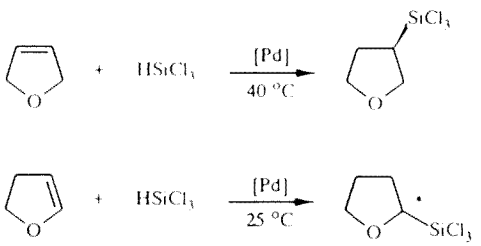


X = Cl, Br, I

It was not possible to synthesize 2,5-bis(trimethylstannyl)furan from 2-trimethylstannylfuran by the lithium synthesis on account of cleavage of the $SN-C_{furan}$ bond by the action of butyllithium. However, this compound is formed quickly and with a high yield (50-60%) in the reaction of 2,5-dibromofuran with trimethylstannyllithium [7]:

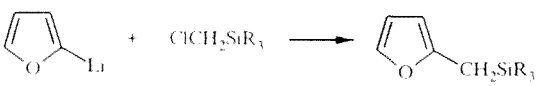


It was not possible to hydrosilylate 2,3- and 2,5-dihydrofurans with alkylhydrosilanes in the presence of various catalysts (elements of group VIII), but trichlorosilane adds to the C=C double bond of dihydrofurans with a high yield. In the presence of a palladium catalyst $[PdCl(\pi\text{-}C_3H_5)]_2$ and (R)-2-methoxy-2'-diphenylphosphino-1,1'-binaphthyl, the reaction takes place with high regioselectivity (optical purity 95%) [113].

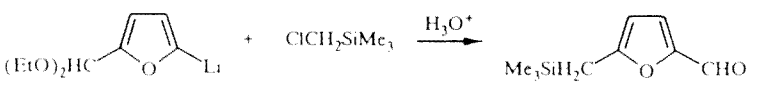


1.2. Synthesis of Compounds of Type II

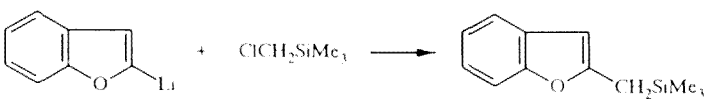
Like compounds of the first type, the furan derivatives of group IVB elements of type II, in which the furan ring is separated from the metal atom by a carbon chain, can be obtained by the lithium synthesis [2-4, 35, 47, 114-117]. Thus, furfurylsilanes [2-4,35,47] and 2-trimethylsilylmethylbenzofuran [116] were obtained during the reaction of the lithium derivatives and chloromethylsilanes.



R = Me [116], Et [4], EtO [47]

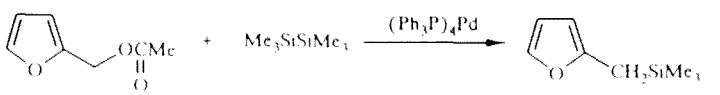


[35]



[116]

An extremely convenient and simple method for the synthesis of furfuryltrimethylsilane is the catalytic conversion of furfuryl acetate by the action of hexamethyldisilane. At 140°C in the presence of tetrakis(triphenylphosphino)palladium, the reaction takes 2 h and gives a yield of 37% [118].



Furfurylchlorodibromogermane is formed with a 44% yield by the insertion of germanium dibromide at the C–Cl bond of furfuryl chloride when the reaction mixture is heated in a sealed tube at 200°C [108].

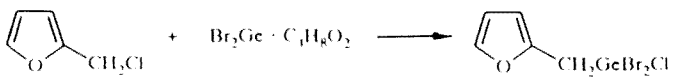
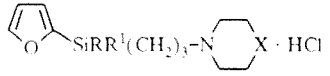
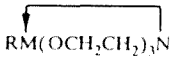


TABLE 14. Physiological Activity of Furylaminopropylsilanes



R	R^1	X	LD_{50}, mg/kg	ED_{50}, mg/kg		
				"rotating rod"	"tube"	hypothermia
Me	Me	NMe	205 (146...287,6)	47,7 (24,8...76,7)	59 (17,0...127,0)	47,7 (24,8...76,7)
Me	Et	NMe	163 (108,7...226,7)	70,8 (43...101,9)	112 (64,8...163,9)	103 (67,6...138,4)
Me	Bu	NMe	258 (168,5...357,1)	56,4 (39,9...74,3)	60 (31,7...93,0)	51,5 (29,1...78,6)
Me	$C_{12}H_{25}$	NMe	163 (108,7...226,7)	7 (4,3...11,5)	6 (3,2...9,3)	28,2 (18,3...37,2)
Et	Et	NMe	282 (182,9...378,7)	70,8 (50,1...92,5)	35,5 (24,9...46,1)	65 (43,8...88,6)
Bu		NMe	103 (67,4...138,4)	51,4 (36,2...69,2)	41 (26,8...55,2)	51,5 (36,2...69,2)
Me	Me	O	447 (313...596)	187 (53...383)	137 (50...262)	129 (84...179)
Me	Bu	O	325 (218,8...454,8)	81,5 (57,7...111)	46 (15,3...86,1)	81,5 (56,7...111)
Me	$C_{12}H_{25}$	O	410 (221...622)	16,3 (10,7...22,7)	12,9 (8,4...17,8)	19 (9,6...30,8)
Et	Et	O	447 (312,6...695,7)	59 (16,7...120,4)	>158	92 (133...174,6)
Me		O	112 (64,8...163,9)	112 (79...147,1)	129 (84,5...178,6)	129 (84,5...178,6)
Bu		O	355 (202...508)	118 (29...240)	129 (84...179)	103 (67,4...138,4)

TABLE 15. Physiological Activity of Furylsilatranes [421, 476] and Furylgermatranes [108]



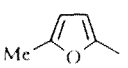
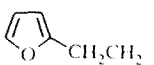
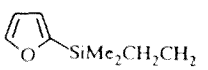
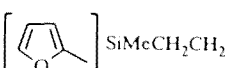
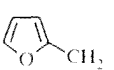
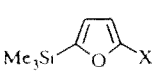
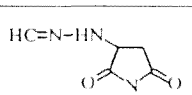
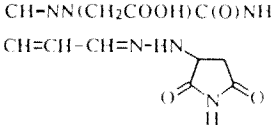
R	M	LD_{50}, mg/kg	ED_{50}, mg/kg			
			"rotating rod"	"tube"	hypothermia	analgesia
	Si	125 (107...146)	14,5 (8...26)	14,5 (8...26)	14,5 (8...26)	9,3 (8...11)
	Si	14,5 (11...19)	1,5 (1...2)	1,5 (1...2)	1,5 (1...2)	>3
	Si	2100 (1273...3465)	10 (6...18)	10 (6...18)	16 (11...20)	16,5 (9,4...28,9)
	Si	235 (147...376)	14 (11...19)	16 (11...25)	14 (11...19)	75 (50...113)
	Si	700 (569...861)	14 (10...22)	20 (13...32)	25 (16...39)	120 (73...198)
	Si	2450 (1600...3675)	92 (59...143)	92 (59...143)	>500	160 (80...320)
	Ge	2050 (1460...2880)	41 (37...55)	41 (37...55)	45 (26...64)	71 (50...93)
	Ge	1630 (1090...2270)	71 (43...102)	82 (45...125)	51 (29...79)	100
	Ge	2960 (930...6122)	21 (15...29)	22 (14...28)	22 (12...33)	100

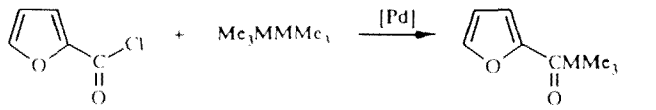
TABLE 16. Antitumor Effect of the Compound



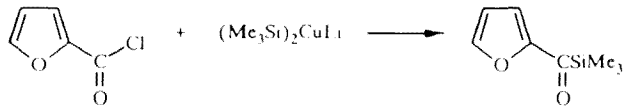
X	Prolongation of life, %		Retardation of tumor growth, %		
	Ehrlich's ascitic tumor	sarcoma 37	carcinoma of the lungs	melanoma B16	adenocarcinoma 755
	—	45	23	45	—
CH=NNHC(O)NH_2	22	28	52	40	18
CH=NNHC(S)NH_2	0	0	33	40	—
CH=NN(CH_2COOH)C(O)NH_2	26	—	62	52	15
	0	26	45	32	—
CH=CHCOOH	—	20	54	60	—

A series of compounds in which there is a functional group in the methylene group separating the metal from the heterocycle have also been synthesized. Thus, in recent years increasing attention has been paid to the chemistry of acylsilanes and stannanes on account of the chemical transformations into which compounds of this type enter. Trimethyl(2-furoyl)silane and trimethyl(2-furoyl)stannane can be obtained by the action of hexamethyldisilazane [119] and hexamethyl-di-

stannane [120, 121] on 2-furoyl chloride in the presence of palladium catalysts or (trimethylsilyl)lithium cuprate at low temperature [122].

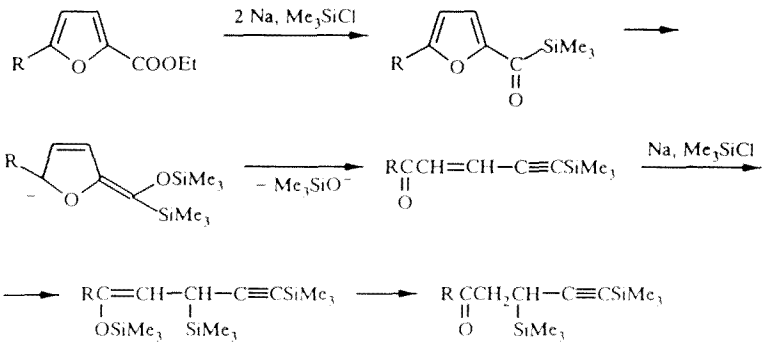


M = Si (60%), Sn (80%)

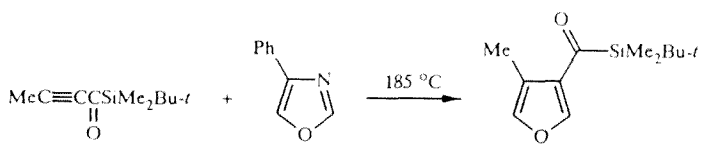


83%

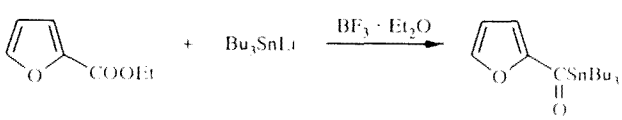
In [123] it was suggested that furyl-containing acylsilanes are formed as intermediate products during the reductive silylation of ethyl 2-furancarboxylates and their 5-substituted derivatives with a mixture of trimethylchlorosilane and sodium in tetrahydrofuran. However, the reaction does not stop at this stage, and subsequent reduction and ring opening occur.



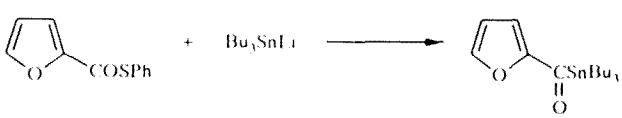
The reaction of methylethynyl dimethyl(*tert*-butyl)silyl ketone with 4-phenyloxazole takes place by a mechanism of the retrodiene synthesis type, and furyl silyl ketone is formed with a 39% yield [124].



Several possible methods for the synthesis of 2-furoylstannanes using trialkylstannyllithium have been described [125]. In the reaction with 2-furoyl chloride a large amount of side products is formed, and the yield of the furoylstannanes is considerably reduced. Better results were obtained in the reaction of tributylstannyllithium with ethyl 2-furancarboxylate in the presence of boron trifluoride etherate or with phenyl 2-furancarbothioate. The reactions are usually conducted in tetrahydrofuran at −78°C. The optimum reagent ratio with the use of ether corresponds to $R_3SnLi-ether-BF_3 \cdot Et_2O$ = 2:1:2.4. The yield of tributyl(2-furoyl)stannane under these conditions amounts to 73%. The product yield in the reaction with the thioether is smaller (47%), but the catalyst is not required and an equimolar amount of stannyllithium is used [125].

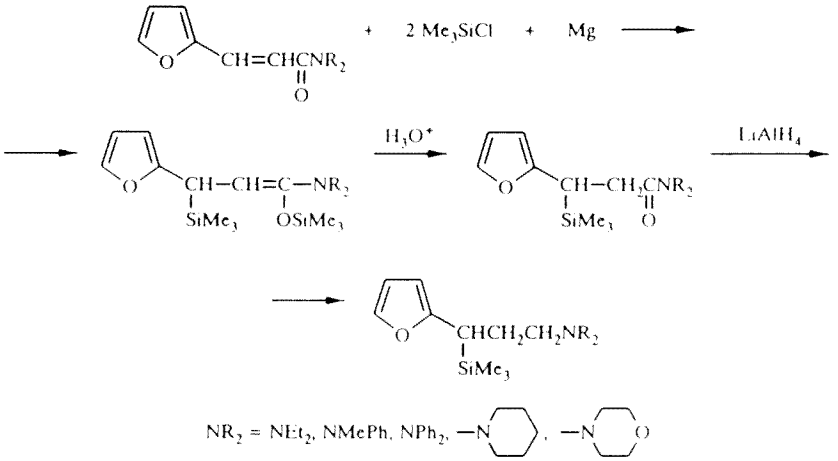


73%

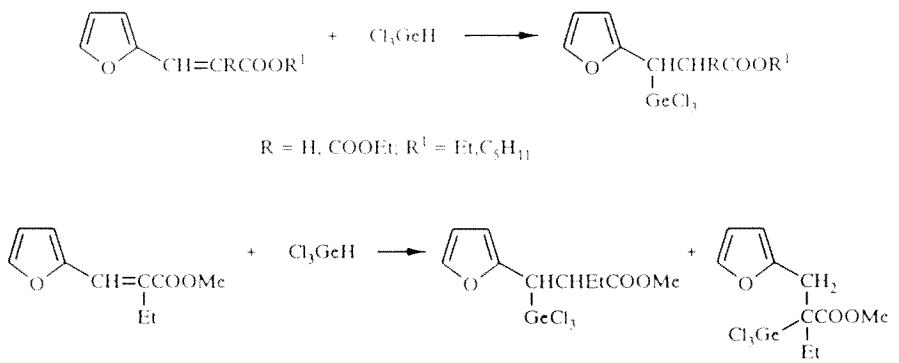


47%

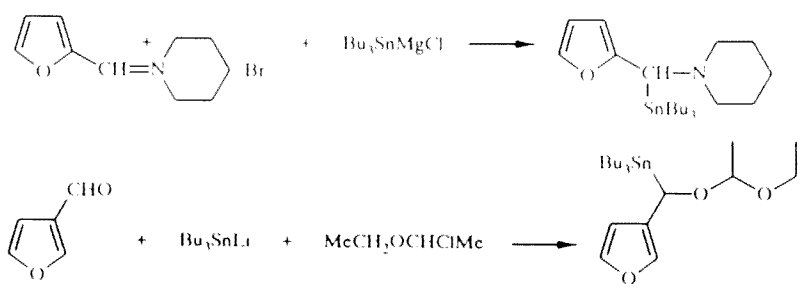
During the silylation of 2-furylacrylamides in the $2Me_3SiCl$ – magnesium – hexamethylphosphorotriamide system, C- and O-silylation occur. After hydrolysis and reduction of the intermediates with lithium aluminum hydride, various α-trimethylsilyl[γ-(2-furyl)propyl]amines were obtained [126].



The hydrogermylation of derivatives of furylacrylic acid was realized with trichlorogermanium. It was found that the addition took place without a catalyst with cooling to −10°C and gave yields of 29-79%. In most cases the reaction is regioselective, and compounds in which the furan ring and the germanium atom are separated by one carbon atom are formed. Only during the hydrogermylation of methyl α-ethyl-β-furylacrylate (R = Et, R^1 = Me) were two isomers obtained [127].

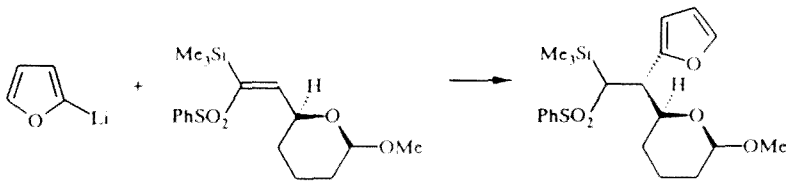


Furan derivatives with a tributylstannylaminomethyl group at the ring can be obtained by the reaction of tributylstannylmagnesium chloride $Bu_3SnMgCl$ with furfurylamine salts [128, 129]. Those with a tributylstannylalkoxymethyl group can be obtained by the reaction of 3-formylfuran and tributylstannyllithium followed by treatment with 1-chloroethyl ethyl ether [130].

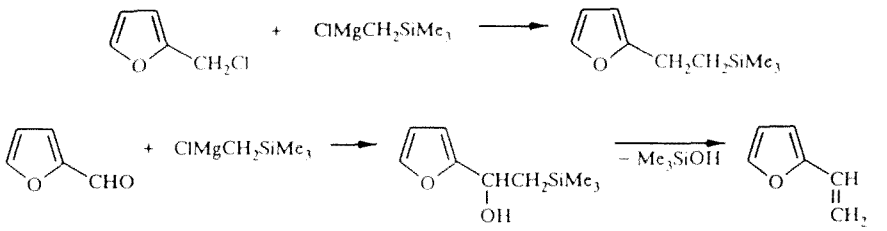


The lithium [117] and magnesium [4] methods were used for the synthesis of β-(2-furyl)ethylsilanes, but the most convenient method is the hydrosilylation of 2-vinylfuran [2, 3, 41, 131, 132].

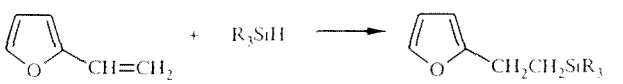
2-Furyllithium adds stereoselectively at the double bond of disubstituted vinylsilane [117].



Trimethylsilylmethylmagnesium chloride reacts with furfuryl chloride readily and with high yield and forms trimethyl(2-furylethyl)silane. The reaction of the same magnesium reagent with furfural leads initially to the formation of furfuryl alcohol with a silyl group at the β position in relation to the furan ring, and this compound then undergoes β-dissociation with the elimination of trimethylsilanol [4].



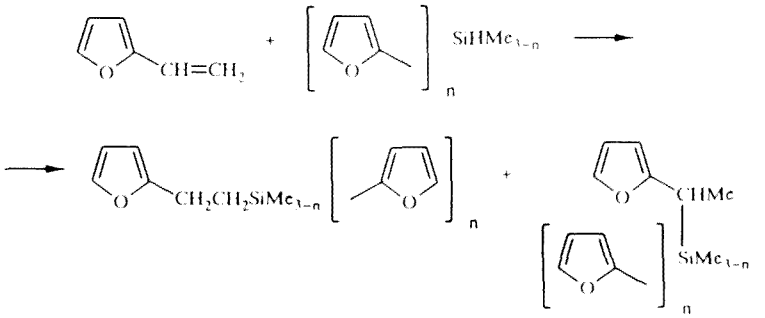
During investigation of the hydrosilylation of 2-vinylfuran it was established that the most varied alkyl-, alkoxy-, and chlorohydrosilanes add in the presence of chloroplatinic acid at the double bond when heated in a glass autoclave with the preferential formation of the β isomer [2, 3, 131].



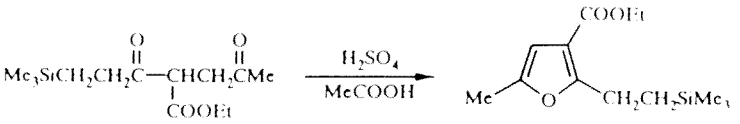
R_3Si = Cl_3Si, $MeCl_2Si$, $EtCl_2Si$, Et_3Si, $Et(EtO)_2Si$, $(EtO)_3Si$

The reactivity of hydrosilanes in this reaction varies. Thus, trichlorosilane adds at the double bond when heated to 80-85°C in an autoclave, and the yield of the products after heating for 18 h amounts to 60%. Methyldichloro- and ethyldichlorosilane react with 2-vinylfuran considerably more vigorously and give higher yields (70%). Triethylsilane exhibits the lowest reactivity, and the yield does not exceed 28% with the most diverse hydrosilylation catalysts ($H_2PtCl_6 \cdot 6H_2O$, 1% Pd/C, 1% Pt/C). Ethyldiethoxy- and triethoxysilane add to vinylfuran more readily than triethylsilane [131]. The main product from the reaction of tetraethyldisiloxane with 2-vinylfuran (ratio 1:2) in the presence of Speier's catalyst was a 1:2 adduct (48%), and only a small amount (6%) of the 1:1 product, in which one Si–H bond is preserved, was isolated [131].

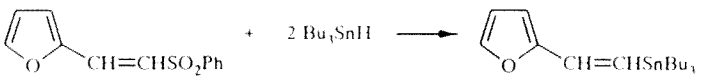
Whereas the only isolated product from addition at the double bond of 2-vinylfuran in all the previous cases was the β isomer, in the reaction of 2-vinylfuran with furylhydrosilanes [41,132] under the influence of $H_2PtCl_6 \cdot 6H_2O$ small amounts of the α isomers (6-16%) are formed. Their fraction in the reaction mixture decreases with increase in the number of furyl groups in the hydrosilane and amounts to 16, 10, and 6% for the hydrosilanes with n = 1, 2, and 3 respectively.



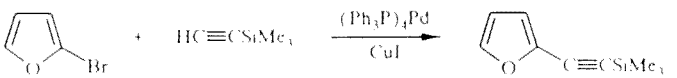
2-Furylethylsilanes can also be obtained by the cyclization of silicon-containing 1,4-dicarbonyl compounds in an acidic medium. However, this method is extremely restricted on account of the poor availability of the initial compounds [133].



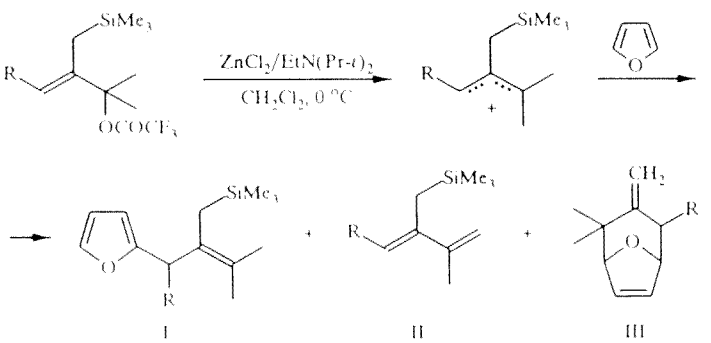
A compound in which the furan ring is separated from the tin atom by a vinyl group was synthesized with a 72% yield from furylvinyl phenyl sulfone and tributylstannane in boiling xylene [134].



The cross coupling of trimethylsilylacetylene with 2-bromofurane, which takes place quickly and with a good yield in pyridine in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium and monovalent copper iodide, gave 2-furylethynyltrimethylsilane [135]. The latter polymerizes under the conditions of catalysis by the derivatives of transition metals with the formation of a polymer containing a conjugated polyene system [136].



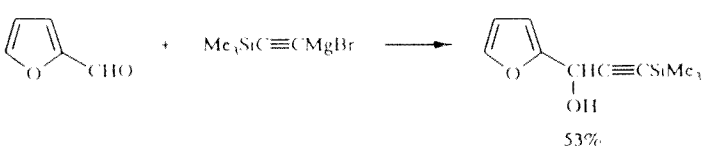
A series of methods have been used for the synthesis of furan derivatives in which the furan ring is separated from the element by three carbon atoms [137-142]. The electrophilic substitution of the hydrogen atom at the second position of the furan ring by a silylmethylallyl cation, obtained from silyl-substituted allyl trifluoroacetates, is interesting [137].



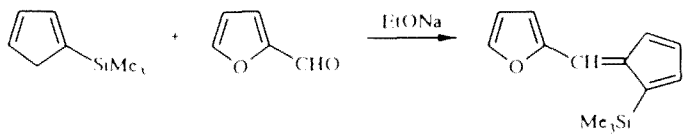
I II III

However, in addition to substitution of the furan, stabilization of the cation by the elimination of a proton is also observed, and it also acts as a dienophile with respect to the furan. The ratios of the reaction products I, II, and III amount to 6:1:3 when R = H and 2:1:1 when R = Me.

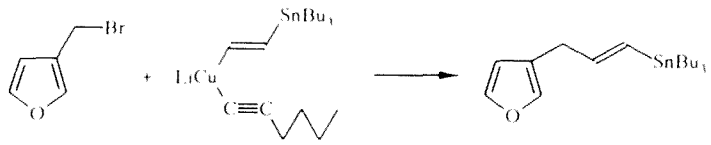
An organomagnesium synthesis was used for the production of furyl-containing silicoalkynyl alcohols [138].



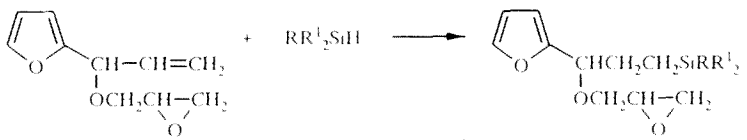
The condensation of furfural with trimethylcyclopentadienylsilane in ethanol under the influence of sodium ethoxide gave the corresponding organosilicon fulvene [139].



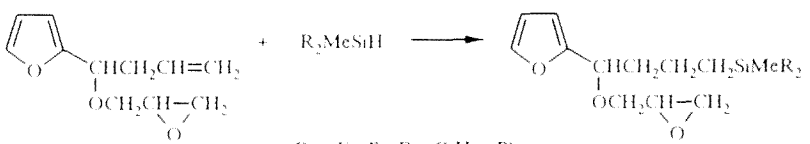
1-Tributylstannyl-3-(3-furyl)prop-1-ene was obtained with a 73% yield from 3-bromomethylfuran by the cuprate method [140, 141].



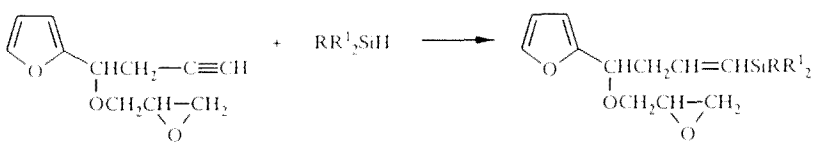
Furylpropylsilane [142] and furylbutylsilane [143-147] are also formed during the hydrosilylation of furyl-containing unsaturated compounds by di- and triorganosilanes in the presence of chloroplatinic acid. The product yields vary between 35 and 90%.



R = Me, R^1 = Et; R = R^1 = OEt

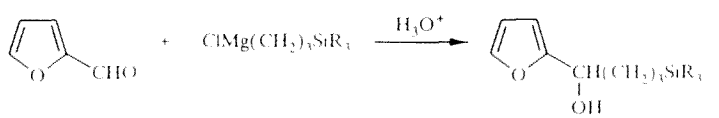


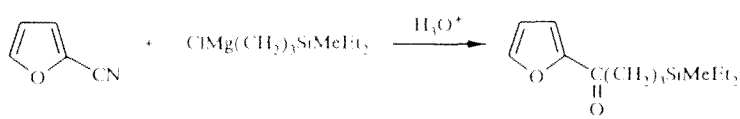
R = Et, Pr, Bu, C_5H_{11}, Ph



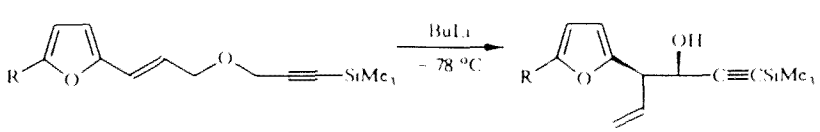
R = Me, R^1 = Et, R = R^1 = OEt; R = Me, R^1_2 = $(CH_2)_4$

Furylbutylsilanes containing a hydroxyl group or carbonyl oxygen atom at the α-carbon atom of the chain are easily obtained by the reaction of silylpropylmagnesium chlorides with furfural [4] or 2-cyanofuran [148].

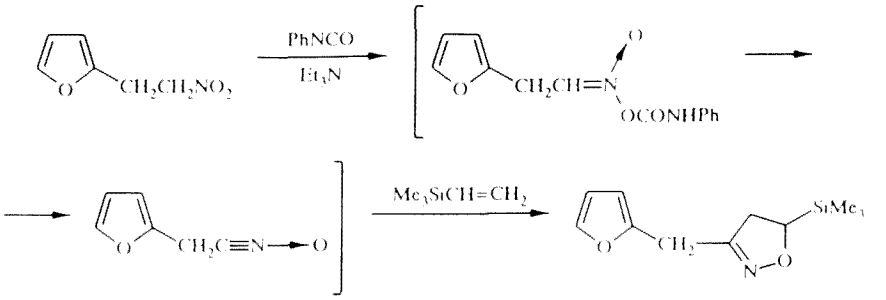




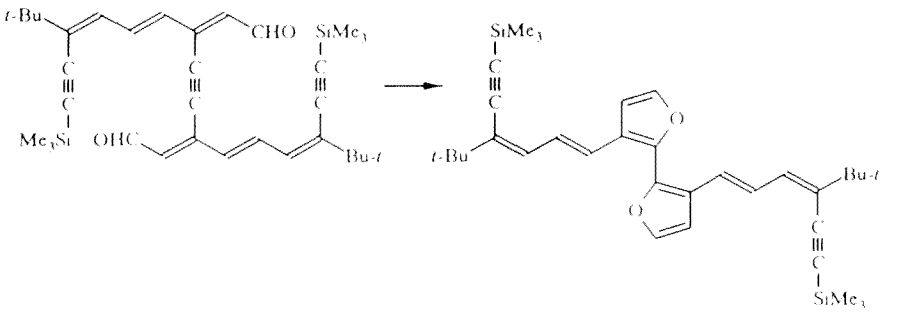
The treatment of propargyl propenyl ether, containing a trimethylsilyl group in the propargyl group and a furan ring in the propenyl group, with butyllithium at −78°C leads to a [2,3]-sigmatropic rearrangement, which takes place with high *erythro* selectivity (95%) [149].



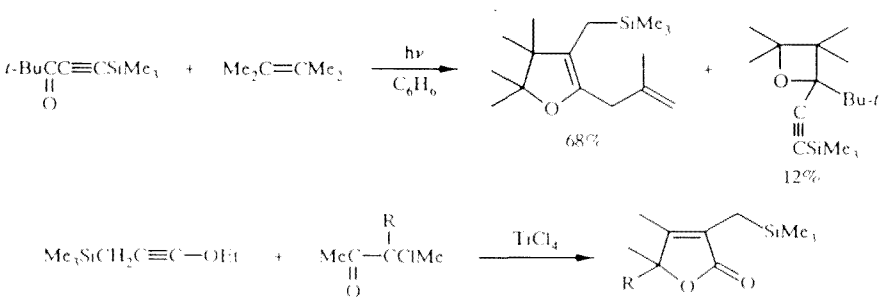
Trimethylvinylsilane enters into 1,3-dipolar cycloaddition to 1,3-diols, generated *in situ* from 2-(2-nitroethyl)furans by the action of phenyl isocyanate in the presence of triethylamine [150].



