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SYNTHESIS OF 3-(2,5-DIHYDROFURYL)-SILANES AND -GERMANES AND THEIR TRANSFORMATIONS UNDER CATALYTIC HYDROGENATION CONDITIONS

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Summary

A number of 3-triorganosilyl- and 3-trimethylgermyl-2,5-dihydrofurans have been prepared by the cyclization of 2-triorganosilyl(germyl)-2-butene-1,4-diols obtained from the hydrosilylation and hydrogermylation products of 1,4-bis(trimethylsiloxy)-2-butyne. It has been found that the liquid-phase heterogeneous hydrogenation of these compounds over palladium catalysts is accompanied by simultaneous isomerization and disproportionation to give the corresponding 3-(4,5-dihydrofuryl)-, 3-tetrahydrofuryl- and 3-furyl- derivatives.

Introduction

Literature data on 3-(2,5-dihydrofuryl)- and 3-tetrahydrofuryl-silanes are scarce [1,2] and there is no information about their properties, and what is more, the corresponding germanium compounds are unknown.

Silicon and germanium derivatives of 2,5-dihydrofuran present a certain interest, because it is possible to use them as the basis for the catalytic synthesis of tetrahydrofuryl-silanes and -germanes as well as furyl- and isomeric dihydrofuryl-silanes and -germanes which are difficult to obtain by other methods. This is feasible since 2,5-dihydrofuran and its homologues are known to undergo similar transformations [3].

Results and discussion

Synthesis of 3-(2,5-dihydrofuryl)-silanes and -germanes

2,5-Dihydrofuran metallation, followed by the interaction of lithium derivative with halosilanes might serve a suitable method for the synthesis of 3-(2,5-dihydrofuryl)silanes (germanes). However, as has been shown [4], when 2,5-dihydrofuran reacts with n-BuLi in the presence of tetramethylethylenediamine at −20°C, the

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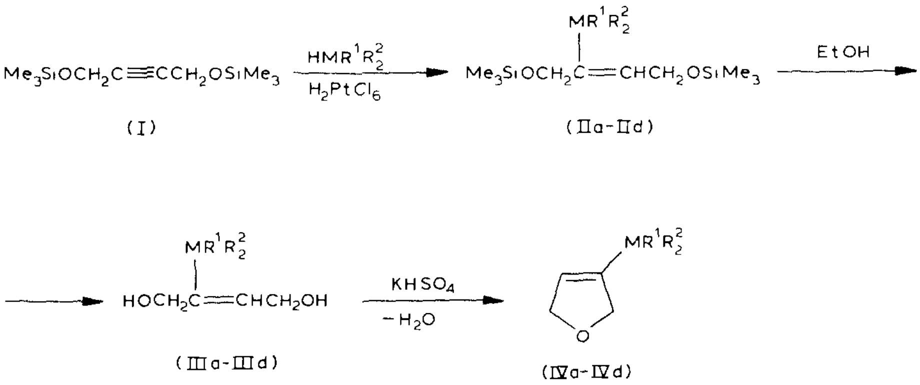
subsequent reaction with trimethylchlorosilane does not lead to 3-(2,5-dihydrofuryl)trimethylsilane formation, but produces *cis*-(1,3-butadienoxy)trimethylsilane as a result of ring cleavage. We have also studied the given metallation reaction at lower temperatures (from −30 to −78°C) using n-BuLi and LDA as metallation agents in an effort to minimize the probability of ring opening. In our experiments, as in ref. 4, the use of n-BuLi and i-Pr_2NLi (LDA) have both led to the opening of the ring, as evidenced by the isolation of the appropriate product from the reaction mixture.

The method for the preparation of 3-(2,5-dihydrofuryl)silanes (germanes) described in [1] involves hydrosilylation (hydrogermylation) of 1,4-butynediol derivatives with subsequent cyclization. Only 2,2,5,5-tetraalkyl(aryl)-(2,5-dihydrofuryl)triethylsilanes (germanes) were obtained with satisfactory yields, whereas the yield of 3-(triethylsilyl)-2,5-dihydrofuran, unsubstituted in the ring, was only 12%. This method appears unsuitable for the preparation of 3-(trimethylsilyl)- and 3-(trimethylgermyl)-2,5-dihydrofurans, since only the dehydrocondensation takes place in the reaction of 1,4-butynediol with $HSiMe_3$ or $HGeMe_3$ in the presence of H_2PtCl_6. That is why 1,4-bis(trimethylsiloxy)-2-butyne (I) was used as the starting compound to prepare 3-(2,5-dihydrofuryl)silanes (germanes) (Scheme 1).