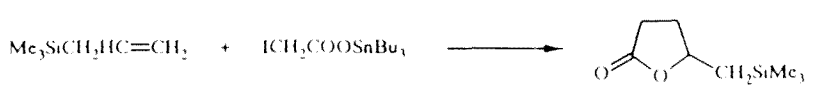
If an acyclic aldehyde with a system of double and triple bonds and trimethylsilylethynyl groups is heated in benzene, cyclization is observed, and a 2,2′-bifuryl derivative is formed with a 67% yield [151].



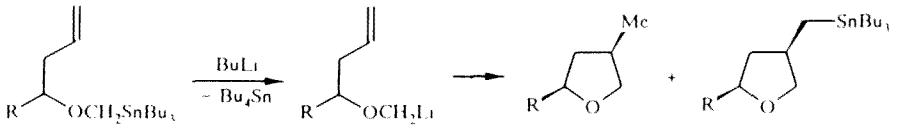
Compounds with a silylmethyl R_3SiCH_2, silylmethylene $R_3SiCH=$ [152-157], stannylmethyl R_3SnCH_2, or stannylmethylene $R_3SnCH=$ group [158-160] in the dihydrofuran, tetrahydrofuran, or tetrahydrofuranone ring were obtained by cyclization. Thus, during the irradiation of *tert*-butyl trimethylsilylethynyl ketone and 2,3-dimethylbut-2-ene in benzene the 3-trimethylsilylmethyl derivative of 4,5-dihydrofuran is formed with a 68% yield together with a small amount of 2,2,3,3-tetramethyl-4-(*tert*-butyl)-4-trimethylsilyloxetane [152]. 1-Ethoxy-3-trimethylsilylprop-1-yne reacts with α-halogeno ketones in the presence of titanium tetrachloride (ratios of silane, ketone, and titanium tetrachloride 4:4:3) and gives 2-trimethylsilylmethyl-3,4-dimethylbut-2-en-4-olides with 40-44% yields [153].



Trimethylallylsilane reacts with tributylstannyl iodoacetate under the influence of azobisisobutyronitrile according to the following scheme [154]:

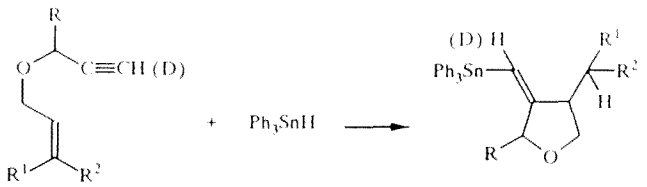


Treatment of the tributylstannylmethyl ethers of but-1-en-4-ols with an excess of butyllithium in tetrahydrofuran at −78°C gives the products from substitution of the stannyl group by lithium, which undergo stereoselective cyclization to 2-R-4-methyltetrahydrofurans when heated to 0°C. 2-R-4-Tributylstannylmethyltetrahydrofurans, probably produced in the reaction of the lithium derivative with tetrabutylstannane, were also detected among the side products [158].



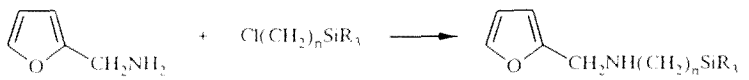
R = *n*-C_6H_{13}, *c*-C_6H_{11}

(Z)-Triphenylstannylmethylenefurans [159, 160] were synthesized by the hydrostannylation of the derivatives of propargyl ethers in the presence of a catalytic amount of triethylborane in toluene at 25°C followed by cyclization.



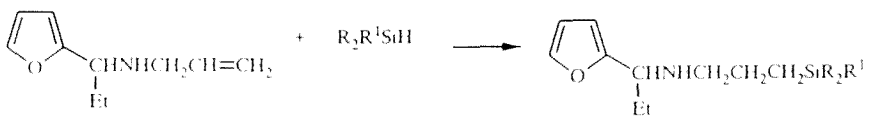
R = H, Bu; $R^1 = R^2 = Me$; $R^1 = H$, $R^2 = Pr$

Various methods of synthesis were used in the production of the silylalkyl derivatives of furfurylamines [148, 161], azomethines [162-164], and alkylsilyl esters of furyl-containing acids [165, 166]. Furfurylamine is alkylated by chloroalkylsilanes when heated [148].

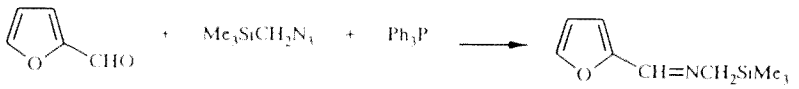


n = 1, 3

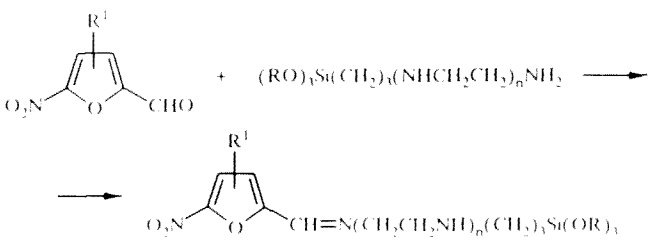
In the presence of $H_2PtCl_6 \cdot 6H_2O$, furfuryl(allyl)amines add hydrosilanes only at the double bond. Reaction at the N−H bond was not observed [161].

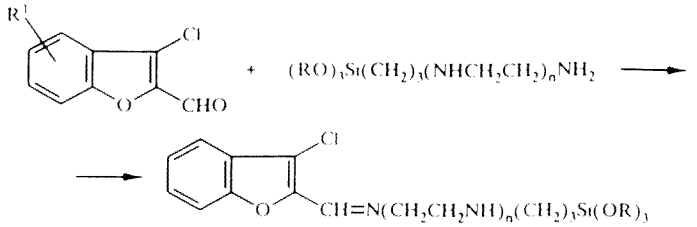


The reaction of trimethylsilylmethyliminotriphenylphosphorane, obtained *in situ* from trimethylsilylmethyl azide and triphenylphosphine, with furfural gave after 2 h the corresponding trimethylsilylmethylimine with a 75% yield [162].



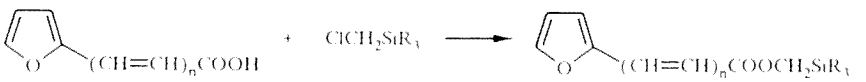
Effective antibacterial and antifungal compounds are formed during the condensation of silylalkylamines with the derivatives of furfural [163] or 2-formylbenzofuran [164] after heating in benzene.





R = Alk, R^1 = H, Alk; n = 0–2

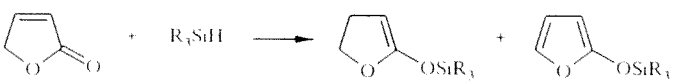
Organosilicon esters were obtained when toluene or xylene solutions of furancarboxylic acids were boiled with chloromethyltrimethyl-, chloromethylmethyldimethoxy-, chloromethylmethyldiethoxy-, and chloromethyltrimethoxysilane in the presence of triethylamine for 12-24 h [165].



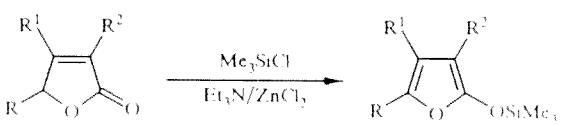
n = 0, 1

1.3. Synthesis of Compounds of Type III

Of the derivatives with a heteroorganic substituent at a heteroatom in the side chain of furans (compounds of type III), the highly reactive trimethylsilyloxyfurans are widely used as intermediate products in organic synthesis. There are several methods for the synthesis of these derivatives. During the hydrosilylation of unsaturated γ-lactones with alkylhydrosilanes in the presence of rhodium catalysts, 2-trialkylsilyloxyfurans were obtained with a yield of 10% in addition to the 1,4-addition product. When the $PdCl_2$–PhSH system was used as catalyst, the yield was increased, but there were difficulties in the separation of the reaction products [167].

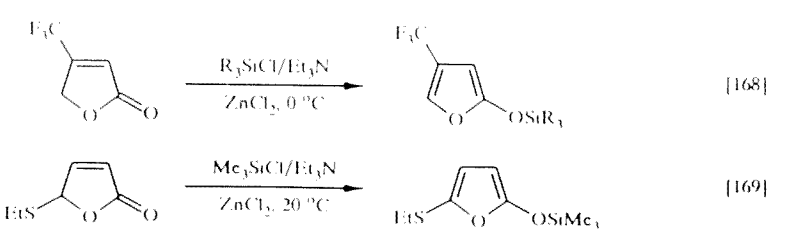


Better results were obtained by treating the γ-lactones and their methyl derivatives with trimethylchlorosilane in the presence of zinc chloride and triethylamine in tetrahydrofuran at 65°C [167].



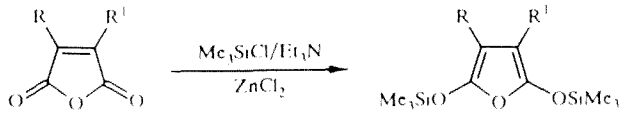
R = R^1 = R^2 = H, Me

A similar process was used for the production of silyloxyfurans with functional groups in the furan ring [168, 169], 2,5-bis(trimethylsilyloxy)furans [170, 171], and 1,3-bis(trimethylsilyloxy)isobenzofurans [172]. 2,5-Bis(trimethylsilyloxy)-furans can be synthesized using a different silylating agent (trimethylsilyl triflate) in a mixture with triethylamine [173] in ether at 0-8°C.

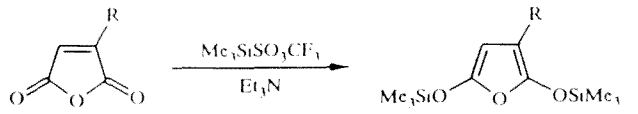


[168]

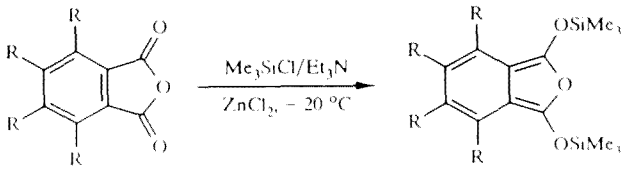
[169]



[170, 171]

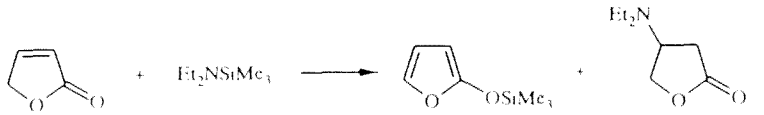


[173]

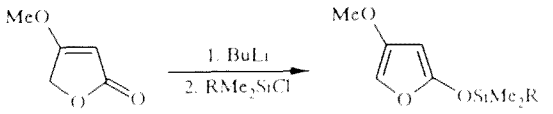


[172]

2-Trimethylsilyloxyfuran is formed with an 80% yield during the reaction of butenolide with N,N-diethylaminotrimethylsilane in ether. A small amount of γ-(β-diethylamino)butyrolactone is also formed in this reaction [174]. The addition of diethylamine to the reaction medium reduces the yield of the silyloxyfuran and increases the yield of the lactone.

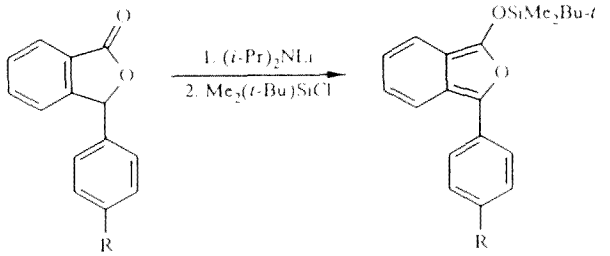


The formation of silyloxyfuran is also observed during the metallation of an unsaturated γ-lactone with butyllithium followed by treatment with trialkylchlorosilanes; the yield of the silylation product depends on the substituents at the silicon. During the action of dimethyl(*tert*-butyl)chlorosilane, the yield is reduced to 20% [175].

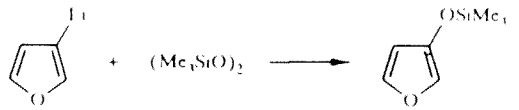


R = Me (94%), *t*-Bu (20%)

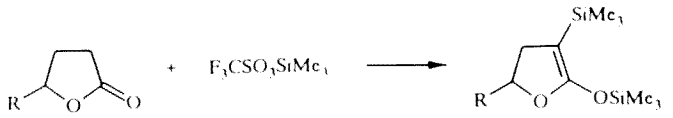
Similarly, metallation with lithium diisopropylamide but not with butyllithium, followed by reaction with dimethyl-(*tert*-butyl)chlorosilane, gave a series of silyloxy derivatives of isobenzofuran [176].



It was possible to synthesize 3-trimethylsilyloxyfuran by lithium synthesis with the cleavage of bis(trimethylsilyl) peroxide by 3-furyllithium [177].

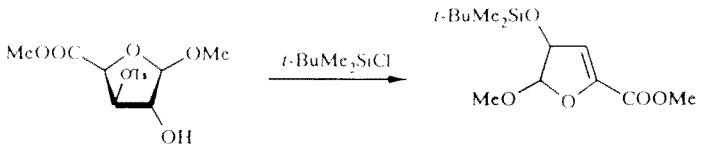


γ-Butyrolactone and valerolactone are silylated by twice the amount of trimethylsilyl triflate not only at the oxygen atom but also at the α-carbon atom with the formation of the C,O-disilyl derivative [178, 179].

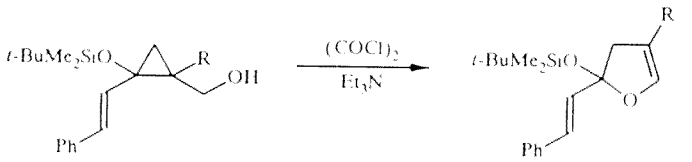


R = H, Me

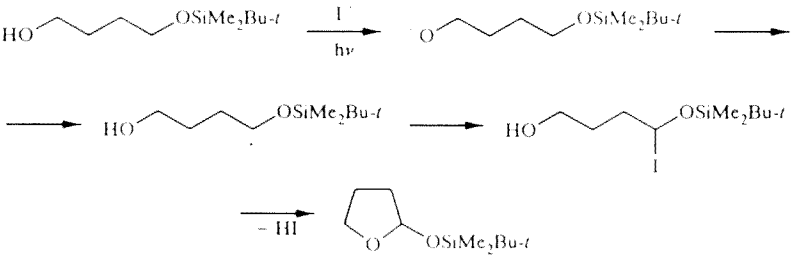
Methyl 1-O-methyl-3-O-tosyl-β-D-xyluronofuranose is silylated at the free OH group by dimethyl(*tert*-butyl)chlorosilane in the presence of imidazole. Subsequent elimination of p-toluenesulfonic acid by the action of 1,8-diazabicyclo-[5.4.0]undec-7-ene leads to 3-silyloxy-substituted 2,3-dihydrofuran [180].



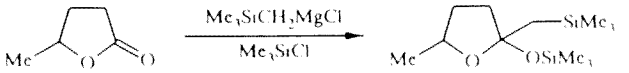
(2-Silyloxycyclopropyl)methanols containing the substituent PhHC=CH at position 2 of the cyclopropane ring are oxidized by oxalyl chloride in the presence of triethylamine with the formation of the 2,3-dihydrofuran derivative [181].



Dimethyl(*tert*-butyl)silyloxytetrahydrofuran and its derivatives can be obtained by the oxidative cyclization of monosilylated butanediols by the action of N-iodosuccinimide [182].

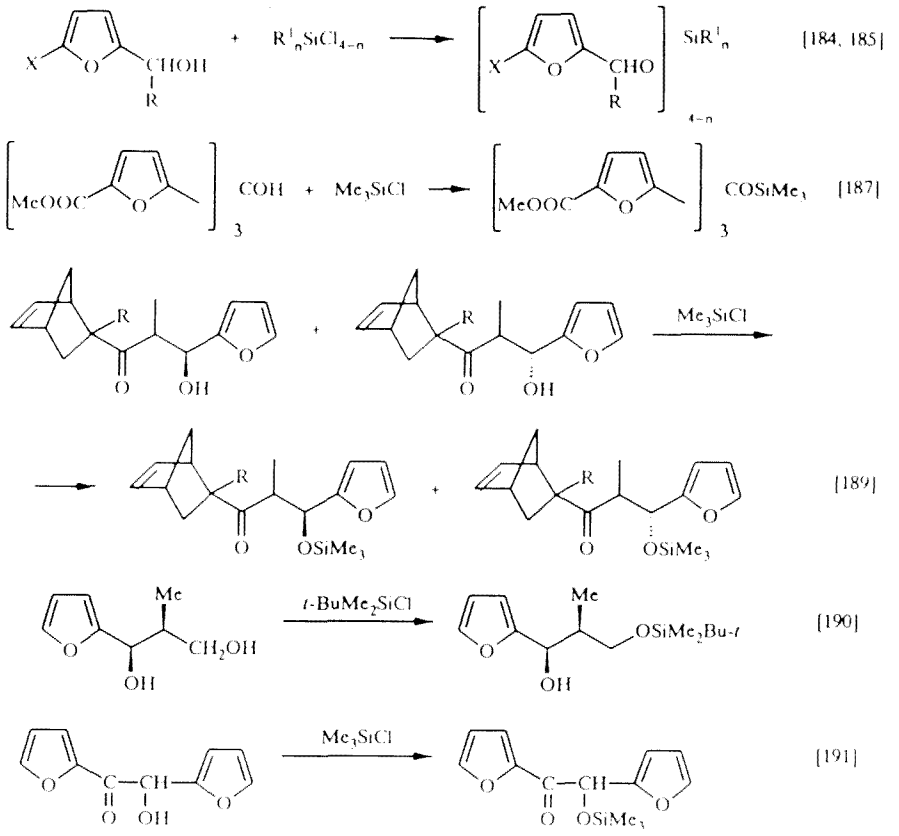


Valerolactone reacts with trimethylsilylmethylmagnesium chloride and trimethylchlorosilane with the formation of the disilyl derivative of tetrahydrofuran [183].

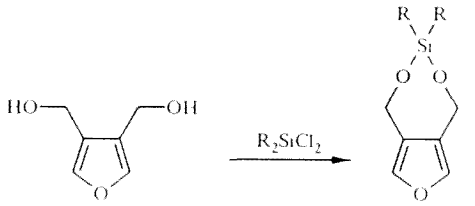


The most general methods for the synthesis of furfuryloxysilanes are the reactions of furfuryl alcohols with chlorosilanes in the presence of amines, with ethoxysilanes, and with hydrosilanes in the presence of metallic sodium or chloroplatinic acid.

Furfuryl alcohol, its 5-substituted derivatives, and furylalkylcarbinols react with organochlorosilanes in the presence of pyridine, triethylamine, or imidazole when heated in ether, hexane, dimethylformamide, or benzene [184-199].

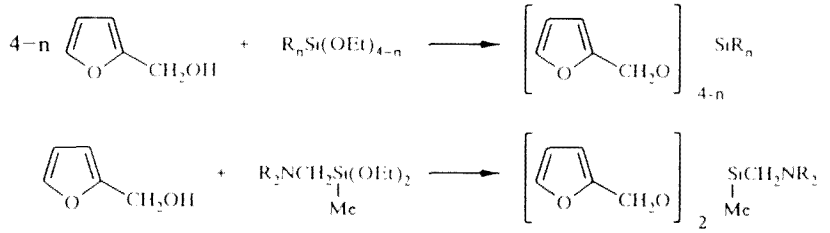


In a highly dilute benzene solution, dimethyl- and dimesityldichlorosilane form a condensed bicyclic product with 3,4-bis(hydroxymethyl)furan [200]:



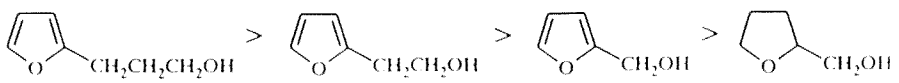
R = Me (51%), Mes (12%)

A simple and convenient method for the production of furfuryloxysilanes is the alcoholysis of alkoxysilanes by alcohols of the furan series [184, 201-207]. The reaction path is easily controlled by the amount of alcohol distilled, but in some cases transetherification takes place slowly and is complicated by the formation of partially substituted products as impurities, while prolonged heating leads to an increase in the yield of polymeric products.

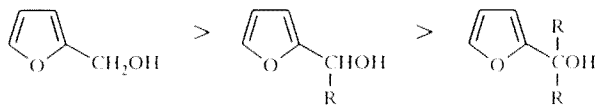


Dehydrocondensation with hydrosilanes in the presence of alkali metals [184, 208, 209] or chloroplatinic acid [5, 185, 208, 210] has often been used for the silylation of alcohols of the furan series. The analogous process with triethylger-

mane was realized by the action of copper [211]. The rate of dehydrocondensation is determined by various factors (by the structure of the alcohol and hydrosilane, by the solvent). The reactivity of furylalkylcarbinols with respect to triethylsilane in toluene at 25°C decreases in the following order:



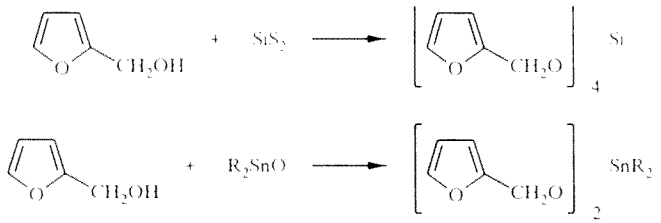
The rate of the process is also affected by steric factors. Thus, a reduction in the reaction rate is observed with branching of the hydrocarbon radical of the alcohol.



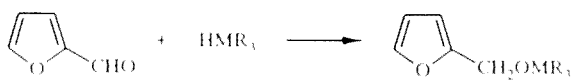
The reaction of furfuryl alcohol with triethylsilane in toluene is considerably faster than in dioxane. The reaction rate decreases particularly strongly in pyridine and dimethylformamide. This is probably due to the formation of complexes with hydrogen bonds [210].

In the reaction of hydrosilanes with furyl-containing unsaturated alcohols in the presence of Speier's catalyst, competition is observed between dehydrocondensation and hydrosilylation, and the direction of the process is therefore determined by structural features of the reacting alcohols. Thus, 3-(2-furyl)allyl alcohol only enters into dehydrocondensation, whereas triethylsilane reacts with 4-(2-furyl)but-1-en-4-ol at the OH and $CH{=}CH_2$ groups [208].

The furfuryloxy derivatives of silicon and tin can be synthesized from furfuryl alcohol in reactions with silicon disulfide [212] or diorganotin oxides [213].

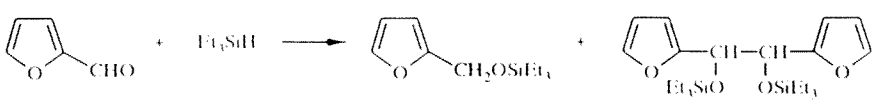


Furfuryloxysilanes and furfuryloxystannanes can also be obtained during the addition of hydrosilanes [214-221] or hydrostannanes [222-224] to the carbonyl group of aldehydes or ketones.



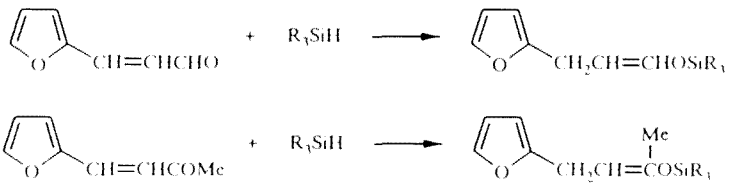
M = Si, Sn

Various catalysts have been used in this reaction: Chloroplatinic acid [214], nickel chloride [216], colloidal nickel [217], various rhodium metal-complex catalysts [218], a 1:2 mixture of dibutyldiacetylacetonatostannane and dibutyldi(cyclohexyloxy)stannane [224], and cesium and rubidium chlorides in the presence of 18-crown-6 [215, 221]. The yield of the products from the hydrosilylation of furfural by hydrosilanes R_3SiH in the presence of chloroplatinic acid is low, and even after heating at 120°C for 78 h more than 50% of the initial reagents remain unreacted. The reaction with 2-acetylfuran takes place with even greater difficulty, and in this case only traces of the product were detected [214]. If nickel chloride or a mixture of nickel chloride with diethyl sulfide is used as catalyst, mixtures of mono- and disilyl products are formed in ratios of 34%:29% and 23%:57% respectively [216]. Similar results were obtained in [217].

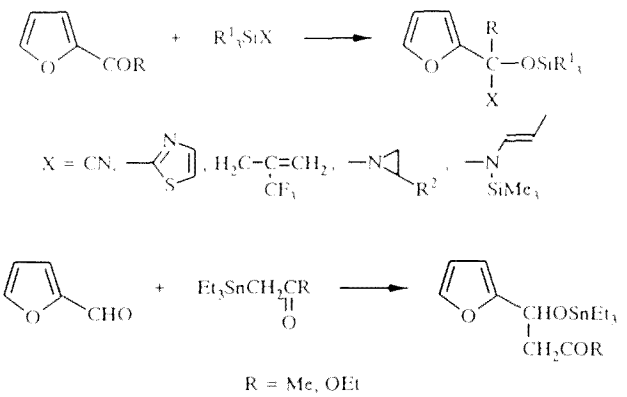


It was possible to increase the yield substantially and to avoid the side processes by conducting hydrosilylation under mild conditions at room temperature in methylene chloride in the presence of catalytic amounts of cesium chloride and the phase-transfer agent 18-crown-6 ether [215]. The yield of the products from hydrosilylation of furfural and 2-acetylfurfural by dimethylphenylsilane under these conditions amounts to 67 and 61% respectively.

With unsaturated furan aldehydes and ketones under the influence of Speier's catalyst, trialkylsilanes react considerably more readily than furfural [214], and they add to 3-(2-furyl)acrolein and furfurylideneacetone at positions 1,4.

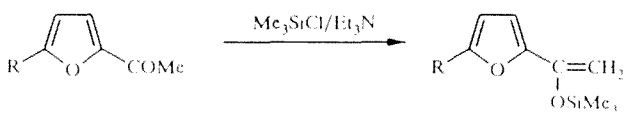


Apart from hydrosilanes, trimethylcyanosilane [225-229], trimethylsilylthiazole [230], 2-(trifluoromethyl)-allyltrimethylsilane [231], N,N-bis(trimethylsilyl)vinylamines [232], triethylaziridinosilanes [233], triethylstannylacetone [234], and ethyl triethylstannylacetate [235] also add to the carbonyl group of aldehydes and ketones. All these reactions take place at room temperature in most cases with a high yield and, as a rule, in the presence of catalysts. Trimethylcyanosilanes add at the carbonyl group under the influence of zinc iodide, triethylazidinosilanes react in the presence of a few drops of an aqueous solution of alkali, while the reactions with trimethylsilylthiazole, 2-(trifluoromethyl)allyltrimethylsilane, N,N-bis(trimethylsilyl)vinylamine, and ethyl triethylstannylacetate require the presence of tetraalkylammonium fluorides (Me_4NF, Bu_4NF).

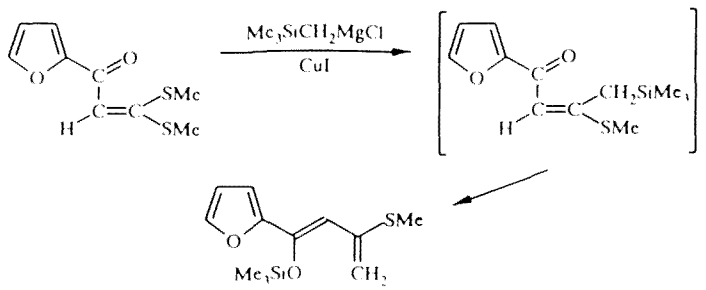


Various furfuryloxysilanes and furfuryloxystannanes with functional substituents at the α position of the side chain are formed in these reactions.

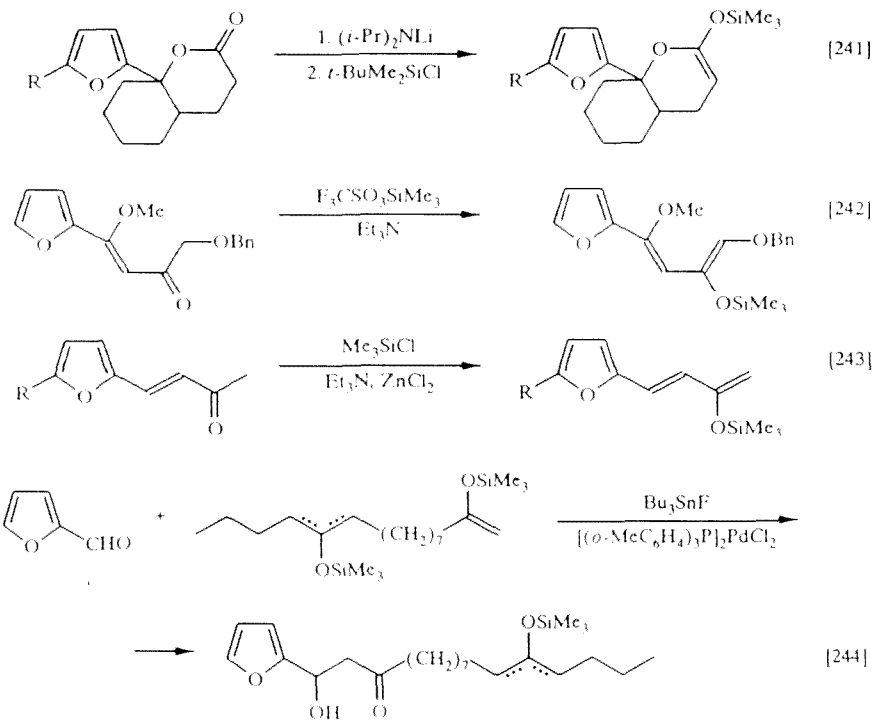
Furyl ketones are starting compounds in the synthesis of the trimethylsilyl ethers of enols. They react readily and with high yields with trimethylsilane in the presence of triethylamine in dimethylformamide [236-239].



1-(2-Furyl)(1-trimethylsilyloxy)-3-methylthio-1,3-butadiene was obtained selectively and with a high yield in the reaction of 2-furyl 1,1-dimethylthiovinyl ketone with trimethylsilylmethylmagnesium chloride in the presence of cupric iodide [240].



Silyl ethers with the silyloxy group separated from the furan ring were obtained from the carbonyl derivatives by various methods: by the action of lithium diisopropylamide and chlorosilanes at −78°C in a mixture of hexamethylphosphorotriamide and tetrahydrofuran [241]; by treatment of a furyl-containing ketone with trimethylsilyl triflate in the presence of triethylamine [242] or trimethylchlorosilane by the action of zinc chloride and triethylamine [243]; by the catalytic condensation of furfural with silyl ethers (Bu_3SnF and $[(o\text{-}MeC_6H_4)_3P]_2PdCl_2$) [244].



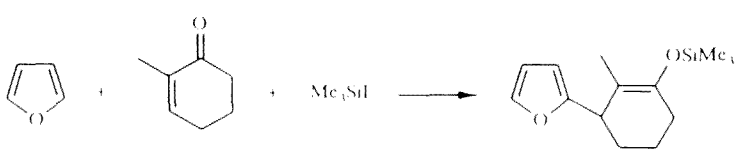
[241]

[242]

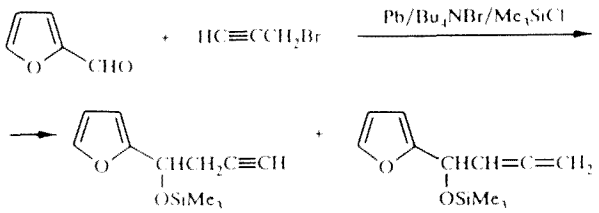
[243]

[244]

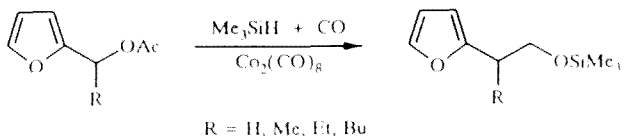
Another method for the synthesis of the silyl ethers of enols is based on the addition of furan to enones under the influence of trimethyliodosilane in methylene chloride at −78°C [245].



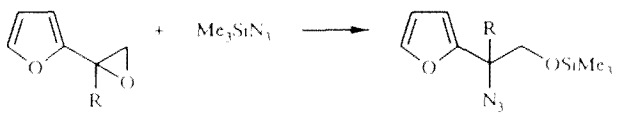
Furfural reacts with propargyl bromide in the lead/Bu_4NBr/Me_3SiCl/dimethylformamide system at room temperature. After treatment of the reaction mixture with sodium bicarbonate in ethyl acetate, a 9:1 mixture of the silyl ethers of the propargyl and allene derivatives is formed with a yield of 83% [246]. The role of the tetrabutylammonium bromide is important but obscure; it may promote the generation of an intermediate organolead compound.



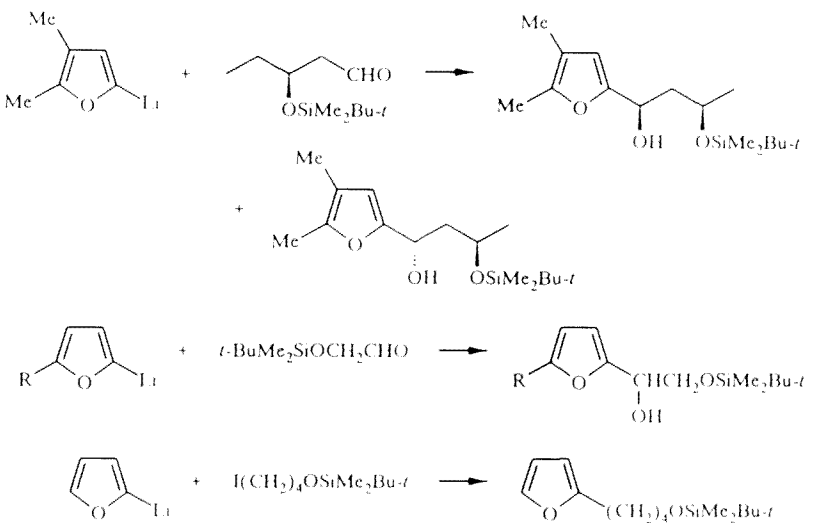
Furfuryl acetates react with trimethylsilane and carbon monoxide under mild conditions (25°C, 1 atm, CO) in the presence of dicobalt octacarbonyl with the formation of the silyl ethers of 2-furylethyl alcohols with yields of 75-90% [247].



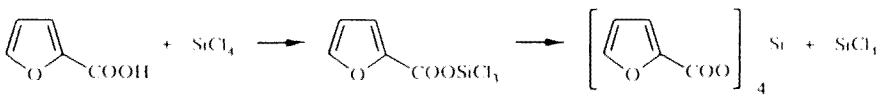
Trimethylazidosilane opens the three-membered ring of (2-furyl)oxiranes in the absence of catalysts, and only one isomer is formed as a result of the reaction [248].



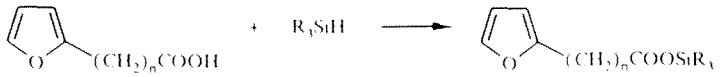
The lithium method has extremely limited use for the synthesis of the silyl ethers of furylalkanols [249-251].



Furoyloxysilanes are formed during the reaction of pyromucic acid with silicon tetrafluoride [252, 253]. With an excess of the acid it is possible to obtain tetra(2-furoyloxy)silane, which is used as a furoylating agent without isolation [254]. It is also formed as a result of disproportionation during the storage of 2-furoyloxytrichlorosilane [253].



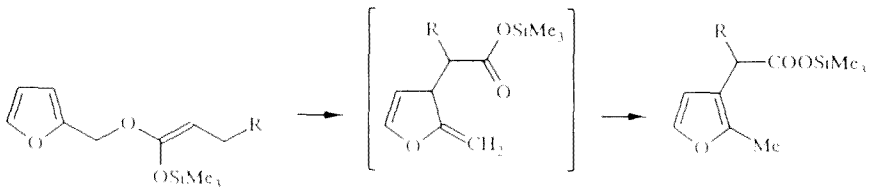
In the presence of Speier's catalyst, furancarboxylic acids react with trialkylsilanes with the release of hydrogen and the formation of trialkyl(2-furoyloxy)silanes [214].



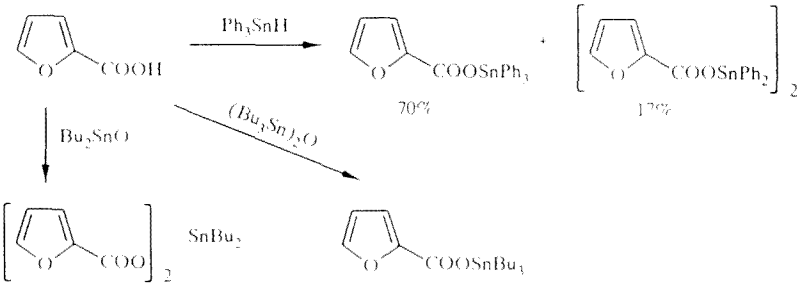
Under analogous conditions 2-furylacrylic acid gives the silyl esters of the saturated acid [214]. They are formed either on account of dehydrocondensation with simultaneous hydrogenation of the C=C double bond by the released hydrogen or as a result of the addition of the trialkylsilanes at positions 1,4.

A very convenient method for the production of trimethyl(2-furoyloxy)silane is the reaction of methyl 2-furancarboxylate with trimethyliodosilane, which takes place quantitatively in 7 h in deuterochloroform with gentle heating [255].

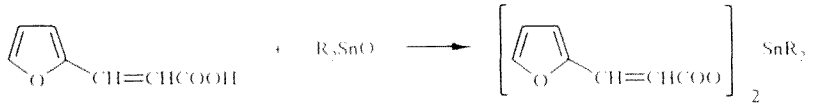
The trimethylsilyl esters of 2-methyl-3-methylcarboxyfuran were synthesized from the silylenol ethers of furfuryl alcohol by a [3,3]-sigmatropic rearrangement. The transformation takes place under mild conditions in 5-22 h in tetrahydrofuran at room temperature or on boiling [256].



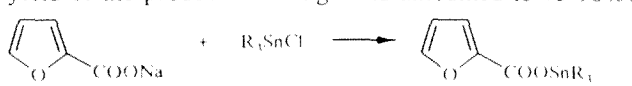
Furoyloxystannanes were synthesized from 2-furancarboxylic acid [257-262] and its 5-substituted nitro derivative [263] by the action of various organotin agents (triphenylstannane [257], dialkyltin oxide [258, 259, 261], hexaalkyldistannoxane [259, 260, 262], or trialkylstannanol [263].



The organotin derivatives of 2-furylacrylic acid were obtained by the action of dimethyl- and dibutyltin oxide [264].

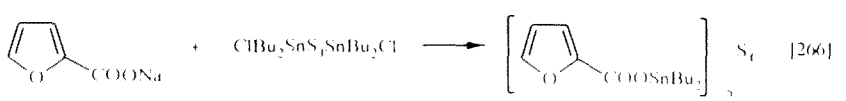


Another method for the synthesis of furoyloxystannanes is the reaction of sodium 2-furancarboxylate with various chlorostannanes [265, 266]. The yield of the products was high and amounted to 75-90%.



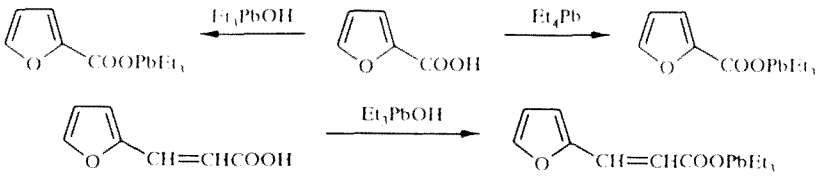
[265]

R = Me, Pr, Bu, Ph

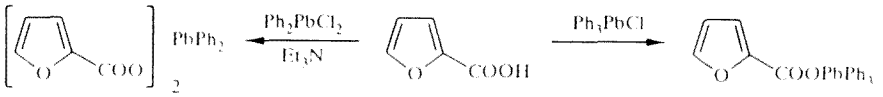


[266]

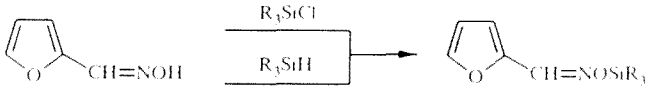
Lead furoates and furylacrylates were obtained with yields of more than 50% by the action of various lead derivatives on the acids [267].



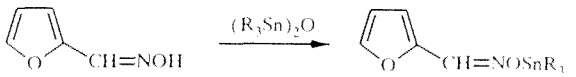
Difuroyldiphenyl- and furoyltriphenylplumbanes are formed in the reaction of 2-furancarboxylic acid with diphenyldichloroplumbane and triphenylchloroplumbane. In the first case triethylamine was used as hydrogen chloride acceptor [268].



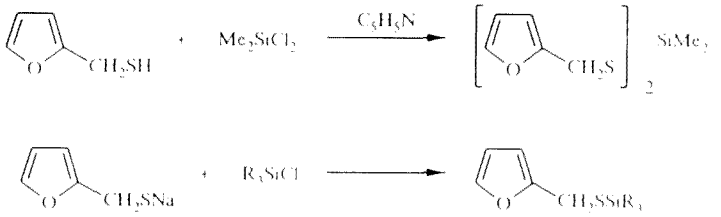
Silylated oximes of furfural were obtained by the action of trialkylchlorosilanes in the presence of triethylamine or of trialkylsilanes in the presence of chloroplatinic acid on the oxime [148]. The yield of the desired product was lower in the second case, and this was due to reduction side processes, which took place with cleavage of the N–O bond.



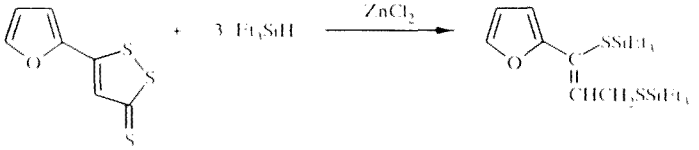
The organotin derivatives of furfural oximes were obtained with almost quantitative yields by the action of hexaalkyldistannoxanes [269, 270].



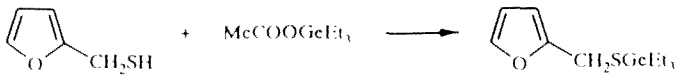
Furfuryl hydrosulfide does not react with triethylsilane in the presence of chloroplatinic acid, but it reacts slowly with dimethylchlorosilane in the presence of pyridine (as hydrogen chloride acceptor) giving a small yield (16%) of dimethyldi(2-furfurylthio)silane. It was possible to increase the yield of furfurylthiosilanes a little (30-35%) in the reaction of alkylchlorosilanes with sodium furfuryl sulfide [148].



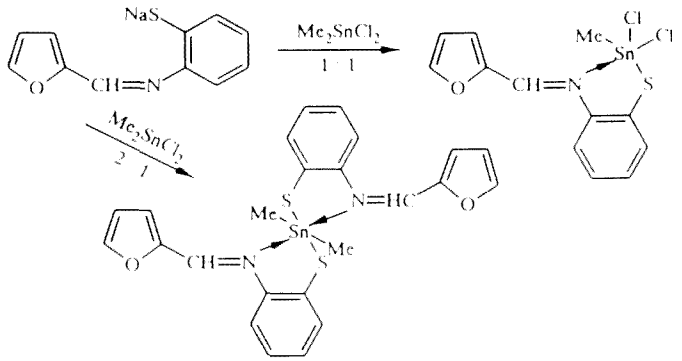
In the reaction of triethylsilane with furyl-containing 1,2-dithiole-3-thione in the presence of zinc chloride, the sulfur-containing ring is cleaved [271].



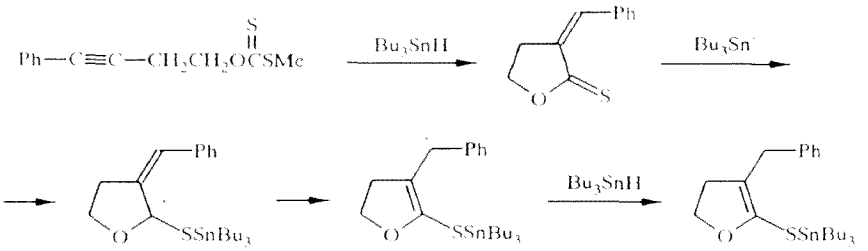
Triethyl(2-furfurylthio)germane was obtained by heating furfuryl hydrosulfide with triethylgermyl acetate [272].



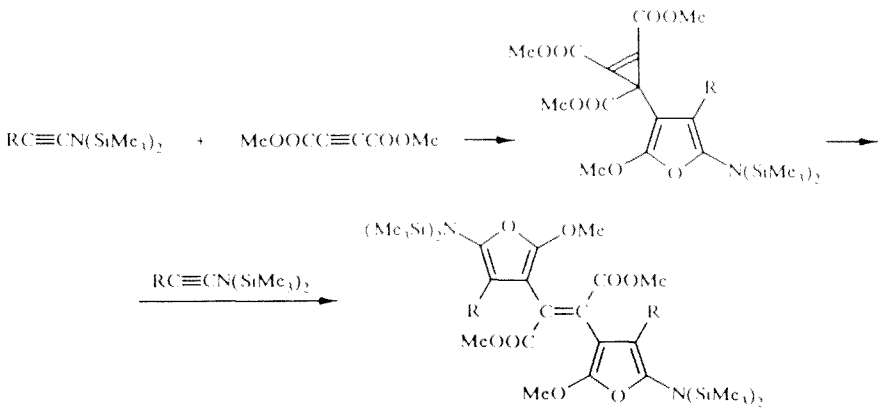
The sodium salt of furyl-substituted benzothiazoline reacts with dimethylchlorostannane, and compounds with five-coordinated (1:1) or six-coordinated (2:1) tin atoms, depending on the ratio of the reagents, are formed [273].



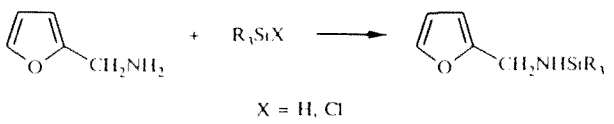
A compound of the 2,3-dihydrofuran series was synthesized by reductive cyclization of the acetylene derivative of S-methyl dithiocarbonate with tributylstannane in the presence of azobisisobutyronitrile [274], which takes place according to the following scheme:



Compounds in which the bis(trimethylsilyl)amino group is attached to the furan ring were obtained with a yield of about 70% by the cyclization of N,N-bis(trimethylsilyl)ynamines with methyl acetylenedicarboxylate in a ratio of 1:2 at −78°C in THF. The furylcyclopropenes formed during the reaction, the structure of which was established by x-ray crystallographic analysis, react with a further equivalent of N,N-bis(trimethylsilyl)ynamine and are converted into bissulfuryl derivatives of dimethyl fumarate [275].

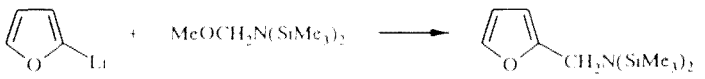


A general method for the synthesis of furfurylaminosilanes is the reaction of chlorosilanes with furfurylamine, which gives a yield of 60% [148]. It was not possible to achieve the dehydrocondensation of triethylsilane with furfurylamine by the action of Speier's catalyst, but it did take place in the presence of potassium 2-furfurylamide [148].

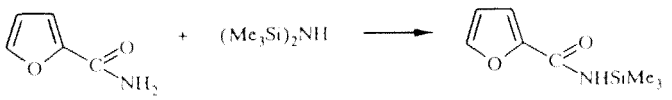


X = H, Cl

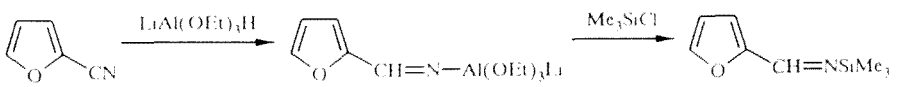
N,N-Bis(trimethylsilyl)furfurylamine was obtained with an 81% yield by the lithium method from 2-furyllithium and N,N-bis(trimethylsilyl)methoxymethylamine in the presence of anhydrous magnesium bromide in ether at room temperature [276].



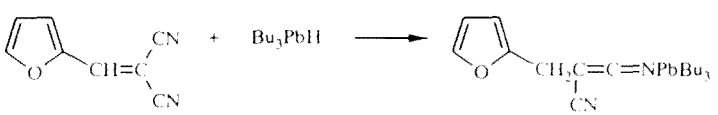
2-Furancarboxamide is silylated very easily with hexamethyldisilazane [148].



N-(Furfurylidene)trimethylsilylamine is formed as intermediate product during the action of lithium triethoxyaluminum hydride and then trimethylchlorosilane on 2-cyanofuran [277-279].



The hydroplumbation of furfurylidenemalononitrile with tributylplumbane takes place at positions 1,4 [280].



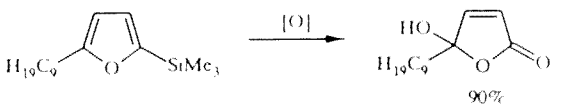
The silyl derivatives of furan of type III have found widespread use in organic synthesis [166-169, 174-179, 188-190, 197, 199, 242-244, 248, 256, 277-279, 281-291]. This is due to the ease of introduction of trialkylsilyl groups into the molecules of alcohols, acids, and amines and their subsequent elimination. In a number of cases silylation makes it possible to conduct chemical transformations regioselectively and stereospecifically. The chemical characteristics of this type of compound will be discussed later in greater detail.

2. CHEMICAL CHARACTERISTICS

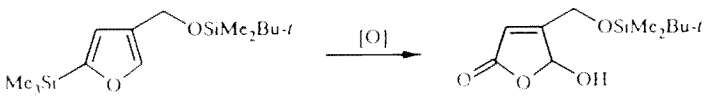
The various chemical transformations in which the furan derivatives of group IVB elements participate can be divided into several types: Reactions taking place with removal of the organometallic group; transformations affecting the furan ring and the functional groups in it; the chemical transformations of functional substituents at the metal atom.

2.1. Demetallation

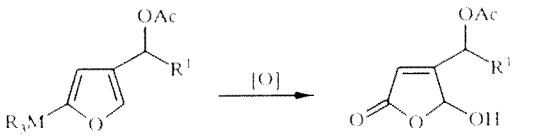
Compounds of the first type, containing a $C_{furyl}-M$ bond, are demetallated when treated with reagents of oxidizing, electrophilic, and nucleophilic character. In a number of cases this process is a side process, e.g., during the metallation of the furan ring of furylsilanes, furylgermanes, and furylstannanes with butyllithium or during chemical transformations at functional groups at the metal or heterocycle. However, demetallation was also used successfully for the synthesis of new types of compounds and for regioselective reactions. Thus, the oxidation of furylsilanes and furylstannanes makes it possible to introduce oxygen selectively into the furan ring and to obtain high yields of butenolides [32, 75, 76, 292-304]. Singlet oxygen (produced by the action of catalytic amounts of bengal rose on molecular oxygen at −78°C or by irradiation) [75, 292-298], m-chloroperbenzoic acid [76], peracetic acid [32, 299, 303] and its sodium salt [300], and dimethyldioxirane [301] were used as oxidizing agents.



[75]



[292]

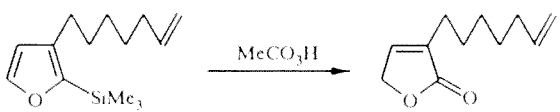


[293]

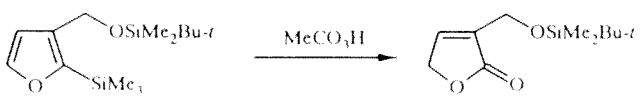
R_3M = Me_3Si, t-$BuMe_2Si$, Bu_3Sn

The yields of the hydroxybutenolides were high and usually exceeded 90%.

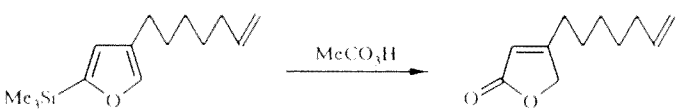
2-Trimethylsilylfurans [32, 299, 303] are oxidized by peracetic acid to the corresponding butenolides in methylene chloride. In most cases the yields of the products fluctuate in the range of 60-80%. However, some of the compounds, e.g., butyl 5-trimethylsilyl-2-furancarboxylate, could not be oxidized under these conditions.



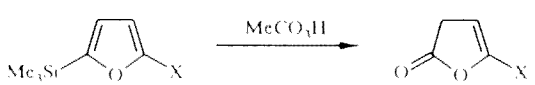
[303]



[32]



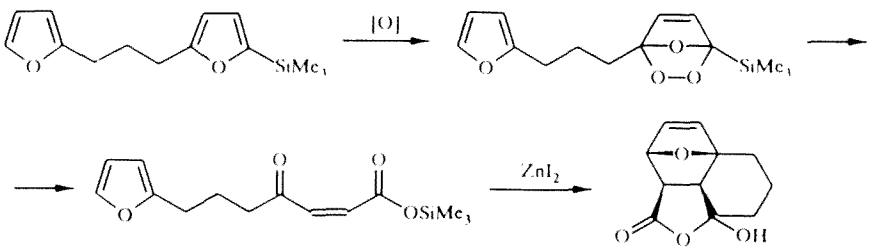
[303]



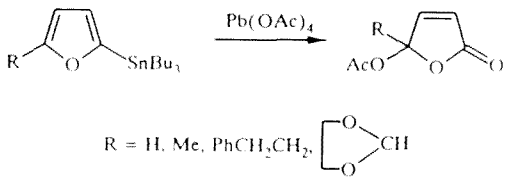
[299]

X = C_6H_{13} (84%), t-$PrCH_2CH_2$ (78%), $CH_2{=}CH(CH_2)_9$ (65%), $(EtO)_2CHCH_2CH_2$ (73%), $C_8H_{17}CH(OH)$ (< 30%), $C_8H_{17}CH(OSiMe_2Bu\text{-}t)$ (64%), $C_8H_{17}CH(OAc)$ (traces)

During the photooxidation of 5-[3-(2-furyl)propyl]-2-(trimethylsilyl)furan in chloroform, the obtained endo-peroxide rearranges to the *cis*-γ-keto-α,β-unsaturated silyl ether, which undergoes partial cyclization during photolysis. Treatment of the reaction mixture at 20°C for 20 h with zinc chloride gives a 58% yield of the cyclic adduct as a single diastereomer [305].

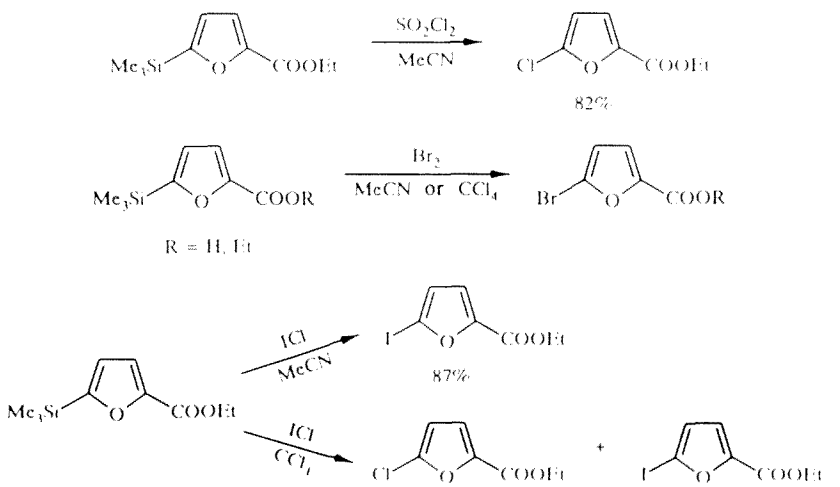


5-Substituted tributylstannanes also undergo oxidative substitution after 32 h under the influence of an equimolar amount of lead tetraacetate in boiling methylene chloride in an inert atmosphere [37].

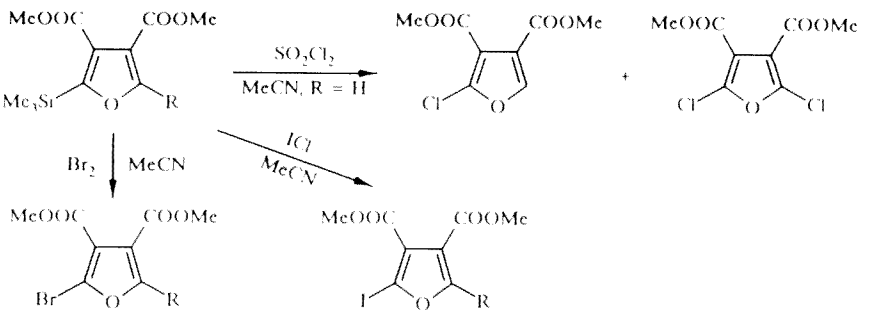


The transformations of trimethyl(5-methyl-2-furyl)silane and trimethyl(5-methyl-2-furyl)germane [306] during vapor-phase oxidation by atmospheric oxygen at the catalyst $V_2O_5-MoO_3-Ag_2O$ (V:Mo:Ag = 1:1:0.02) at 300-450°C were investigated. It was not possible to achieve selective oxidation of the methyl group to aldehyde, and the yields of the silyl- and germylfurfural were not higher than 7%. Under these conditions the initial compounds underwent demetallation and were converted into various products containing a five-membered ring (furan, sylvane, furfural, maleic anhydride), siloxanes or germoxanes, and the products from more extensive oxidation (CO, CO_2, H_2O).

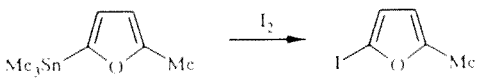
The action of various halogenating agents (sulfuryl chloride, bromine, iodine monochloride) on 5-trimethylsilyl-2-furancarboxylic acid [307], its ethyl ester [308], and 2-trimethylsilyl-3,4-bis(methoxycarbonyl)furans [309] led to electrophilic substitution of the silyl group. Cleavage of the $Si-C_{furyl}$ bond in 5-trimethylsilyl-2-furoic acid and its ester with bromine gave a high yield (more than 80%) both in carbon tetrachloride [307-309] and in acetonitrile [308], but demetallation of the ethyl ester [308] by sulfuryl chloride with the formation of the corresponding chlorine derivative (yield 82%) was only observed in acetonitrile. In the same solvent iodination by iodine monochloride took place smoothly at room temperature [308]. Treatment of ethyl 5-trimethylsilylfurancarboxylate with iodine chloride in carbon tetrachloride gave a mixture of the chlorine and iodine products (15 and 85% respectively).



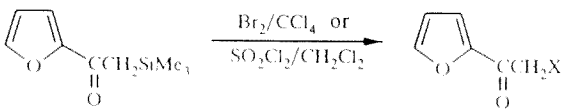
Desilylation products were also obtained from 2-trimethylsilyl-3,4-bis(methoxycarbonyl)furan in acetonitrile by the action of sulfuryl chloride, bromine, and iodine monochloride. However, in the reaction with sulfuryl chloride, 2,5-dichloro-3,4-bis(methoxycarbonyl)furan was obtained in addition to the usual product from substitution of the silyl group. The introduction of a methyl group at position 5 of the ring in 2-trimethylsilyl-3,4-bis(methoxycarbonyl)furan increased the reaction time, and the yields of the chlorine, bromine, and iodine products amounted to 73, 68, and 74% [309].



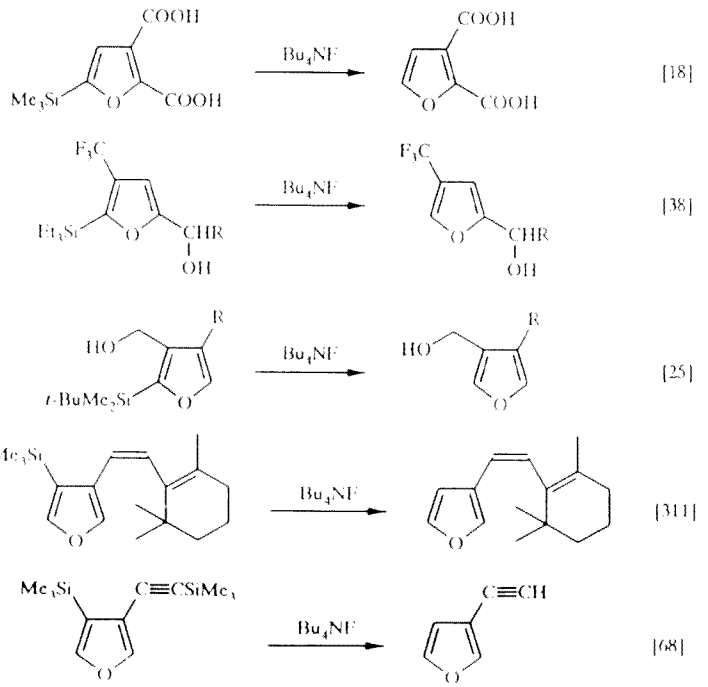
The $Sn-C_{furyl}$ bond in 2-methyl-5-trimethylstannylfuran is very easily broken by the action of iodine [31].



From 2-furyl trimethylsilylmethyl ketone [310] by the action of bromine in carbon tetrachloride or of sulfuryl chloride in methylene chloride the corresponding halogenomethyl ketones were obtained.



The reaction of furylsilanes with compounds that are sources of fluoride ions is often used for the elimination of the silyl group [18, 25, 38, 68, 76, 311], since the fluoride ion is the most suitable nucleophile for the silyl group. Tetrabutylammonium fluoride is most often used as fluorine-containing compound.