$M = Si$, $R^1 = R^2 = Me$ (a), $R^1 = R^2 = Et$ (b); $R^1 = Ph$, $R^2 = Me$ (c);
$M = Ge$, $R^1 = R^2 = Me$ (d)

SCHEME 1

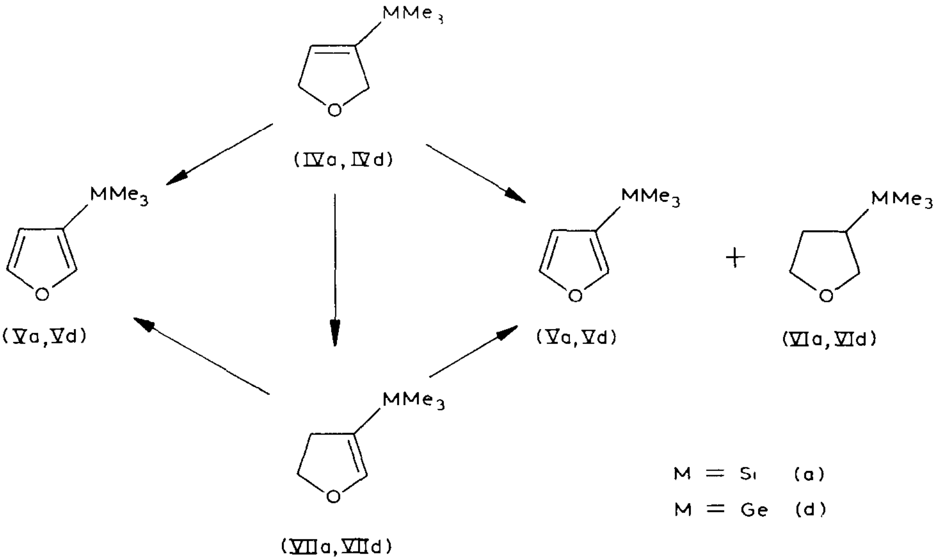
2-Triorganosilyl(germyl)-1,4-bis(trimethylsiloxy)-2-butenes (IIa–IId) were obtained in high yields by the hydrometallation of I in the presence of H_2PtCl_6 at 90–100°C. Silyl protection was removed quantitatively by refluxing IIa–IId in ethanol for 30 min to give IIIa–IIIc. The mixture of $KHSO_4$ with dithizon was used as dehydrating agent to attain the cyclization of IIIa–IIIc to 3-(2,5-dihydrofuryl)silanes (IVa–IVc) [1].

The yields reached 68–80%. On the contrary, the yield of 3-(trimethylgermyl)-2,5-dihydrofuran (IVd) did not exceed 10% as a result of the Ge–C bond cleavage. Therefore to prepare IVd we have used as a mild dehydrating agent the mixture of triphenylphosphine with diethyl azodicarboxylate [5], thus increasing the yield of IVd by 50%.

Transformations of 3-(2,5-dihydrofuryl)-silanes and -germanes in the presence of hydrogenation catalysts

Catalytic hydrogenation of IVa–IVd was carried out in the liquid phase in the presence of supported metallic palladium (Pd/C, Pd/Al_2O_3) as well as organometallic complexes of Pd^0, Pd^{II}, Rh^I and Ru^{II}.