[18]

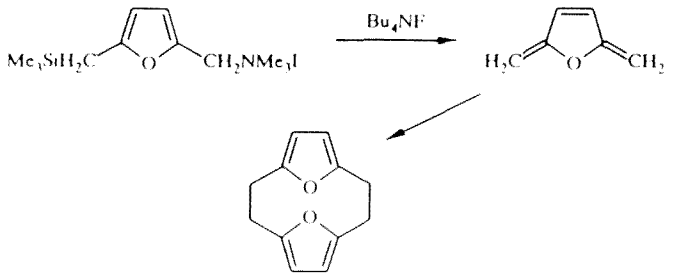
[38]

[25]

[311]

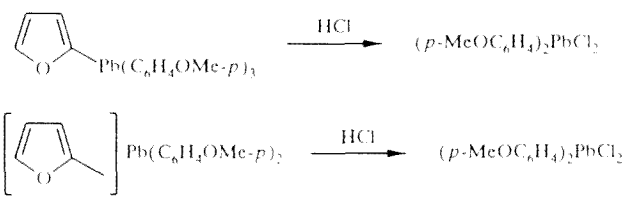
[68]

When heated with tetrabutylammonium fluoride in acetonitrile 2-dimethylaminomethyl-5-trimethylsilylmethylfuran, in which the silyl group is separated from the furan ring by a methylene group, is simultaneously desilylated and deaminated, giving a small yield of furanophane as a result of subsequent dimerization. The yield can be increased to 73% by conducting the reaction in a sealed tube at 110°C [312].



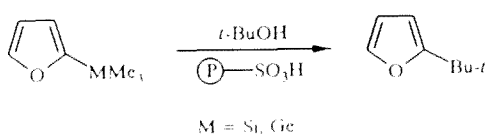
The acid removal of the trimethylsilyl group in methanol was investigated [313, 314], and it was established that the protodesilylation of 2-trimethylsilylfuran with perchloric acid takes place instantly; 3-trimethylsilylfuran is less reactive [313]. Opening of the furan ring probably competes with the cleavage of the Si−C bond in furylsilanes by hydrogen chloride in glacial acetic acid [9].

Bond cleavage by hydrogen chloride in tri(p-methoxyphenyl)(2-furyl)plumbane and di(p-methoxyphenyl)di(2-furyl)-plumbane [65] stops at the formation of di(p-methoxyphenyl)dichloroplumbane.



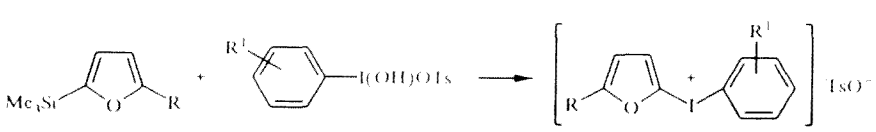
The electrophilic substitution of the trimethylsilyl [315-318] and trimethylgermyl [315] groups in 2-trimethylsilyl-furan, 2-trimethylsilylbenzofuran, and 2-trimethylgermylfuran was studied.

During the alkylation of 2-trimethylsilyl- and 2-trimethylgermylfurans by *tert*-butanol in the presence of Amberlist 15 ion-exchange resin, the silyl and germyl groups and not the hydrogen of the ring underwent electrophilic substitution [315], and the silyl group was substituted more easily than the germyl group.



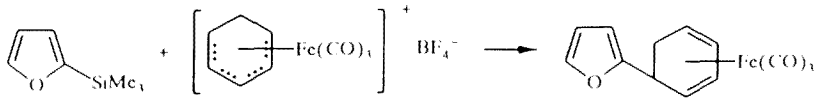
M = Si, Ge

[Hydroxy(tosyloxy)iodo]benzenes react with 2-trimethylsilylfuran when boiled in an acetonitrile−methanol mixture in a ratio of 1:1 and form low yields (9-20%) of the respective aryl(2-furyl)iodonium tosylates. Higher yields (61-74%) of the products were obtained from 2,5-bis(trimethylsilyl)furan, for which substitution of one silyl group is observed under these conditions [316].

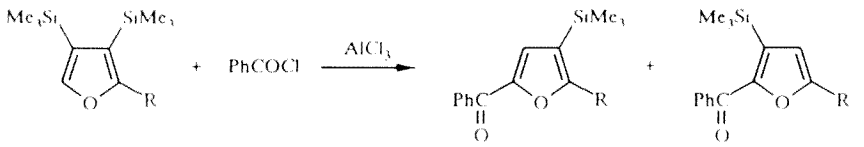


R = H, Me, Me_3Si

Electrophilic attack by the cation of the iron-containing complex $[Fe(CO)_3(C_6H_7)]^+BF_4^-$ on 2-trimethylsilylfuran in nitromethane also leads to *ipso* substitution of the silyl group [317].

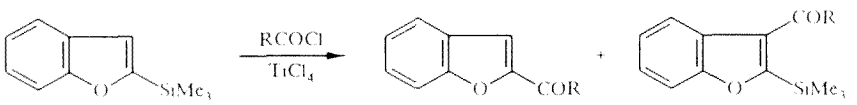


The acylation of 3,4-bis(trimethylsilyl)- and 2-methyl-3,4-bis(trimethylsilyl)furans by benzoyl chloride with aluminum chloride takes place with simultaneous desilylation and the formation of a mixture of two isomers (yields 56 and 40% respectively). The formation of the products from *ipso* substitution of the silyl groups was not observed [69].

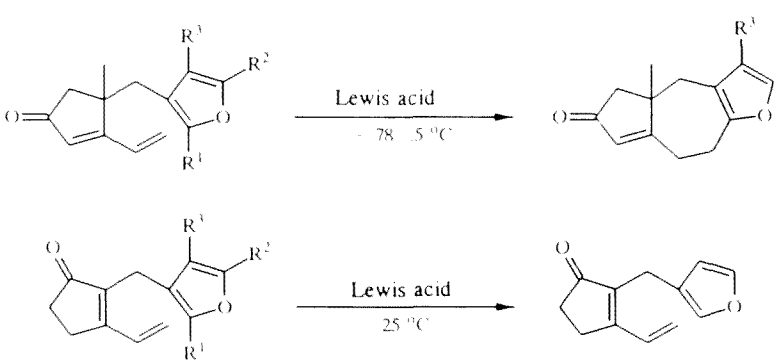


R = Me (1 : 3), H (1 : 1)

2-Trimethylsilylbenzofuran reacts very quickly with acid chlorides in the presence of titanium tetrachloride at −78°C with the formation of the respective 2-acylbenzofurans. As well as substitution of the silyl group, acylation occurs to a small degree (up to 5%) at position 3 of the benzofuran [318].

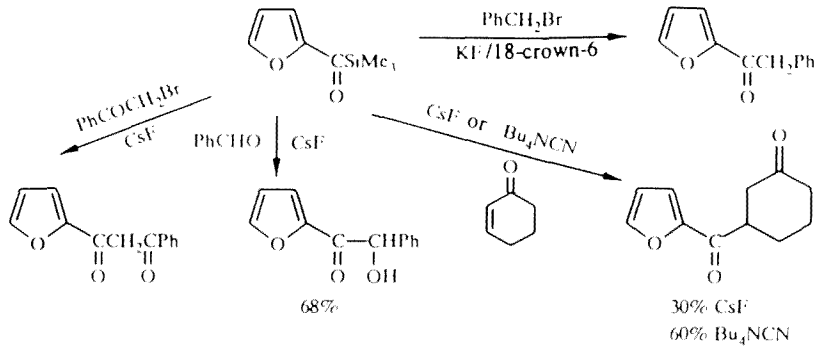


The intramolecular cycloalkylation of conjugated dienones containing trimethylsilylfuryl substituents by the action of Lewis acids ($FeCl_3$, $BF_3 \cdot Et_2O$) with cooling to −78°C proved an extremely useful method for the synthesis of condensed tricyclic compounds with yields of 85-96%. It should be noted that removal of the Me_3Si group was observed for 2- and 5-silylfurans, while in the case of the 3-silyl derivative the Si−C bond was stable under the given conditions. At room temperature only rapid desilylation occurred not only in the 2- and 5-silyl-substituted furans but also in the 3-substituted isomer [319].

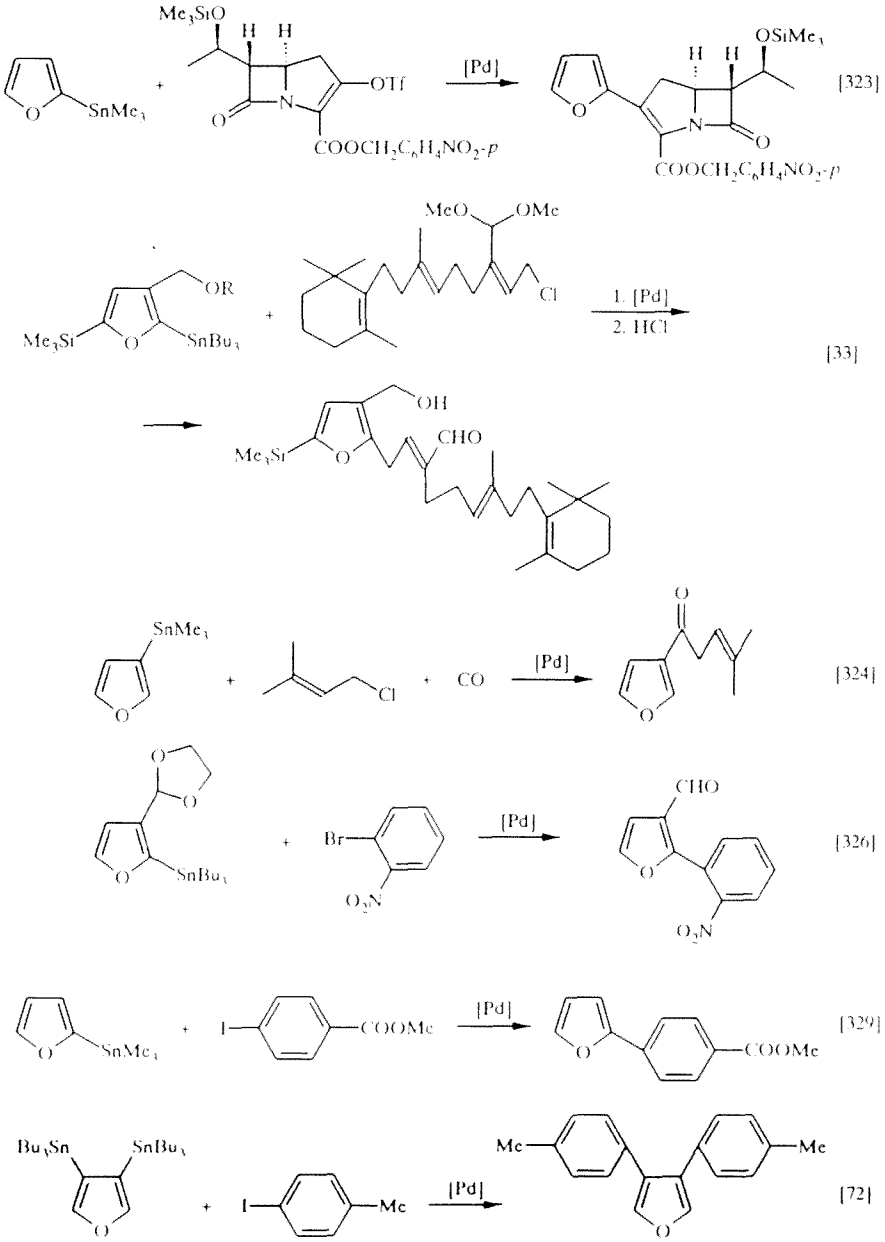


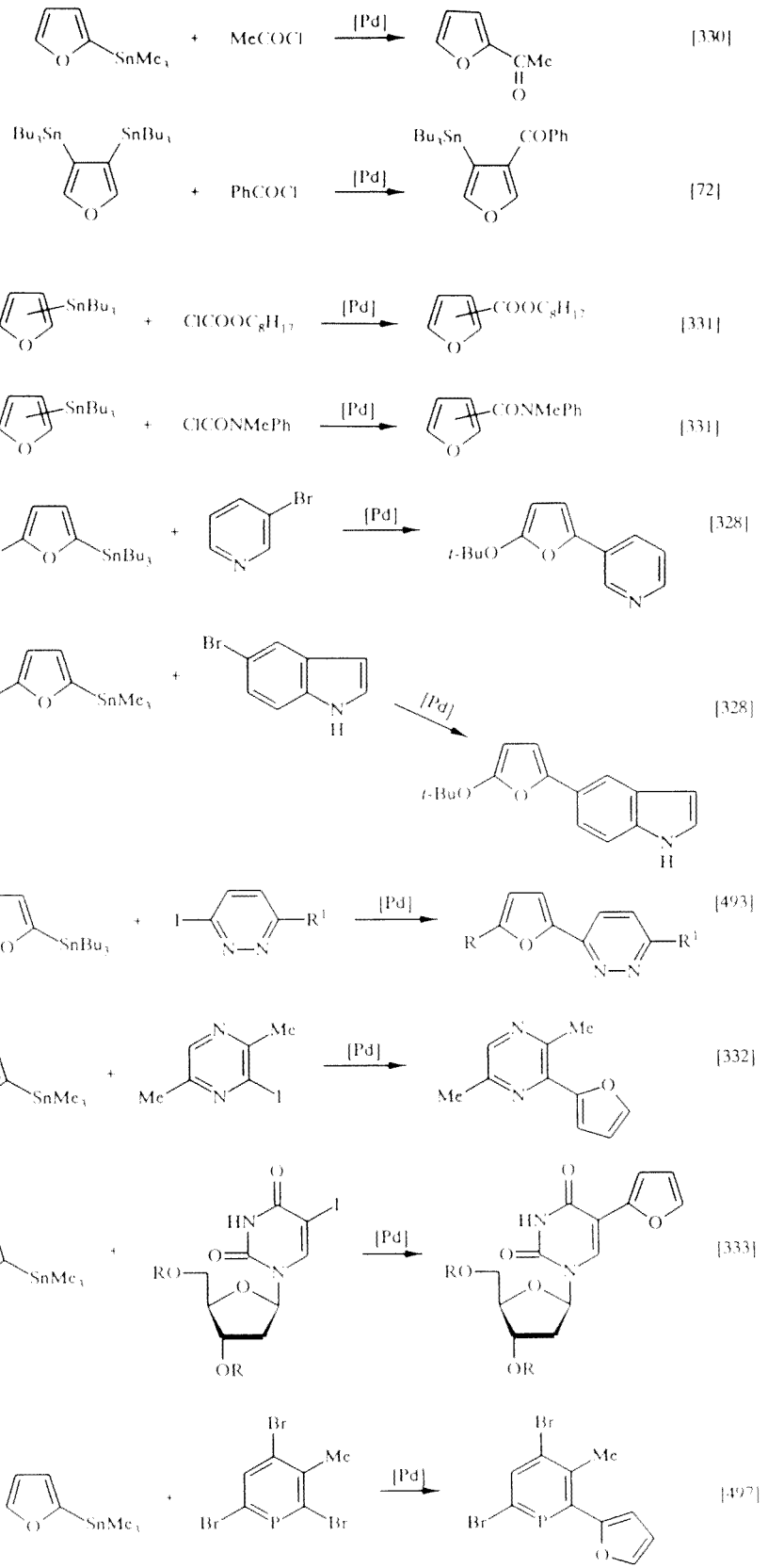
$R^1 = Me_3Si$, $R^2 = R^3 = H$; $R^2 = Me_3Si$, $R^1 = R^3 = H$; $R^3 = Me_3Si$, $R^1 = R^2 = H$

In the presence of CsF, KF/18-crown-6 [119], and Bu_4NCN [320] furoyltrimethylsilane reacts with various electrophiles with cleavage of the Si−C bond, i.e., furoylsilane can be regarded as a nucleophilic acylating agent in these processes.

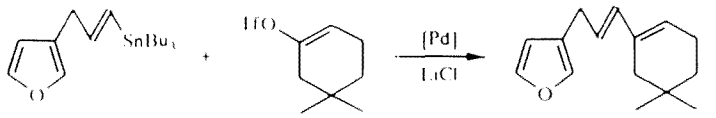


In the presence of palladium catalysts 2- and 3-substituted furylstannanes [33, 72, 321-333] enter into cross-coupling with triflates [323], alkenyl halides [33, 72], allyl halides and carbon monoxide [324, 325], aryl bromides [30, 72, 326-328] and aryl iodides [72, 329], acid chlorides [72, 330], octyl chloroformate [331], carbamoyl chlorides [331], bromine and iodine derivatives of nitrogen-containing heterocycles [328, 332, 333, 493], and bromophosphorinanes [497].

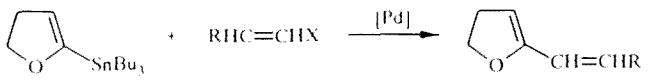




The method is distinguished by high yields, regioselectivity, and stereospecificity. It can be used for dihydrofurylstannanes [334] and benzofurylstannanes [335] and also for compounds in which the furan ring and the tin atom are separated by an alkenyl chain [140, 141].

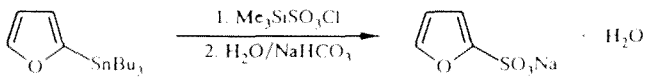


[140, 141]

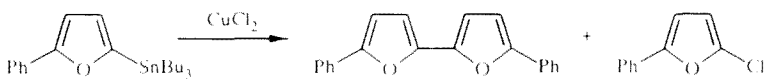


[334]

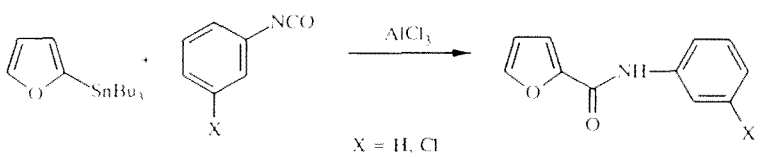
By the action of trimethylsilyl chlorosulfonate on 2-tributylstannylfuran it was possible to substitute the tributylstannyl group selectively. The reaction was realized under mild conditions at room temperature without a catalyst, and the 2-furylsulfonate was obtained with a 95% yield after only 1 h [495].



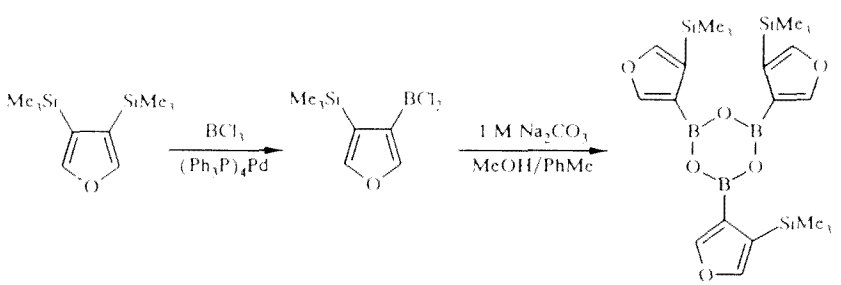
The reaction of 5-phenyl-2-tributylstannylfuran with an equimolar amount of $CuCl_2$ at 67°C gives a mixture of two products 5,5′-diphenyl-2,2′-bifuran (21%) and 5-phenyl-2-chlorofuran (73%). In contrast to the oxidative coupling of the analogous lithiofurans, the product from substitution of the stannyl group by chlorine is formed preferentially [496].



2-Tributylstannylfuran reacts with aryl isocyanates under mild conditions (20°C) in the presence of aluminum chloride. This method is convenient for the synthesis of the arylamides of furancarboxylic acid [336].

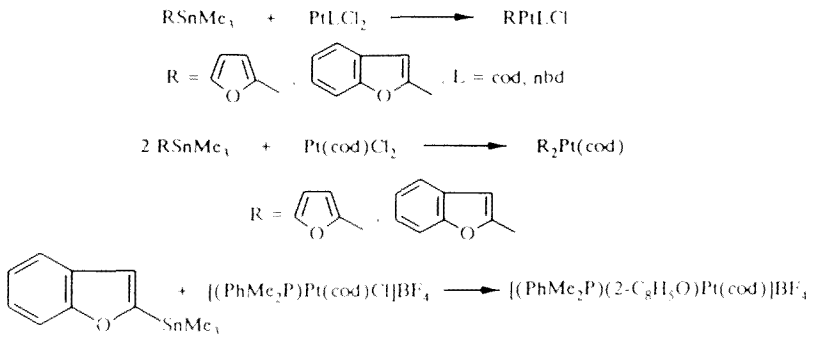


Unlike stannylfurans, silylfurans proved completely unreactive in cross-coupling reactions with aryl and alkenyl halides in the presence of palladium catalysts. It was found that the silyl group of 3,4-bis(trimethylsilyl)furan could only be substituted by the action of a strong Lewis acid — boron trichloride and the palladium catalyst $(Ph_3P)_4Pd$ [70].

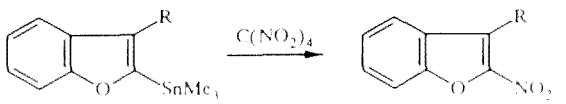


In methylene chloride and 1,1,2,2-tetrachloroethane, the platinum complexes $[Pt(cod)Cl_2]$, $[Pt(nbd)Cl_2]$ [337], and $[(PhMe_2P)Pt(cod)Cl]BF_4$ [338] react with 2-trimethylstannylfurane [338] and 2-trimethylstannylbenzofuran [337, 338] with substitution of one or two chlorine atoms by the heteroatomic group. The $Sn-C_{furyl}$ bond is easily cleaved by the action of the platinum complexes, and the yields of the reaction products amount to 70-90%. On the other hand, after 40 h at 30°C in

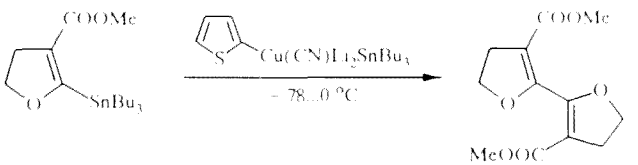
methylene chloride 2-trimethylgermylbenzofuran and the complex $[Pt(nbd)Cl_2]$ in a ratio of 4:1 only form the monoaryl complex with a yield of 10% [337].



Removal of the trimethylstannyl group is also observed during the action of tetranitromethane on derivatives of 2-trimethylstannylbenzofuran in dimethyl sulfoxide. This reaction makes it possible to realize nitration regioselectivity at position 2 of benzofuran [339].

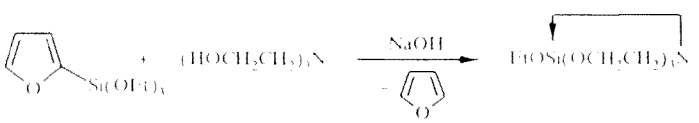


The action of a thienyl-containing cuprate on tributyl[2-(3-carboxymethyl-4,5-dihydrofuryl)]stannane gives a low yield (15%) of a dimeric product [340].



Reactions involving the removal of a silyl group by the action of an aqueous alcohol solution of potassium hydroxide [341] and of amines in the presence of catalytic amounts of alkali metals [24, 44, 342] are known. The rate constants for the demetallation of furylsilanes, furylstannanes, benzofurylsilanes, benzofurylgermanes, and benzofurylstannanes by sodium methoxide in methanol at 50°C were measured [343]. It was established that the stannyl group is removed most easily. In the series of 2-substituted benzofurans, the trimethylsilyl group is 1300 times more reactive than the trimethylgermyl group. The rate of desilylation also depends on the alkyl substituent at the silicon atom. Thus, the $ArSiMe_3$ compounds are demetallated 130-190 times more quickly than $ArSiEt_3$ [343].

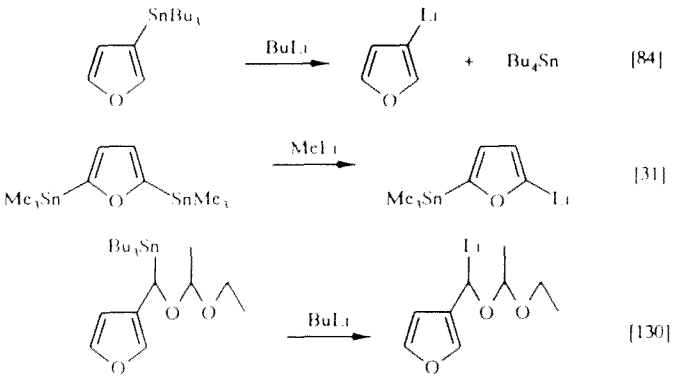
Attempts to obtain 2-furylsilatrane from 2-furyltriethoxysilane and triethanolamine in the presence of basic catalysts (sodium hydroxide, metallic sodium) did not lead to the desired results, since removal of the furyl group and the formation of ethoxysilatrane were observed under these conditions [344].



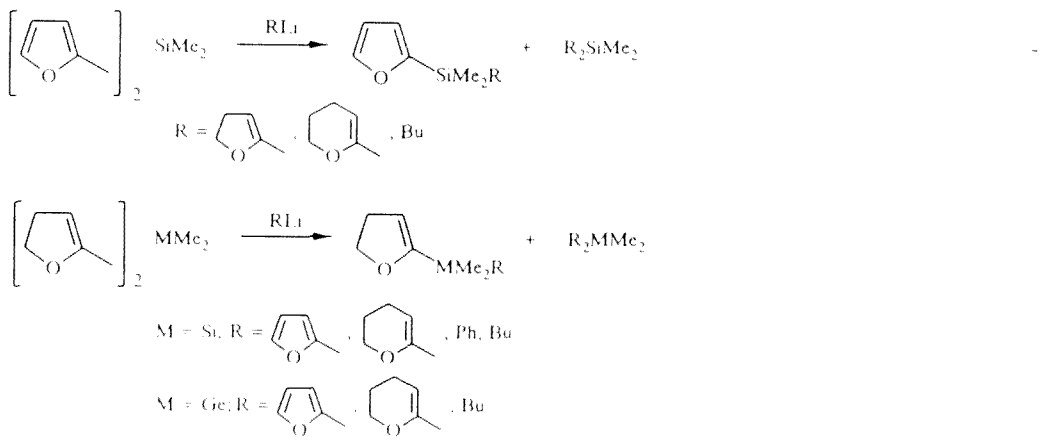
The action of a methanol solution of sodium methoxide [116] or an ethanol solution of sodium hydroxide [151] led to the desilylation of furan derivatives containing silicon in the side chain.

Butyllithium can react with the furan derivatives of group IVB elements in two directions, i.e., metallation of the furanring or cleavage of the $M-C_{furyl}$ bond [7, 31, 43, 84]. Thus, for trimethyl(2-furyl)silane, desilylation (yield 50%) takes

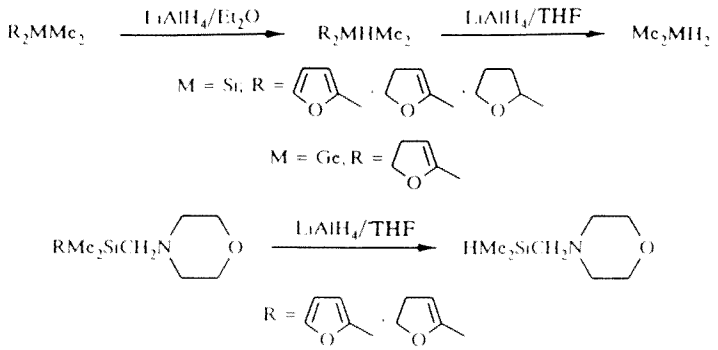
place in addition to metallation of the ring by the butyllithium (yield 35%) [7]. Trimethyl(2-furyl)stannane reacts with butyllithium in the range between −70 and 0°C with cleavage of the $Sn-C_{furyl}$ bond [7]. In a series of papers, this property was used to obtain lithium derivatives of furan [31, 84], including compounds containing the lithium atom in the side chain [130].



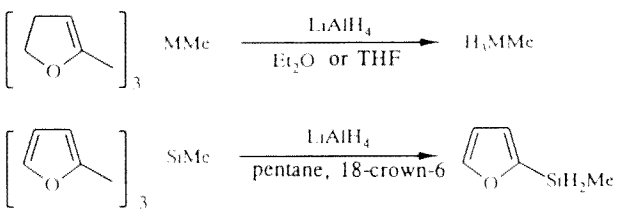
Cleavage of the Si−C and Ge−C bonds was observed in the reaction of dimethyl(2-furyl)- and dimethyldi[2-(4,5-dihydrofuryl)]silanes and dimethyldi[2-(4,5-dihydrofuryl)]germane with organolithium compounds. The reactions were usually conducted with equimolar amounts of the reagents in a mixture of THF and hexane (8:1) at −30°C (30 min), and the temperature was then raised to room temperature. Among the employed organolithium compounds the most active was butyllithium, which reacts with the above-mentioned furan compounds more selectively with the formation of only the monosubstituted products and with a high degree of conversion (67-89%). In the reaction with the lithium derivatives of heterocycles, the degree of conversion was lower (35-60%), and the amount of the products from exhaustive substitution of the heterocycles in the initial furylsilanes and furylgermanes was small (3-12%). Phenyllithium proved unreactive and only reacted with the most reactive dimethyldi[2-(4,5-dihydrofuryl)]silane [345].



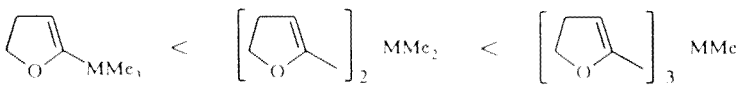
Lithium aluminum hydride was used for the cleavage of the Si−C and Ge−C bonds in the furyl and dihydrofuryl derivatives of silicon and germanium [346-348]. The hydride ion substitutes the heterocyclic group in dimethyldi(2-furyl)-, dimethyl(2-furyl)morpholinomethyl-, dimethyldi[2-(4,5-dihydrofuryl)]-, dimethyl[2-(4,5-dihydrofuryl)]morpholinomethyl-, and dimethyl(2-tetrahydrofuryl)silanes and dimethyl[2-(4,5-dihydrofuryl)]germane. For the compounds containing heterocyclic substituents at the element the reaction in diethyl ether takes place selectively with the substitution of one heterocycle, while in the more polar tetrahydrofuran dimethylsilane and dimethylgermane are formed exclusively [346].



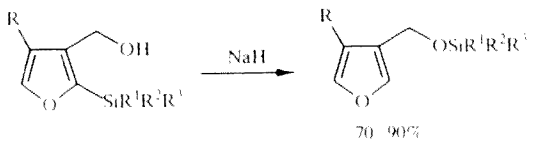
Methyltris[2-(4,5-dihydrofuryl)]silane and methyltris[2-(4,5-dihydrofuryl)]germane lose the dihydrofuryl group more readily than the bisdihydrofuryl analogs, and as a rule exhaustive substitution is observed in ether and tetrahydrofuran. Methyl(2-furyl)silane can be obtained under the mild conditions of phase-transfer catalysis in benzene, pentane, or hexane:



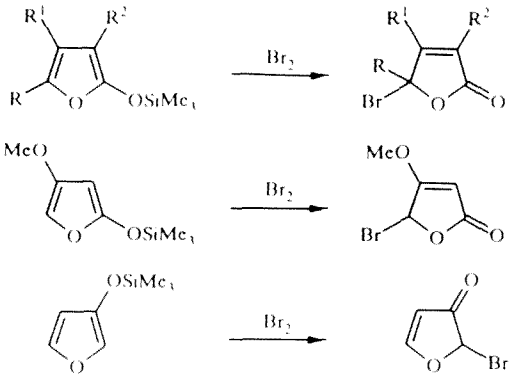
Trimethyl(2-furyl)-, trimethyl[2-(4,5-dihydrofuryl)]-, trimethyl(2-tetrahydrofuryl)silanes and trimethyl[2-(4,5-dihydrofuryl)]germane, containing three alkyl substituents at the metal atom, are stable to the action of lithium aluminum hydride, and substitution of the heterocycle is not observed even after prolonged boiling in THF [347]. The results from investigations into the reaction of heterylsilanes and heterylgermanes with lithium aluminum hydride showed that their reactivity depended on the number of heterocycles, increasing in the order:



During the action of sodium hydride on 2-trialkylsilyl-3-hydroxymethylfurans in THF and DMFA 1,4-C−O silyl migration is observed, and this results in cleavage of the Si−C bond and the simultaneous silylation of the hydroxymethyl group [349].