The ability of 2,5-dihydrofuran and of some of its homologues to undergo various transformations when using Pd/carrier type catalysts in the absence of hydrogen has been shown [3,6,7]. Therefore in order to use the liquid-phase hydrogenation conditions the stability of IVa–IVd was first studied with IVa and IVd in the presence of a supported palladium catalyst in solvents of different polarity. The experiments demonstrate (Table 1) that IVa and IVd do not undergo any transformations in the low-polarity ether and pentane. In methanol, IVa was converted to 3-furyl- (Va) and (3-tetrahydrofuryl)-trimethylsilane (VIa), and already at room temperature (r.t.) a small amount of the isomeric 3-(4,5-dihydrofuryl)trimethylsilane (VIId) was also found. The formation of VIa under such conditions proceeds only by way of IVa disproportionation and in the given case probably runs in parallel with dehydrogenation, since the amount of Va always exceeds that of VIa. The rate of disproportionation and dehydrogenation increases with growing concentration of IVa in solution. The temperature increase to 100°C exerts practically no effect upon these processes, whereas the isomerization product (VIIa) disappears from the reaction mixture, obviously due to its ability to undergo disproportionation and dehydrogenation similarly to that of IVa (Scheme 2).

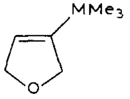


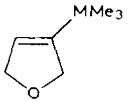
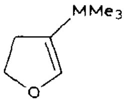
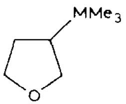
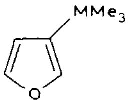
SCHEME 2

In ethanol at elevated temperature (100°C), IVa is subject to disproportionation and dehydrogenation when the solution is sufficiently concentrated (0.7 *M*). The germane IVd fails to undergo any alterations in low-polarity solvents in the presence

(Continued on p. 288)

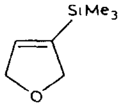
TABLE 1

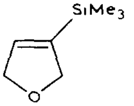
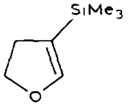
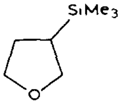
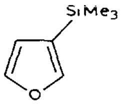
TRANSFORMATIONS OF  IN VARIOUS SOLVENTS [a]

M	Solvent	Substrate concentration (M)	Temperature (°C)	Reaction time (h)	Ratio of reaction mixture components [b]			
								
Si	MeOH	0.1	25	1	100	–	–	–
				8	77	–	8	15
				16	52	4	16	28
				32	45	6	19	30
			100	3.5	41	–	19	40
Si	MeOH	0.7	25	1	100	–	–	–
				8	43	7	18	32
				16	22	4	23	51
				32	14	2	26	58
			100	3.5	9	–	28	63
Si	EtOH	0.1	25	32	100	–	–	–
			100	3.5	100	–	–	–
Ge	EtOH	0.1	25	32	100	–	–	–
			100	3.5	100	–	–	–
Si	EtOH	0.7	25	32	100	–	–	–
			100	3.5	–	–	19	81
Ge	EtOH	0.7	25	32	100	–	–	–
			100	5	8	–	30	62
				12	–	–	32	68
Si	pentane	0.1	25	32	100	–	–	–
Ge	pentane	0.1	25	32	100	–	–	–
Si	pentane	0.7	25	32	100	–	–	–
Ge	pentane	0.7	25	32	100	–	–	–

[a] Catalyst 2% Pd/C, [substrate]:[Pd] = 50. [b] According to GLC.

TABLE 2

HYDROGENATION OF  IN VARIOUS SOLVENTS[a]

Solvent (ε)	Reaction time (h)	Ratio of reaction mixture components[b]			
					
Ethanol (24.3)	1.0	86	3	7	4
	1.5	75	5	13	7
	2.0	55	8	21	16
	3.0	20	10	51	19
	3.5	4	8	70	18
	4.0	–	6	80	16
	6.0	–	–	88	12
Ether (4.34)	2.0	60	12	25	3
	4.0	26	20	50	4
	6.0	–	24	68	8
	8.0	–	18	78	8
Pentane (1.84)	3.5	95	3	–	2
	4.5	76	7	13	4
	10	68	8	20	4
	14	64	8	24	4

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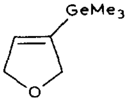
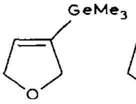
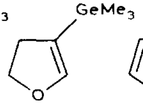
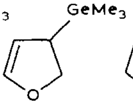
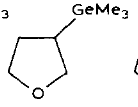
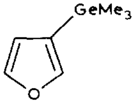
[a] At 25°C, 1 atm H_2, 0.1 *M* solution, [substrate]:[Pd] = 50. [b] According to GLC.

TABLE 3

HYDROGENATION[a] OF 

Solvent	Reaction time (h)	Ratio of reaction mixture components				
						
Ethanol	0.5	33	–	–	66	1
	1.0	–	3	1	91	5
	2.0	–	–	–	95	5
	3.0	–	–	–	95	5
Ether	0.5	71	2	1	23	3
	1.5	–	2	–	95	3
	2.5	–	1	–	96	3
	3.5	–	–	–	97	3
Pentane	0.5	97	2	–	–	1
	1.5	97	2	–	–	1
	3.0	66	2	–	31	1
	3.5	54	2	–	43	1
	4.0	41	1	–	58	1

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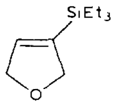
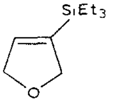
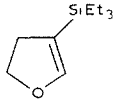
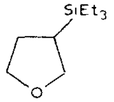
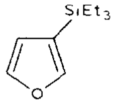
[a] For experimental conditions see Table 2.

TABLE 4

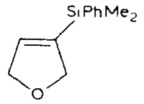
HYDROGENATION [a] OF 

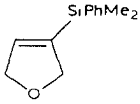
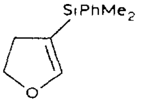
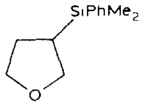
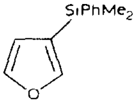
Solvent	Reaction time (h)	Ratio of reaction mixture components			
					
Ethanol	1	72	1	20	7
	2	53	-	36	11
	3	35	-	50	15
	5	14	-	64	22
	10	-	-	81	19
Ether	1	92	2	4	2
	3	87	3	7	3
	5	79	5	13	3
	10	53	12	32	3
	20	31	12	52	5

[a] For experimental conditions see Table 2.

of Pd/C (Pd/Al_2O_3), while in ethanol it undergoes disproportionation and dehydrogenation like the silane IVa, but at a much slower rate. Thus, the reactions of IVa and IVd, being in contact with the palladium catalyst in a polar solvent may serve,

TABLE 5

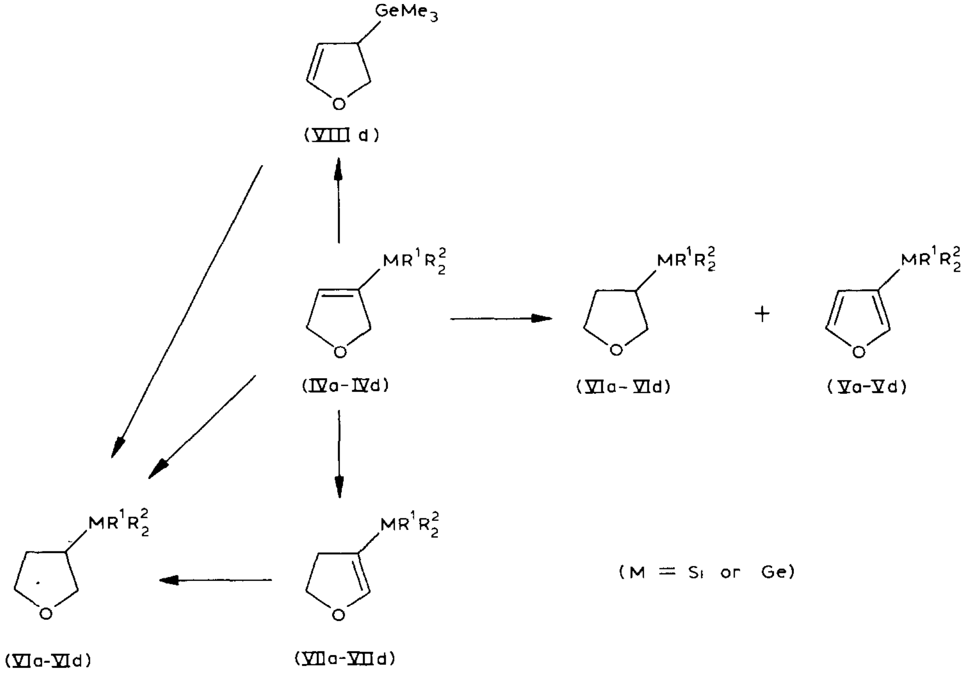
HYDROGENATION [a] OF 

Solvent	Reaction time (h)	Ratio of reaction mixture components			
					
Ethanol	0.5	70	10	13	7
	1.0	40	11	40	9
	1.5	16	9	64	11
	2.0	-	8	80	12
	3.0	-	-	100	-
Ether	0.5	10	54	35	1
	1.0	-	52	46	2
	2.0	-	42	56	2
	3.0	-	32	64	2
	5.0	-	21	77	2
	10.0	-	17	81	2
Pentane	1.0	91	7	-	2
	2.0	56	20	22	2
	3.0	41	31	25	3
	5.0	32	39	26	3
	10.0	-	44	51	5