Of compounds of type III, silyloxyfurans have been used most widely in organic synthesis; by their desilylation with various agents it is possible to obtain the most varied furan derivatives [350-375]. Compounds of this type are extremely active in reactions with bromine [167, 175, 177], and the reactions give high yields and are highly regiospecific.

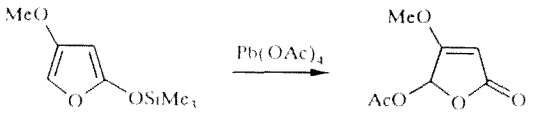


[167]

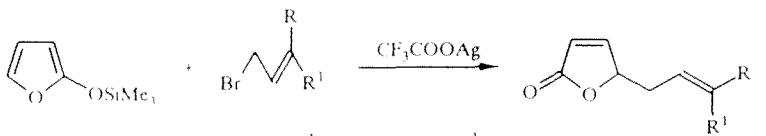
[175]

[177]

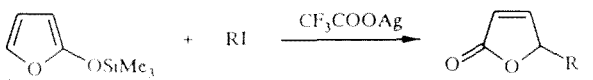
Lead tetraacetate reacts with 2-trimethylsilyloxy-4-methoxyfuran with an 85% yield of butenolide, containing an acetoxy group at position 5 [175].



2-Trimethylsilyloxyfuran reacts with bromo- and iodoalkenes under the influence of silver trifluoroacetate [350-352]. The yields amount to 95%, and the alkylation is regioselective.

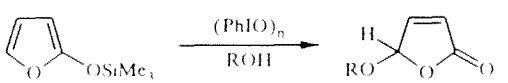


R = H, R^1 = Me, Ph; R = R^1 = Me



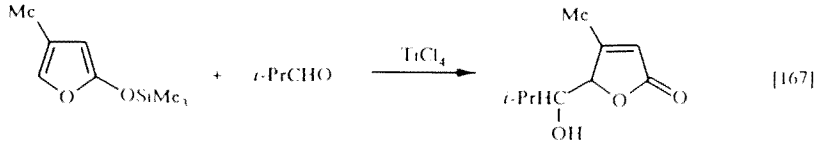
R = Et, Pr, Bu, C_5H_{11}, C_9H_{19}, CH_2CN, CH_2COOMe, CH_2COOEt

The oxidation of 2-trimethylsilyloxyfuran with iodosobenzene in the presence of nucleophiles under the influence of boron trifluoride etherate in methylene chloride at room temperature gave 5-substituted 2(5H)-furans [353].



R = Ac, $MeSO_2$, p-$MeC_6H_4SO_2$, Et

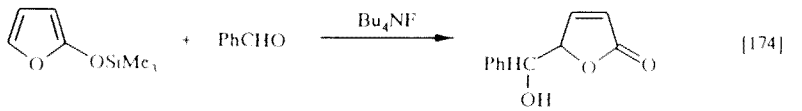
The reactions of silyloxyfurans with carbonyl-containing compounds are most often used in organic synthesis. They take place in the presence of the following catalysts: $TiCl_4$, $SnCl_4$, $ZnBr_2$, $BF_3 \cdot Et_2O$, Bu_4NF [167, 168, 171, 174, 175, 178, 354-362, 498].



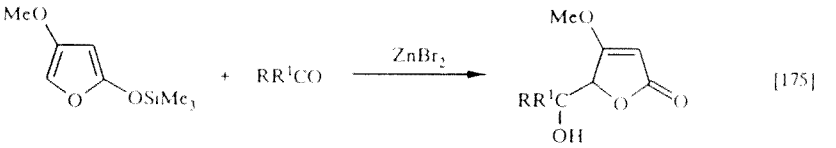
[167]

[168]

R = $PhCH_2OCH_2$, C_6H_{13}, $PhCH_2CH_2$

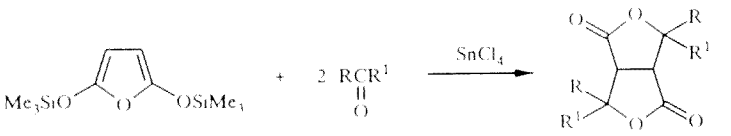


[174]

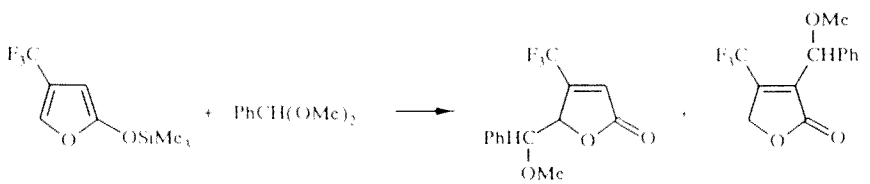


[175]

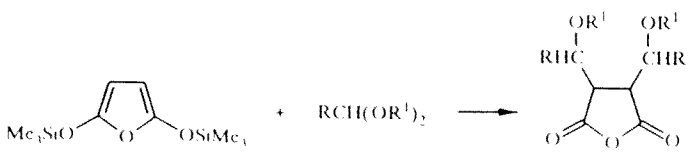
In analogous processes 2,5-bis(trimethylsilyloxy)furan forms dilactones with yields of 66-72% [171, 358].



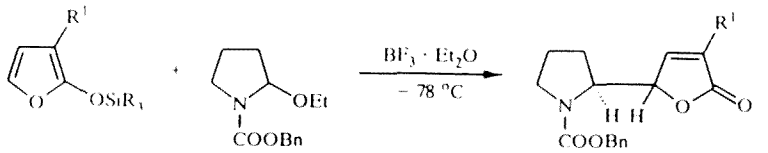
In methylene chloride at low temperatures (−78 to −60°C), 4-substituted 2-silyloxyfurans and also 2,5-bis(trimethylsilyloxy)furan react with acetals [168, 173], ortho esters [175], N,O-acetals [363], and nitrones [364] under the influence of the following catalysts: $ZnBr_2$ [175], $TiCl_4$ [168], $BF_3 \cdot Et_2O$ [168, 363], and $F_3CSO_3SiMe_3$ [173, 364]. Benzaldehyde dimethyl acetal reacts with 4-trifluoromethyl-2-trimethylsilyloxyfuran in methylene chloride in the presence of titanium tetrachloride at −78°C. Under these conditions 4-trifluoromethyl-5-phenyl(methoxy)methyl-2(5H)-furan is formed selectively with a yield of 26% after 15 min. If the reaction time and temperature are increased and the catalyst is changed (boron trifluoride etherate), the yield is increased to 36-62%. However, the selectivity is lost, and the 3-isomer is formed in addition to the 5-substituted product. The ratio of the isomers depends on the process conditions and varies between 4:1 and 1:2 [168].



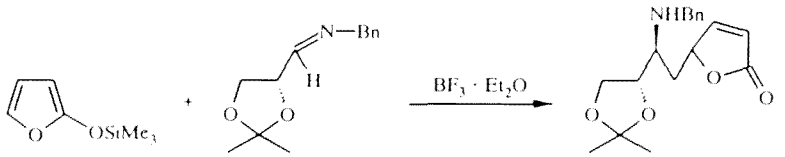
The products from the reaction of 2,5-bis(trimethylsilyloxy)furan with acetals and ortho esters are bissubstituted derivatives of succinic anhydride [173].



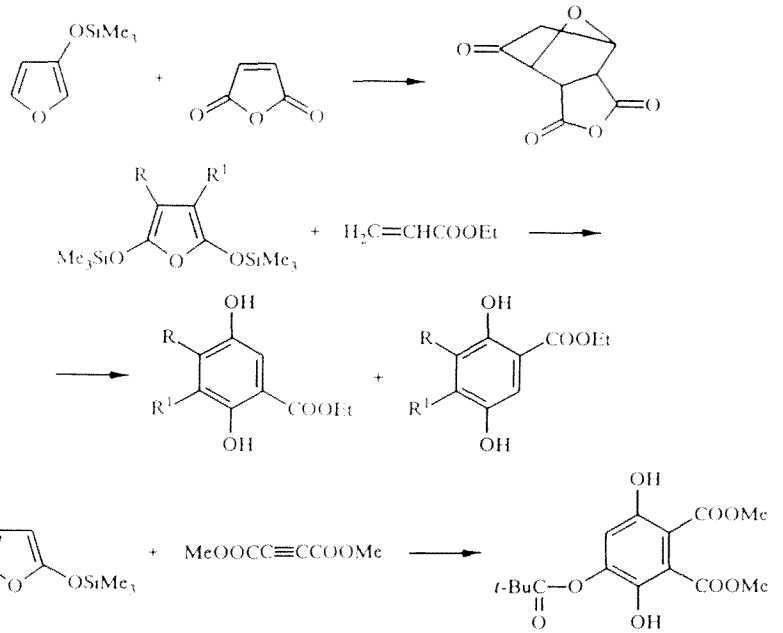
The addition of 2-trimethylsilyloxyfuran and 2-(*tert*-butyldimethylsilyloxy)-3-methylfuran to the cyclic N-acyliminium ion obtained during the treatment of 1-benzyloxycarbonyl-2-ethoxypyrrolidine with boron trifluoride etherate leads to a mixture of *threo/erythro* isomers in ratios of 8.5:1 and 6:1 respectively [365].



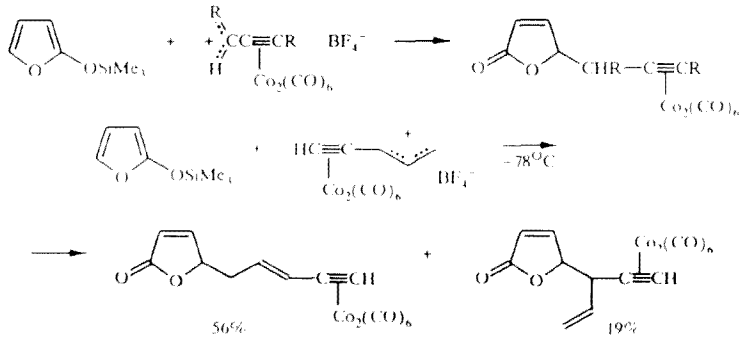
In the reaction of benzylimine derivatives with trimethylsilyloxyfuran in the presence of boron trifluoride etherate, the 5-substituted 2(5H)-furanones are formed as a 1:1 mixture of the two epimers at $C_{(4)}$ [366, 367].



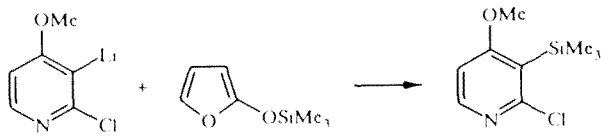
Silyloxyfurans enter into the Diels–Alder reaction with maleic anhydride [167, 177], ethyl acrylate [170], and dimethyl acetylenedicarboxylate [368].



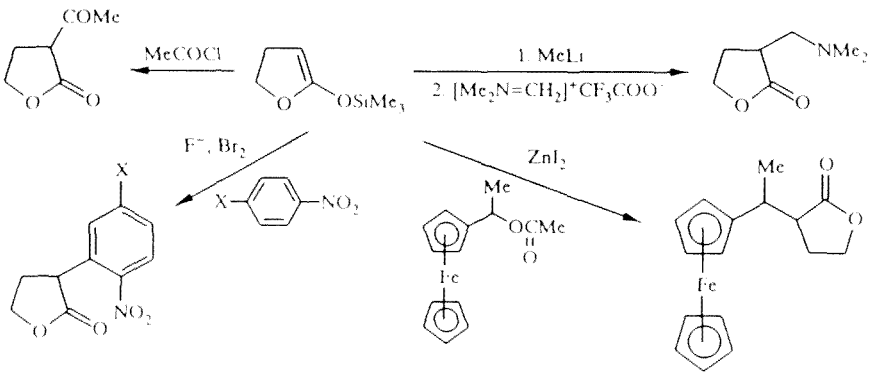
The alkylation of silyloxyfurans by the acetylene complexes of cobalt was investigated [369]. The reaction of silyloxyfuran with the propynyl cationic complexes in methylene chloride at 45°C is complete in 10 min. The cationic complex with the positive charge delocalized at the allylic system forms a mixture of two isomers.



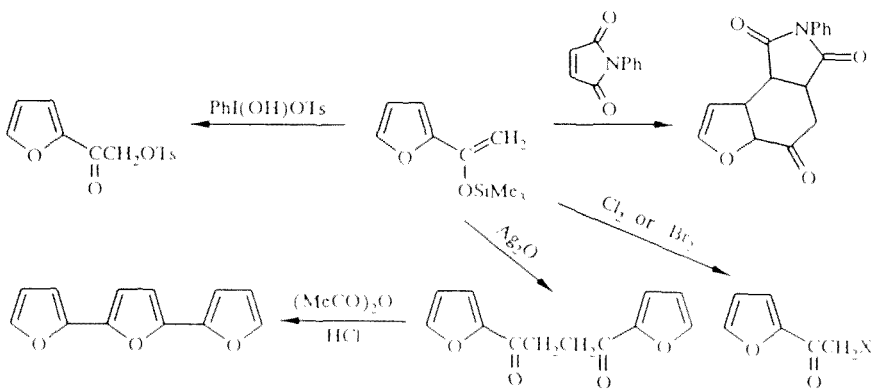
Trimethylsilyloxyfuran can also be used as a silylating agent in reaction with the lithium derivative of pyridine [370].



2-Trimethylsilyloxy-4,5-dihydrofurans have properties characteristic of silyloxyfurans. They react with lead tetraacetate and tetrabenzoate [376], aldehydes and ketones [377-380], and diacetals [381]. Their transformations under the influence of acetyl chloride [382], methyllithium and dimethylmethyleneammonium trifluoroacetate [383], aromatic nitro compounds [384, 385], and 1-acetoxy-1-ferrocenylethane [386] were also investigated.

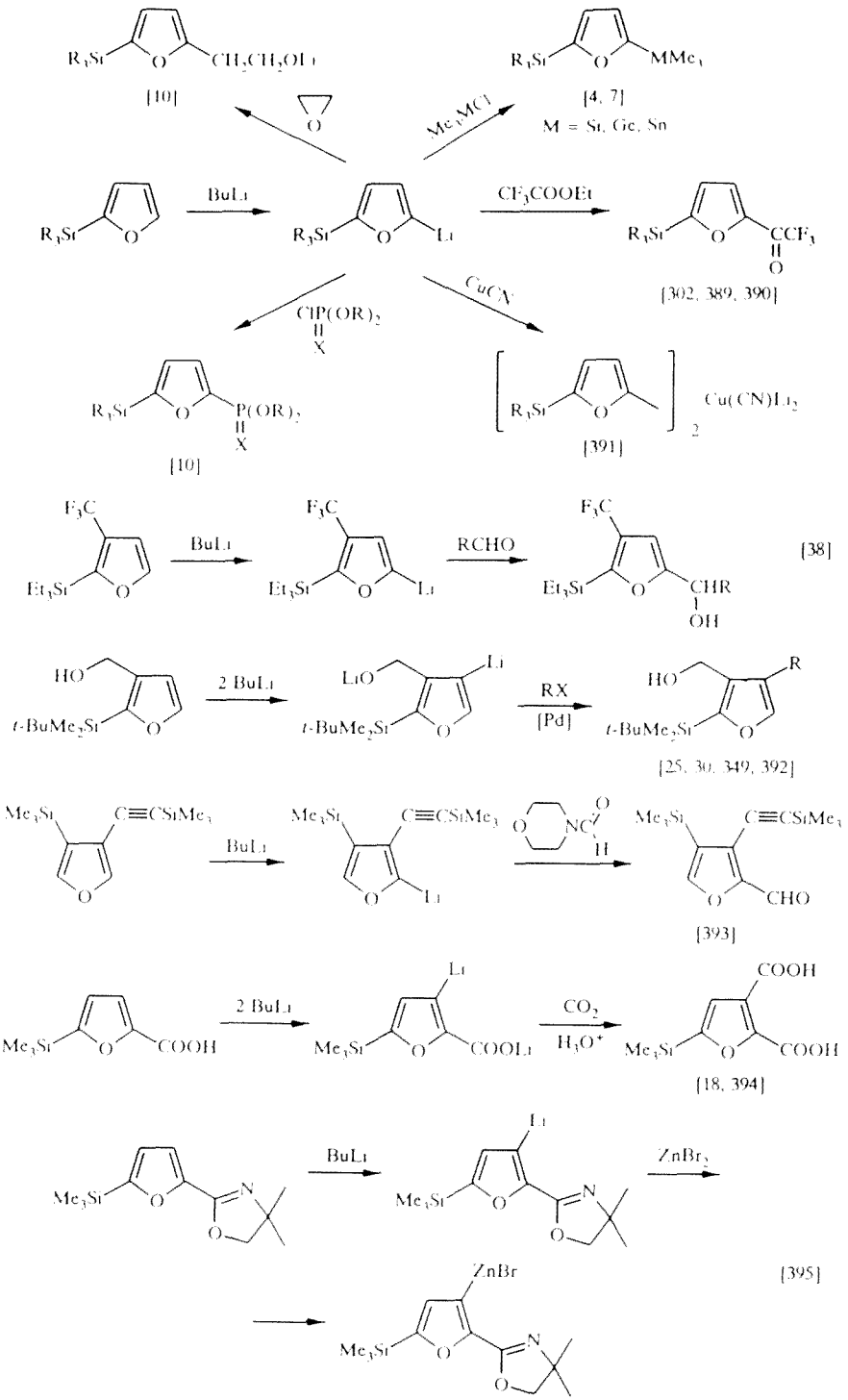


In addition to silyloxyfurans, the trimethylsilyl ethers of furyl-containing enols are also used in organic synthesis [236-239, 387, 388]. Some transformations of 2-(1-trimethylsilyloxyvinyl)furan were investigated. Thus, when treated with silver oxide, it gave 1,2-bis(2-furoyl)ethane, which in turn underwent cyclization to terfuryl with an overall yield of 65% [326]. The reaction with [hydroxy(tosyloxy)iodo]benzene at room temperature was used for the production of tosyloxy ketones [238]. The silyl ether acts as a diene toward N-phenylmaleimide [387].

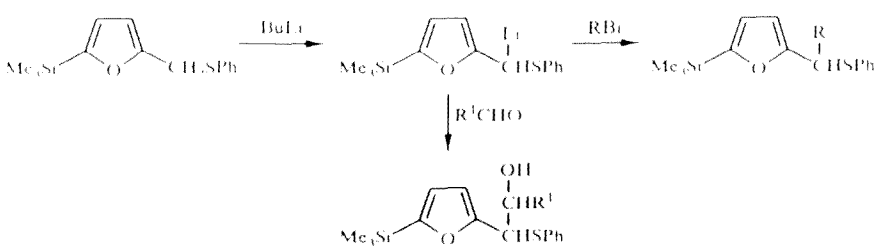


2.2. Reactions Involving the Furan Ring and the Functional Groups of the Organic Substituents

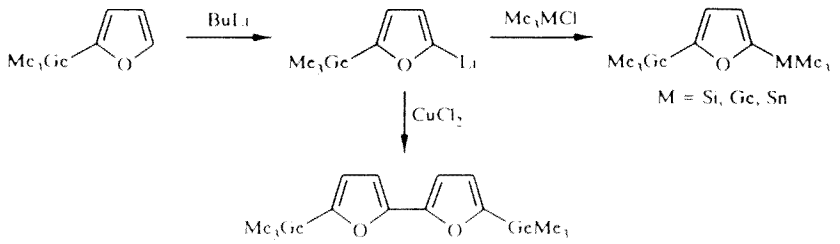
The reaction of trialkylfurylsilanes and their derivatives with butyllithium results in metallation of the furan heterocycle [1-4, 7, 10, 18, 25, 30, 38, 302, 349, 389-392]. This process is widely used for the introduction of various functional groups into the furan ring of silylfurans.



However, as already mentioned in Section 2.1, during the action of butyllithium desilylation occurs in addition to lithiation [7, 43]. Sometimes, metallation occurs not at the furan but at a methylene group in the functional substituents [396].

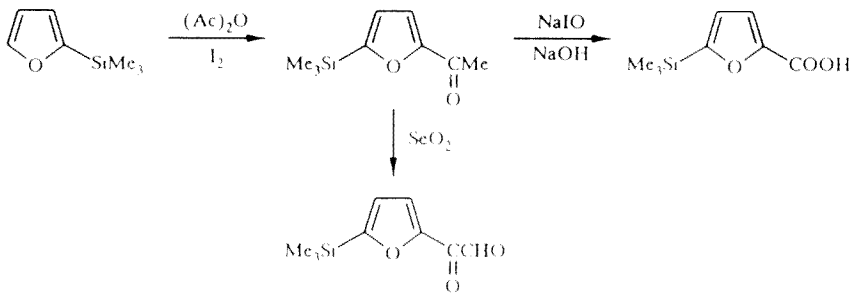


Trimethyl(2-furyl)germane also undergoes metallation with butyllithium [7, 315] with the formation of trimethyl(5-lithio-2-furyl)germane, which is used as the starting compound in the synthesis of 2,5-disubstituted furans.

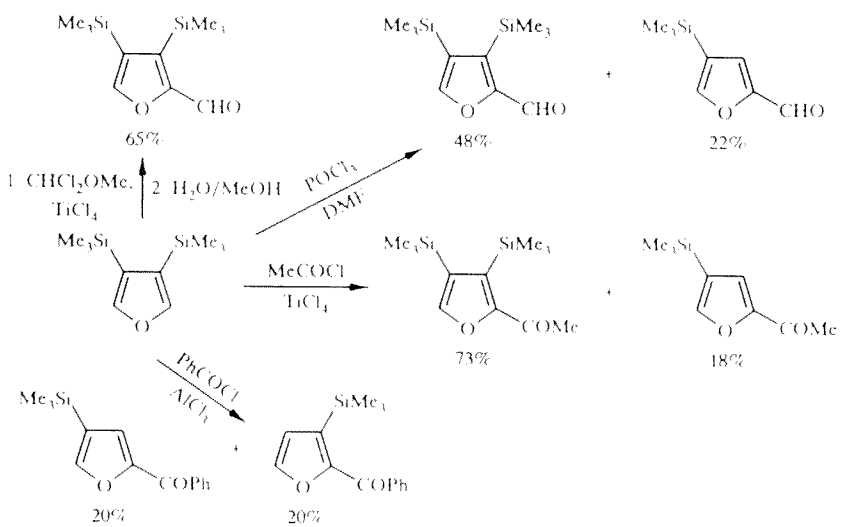


For stannylfurans, cleavage of the $Sn-C_{furyl}$ bond by the action of butyl- and methyllithium is the main process [7, 31, 84].

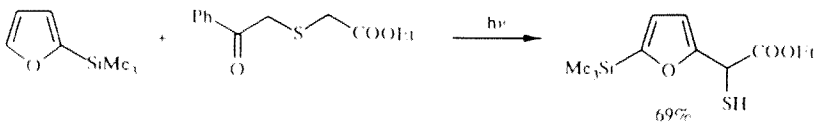
Trimethyl(2-furyl)silane is acylated with a small yield (25%) by acetic anhydride in the presence of iodine [307], and the obtained ketones are easily oxidized by sodium hypoiodite NaIO or selenium dioxide [307, 397].



In [70] the possibilities of acylation of 3,4-bis(trimethylsilyl)furan were investigated. The Friedel–Crafts reaction with dichloromethyl methyl ether under the influence of titanium tetrachloride gave after hydrolysis 2-formyl-3,4-bis(trimethylsilyl)furan. During formylation by the Vilsmeier method and acylation with acetyl chloride (titanium tetrachloride) the products from desilylation at position 3 were also formed, in addition to the products from substitution at position 2 of the furan ring. The reaction of bis(trimethylsilyl)furan with benzoyl chloride in the presence of aluminum chloride leads to simultaneous acylation at position 2 and desilylation of one of the trimethylsilyl groups.

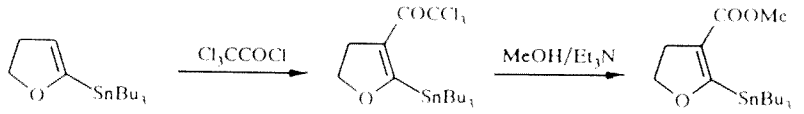


Functionalization of position 5 of the ring in trimethyl(2-furyl)silane can be achieved by photolysis with phenacyl sulfides [398].

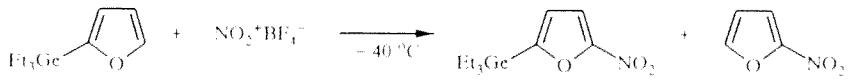


The acylation of triethyl(2-furyl)germane with trifluoroacetic anhydride is not accompanied by cleavage of the Ge–C bond. The only product triethyl(5-trifluoroacetyl-2-furyl)germane (64%) was obtained as a result of electrophilic substitution [315].

The reaction of tributyl[2-(4,5-dihydrofuryl)]stannane with trichloroacetyl chloride in the presence of Hünig's base gave 3-trichloroacetyl-2-tributylstannyl-4,5-dihydrofuran with a 65% yield. In reaction with a methanol solution of triethylamine, the product was converted into a carboxymethyl derivative [399].

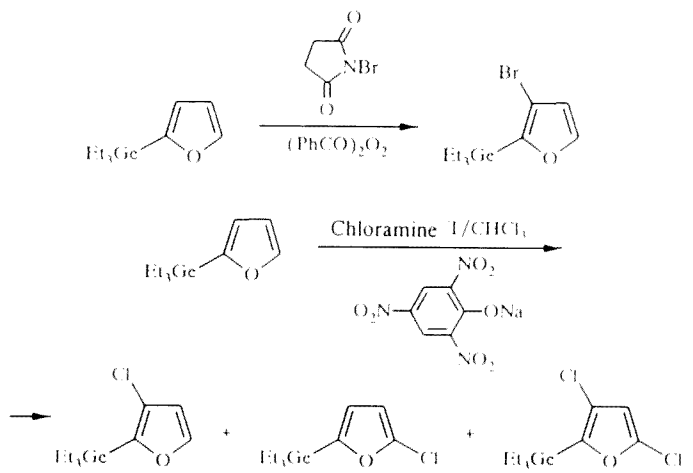


The usual method of nitration with acetyl nitrate is unsuitable for furylsilanes and furylgermanes on account of strong resinification of the reaction mixture. Resinification is also observed in the presence of the neutral nitrating agent nitronium tetrafluoroborate, but the corresponding 5-nitro-substituted derivative was obtained with a small yield (10%) from triethyl(2-furyl)germane [315].

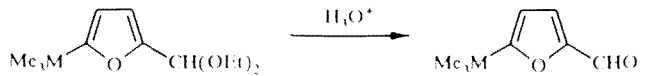


Under analogous conditions, trimethyl(2-furyl)silane forms about 4% of the nitration product. A small amount of 5-nitrofuran was formed as a result of desilylation and degermylation [315].

Whereas the bromination of triethyl(3-bromo-2-furyl)germane with dioxane dibromide takes place exclusively as *ipso* substitution, triethyl(3-bromo-2-furyl)germane was obtained with a 43% yield by the action of N-bromosuccinimide in the presence of benzoyl peroxide under radical conditions [315]. The chlorination of furylgermane was realized with Chloramine T in the two-phase chloroform–water system with sodium picrate as catalyst. The main reaction product was triethyl(3-chloro-2-furyl)germane (35%), and the 5-substituted isomer and dichloro-substituted furylgermane were also formed [315].

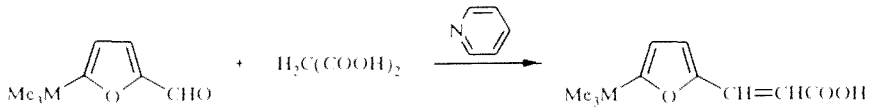


The various chemical transformations of the aldehyde group in 5-trimethylsilylfurfural [400-402] and 5-trimethylgermylfurfural [27, 221], obtained by hydrolysis of the corresponding acetals, have been widely investigated.



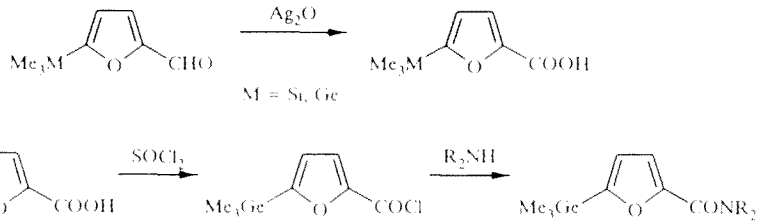
M = Si, Ge

During the condensation of equimolar amounts of malonic acid with silyl- or germylfurfurals in the presence of pyridine 5-substituted furylacrylic acids are formed with yields of 63 and 73%.



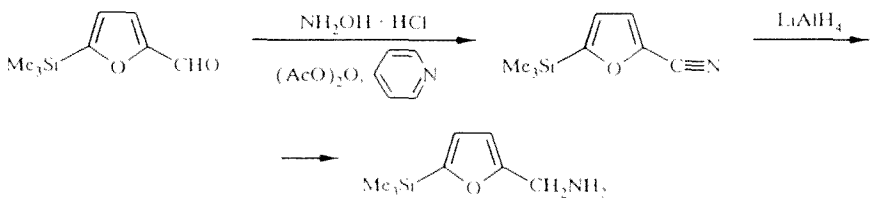
M = Si, Ge

The oxidation of the aldehyde group by freshly precipitated silver oxide or potassium permanganate in an alkaline medium resulted in the formation of silyl- and germylfurancarboxylic acids [27, 401]. 5-Trimethylgermylfurancarboxylic acid in turn was transformed by the action of thionyl chloride into 5-trimethylgermylfuroyl chloride with an 86% yield. Treatment of the latter with an aqueous solution of ammonia or with an excess of diethylamine gave the corresponding amides [110].

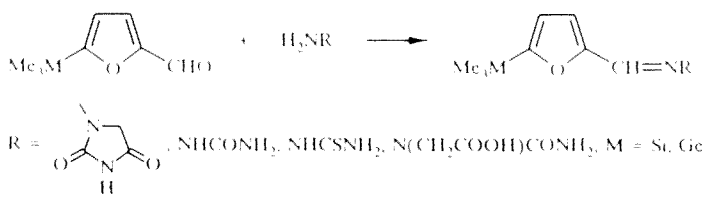


M = Si, Ge

When 5-trimethylsilylfurfural was heated with hydroxylamine hydrochloride in the presence of pyridine and acetic anhydride, 5-trimethylsilyl-2-cyanofuran was formed with an 85% yield. The product was easily reduced to 5-trimethylsilyl-2-furfurylamine with lithium aluminum hydride in ether [401].

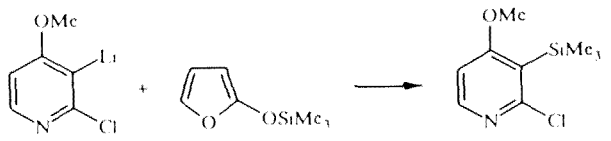


The condensation of the silyl and germyl derivatives of furfural with aminohydantoin, semicarbazide, and semicarbazidoacetic acid on heating in an alcohol or aqueous alcohol medium was investigated. Removal of the trimethylsilyl or trimethylgermyl group was not observed under these conditions, and the azomethine derivatives were formed with yields of 60-90% [27, 400].

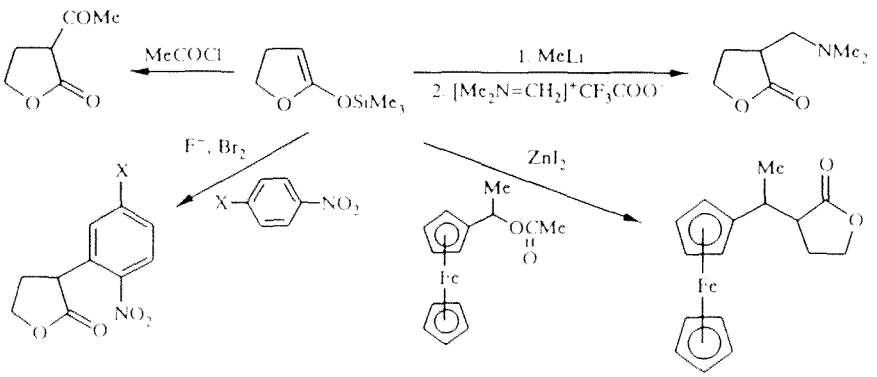


The enantioselective synthesis of 5-trimethylsilylfurfuryl alcohols by the asymmetric addition of diethylzinc to 5-tri-methylsilylfurfural in the presence of the chiral amines 1-4 was investigated [402].

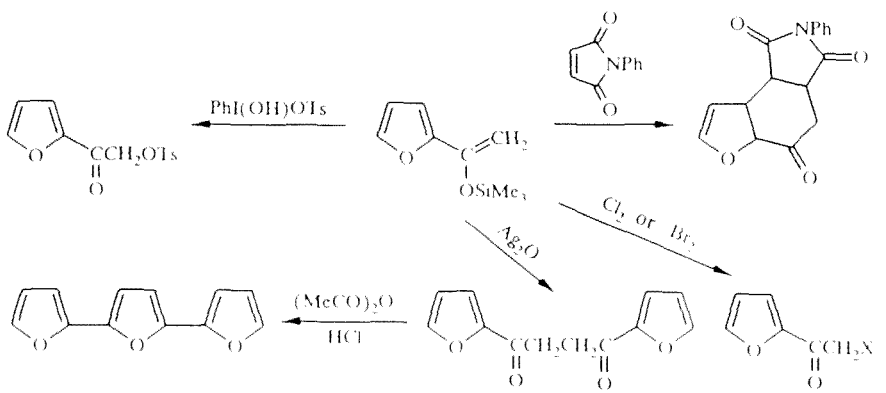
Trimethylsilyloxyfuran can also be used as a silylating agent in reaction with the lithium derivative of pyridine [370].



2-Trimethylsilyloxy-4,5-dihydrofurans have properties characteristic of silyloxyfurans. They react with lead tetraacetate and tetrabenzoate [376], aldehydes and ketones [377-380], and diacetals [381]. Their transformations under the influence of acetyl chloride [382], methyllithium and dimethylmethyleneammonium trifluoroacetate [383], aromatic nitro compounds [384, 385], and 1-acetoxy-1-ferrocenylethane [386] were also investigated.



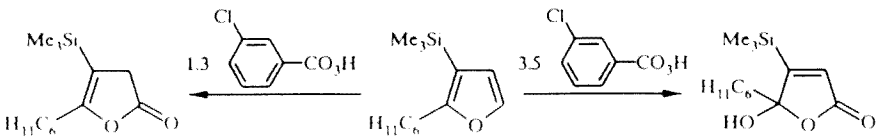
In addition to silyloxyfurans, the trimethylsilyl ethers of furyl-containing enols are also used in organic synthesis [236-239, 387, 388]. Some transformations of 2-(1-trimethylsilyloxyvinyl)furan were investigated. Thus, when treated with silver oxide, it gave 1,2-bis(2-furoyl)ethane, which in turn underwent cyclization to terfuryl with an overall yield of 65% [326]. The reaction with [hydroxy(tosyloxy)iodo]benzene at room temperature was used for the production of tosyloxy ketones [238]. The silyl ether acts as a diene toward N-phenylmaleimide [387].



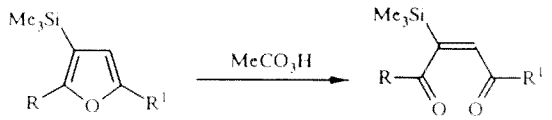
2.2. Reactions Involving the Furan Ring and the Functional Groups of the Organic Substituents

The reaction of trialkylfurylsilanes and their derivatives with butyllithium results in metallation of the furan heterocycle [1-4, 7, 10, 18, 25, 30, 38, 302, 349, 389-392]. This process is widely used for the introduction of various functional groups into the furan ring of silylfurans.

Chemical transformations of the furan ring, including opening, were observed under the influence of a series of reagents (hydrogen, oxidizing agents, dichlorocarbene, lithium cuprates) and also under the conditions of irradiation and vacuum flash pyrolysis. The treatment of 2-cyclohexyl-3-trimethylsilylfuran with m-chloroperbenzoic acid in methylene chloride takes place in two directions, depending on the ratio of the initial reagents [76].

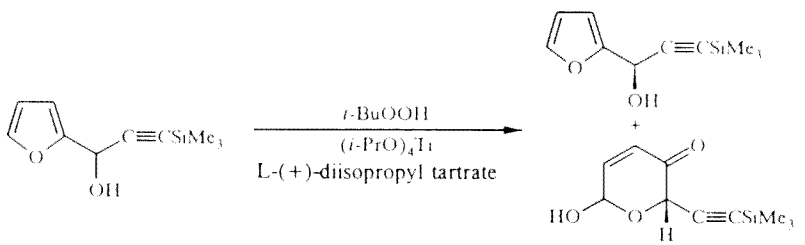


If peracetic acid is used as oxidizing agent, it is possible to achieve successful conversion of 2,5-dialkyl-3-trimethylsilylfurans in methylene chloride at 0°C into *cis*-1,2-diacetylethylenes with high yields (70-90%). Thus, the reaction does not stop at the formation of butenolides, but complete opening of the heterocycle occurs [404].



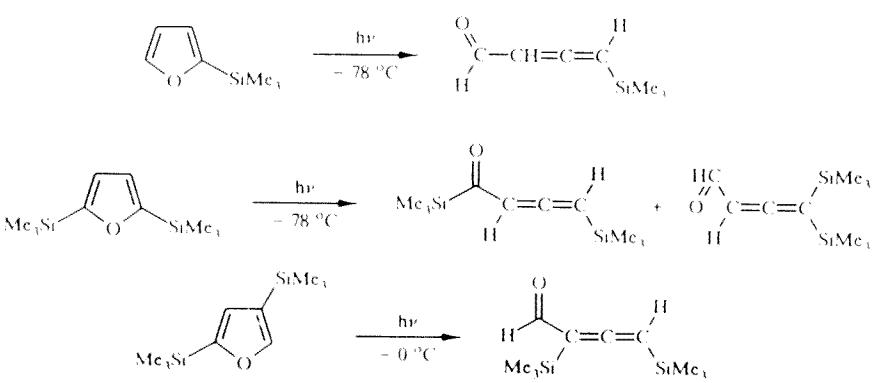
R = Me, Pr; R^1 = Et, Pr, Ph

Kinetic resolution, based on the different epoxidation rates of the R and S isomers of *tert*-butyl hydroperoxide in the presence of the chiral diisopropyl tartrate catalyst, was used to produce an optically active silicon-containing furylcarbinol [405].

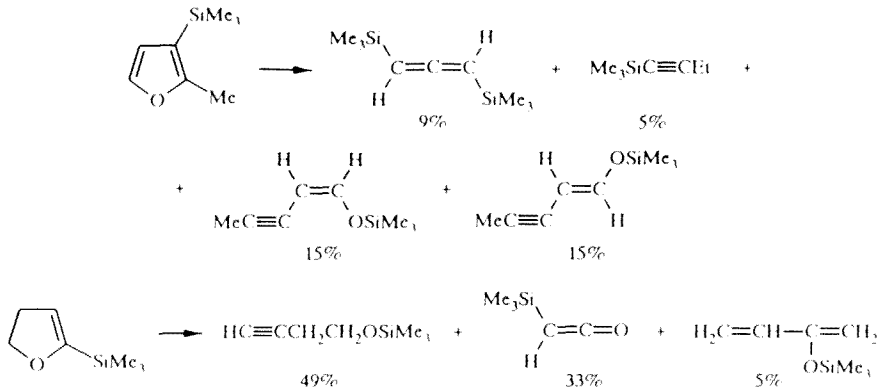


The S enantiomer is oxidized preferentially under these conditions to 2H-pyran-3(6H)-one, while the R enantiomer reacts more slowly. It was therefore isolated with a yield of 38% (optical purity 88%).

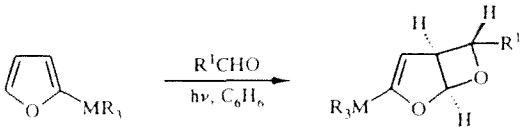
Cleavage of the furan ring was observed during the irradiation of 2-trimethylsilylfuran and 2,5- and 2,4-bistrimethylsilylfurans in pentane at −78°C or 0°C. Together with the initial compounds, the reaction mixtures contained various silylallene compounds [406]:



Under the conditions of vacuum flash photolysis at 800°C, the conversion of 2-methyl-3-trimethylsilylfuran does not exceed 55%. 2-Trimethylsilyl-4,5-dihydrofuran is less stable, and its conversion at 650°C is greater than 85% [85].

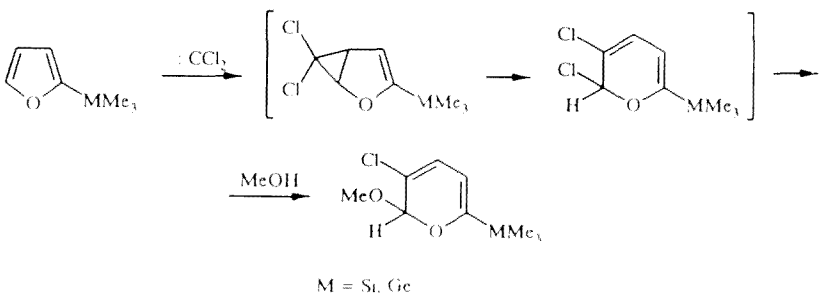


The photochemical cycloaddition of aldehydes to silyl- and stannyl-substituted furans was studied [407].

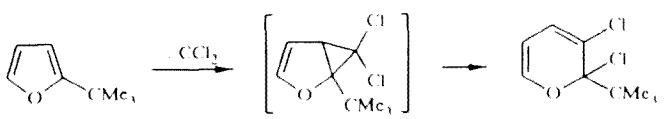


In all cases a mixture of two isomers is formed as a result of addition of the aldehydes at the $C_{(2)}-C_{(3)}$ and $C_{(4)}-C_{(5)}$ bonds of the furan ring. However, the isomer with the silicon or tin atom attached to the acetal carbon atom is unstable and is always a minor component of the reaction mixture. Among the silylfurans the tri(isopropyl)silyl group helps to increase the selectivity of the reaction. In the reaction of [2-tri(isopropyl)silyl]furan with benzaldehyde, the ratio of the isomers is >20:1.

The addition of dichlorocarbene, produced by various versions of two-phase catalysis, to trimethyl(2-furyl)silane and trimethyl(2-furyl)germane and also to 3-trimethylsilyl-2,5-dihydrofuran and 2-trimethylsilyl-4,5-dihydrofuran was studied [315, 408]. In the reaction of trimethyl(2-furyl)silane with dichlorocarbene, generated by the action of solid sodium hydroxide on methanol-containing chloroform in the presence of a phase-transfer catalyst, 6-trimethylsilyl-3-chloro-2-methoxy-2H-pyran is formed. Under similar conditions trimethyl(2-furyl)germane is converted into the corresponding germyl derivative [315].

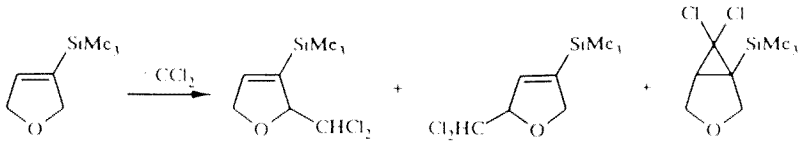


Thus, in the given reaction dichlorocarbene adds at the $C_{(4)}=C_{(5)}$ bond of the furan ring with subsequent isomerization of the bicyclic adducts to 2H-pyrans and substitution of the chlorine atom at the second position by a methoxy group. Dichlorocarbene adds to the carbon analog of trimethyl(2-furyl)silane and trimethyl(2-furyl)germane, i.e., 2-*tert*-butylfuran, at the $C_{(2)}=C_{(3)}$ bond of the furan ring [315].

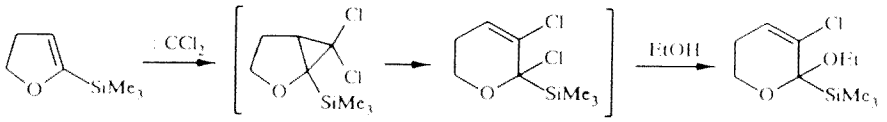


In the reaction of 3-trimethylsilyl-2,5-dihydrofuran with dichlorocarbene, both possible isomers of the product from insertion of $:CCl_2$ at the C–H bonds of the ring at positions 5 and 2 and the product from addition of the carbene at the C=C

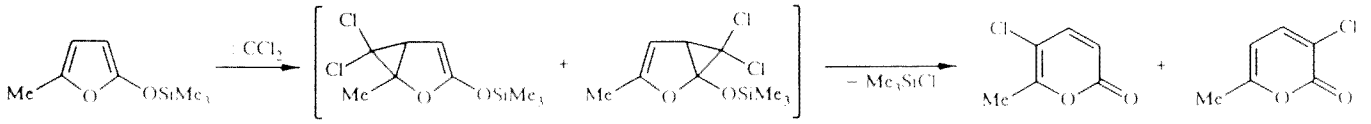
bond are formed with an overall yield of 60-80%. The ratio of the insertion and addition products is determined by the method of generation of the $:CCl_2$ [408] (Table 1).



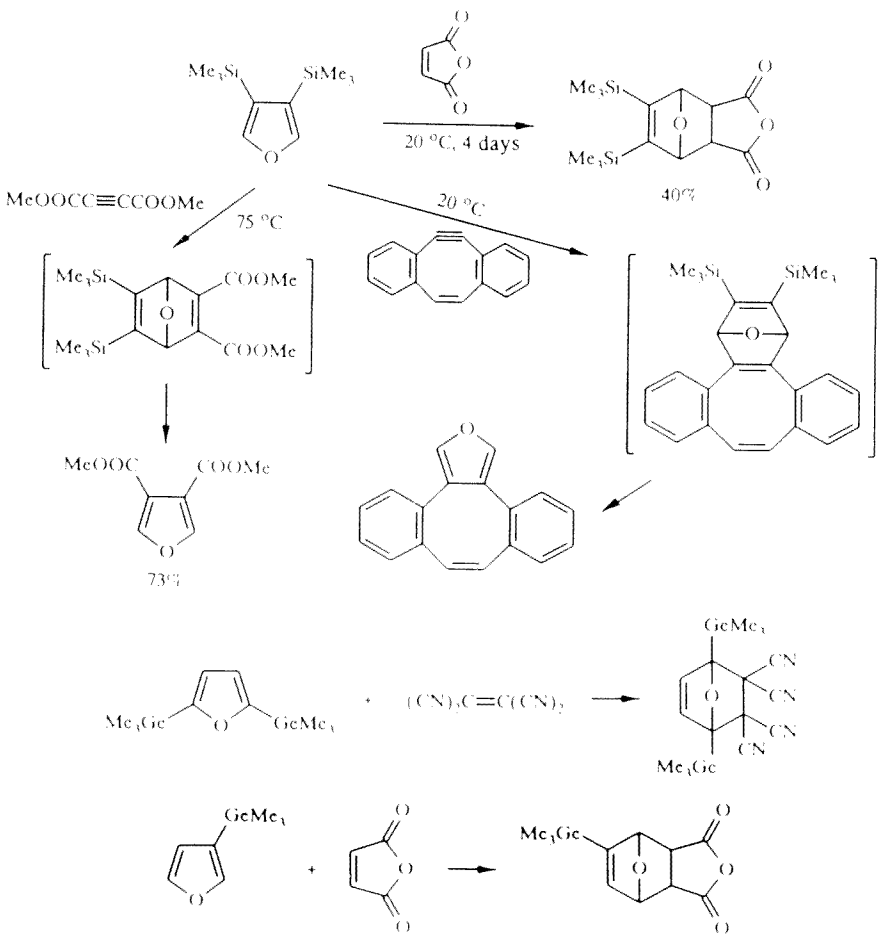
Substantial differences are observed in the reaction of 2-trimethylsilyl-4,5-dihydrofuran with dichlorocarbene. If commercial chloroform, containing 1% of ethanol, is used, 2-trimethylsilyl-2-ethoxy-3-chloro-5,6-dihydro-2H-pyran is formed as the main product [408]. This indicates that the reaction takes place through the bicyclic product from addition of the dichlorocarbene, which then isomerizes with ring enlargement.



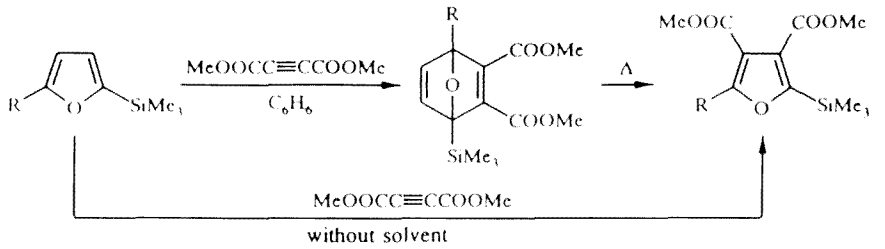
The addition of dichlorocarbene to 2-methyl-5-trimethylsilyloxyfuran was studied. Initially, the products from addition at the $C_{(2)}=C_{(3)}$ and $C_{(4)}=C_{(5)}$ bonds are formed, and they eliminate trimethylchlorosilane when heated with the simultaneous transformation of the bicyclic system [167].



3,4-Bis(trimethylsilyl)furan [302, 389], 2,5-bis(trimethylgermyl)furan [7], and 3-trimethylgermylfuran [409] enter into the Diels–Alder reaction under mild conditions.

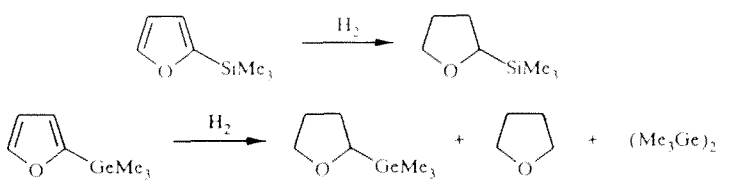


5-Substituted trimethyl(2-furyl)silanes also act as dienes toward dimethyl acetylenedicarboxylate. In benzene or xylene their reaction leads to a bicyclic adduct, which decomposes when heated to 200°C into acetylene and 2-trimethylsilyl-3,4-bis(methoxycarbonyl)furans [310]. If the reaction is conducted with heat and without the solvent, it is not possible to detect the bicyclic adduct on account of its rapid decomposition [410].

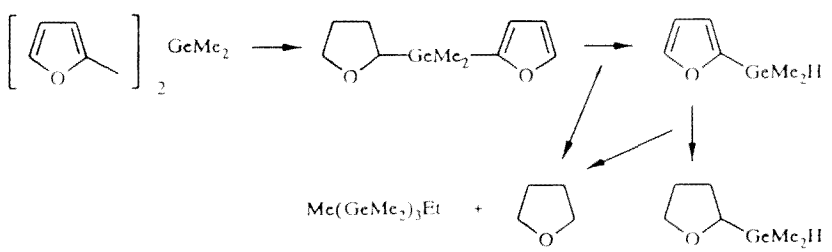


R = H, Me, CH_2OSiMe_3

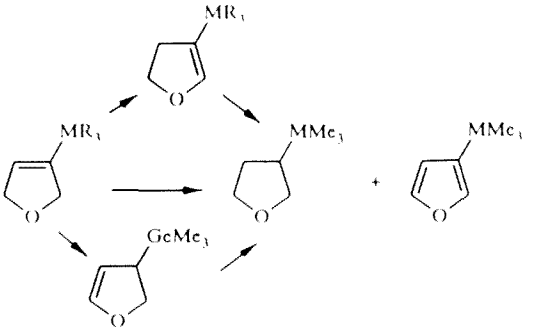
The catalytic hydrogenation of trimethyl(2-furyl)silane and a series of furylgermanes over Raney nickel and platinum and palladium black in the liquid phase and over Pd/C in the gas phase was investigated. However, platinum and palladium black in the liquid phase and Pd/C in the gas phase proved unsuitable for furylsilanes and furylgermanes on account of the low activity of the first two catalysts and the removal of the MMe_3 group during vapor-phase hydrogenation over Pd/C. When the reaction was carried out at Raney nickel, it was possible to hydrogenate the furan ring. However, in the case of trimethyl(2-furyl)germane, for which the degree of transformation after 10 h amounts to 73%, cleavage of the Ge−C bond and the formation of tetrahydrofuran (22%) and hexamethyldigermane (10%) were also observed [411].



Triethyl(2-furyl)germane is hydrogenated slowly but selectively with the formation of triethyl(2-tetrahydrofuryl)germane. The transformation of dimethyldi(2-furyl)germane under the conditions of hydrogenation at Raney nickel leads to hydrogenation of one of the two furan rings with the formation of 10% of dimethyl(2-tetrahydrofuryl)(2-furyl)germane. Dimethyl(2-furyl)germane, dimethyl(2-tetrahydrofuryl)germane, and tetrahydrofuran were also found in the reaction mixture [412].

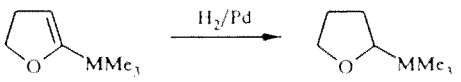


The catalytic hydrogenation of 3-silyl- and 3-germyl-substituted 2,5-dihydrofurans was realized in ethanol at room temperature in the presence of metallic palladium on a support (Pd/C, Pd/Al_2O_3). Dehydrogenation of the 3-substituted 2,5-dihydrofurans to the corresponding furans and also isomerization of the initial compounds to the 3-(4,5-dihydrofuryl) derivatives and 2,3-dihydrofurylgermane were observed in parallel with the formation of the tetrahydrofurylsilanes and tetrahydrofurylgermanes. The isomeric products are converted under the hydrogenation conditions into the tetrahydrofuryl derivatives [90].



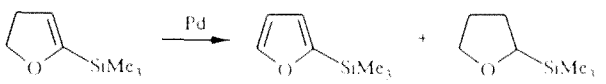
Depending on the structure of MR_3, the hydrogenation rate decreases in the following order: $GeMe_3$ > $PhSiMe_2$ > $SiMe_3$ > $SiEt_3$.

Trimethyl[2-(4,5-dihydrofuryl)]silane and trimethyl[2-(4,5-dihydrofuryl)]germane are transformed selectively at 5% Pd/Al_2O_3 in ethanol under mild conditions (25°C, 1 atm H_2) into tetrahydrofuryl compounds, and the germane in hexane is hydrogenated considerably more slowly than the silane [413, 414].

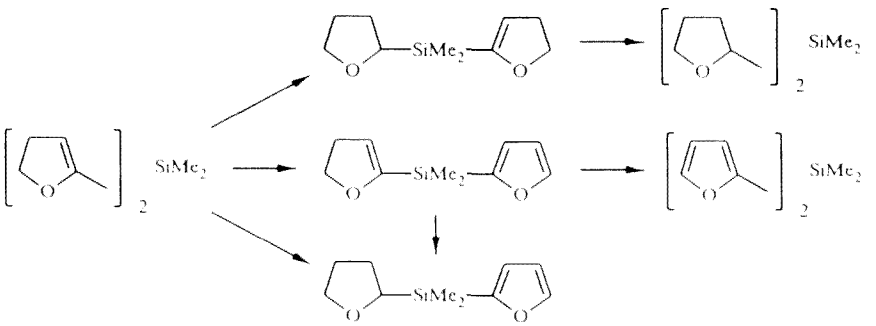


M = Si, Ge

The transformations of trimethyl[2-(4,5-dihydrofuryl)]silane at the palladium catalyst are more complicated in nature, and a mixture of trimethyl(2-tetrahydrofuryl)- and trimethyl(2-furyl)silanes in a ratio of 17:83 is formed.

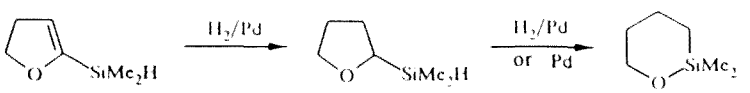


A series of products were obtained during the hydrogenation of dimethylbis[2-(4,5-dihydrofuryl)]silane in hexane at 5% Pd/Al_2O_3, i.e., dimethyl[2-(4,5-dihydrofuryl)](2-tetrahydrofuryl)silane, dimethyl(2-furyl)(2-tetrahydrofuryl)silane, dimethyl(2-furyl)[2-(4,5-dihydrofuryl)]silane, and dimethyldi(2-furyl)silane.

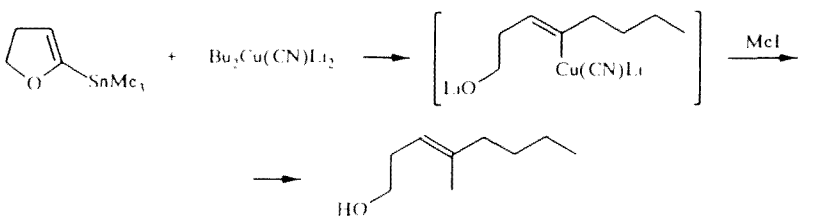


With increase in the amount of catalyst, the dimethylbis[2-(4,5-dihydrofuryl)]silane can be converted into dimethylbis(2-tetrahydrofuryl)silane.

Dimethyl[2-(4,5-dihydrofuryl)]silane is hydrogenated quickly and quantitatively under mild conditions (20°C, 1 atm H_2, 5% Pd/Al_2O_3) to the corresponding tetrahydrofuryl derivative. After complete conversion of the initial compound, this rearranges into 2,2-dimethyl-1-oxa-2-silacyclohexane [59].



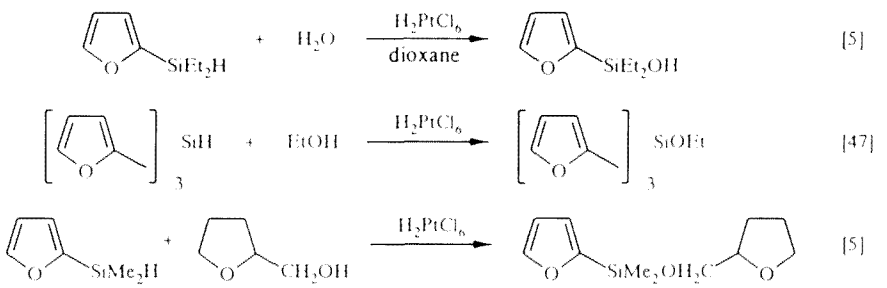
Opening of the heterocycle is observed during the treatment of trimethyl[2-(4,5-dihydrofuryl)]stannane with the lithium cyanocuprate $Bu_2Cu(CN)Li_2$ [62]. This reaction can be used for the stereoselective synthesis of acyl cyanocuprates.



2.3. Reactions of Functional Substituents at Elements of Group IVB

The functional groups at the metal atom in the furan derivatives of group IVB elements can undergo various chemical transformations.

The most widely studied are the properties of furylhydrosilanes. These compounds enter readily into dehydrocondensation with various hydroxyl-containing compounds in the presence of chloroplatinic acid or organic bases. Most often these reactions take place readily and give good yields.



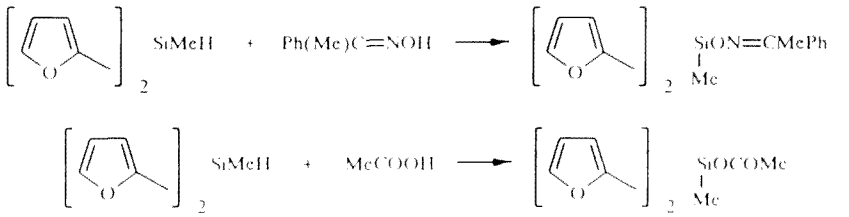
[5]

[47]

[5]

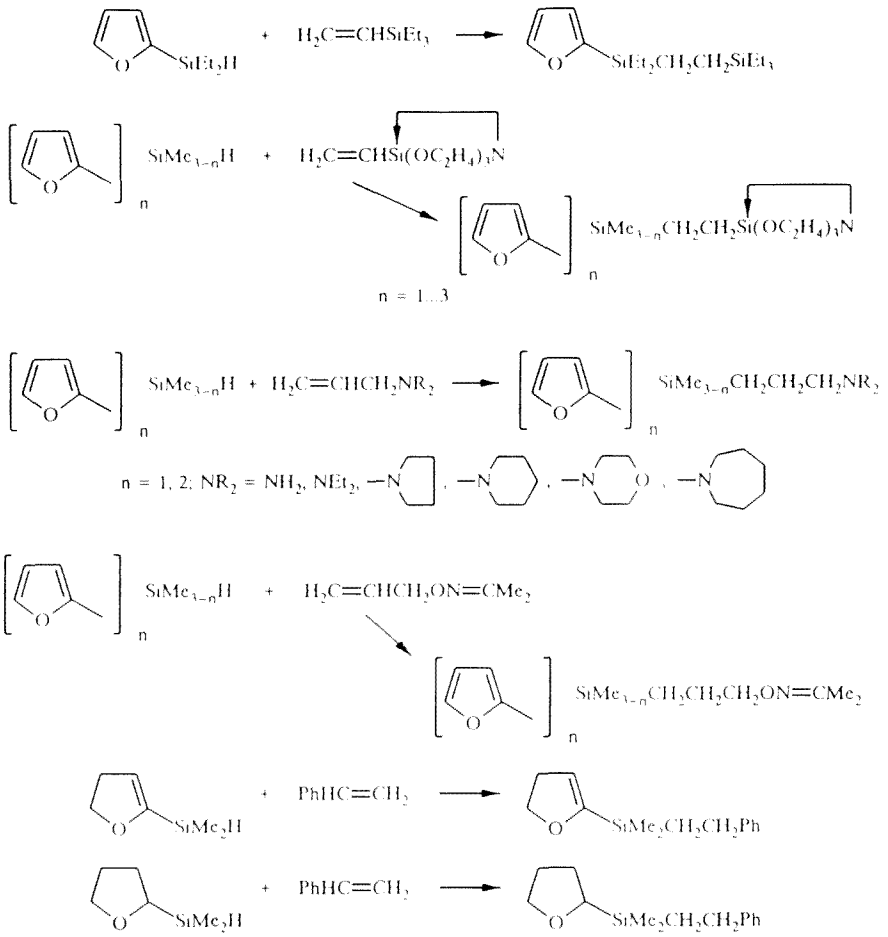
The effects of the structure of the alkanol, the basicity of the catalyst, and the nature of the solvent on the rate of dehydrocondensation of methyldi(2-furyl)silane with alcohols were investigated, and it was established that the reaction rate increases with increase in the electron-accepting power of the substituents in the alcohol molecule. The dehydrocondensation of ethanol with methyl(2-furyl)silane did not take place under the influence of pyridine and N,N-diethylaniline. Very slow release of hydrogen was observed in the presence of N-allylmorpholine. With further increase in the basicity of the amine the reaction rate increased, and it was highest under the influence of piperidine [415]. The reaction of methyl(2-furyl)- and methyl(3-furyl)silanes with amino alcohols is autocatalytic [416]. It was shown in the case of the reaction with 2-diethylaminoethanol that dehydrocondensation is accelerated with increase in the dielectric constant and the dipole moment of the solvent; the highest reaction rate was observed in dimethylformamide [416].