[a] For experimental conditions see Table 2.

at the same time, to prepare 3-furyl- and 3-tetrahydrofuryl silanes (germanes) which are difficult to obtain by other methods.

Taking into account the available results, IVa–IVd hydrogenation was studied in the 0.1 *M* ethanol, ether and pentane solutions at r.t. The experiments show (Tables 2–5, Scheme 3) that under mild conditions compounds IVa–IVd produce the corresponding tetrahydrofuryl derivatives (VIa–VId) in a high yield, the rate of this process being intensified with increasing solvent polarity.



SCHEME 3

The catalytic hydrogenation of 3-(2,5-dihydrofuryl)-silanes, -germanes is obviously the most convenient method for the preparation of (3-tetrahydrofuryl)-silanes and -germanes, since, according to the literature [8] and our own findings, the other likely synthetic methods (hydrosilylation or hydrogermylation of 2,5-dihydrofuran; 3-bromotetrahydrofuran metallation, followed by the reaction with halosilane (germane); and, finally, 1,4-butenediol hydrosilylation with subsequent cyclization) do not lead to the desired goal.

Under the conditions of catalytic hydrogenation of IVa–IVd, the formation of tetrahydrofuryl-derivatives VIa–VId occurs concurrently with the conversion of IVa–IVd to the corresponding 3-furylsilanes Va–Vd and 3-furylgermane Vd, as well as IVa–IVd isomerization to 3-(4,5-dihydrofuryl)-derivatives (VIIa–VIId) and 3-(2,3-dihydrofuryl)germane (VIIId) (Scheme 3). The formation of Va–Vc is solely the result of IVa–IVd disproportionation, since in the absence of hydrogen in the solvents the dehydrogenation of IVa–IVd fails to take place (Table 1).

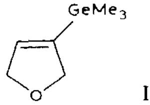
The isomerization products (VIIa–VIId and VIIId) under hydrogenation conditions are involved in consecutive reactions. These compounds are hydrogenated to VIa–VId at a somewhat lower rate than the rate of disappearance of the starting products IVa–IVd, as indicated by their presence in the reaction mixture after the total conversion of IVa–IVd. However, 3-organosilyl- and 3-(trimethylgermyl)-furans (Va–Vd) under the present conditions are not hydrogenated. A comparison of these data shows that the hydrogenation rates of IVa–IVd decrease in the following order: IVd > IVc > IVa > IVb.

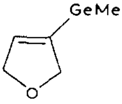
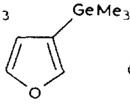
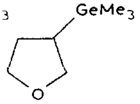
Apparently the highest reactivity of IVd is connected with the weaker p_π–d_π-interaction in organogermanium compounds as compared with their silicon analogues [9,10]. The greatest reactivity of IVc among silicon-containing 2,5-dihydrofurans is probably due to the competitive p_π–d_π-interaction of the vinyl and the phenyl group with the silicon 3*d*-orbitals. Compound IVa was hydrogenated more readily than IVb, obviously due to steric factors.

The ability of all the studied 3-organosilyl-2,5-dihydrofurans to undergo isomerization to the corresponding 3-organosilyl-4,5-dihydrofurans during hydrogenation is probably the result of an increasing degree of conjugation owing to the involvement of the oxygen *p*-electrons. During IVd hydrogenation the content of isomers in the reaction mixture was negligible (Table 5). On the one hand this may be connected with the higher hydrogenation rate of IVd when compared to isomerization.