Methyldi(2-furyl)silane also reacts with acetophenone oxime [417] and acetic acid [418] in the presence of piperidine.



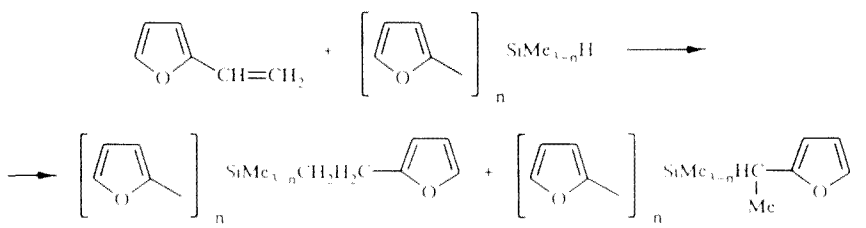
Investigation of the kinetics of dehydrocondensation of methyl(2-furyl)hydrosilanes with aminoalkanols showed [419] that the reactivity in the $R_nSiMe_{3-n}H$ series increases with increase in the number of furyl groups R in the molecule. For alkyldi(2-furyl)silanes the reactivity decreases with increase in the alkyl substituent (Me > Et > Bu), and methyldi(2-furyl)silane reacts more quickly than methyldi(3-furyl)silane [419].

Furylhydrosilanes exhibit high reactivity in the hydrosilylation reactions of unsaturated compounds in the presence of chloroplatinic acid [5, 34, 41, 44, 59, 132, 420, 421]. The reactions with vinylsilanes [5, 132, 421], styrene [59], allylamines [34, 41, 44, 132, 420], and acetoxime allyl ether [41] take place with the formation of only the β-products with yields of 60-80%.

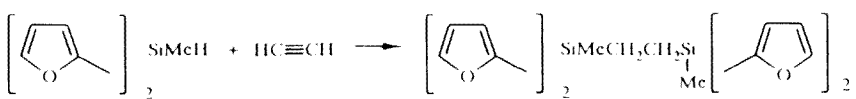


2-Vinylfuran is hydrosilylated by furylhydrosilanes in several minutes with yields of 80-85%. In this case, however, a mixture of two isomers, i.e., the products from α- and β-addition of the silyl group, is formed [41, 132].

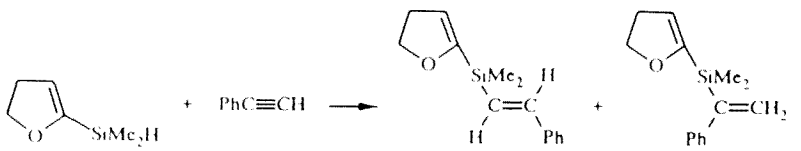
The content of the β isomer increases with increase in the number of furyl groups in the hydrosilane and amounts to 84, 90, and 94% for n = 1, 2, and 3 respectively.



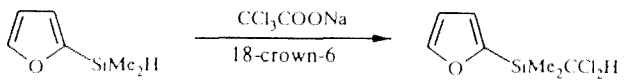
Acetylene is very active in hydrosilylation. Thus, the reaction between acetylene and methyldi(2-furyl)silane in the presence of Speier's catalyst begins at room temperature and takes place exothermically [41, 132]. The main product is a derivative of bissilylethane.



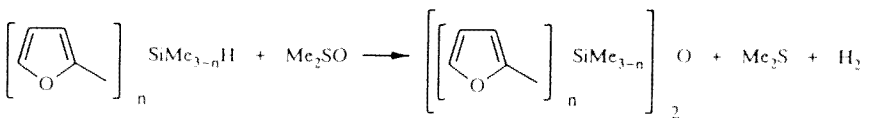
The addition of dimethyl[2-(4,5-dihydrofuryl)]- and dimethyl(2-tetrahydrofuryl)silane to the C≡C triple bond of phenylacetylene in the presence of chloroplatinic acid leads to the formation of two isomers (*β-trans* and α), the yields of which amount to 77 and 9% for dihydrofurylsilane and 62 and 25% for tetrahydrofurylsilane [59].



The dichlorocarbene generated from sodium trichloroacetate under the conditions of phase-transfer catalysis enters at the Si−H bond of dimethyl(2-furyl)silane with the formation of dimethyl(dichloromethyl)(2-furyl)silane (yield 42%) [422].

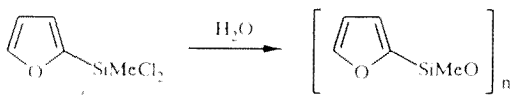


It was found that furylhydrosilanes have high reactivity in reaction with dimethyl sulfoxide in the presence of Speier's catalyst. The reaction can be used for the synthesis of siloxanes under conditions requiring the absence of moisture [423].



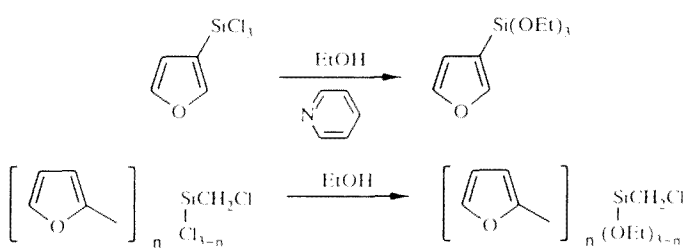
n = 2, 3

Methyl(2-furyl)dichlorosilane is hydrolyzed by the action of an aqueous solution of potassium carbonate with the formation of cyclotri-, cyclotetra-, and cyclopentasiloxanes [424].

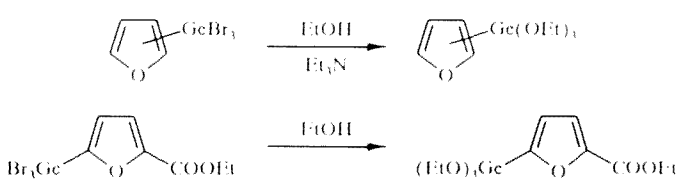


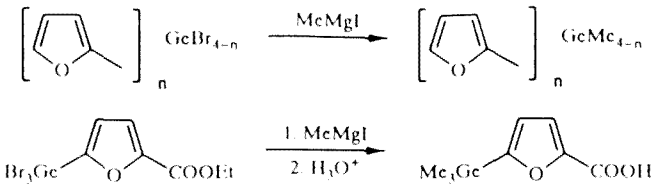
n = 3...5

Furyloxysilanes, obtained by the lithium synthesis from 2- and 3-furyllithium and chlorosilanes, were subjected without isolation to alcoholysis with ethanol for the synthesis of furylethoxysilanes [43, 47]

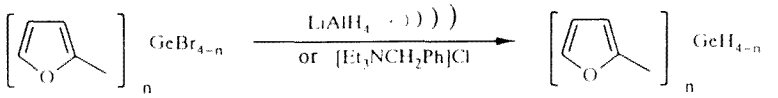


Furylbromogermanes also enter into a similar reaction [108, 110]. The action of methylmagnesium iodide on these compounds leads to substitution of the bromine by a methyl group [28, 110].



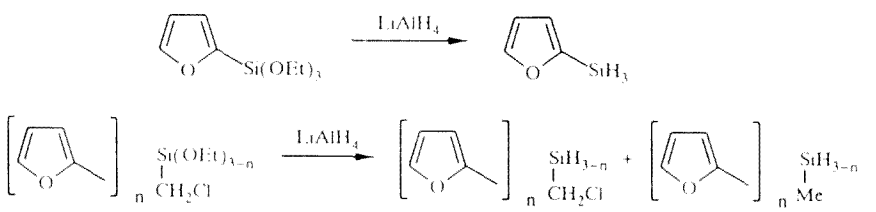


2-Furylbromogermanes are reduced to the corresponding hydrogermanes by lithium aluminum hydride in nonpolar solvents (benzene, toluene, hexane) with ultraviolet irradiation [28] or under the influence of phase-transfer catalysts [425].



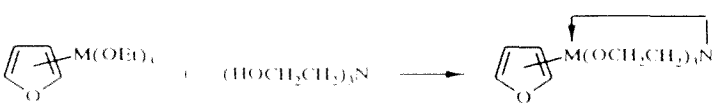
The reduction is conducted at room temperature or with gentle heat. The yield is high and is in a number of cases close to quantitative.

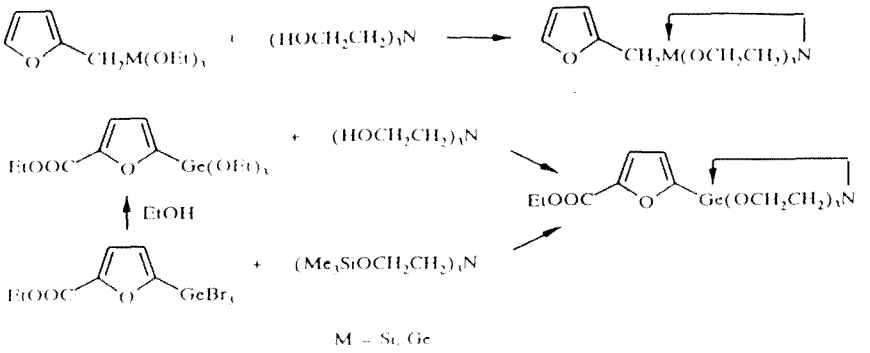
The reduction of ethoxysilanes with lithium aluminum hydride was used for the synthesis of 2-furylsilane and furylsilanes containing a chloromethyl group and a hydrogen atom at the silicon atom. In order to avoid cleavage of the Si−C bond, the lithium aluminum hydride was added to an ether solution of the silane, cooled to −25°C, in an inert atmosphere. However, the yield of 2-furylsilane was small (35%) even under these conditions, and in the case of the chloromethyl derivatives reduction of the chloromethyl group also occurred [43].



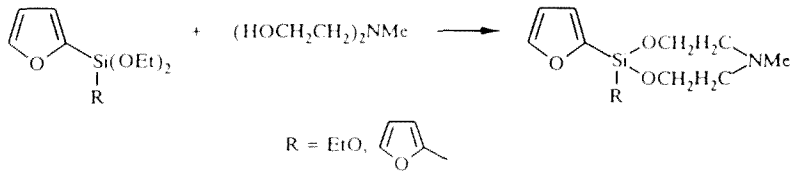
Dimethyl[2-(4,5-dihydrofuryl)]methoxysilane and dimethyl(2-tetrahydrofuryl)methoxysilane were reduced quantitatively by lithium aluminum hydride in deuterocyclohexane after 2-3 h at 25°C under the influence of ultrasonic radiation [426].

The transetherification of furylethoxysilanes and furylethoxygermanes with triethanolamine was studied [108, 110, 344, 427]; the most varied silatranes and germatranes were obtained by this method. The reaction conditions are determined by the structure of the heterocyclic substituent at the silicon atom. 2-Furyltriethoxysilane reacts with triethanolamine without a catalyst with the formation of 2-furylsilatrane with a yield of 76%. With chloroplatinic acid as catalyst it was possible to increase the yield of 2-furylsilatrane by 12%. In the presence of the hydroxides of alkali metals (the usual catalysts for transetherification), the reaction of 2-furyl- and 5-methyl-2-furyltriethoxysilanes took place with cleavage of the Si−C bond and the formation of ethoxysilatrane. Silatranes in which the silicon atom was separated from the heterocycle by one or two methylene groups and also was introduced at position 3 of the furan ring were only obtained during transetherification in the presence of basic catalysts [344]. The transetherification of furyltriethoxygermanes with triethanolamine does not require a catalyst and gives a yield of 54-64% [108, 110]. 5-Ethoxycarbonyl-2-furylgermatrane was obtained both in the reaction of the corresponding triethoxygermane with triethanolamine [108] and in the reaction of 5-ethoxycarbonyl-2-furyltribromogermane with silylated triethanolamine [428].

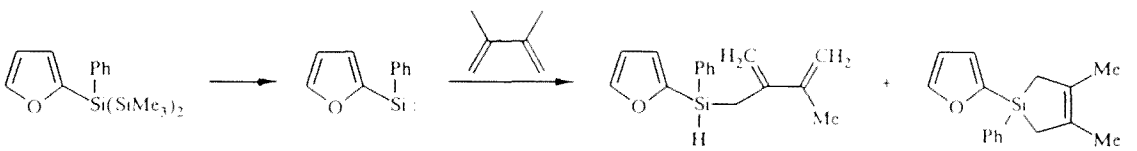




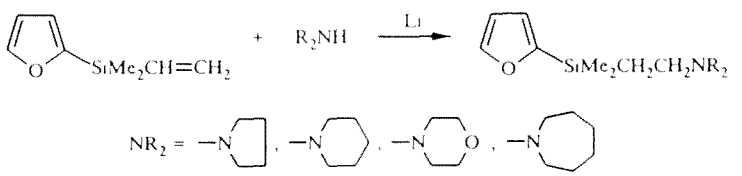
2-Furyltriethoxysilane and di(2-furyl)diethoxysilane react with N-methyldiethanolamine with the formation of cyclic aminoalkoxysilanes. The yield of the product with the ethoxyl substituent at the silicon atom is lower (38%) than with furyl (72%), since significant amounts of polymeric products are formed in the former case [344].



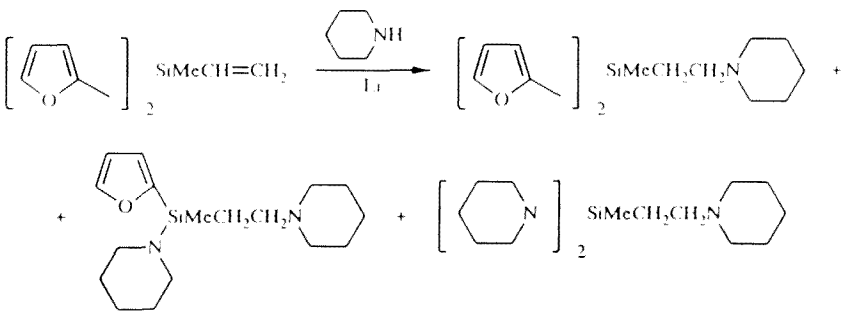
2-Furylphenylsilylene is formed during the photolysis of 2-(2-furyl)-2-phenylhexamethyltrisilane. In reaction with 2,3-dimethylbutadiene it forms both a cyclic product and the product from insertion of the methyl group into the C–H bond [429, 430].



When heated at 70°C in tetrahydrofuran for 5 h [44], dimethyl(2-furyl)vinylsilane enters into reaction with secondary heterocyclic amines in the presence of catalytic amounts of metallic lithium with the formation of β-substituted aminoethylsilanes.

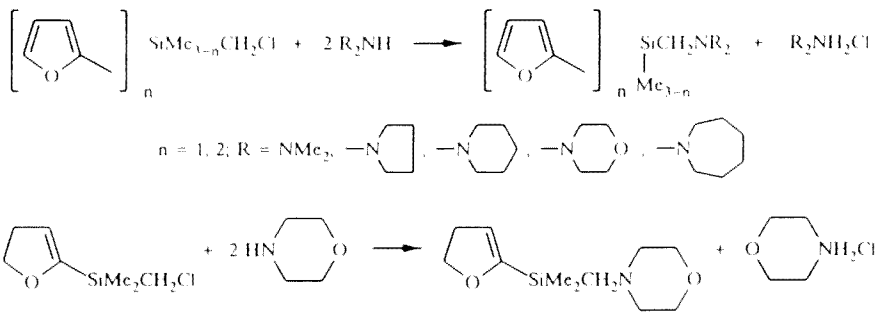


The yield of the aminoethylsilanes amounts to 25%, and the highest yield (65%) is observed during the addition of piperidine. The reaction of amines with methyldi(2-furyl)vinylsilane takes place in a more complicated manner. As well as the addition of the amine at the double bond, the elimination of one or two of the furan rings is observed.



Methyldi(2-furyl)- and dimethyl(2-furyl)vinylsilane polymerize by 60 and 20%, respectively, under the influence of ethyllithium after 2 h at room temperature. (According to the IR spectra, polymerization takes place at the vinyl group [46]).

Furylaminomethylsilanes were obtained with yields of 50-80% during the alkylation of secondary amines in hexane [44] or without a solvent [348]. The reaction requires a large amount of heat (70°C).



3. PHYSICOCHEMICAL PROPERTIES

In connection with the electronegativity of group IVB elements compared with the carbon atom, the trimethylsilyl, trimethylgermyl, and trimethylstannyl groups are electron donors. However, the uniqueness of these groups lies in the fact that in compounds of the Me_3SiX type, where X is an atom with an unshared electron pair or a π system, electronic effects not corresponding to the simple induction effect operate.

Since the π-electronic system of furan is extremely sensitive to the action of the substituents, furylsilanes, furylgermanes, and furylstannanes are suitable subjects for the study of the electronic effects of heteroorganic groups by various physicochemical methods.

3.1. NMR Spectroscopy

The general nature of the NMR spectra of furan derivatives is determined by the donor–acceptor effect of the substituents. The NMR method has therefore been widely used for the investigation of the electronic effects of heteroorganic groups with reference to the π-electronic system of the heterocycle in R_nMMe_{4-n} compounds (R = 2-furyl, 3-furyl, 2-(4,5-dihydrofuryl), M = Si, Ge, Sn, Pb, n = 1-4) [7, 8, 58, 431-439]. In spite of the lower electronegativity of group IVB elements compared with carbon, in the direct bond with the ring they behave as electron acceptors [8, 433, 434] (Table 2), since the chemical shifts of the protons of the heterocycle in the spectra of 2- and 3-substituted heteroorganic furan compounds are downfield from the carbon analogs. In the PMR spectrum of trimethyl[2-(4,5-dihydrofuryl)]silane, $\delta H_{(3)}$ also shows a downfield shift of 0.23 ppm in relation to 2,3-dihydrofuran, whereas the methyl group in 2-methyl-4,5-dihydrofuran shifts the $H_{(3)}$ signal upfield by 0.39 ppm [58]. A downfield shift of the signals for the protons of the ring and the methyl groups in all the types of compounds presented in Table 2 is observed with increase in the number of heterocyclic substituents at the element.

As in the case of PMR, the *tert*-butyl group differs qualitatively from the heteroorganic group in its effect on the ^{13}C chemical shifts of the ring. In the series of 2- and 3-substituted furans, the heteroorganic substituents shift all the $\delta^{13}C$ signals downfield in relation to unsubstituted furan, whereas the 2-*tert*-butyl group screens the $C_{(3)}$ and $C_{(5)}$ nuclei and the 3-*tert*-butyl group screens the $C_{(2)}$, $C_{(4)}$, and $C_{(5)}$ nuclei [8, 434].

Increase in the number of furyl groups leads to screening of the carbon atom to which the heteroorganic substituent is attached and to descreening of the other carbon atoms.

Substitution of the methyl group in tetramethylsilane, tetramethylgermane, tetramethylstannane, and tetramethylplumbane by 2-furyl, 3-furyl, or 2-(4,5-dihydrofuryl) leads to an upfield shift of the silicon, germanium, tin, and lead signals. This shows that these elements have an accepting effect on the π-electronic system of furan. With increase in the number of heterocyclic groups, a linear increase is observed in the screening of the silicon, germanium, and tin atoms. Here the electronic interaction between the group IVB element and the π-electrons of the ring decreases in the order 2-furyl > 2-(4,5-dihydrofuryl) > 3-furyl [8, 58, 434, 438].

The ^{13}C, ^{29}Si, and ^{119}Sn chemical shifts of the substituents MMe_3 [7, 434] (Table 3) in the spectra of the 2,5-disubstituted furans differ little from the corresponding shifts of the monosubstituted compounds, while the chemical shifts of the $C_{(2)}$ and $C_{(5)}$ nuclei are shifted downfield.

The effect of the structure of furylhydrosilanes on the chemical shift of the proton of the Si–H bond, the spin–spin coupling constant $^1J_{Si-H}$, and the chemical shift of the oxygen and silicon nuclei was investigated (Table 4). As in the series of furylalkylsilanes, increase in the number of furyl groups leads to an upfield shift of the $\delta^{29}Si$ signals, while the $\delta H_{(Si)}$ signals are shifted downfield [419].

According to the NMR data, the silicon-containing substituents at the heterocycle in furylalkoxy- and furylaminoalkoxysilanes also act as electron acceptors in relation to the π-electronic system of furan [344] (Table 5). This effect decreases in the order $Si(OEt)_3$ > $EtOSi(OCH_2CH_2)_2NMe$ > $Si(OCH_2CH_2)_3N$ on account of the increase of the competing interaction between the silicon and the functional groups. With increase of n in the $R_nSi(OEt)_{4-n}$ series (R = 2-furyl) the signals of the $H_{(4)}$ and $H_{(5)}$ protons and also of the $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, and $C_{(5)}$ carbon nuclei are shifted downfield, while the dependence of the chemical shifts of the silicon $\delta^{29}Si$ on n is parabolic in nature with a minimum at n = 3. The introduction of one furyl substituent into tetraethoxysilane gives rise to a downfield shift of $\delta^{29}Si$ by 14.4 ppm, which shows that the π-electronic system of the furan makes a smaller contribution to the screening of the silicon than the ethoxy group [344].

According to PMR spectroscopy, the bromogermyl groups in the series of furylbromogermanes $(2\text{-furyl})_nGeBr_{4-n}$ (n = 1-3) have π-accepting activity in relation to the furan heterocycle [28].

During investigation of the spin–spin coupling constants $^1J_{(^{29}Si-^{13}C\alpha)}$ in the furyl derivatives of silicon, it was found that in (2-furyl)vinylsilanes they differ substantially for the α-carbon of the furan ring and the vinyl group [78.0 and 69.0 Hz respectively in dimethyl(2-furyl)vinylsilane and 85.3 and 73.4 Hz in methyldi(2-furyl)vinylsilane] [440], in spite of the formally identical state of hybridization of these carbon atoms. Such a difference in the spin–spin coupling constants cannot be due to differences in the induction effects, since the positive charge at the silicon atom must have an identical effect on the values of these constants. A relation was established between the spin–spin coupling constants and the sum of the induction constants of the substituents σ^* at the silicon atom (the spin–spin coupling constants of other furylsilanes were also used):

$$^1J(^{29}Si—^{13}C\alpha) = 69{,}0 + 6{,}5\Sigma\sigma^*$$

Electron-withdrawing groups (carboxyl, aldehyde, oxime, and cyano) at position 5 of trimethyl(2-furyl)silane and trimethyl(2-furyl)germane descreen the $H_{(3)}$ and $H_{(4)}$ protons and the $C_{(3)}$ and $C_{(4)}$ carbon nuclei (Table 6) [401, 441, 442]. For the 5-trimethylsilyl 2-carbofunctional derivatives of furan the contributions of the trimethylsilyl and functional groups to the change in the screening of the carbon nuclei of the furan, ring in 5-trimethylsilylfurfural and 5-trimethylsilyl-2-cyanofuran, calculated by the LCAO CNDO/2 MO method, are additive [401].

The $\delta^{17}O$ chemical shifts of the carbonyl group in 5-substituted furfurals were investigated. In this series 5-nitrofurfural has the largest $\delta^{17}O$ shift, since the nitro group polarizes the π-electronic system of the furan and thereby weakens the conjugation. The methyl and *tert*-butyl groups have the opposite effect. It could be expected that the heteroorganic substituents $SiMe_3$ and $GeMe_3$ would screen the carbonyl oxygen more than methyl. However, the observed shifts with reference to furfural are only −0.7 and −4.8 ppm for the silyl and germyl derivatives (−16 ppm for 5-methylfurfural). This may be due to the π-accepting effect of the silicon and germanium atoms (Table 7).

3.2. Photoelectron Spectroscopy

In order to study the electronic interactions between the π-system of furan and the silicon [443-447] and tin [444] atom, the photoelectron spectra were recorded for monofuryl- and difurylhydrosilanes [443], trimethyl(2-furyl)silane [443-445], trimethyl(2-furyl)stannane [444], trimethylfurfurylsilane [444], and 2,5-bis(trimethylsilyl)furan, and quantum-chemical

calculations were made by the CNDO/2 [443] and CNDO/S [445] methods with and without allowance for the d orbitals. The experimental data are given in Table 8.

Analysis of the correlations between the experimental ionization potentials and the energies of the π_1 and π_2 orbitals, calculated in the sp and spd basis sets, showed that the best agreement was obtained in the spd set [443]. However, according to published data [445], the ionization potentials calculated with and without allowance for the d orbitals differed little.

In 2-furylsilane and trimethyl(2-furyl)silane, high stabilization of the π_1 and π_2 molecular orbitals is observed in comparison with the carbon analogs. This shows that the silyl group has an accepting effect in relation to the furan system. A comparative analysis of the first two ionization potentials of 2-furylsilanes $RSiH_nMe_{3-n}$ shows greatest stabilization of the molecular orbitals in 2-furylsilane. Replacement of the hydrogen atoms by methyl groups leads to a decrease of the ionization potentials and, consequently, to destabilization of the molecular orbitals [443].

3.3. UV Spectroscopy of Charge-Transfer Complexes

The electronic spectra of the charge-transfer complexes (CTC) of the heteroorganic derivatives of furan with tetracyanoethylene (TCE), which are complexes of the π,π type, were investigated [448-452].

The long-wave band in the spectra of the charge-transfer complex shows the highest sensitivity to the effect of the substituents.

The introduction of electron-withdrawing substituents into the furan ring leads to a reduction in the energy of the highest occupied molecular orbital and to an increase in the difference between the energy of this orbital and the lowest unoccupied orbital of TCE. Experimentally this shows up as an increase in the charge transfer frequency (ν_{ct}).

In the transition from 2-*tert*-butylfuran and 3-*tert*-butylfuran to the corresponding trimethylfurylsilanes and trimethylfurylgermanes (Table 9) the ν_{ct} values in the spectra of the CTC increase, which demonstrates the accepting action of the heteroorganic substituents. On the whole a systematic increase in the frequency is observed with the introduction of a furyl group into the molecule. The separation of the trimethylsilyl group from the furan ring by one or two methylene groups is accompanied by a decrease of ν_{ct} and by loss of the accepting ability of the trimethylsilyl group.

A comparison was made of the effects of the substituents in a series of furylsilanes and furylgermanes in the ground and excited states [451]. IR spectroscopy of a $\pi\cdots H-O$ hydrogen bond with phenol was used to study the π-electron-donating capacity of the furan ring in the ground state, and the parameter characterizing the effect of the substituent was the shift of the frequency $\Delta\nu$ for the stretching vibration ν_{O-H} of the phenol during the formation of the complex. It was established that a linear relation between ν_{ct} and $\Delta\nu$ is observed for furan and its derivatives.

There is also a linear relation between the charge transfer frequency of the complexes of furan derivatives with TCE and the σp^+ constant for substituents in the benzene series [452]. However, this relation is not observed for all the compounds. For example, 2-trimethylsilyl-5-trimethylgermylfuran (ν_{ct} = 17,700 cm^{-1}) and 2-dimethylsilyl-5-trimethylgermyl-furan (ν_{ct} = 18,200 cm^{-1}) are characterized by anomalously low ν_{ct} values and by the absence of a correlation.

3.4. Vibrational Spectra

The IR absorption spectra and also the Raman spectra of 2-furylsilanes, 2-furylgermanes, and 2-furylstannanes [453-456], furylhydrosilanes [453, 454], furfuryloxysilanes [453], silyl 2-furancarboxylates [453], and N-silyl-2-furancarboxamides [453] were studied. The frequencies and the forms of the normal vibrations were calculated for the molecules of trimethyl(2-furyl)silane, trimethyl(2-furyl)germane, and trimethyl(2-furyl)stannane, and the absorption and Raman spectra of R_nMMe_{4-n} (R = 2-furyl) were interpreted [456].

Three very weak signals, belonging to the stretching vibrations of the C–H bonds in the ring, were recorded in the short-wave region of the IR spectra. Their intensity increases with increase in the number of furyl groups in the molecule. The corresponding lines in the Raman spectra are fairly strong. Within the experimental error limits, the frequencies for the stretching vibrations of the C–H bond for 2-furylsilanes, 2-furylgermanes, and 2-furylstannanes coincide [456]. The bands at 2962 and 2902 cm^{-1} in the spectrum of trimethyl(2-furyl)silane belong to the stretching vibra-

tions of the methyl C−H bonds. Their intensity decreases with decrease in the number of methyl groups. In trimethyl(2-furyl)germane and trimethyl(2-furyl)stannane, these frequencies are 10-20 cm^{-1} and 7-25 cm^{-1} respectively higher than in the silane.

The deformation vibrations of the methyl groups due to the change in the HCH angles have a frequency of 1410 cm^{-1} in the IR spectrum. In the region of 1252-1260 cm^{-1}, the IR spectrum of trimethyl(2-furyl)silane contains two strongly overlapping bands, which also belong to the deformation vibrations of the methyl groups. The analogous vibrations in the 2-furylgermanes are in the regions of 1410-1420 and 1240-1250 cm^{-1}.

The bands at 1555, 1462, 1362, 1204, 1150, 1109, 1074, 1008, 902, and 887 cm^{-1} in the IR spectrum of trimethyl(2-furyl)silane belong to the planar vibrations of the furyl fragment. Of the analogous bands that appear in the region of 880-1560 cm^{-1} in the IR spectrum of trimethyl(2-furyl)germane, only the band of a complex vibration, in which practically all the bond lengths of the ring (breathing vibrations) vary, at 1093 cm^{-1} is shifted strongly ($\Delta\nu$ = 16 cm^{-1}) toward the long-wave region compared with the silane. The shift in the same direction for the other bands does not exceed 7 cm^{-1}. The same tendency is observed for the planar vibrations of the furan ring of trimethyl(2-furyl)stannane [456].