On the other hand, this germanium-containing compound appears to be less subject to increased conjugation involving the Ge atom. This was confirmed by the occurrence of isomer VIIId (with the double bond isolated from Ge) in the reaction mixture. In such conditions, the preparative isolation of VIId and VIIId proved impossible and these compounds were identified by GLC-MS (see Table 11). The fragmentation pattern of VIId is similar to that of its silicon analogue VIIa, whereas the spectrum of VIIId corresponds to the dihydrofuryltrimethylgermane structure (*m/e* 188 (M^+), 119 ($GeMe_3^+$) and 69 (dihydrofuryl$^+$)) and is distinguishable from the VIIa and VIId spectra.

TABLE 6

TRANSFORMATIONS OF  IN THE PRESENCE OF COMPLEX CATALYSTS[a]

Catalyst	Temperature (°C)	Reaction time (h)	Ratio of reaction mixture components		
			 GeMe3	 GeMe3	 GeMe3
$Pd(PPh_3)_2Cl_2$	20	24	100	–	–
	100	1	81	9	9
		3	72	14	14
		5	68	16	16
$RhCl(PPh_3)_3$	20	24	100	–	–
	100	1	83	8.5	8.5
		3	80	10	10
		5	76	12	12
$RuCl_2(PPh_3)_3$	20	24	100	–	–
	100	1	94	3	3
		3	87	6.5	6.5
		5	85	7.5	7.5

[a] 0.1 *M* Benzene solution, [substrate]:[catalyst] = 10:1.

A comparison of the amounts of the furyl derivatives (Va–Vd) obtained in the course of IVa–IVd hydrogenation (Table 2–5) shows that, as expected, the Va–Vd content in the reaction mixtures drops with the increasing rate of hydrogenation of the starting compounds.

We have also explored the possibility of homogeneous hydrogenation of IVa–IVd with organometallic complex catalysts used for the hydrogenation of the C=C bonds in alkenes and cycloalkenes [11,12]. However, the experiments showed that IVa–IVd did not undergo any changes in the presence of $\mathrm{RhCl(PPh_3)_3}$, $\mathrm{RhH(CO)(PPh_3)_3}$, $\mathrm{Pd(PPh_3)_2Cl_2}$ and $\mathrm{Pd(PPh_3)_4}$ under the same conditions as described for the heterogeneous hydrogenation.

The ability of IVa–IVd to undergo isomerization discovered in the course of catalytic heterogeneous hydrogenation has prompted us to investigate the possibility of selectively carrying out this reaction, as described in [13] for 2,5-dihydrofuran and some of its homologues, using $\mathrm{Pd^{II}}$, $\mathrm{Rh^{I}}$ and $\mathrm{Ru^{II}}$ complexes as catalysts. However, it was found that at r.t. these Pd, Rh and Ru complexes are inactive with respect to germane IVd but at higher temperature (100°C) they bring about its disproportionation (Table 6).

Experimental

^{1}H NMR spectra were obtained on a Bruker WH-90/DS spectrometer using $\mathrm{CDCl_3}$ as solvent and TMS and cyclohexane as internal standards. IR spectra were recorded on a Perkin–Elmer Model 580 B spectrometer. Mass spectra were obtained on a Kratos MS-25 GC/MS system (70 eV).

1,4-Bis(trimethylsiloxy)-2-butyne (I) was prepared as described in [14]. $\mathrm{HSiMe_3}$, $\mathrm{HSiEt_3}$, $\mathrm{HSiMe_2Ph}$ and diethyl azodicarboxylate were purchased from Fluka and $\mathrm{HGeMe_3}$ was obtained by the reduction of $\mathrm{ClGeMe_3}$ using $\mathrm{LiAlH_4}$ according to a routine procedure. All the synthetic procedures were carried out in absolute solvents under dry argon.

Commercially available 2 wt.% Pd/C and 5 wt.% $\mathrm{Pd/Al_2O_3}$ catalysts were used for hydrogenation. The complexes $\mathrm{Pd(PPh_3)_2Cl_2}$, $\mathrm{RhCl(PPh_3)_3}$, $\mathrm{RhH(CO)(PPh_3)_3}$, $\mathrm{RuCl_2(PPh_3)_3}$ were purchased from Fluka. $\mathrm{Pd(PPh_3)_4}$ was prepared according to a known method [15].