The rocking vibrations of the methyl groups appear in the region of 880-800 cm^{-1} in the form of strong and broad bands, where they overlap with the band for the out-of-plane vibrations of the ring. In the Raman spectrum the rocking vibrations are either inactive or appear in the form of very weak depolarized lines.

The stretching vibrations of the $M-C_{furyl}$ bonds in the IR spectra of trimethyl(2-furyl)silane and trimethyl(2-furyl)germane appear at 416 and 320 cm^{-1} respectively. The broad polarized line at 267 cm^{-1} in the Raman spectrum of trimethyl(2-furyl)stannane was also assigned to the stretching vibration of the $Sn-C_{furyl}$ bond [456].

On account of the highly characteristic nature of the Si−H stretching vibrations, an important source of information on the nature of the electronic interactions in the molecules of hydrosilanes can be the frequencies and intensities of the absorption bands for the νSi−H stretching vibrations in the IR spectra [453, 454] (Table 10). The frequencies of the Si−H vibrations of furylhydrosilanes calculated from the Taft induction constants differ substantially from the experimental values. This is due to the effect of conjugation between the π-electronic system of the furan and the silicon atom, which operates in the opposite direction to the −I effect of the furan ring. The value of $\Delta\nu = \nu_{calc} - \nu_{expt}$ increases with increase in the number of furan substituents at the silicon and amounts to 12, 28, and 43 cm^{-1} for 2-furyl-, di(2-furyl)-, and tri(2-furyl)silanes respectively.

IR spectroscopy of the hydrogen bond in complexes of the $\pi\cdots H-O$ type, where the electron acceptor is phenol, was used to study the π-electron-donating power of the furan derivatives of group IVB elements [451, 457]. A parameter that characterizes the π-donating properties, i.e., reflects the effect of the substituents in the furan ring, is the shift of the frequency ($\Delta\nu$) for the stretching vibration ν_{OH} of phenol during the formation of the H complex. If the frequency shifts $\Delta\nu$ of 2-silylfuran ($\Delta\nu$ = 48 cm^{-1}) and 2-trimethylsilylfuran ($\Delta\nu$ = 67 cm^{-1}) are compared with the shifts of their carbon analogs (66 and 72 cm^{-1} respectively), it is possible to see the strong π-donating ability of the furan ring in alkylfurans.

3.5. Mössbauer Spectroscopy

A series of 2-furyl- and 3-furylstannanes were studied by Mössbauer spectroscopy [111, 112, 260, 458] (Table 11).

A considerable shift was observed in the isomer shifts of furylstannanes compared with phenylstannanes (e.g., for tetraphenylstannane δ = 1.26 mm/sec). This may be due either to increase in the induction effect of the heterocycle, which reduces the s-electron density at the tin atom, or to interaction between the tin atom and the furan π-system. The isomer shift of tributylstannyl 2-furoate is 1.48 mm/sec [260].

3.6. Chromatographic Investigations

During chromatographic investigation of 2-furylsilanes, 2-furylgermanes, and 2-furylstannanes, it was established that the retention indices (I) increase sharply with increase in the number of furan rings in the molecule, while increase in the mass of the atom M in R_nMMe_{4-n} compounds (R = 2-furyl) has a lesser effect on the value of I. The difference between the retention at polar and nonpolar stationary phases (ΔI) also depends strongly on the number of heterocycles and depends little

on the nature of the element [6]. The successive replacement of the methyl groups by furyl groups probably leads to an increase in the role of induction and orientation forces in the overall chromatographic retention.

During investigation of furylsilatranes [459, 460] it was shown that their thermal stability and vapor pressure are fairly high. The compounds can therefore be chromatographed on polar and nonpolar stationary phases, deposited on silylated Chromosorb.

The difference between the retention indices at the polar and nonpolar stationary phases for the various furylsilatranes amounts to 600-1300 units (Table 12) and considerably exceeds the values for such chromatographic polarity standards as butanol, nitropropane, and pyridine.

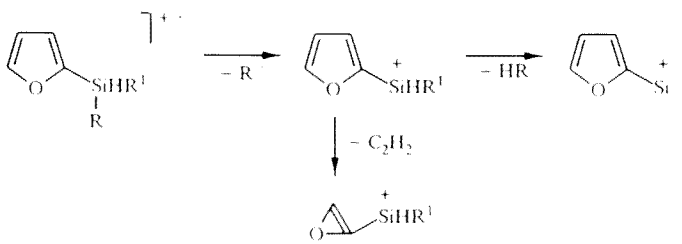
Additive calculation of the indices of the silatranes leads to low values compared with the experimental values. The difference between the experimental and calculated values of the retention indices is determined by the presence of the silatrane fragment with a transannular N → Si bond, and depends on the nature of the substituent R in the molecule of the silatrane $RSi(OCH_2CH_2)_3N$. This is supported by the fact that, in spite of the large molecular weight, 2-(2-furyl)-2-ethoxy-6-methyl-1,3-dioxa-6-aza-2-silacyclooctane and β-(2-furyl)ethylsilatrane are eluted 9.6 and 4.4 times respectively more quickly than (2-furyl)silatrane.

The ΔI and δI values decrease with increase in the chain of atoms between the furan ring and the silicon of the silatrane skeleton.

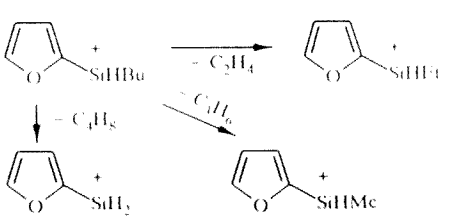
3.7. Mass-Spectrometric Investigations

Mass-spectrometric dissociation under electron impact has been studied for various furan derivatives of silicon: Furylhydrosilanes [43], furylalkylsilanes [43], 2,5-bis(trimethylsilyl)furan [461], furylethoxysilanes [462, 463], furylsilatranes [464], and 2-carbofunctional 5-furylsilanes [34].

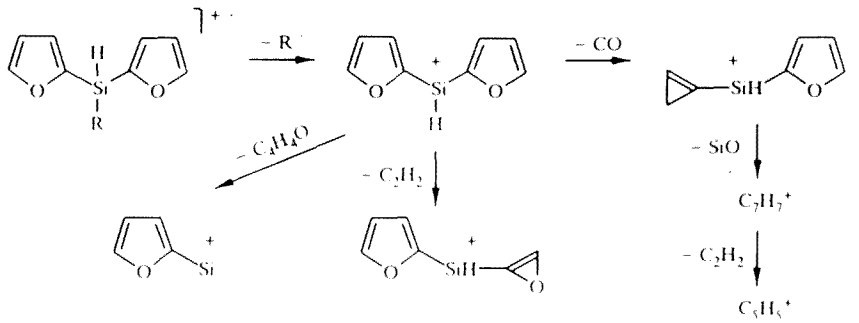
The mass spectra of monofurylhydrosilanes are characterized by a wide range of molecular ion stability (4-95% of the maximum peak). The common dissociation process of these compounds is homolytic cleavage of the Si−alkyl bond. If there are various alkyl substituents at the silicon, the bulkier one is removed preferentially. As a result of possible delocalization of the charge in the conjugated system of the furan ring, the removal of the furyl radical is energetically unfavorable. The $(M - R)^+$ ion then eliminates a molecule of acetylene and a molecule of the alkane in parallel [43].



An exception from the general scheme is the dissociation of dibutyl(2-furyl)silane. In this case after initial removal of the butyl radical, a molecule of olefin is eliminated, but degradation of the furan ring and the ejection of an alkane molecule are not observed.



The dissociation of difurylhydrosilanes, like the dissociation of monofurylsilanes, begins with homolytic cleavage of the Si–R bond. The parallel elimination of furan, acetylene, and carbon monoxide molecules then occurs and is followed by skeletal rearrangement and by the formation of a tropylium ion [43].



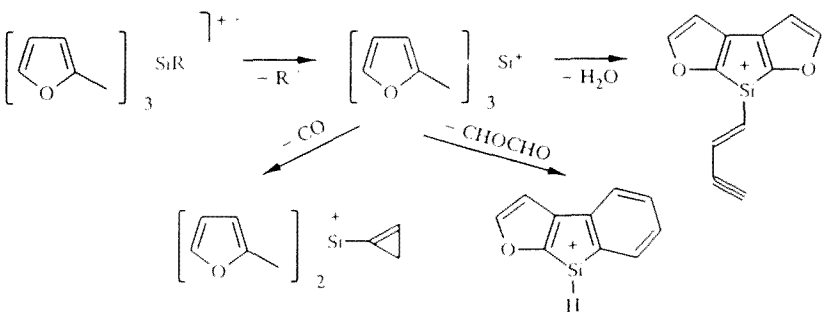
The introduction of a second furyl substituent into the molecule stabilizes the molecular ion as a result of delocalization of the unshared electron pair among the two furan rings, as indicated by the intensity ratio of the molecular ion and the $(M - R)^+$ ion. With identical alkyl substituents, the I_M/I_{M-R} ratio is higher for the difuryl derivatives than for the monofurylsilanes [43].

The mass-spectrometric dissociation of tri(2-furyl)silanes also includes initial removal of the substituent R. With the introduction of a third furan ring into the molecule, two competing factors begin to operate: On the one hand, the delocalization of the charge among the three furan rings stabilizes the molecular ion; on the other, the presence of the three bulky substituents in the molecule assists removal of the substituent R, thereby increasing the intensity of the signal of $(M - R)^+$.

The intensity ratios $I_M/I_{(M-R)}$ for compounds of the $(2\text{-furyl})_nSiH_{4-n}$ type (n = 1-4) indicate that the stability of the molecular ion increases with increase in the number of furyl groups. The dependence of the $I_M/I_{(M-R)}$ ratio on n is described by the equation:

$$\lg I_M/I_{(M-R)} = -0{,}44 + 0{,}46\ n$$

The steric hindrance of the trifurylsilanes favors the occurrence of specific skeletal rearrangements — the elimination of water and glyoxal molecules from the $(M - R)^+$ ion [43].



Analysis of the mass spectra of the furylgermanes $(2\text{-furyl})_nGeX_{4-n}$ (X = H, Me, Br) showed that their fragmentation is similar in character to the fragmentation of furylsilanes. The main direction in the dissociation of the molecular ions is the removal of the substituent X [28].

During comparison of the mass spectra of (2-furyl)hydrosilanes and 2-(4,5-dihydrofuryl)hydrosilanes R_nSiHMe_{3-n} it was shown that the stability of the molecular ions of the furylsilanes is higher than that of the dihydrofurylsilanes. This is due to the reduced possibility of delocalization of the positive charge in the transition from the furyl systems to the less conjugated dihydrofuryl systems [63]. The main process in the dissociation of 2-(4,5-dihydrofuryl)silanes during electron impact involves cleavage of the Si–C bond and removal of the methyl and dihydrofuryl radicals followed by cleavage of the dihydrofuran ring and elimination of the neutral C_2H_4 and CH_2O molecules.

The mass-spectrometric transformations of 2-carbofunctional 5-furylsilanes were studied [34]. The introduction of the trimethylsilyl group at position 5 of 2-substituted furans substantially alters the fragmentation path of the compounds. System-

atic treatment of the obtained results is hindered by the many types of the functional groups and by the equally probable cleavage of the bonds, accompanied by the large number of rearrangements. The fragmentation characteristic of the nonsilyl derivatives with cleavage of the furan ring and the ejection of CO and cyclopropylene shows up little in the furylsilyl compounds. This is clearly due to the stabilizing effect of the silyl group.

3.8. Structural Investigations

The molecular structure of some furan derivatives of group IVB elements was investigated by electron diffraction [465] and x-ray crystallographic analysis [261, 275, 466-472]. The structural parameters of the 2-furylsilane molecule in the gas phase were obtained during calculation of the electron-diffraction data on the assumption that the furan ring is planar and has C_{2v} symmetry, while the SiH_3 group has C_{3v} symmetry, and that one of the SiH_3 groups lies in the plane of the furan ring. The length of the Si−C bond is 1.871 Å, the SiCC bond angle is 127.8°, and the SiCO angle is 121.2°. In the transition from 2-furylsilane to di(2-furyl)- and tri(2-furyl)silane, some shortening of the Si−C bond to 1.869 and 1.857 Å respectively is observed. The molecule of tri(2-furyl)silane has the form of a propeller, in which each ring forms an angle of 38.6° with the HSiC plane [465].

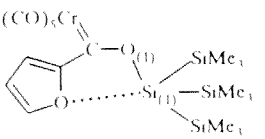
According to the data from low-temperature x-ray crystallographic analysis, weak intramolecular $Si\cdots O_{furyl}$ interaction (2.795 Å) is observed for di(2-furyl)- and tri(2-furyl)silanes. In di(2-furyl)silane both furyl groups are included in this interaction, whereas in tri(2-furyl)silane one of the groups does not participate in this interaction for steric reasons. The SiCC bond angle is 12-16° smaller than SiCC for the furyl substituents included in additional coordination [466].

The probable conformations of the furylsilanes R_nSiH_{4-n} (R = 2-furyl) in solution were determined during comparison of the experimental and calculated values of the Kerr constants and dipole moments [473].

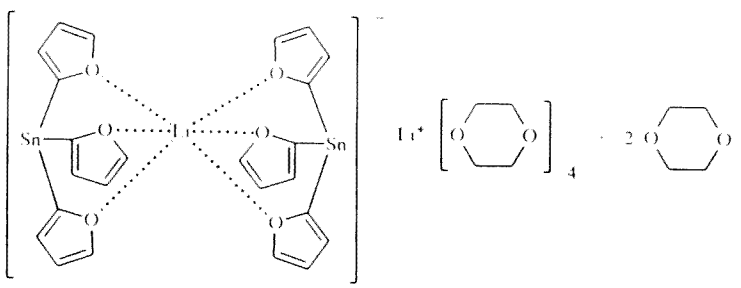
According to the data from x-ray crystallographic analysis [467], the furan rings in the molecules of (2-furyl)- and (3-furyl)silatrane are planar. Except for a slightly increased $C_{(2)}-O$ bond length (1.39 Å), the interatomic separations in (2-furyl)silatrane correspond to those in crystalline furan. The heterocycle in (3-furyl)silatrane is characterized by a large spread in the bond lengths, but they do not fall outside the familiar limits for substituted furans. The silicon atom in silatranes is pentacoordinated and has a trigonal-bipyramidal environment. The length of the transannular N → Si bond in (2-furyl)- and (3-furyl)silatranes is 2.112 and 2.170 Å respectively. The Si−C distances in these compounds are 1.894 and 1.859 Å. The electronic structures of 2-furylsilatrane and 2-furyltriethoxysilane (the charges at the atoms, the additive populations of the atomic orbitals, and the multiplicities of the chemical bonds) were analyzed by the CNDO/2 LCAO MO method [474].

The furan ring in (5-ethoxycarbonyl-2-furyl)germatrane is also planar, and the coordination polyhedron of the germanium atom (like that of the silicon atom in silatranes) is a trigonal bipyramid with an N−Ge distance of 2.165 Å [428].

The structure of the pentacarbonyl chromium complex, in which the tris(trimethylsilyl)silyl group is separated from the furan ring by a C−O fragment, was determined by x-ray crystallographic analysis. The central silicon atom has a distorted trigonal-bipyramidal environment with the $O_{(1)}$ atom and two silicon atoms in the equatorial plane, while the oxygen of the furyl group and the third silicon atom occupy axial positions. It should, however, be noted that the $Si_{(1)}\cdots O_{furyl}$ distance is fairly large and equal to 2.92 Å [468]:



The complex of tri(2-furyl)stannyllithium with dioxane has an ionic structure [470]:



The length of the Sn−C bond in the anion is 2.188 Å, while the $Li-O_{furan}$ distances are nonequivalent. The average length of the $Li-O_{ax}$ bond (2.29 Å) is larger than that of $Li-O_{eq}$ (2.06 Å).

In the crystalline state, trimethylplumbyl furoate $RCOOPbMe_3$ (R = 2-furyl) forms chains through intermolecular interaction between the lead atom and the oxygen of the carbonyl group [r(Pb···O) = 3.17 Å]. For this reason the lead has a trigonal-bipyramidal environment with the methyl groups in the equatorial positions and the oxygen atoms in the axial positions. Interaction with the oxygen atom of the furan ring is also observed, and the $Pb\cdots O_{furan}$ distance is 3.55 Å. The bond lengths and angles in the furan ring differ very little from those in 2-furancarboxylic acid [472].

4. BIOLOGICAL ACTIVITY

Compounds possessing physiological activity have been found among the furan derivatives of silicon and germanium. The psychotropic activity of furylaminoalkylsilanes and their hydrochlorides [44, 420, 475] and of furylsilatranes [421, 476] and furylgermatranes [108, 477] has been studied most comprehensively. In the series of furylaminoalkylsilanes, the effect of such factors as the nature of the substituents at the silicon and nitrogen atoms and the length of the carbon chain between them on the biological effects was analyzed.

All the investigated aminoalkylsilanes with a furyl group at the silicon [44, 420, 475] have psychotropic activity of the decalming type. Here there is a definite relationship between the appearance of the decalming effect, the toxicity, and the chemical structure of the compounds (Tables 13 and 14).

The acute toxicity has a tendency to increase with increase in the length of the chain between the silicon and the nitrogen, although the difference is statistically insignificant. The highest activity in the "tube" and "rotating rod" tests is found in the furyl derivative of perhydroazepinoalkylsilane with a methylene bridge consisting of two CH_2 groups (Table 13).

In the series of 2-furyl-γ-(N-methylpiperazino)propylsilanes, the replacement of the methyl groups by ethyl groups leads to some decrease in the decalming activity with the exception of the "tube" test. The acute toxicity indices in both compounds do not differ with statistical reliability. The replacement of one methyl group by butyl slightly reduces both the acute toxicity and the pharmacological activity, whereas the introduction of a dodecyl group increases the decalming activity by 10-18 times (Table 14). On the whole, analogous relationships are observed in the series of 2-furyl-γ-(morpholino)propylsilanes; the dodecyl derivative showed the strongest decalming effect. It should also be noted that the derivatives of morpholinopropylsilane are less toxic than the corresponding derivatives of perhydroazepino- and N-methylpiperazinopropylsilanes [44, 420].

The introduction of a second furyl group into the molecule of N-methylpiperazinopropylsilane leads to an increase in the acute toxicity, as also in the case of methyldi(2-furyl)-γ-aminopropylsilane [420]. In the corresponding morpholinopropyl compounds, the toxicity does not differ reliably [475].

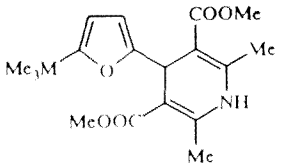
The results from an experimental trial on furylsilatranes and furylgermatranes in female mice of the BALB/c strain with intraperitoneal administration are given in Table 15. With the exception of (2-furyl)silatrane and β-(2-furyl)ethylsilatrane all the compounds in the table exhibit neurotropic activity of the decalming type. The most toxic among the furylsilatranes is 3-furylsilatrane, and the lethal dose for the 2-isomer is 8.6 times larger. If the 2-furyl radical is removed from the silatrane skeleton and also if a methyl group is introduced at position 5 of the furan ring, the toxicity of the compounds is substantially reduced. Analogous relationships are observed for furylgermatranes, the toxicity of which is very low.

The antitumor activity of the various derivatives of 5-trimethylsilylfurfural [400] (Table 16) and 5-trimethylgermylfurfural [27] was investigated. The most clearly defined antitumor activity among the compounds examined in the table is observed in Lewis carcinoma of the lungs and melanoma B_{16}, the growth of which is retarded to 60-62%. Ehrlich's ascitic tumor and sarcoma 37 proved less sensitive to the compounds [400]. The germyl derivatives were even less active toward Lewis carcinoma of the lungs (48%) and melanoma B_{16} (43%) [27].

The cytotoxicity of 5-trimethylsilylfurfural and some of its derivatives was studied on a culture of melanoma B_{16} cells [478]. The strongest cytotoxic activity was found in 5-trimethylsilylfurfural (EC_{50} = 1.8, 3.8 μg/ml). In the transition to the diethyl acetal, the cytotoxicity was reduced to less than a third, and replacement of the diacetal group by 1,3-dioxolane further reduced the activity to a third. The cytotoxicity of 5-trimethylsilylpyromucic acid (10 μg/ml) is three times higher than that of the carbon analog and lower than that of 5-trimethylsilylfurfural.

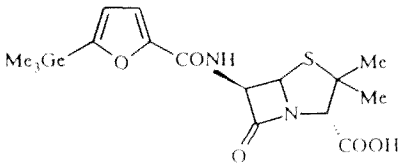
The thiosemicarbazones of 5-silyl-substituted furfural exhibit cytotoxic activity of the decalming type [479].

During investigation of the cardiovascular action of 2,6-dimethyl-3,5-bis(methoxycarbonyl)-4-(5-trimethylsilyl-2-furyl)-1,4-dihydropyridine it was established that it reduces the blood pressure. With oral administration to rats at a dose of 10 mg/kg, it reduces the cystolic pressure by 21%. The blood pressure remains reduced by 17% after 24 h, whereas nifedipine is already ineffective after this time [480]. Moreover, the toxicity of the silylfuryl derivative (LD_{50} > 1000 mg/kg) in experiments on mice is considerably lower than that of nifedipine (185 mg/kg). The replacement of the trimethylsilyl group by trimethylgermyl leads to a threefold reduction of the toxicity [481].

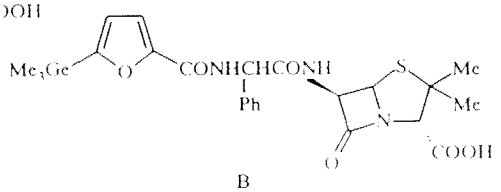


M = Si, Ge

The derivatives of 6-aminopenicillanic acid containing 5-trimethylgermylfuryl substituents have some bacteriostatic activity on the gram-positive bacteria *Staphylococcus aureus* (1.5 and 12.5 μg/ml for compounds A and B respectively) and are inactive toward the gram-negative bacteria *Escherichia coli* (>200 μg/ml).



A



B

The silylamides of 5-nitrofurylacrylic acid (R = 5-nitro-2-furyl, R^1, R^2 = Alk) RCH=CH−CONH$(CH_2)_3SiR^1R^2_2$ do not exhibit bacteriostatic and fungistatic activity [482].

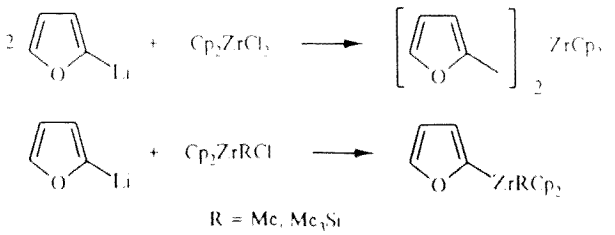
Organosilicon derivatives of the (2-furyl)$CH_2NH(CH_2)_mSiRR^1_2$ type (m = 1, 3) suppress many strains of pathogenic fungi extremely effectively. (During analysis of the activity the strongest antibacterial and antifungal effect was predicted for the compound with R = Me, R^1 = Bu, and m = 3 [483].)

The insect-repellant activity of N-furfurylaminomethyltriethoxysilane [484] was also investigated with respect to an insect strain of the flea *X. cheopsis*. The coefficient of the repellant activity of the compound amounted to 82, 79, and 89% at concentrations of 5, 20, and 40 g/m^2 respectively. The duration of the activity was identical and amounted to 4 days both at 20 g/m^2 and at 40 g/m^2.

Dimethyl(2-furyl)(γ-aminopropyl)silane exhibits weak activity toward rust in wheat (reduction of infestation 50%), phytophthora infection in tomatoes (8%), and powdery mildew in cucumbers (6%) [485].

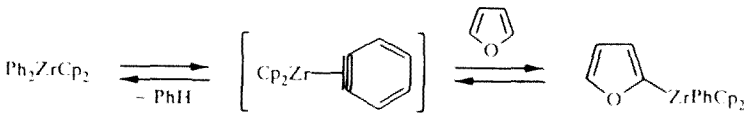
5. DERIVATIVES OF TITANIUM AND ZIRCONIUM

Investigations in the region of the furan derivatives of titanium and zirconium are few. The first compound with a $C_{furyl}-Zr$ bond was obtained with a 74% yield by a lithium synthesis in the reaction of bis(η-cyclopentadienyl)zirconium dichloride with 2-furyllithium. Compounds with one furyl group at the zirconium atom were obtained similarly [487].

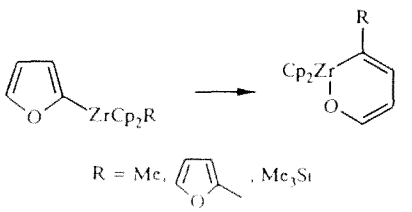


R = Me, Me_3Si

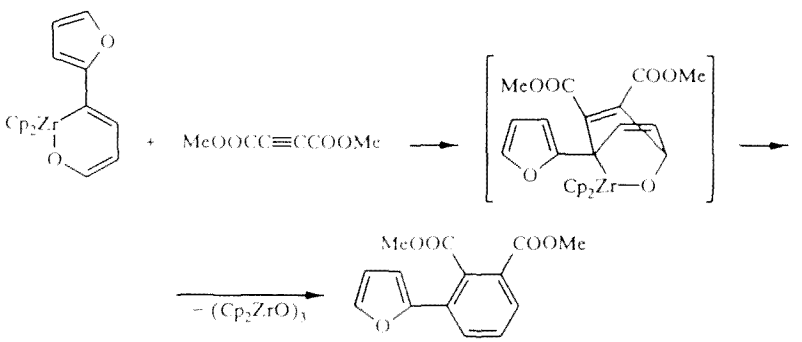
The substitution of one of the phenyl groups of diphenylzirconocene by 2-furyl by the action of a 10-fold excess of furan at 90°C was used to obtain phenyl(2-furyl)zirconocene [487]. In the opinion of the authors the reaction takes place through the formation of an intermediate complex of zirconium with dehydrobenzene.



Bis(2-furyl)zirconocene is fairly thermally stable and only rearranges quantitatively to zirconooxacyclohexadiene at 185°C. The rearrangement of other 2-furylzirconocenes Cp_2ZrR(2-furyl) also takes place as insertion of the Cp_2Zr group into the $C_{(2)}-O$ bond of the furan ring and migration of the substituent R from the zirconium to the carbon atom of the zirconaoxacyclohexadiene system. The temperature at which the reaction occurs is determined by the substituent R and amounts to 200°C (Me), 185°C (2-furyl), and <0°C ($SiMe_3$) [487, 488].

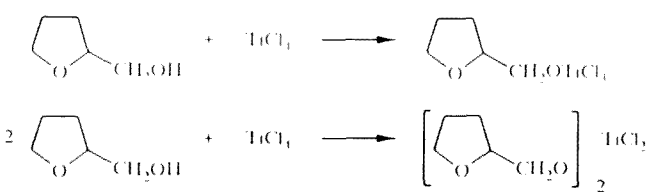


The zirconaoxacyclohexadiene with R = 2-furyl reacts with dimethoxycarbonylacetylene in toluene at 105°C after 18 h and forms a furyl-substituted phthalate [486]

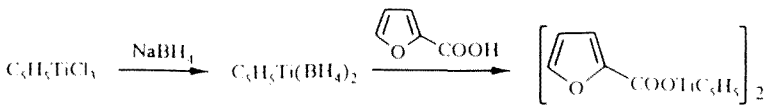


3-(2-Furyl)-2,2-di(η-cyclopentadienyl)-1-oxa-2-zirconacyclohexadiene was characterized by x-ray crystallographic analysis. The compound is monomeric in the crystalline state, and the central six-membered heterocycle is nonplanar. The furyl group is turned so that the oxygen is directed toward the zirconium atom. All the bond lengths and angles in the furan ring have the usual values: $C_{(2)}-C_{(3)}$ = 1.360 Å, $C_{(3)}-C_{(4)}$ = 1.408 Å, $C_{(4)}-C_{(5)}$ = 1.330 Å, $C_{(2)}-O$ = 1.379 Å, and $C_{(5)}-O$ = 1.352 Å; bond angle $C_{(2)}$ = 107.7°, $C_{(3)}$ = 107.8°, $C_{(4)}$ = 106.3°, $C_{(5)}$ = 111.0°, and O = 107.1° [488].

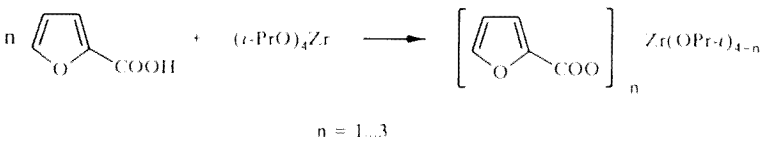
The other compounds of this type are derivatives of tetrahydrofurfuryl alcohol [489], 2-furancarboxylic acid [490, 491], and furfural semicarbazone [492]. In the reaction of tetrahydrofurfuryl alcohol with titanium tetrachloride in anhydrous carbon tetrachloride in an atmosphere of nitrogen, depending on the reagent ratio, tetrahydrofurfuryloxytrichlorotitanium and di(tetrahydrofurfuryloxy)dichlorotitanium were obtained with yields of 91 and 88% [489].



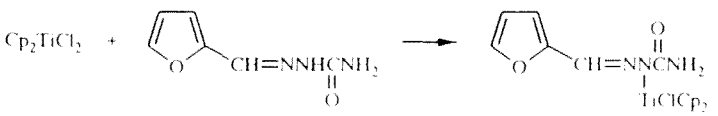
The furoyloxy derivative of trivalent titanium was synthesized by the reduction of cyclopentadienyltrichlorotitanium with sodium borohydride in tetrahydrofuran followed by treatment with 2-furancarboxylic acid at 20°C in benzene [490].



Tetraisopropoxyzirconium reacts with 2-furancarboxylic in anhydrous benzene. Depending on the ratio, it forms a series of carboxylate derivatives in which the COO group is bonded symmetrically to the zirconium atom [491].



In reaction with furfural semicarbazone (ratio 1:1) in tetrahydrofuran at room temperature in the presence of triethylamine dicyclopentadienyldichlorotitanium forms the product from substitution of one Ti–Cl bond [492].



CONCLUSION

While summarizing the published results and the results of our own investigations, among the furan derivatives we note that the methods of synthesis and the chemical properties of silylfurans have been investigated most comprehensively. Furylsilanes, furylgermanes, and furylstannanes have proved extremely convenient models for the investigation of the electronic effects of heteroorganic substituents by various physicochemical methods. The variety of chemical transformations, the high regioselectivity, and the stereospecificity of the reactions of silyl- and silyloxyfurans open up broad possibilities for their use in organic synthesis. Compounds with high biological activity have been found among the aminoalkylsilylfurans, furylsilatranes, and furylgermatranes.

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