Metallation of 2,5-dihydrofuran by LDA followed by the reaction with $\mathrm{Me_3SiCl}$

To a solution of $\mathrm{i\text{-}Pr_2NLi}$ (prepared from 10.1 g (0.1 mol) $\mathrm{(i\text{-}Pr)_2NH}$ and 63.1 ml of 1.6 *M* n-BuLi hexane solution at −10°C) cooled to −78°C, 80 ml of THF, and a solution of 7.0 g (0.1 mol) of 2,5-dihydrofuran in THF (20 ml) were added. The mixture was stirred for 30 min at −78°C then 12.5 g (0.115 mol) of $\mathrm{Me_3SiCl}$ was added to this solution, dropwise, over 30 min, and then the temperature was raised to r.t. After filtration, *cis*-(1,3-butadienoxy)trimethylsilane (9.7 g, 0.07 mol) was obtained by distillation; yield 68%; b.p. 125°C, 752 mmHg; $n_D^{20} = 1.4210$; ^{1}H NMR $\mathrm{Me_3SiO}\underset{(1)}{\mathrm{CH}}{=}\underset{(2)}{\mathrm{CH}}-\underset{(3)}{\mathrm{CH}}{=}\underset{(4,5)}{\mathrm{CH_2}}$ (δ, ppm, *J*, Hz) 6.84 (m, H_3, *J*(3,4) 17.8, *J*(3,5) 10.5), 6.26 (d, H_1, *J*(1,2) 5.9), 5.31 (m, H_2, *J*(2,3) 11.0), 5.15 (dd, H_4, *J*(4,5) 1.3), 4.97 (dd, H_5).

1,4-Bis(trimethylsiloxy)-2-(trimethylsilyl)-2-butene (IIa)

115 g (0.5 mol) I, 37.1 g (0.5 mol) $\mathrm{Me_3SiH}$ and 3×10^{-3} mol $\mathrm{H_2PtCl_6}$ (THF

solution) were mixed in a stainless steel autoclave at −20°C. The reaction mixture was heated in a boiling water bath for 2 h, cooled and distilled in vacuo to give IIa (134.2 g, 0.44 mol); yield 88.2%; b.p. 80°C, 0.5 mmHg; $n_D^{20} = 1.4380$; ^{1}H NMR (δ, ppm) 5.80 (m, 1H, C*H*=C), 4.26 (m, 4H, O–CH_2–C=) and 0.11 (s, 9H, $\equiv$Si–CH_3); IR (cm^{-1}) 1620 (ν(C=C)).

2-(Trimethylsilyl)-2-butene-1,4-diol (IIIa)

A solution of 134.2 g (0.44 mol) IIa in 300 ml of absolute ethanol was heated under reflux for 30 min, the excess ethanol and trimethylethoxysilane were distilled off and the residue was distilled in vacuo to give IIIa (67.3 g, 0.42 mol); yield 95.3%; b.p. 102–103°C, 1 mmHg; $n_D^{20} = 1.4850$; ^{1}H NMR (δ, ppm) 6.11 (t, 1H, CH_2–C*H*=C), 4.29 (m, 4H, O–CH_2), 0.13 (s, 9H, $\equiv$Si–CH_3); IR (cm^{-1}) 3150 (ν(OH)), 1620 (ν(C=C)).

3-(Trimethylsilyl)-2,5-dihydrofuran (IVa)

A mixture of 30.0 g (0.19 mol) IIIa, 30.0 g (0.02 mol) $KHSO_4$ and 1.0 g (0.004 mol) dithizon was heated under reflux for 30 min, the crude product obtained by distillation in vacuo was dried ($MgSO_4$) and redistilled to give IVa (21.4 g, 0.15 mol); yield 80.4%; b.p. 65°C, 40 mmHg; $n_D^{20} = 1.4485$; MS (*m/e*, relative intensity,% *) 142 (M^+, 24), 127 (52), 97 (16), 74 (33), 73 (100), 59 (64), 45 (30), 43 (29); ^{1}H NMR (δ, ppm): 6.02 (m, 1H, CH_2–C*H*=C), 4.66 (m, 4H, O–CH_2) and 0.13 (s, 9H, $\equiv$Si–CH_3); IR (cm^{-1}) 1600 (ν(C=C)).

3-(Triethylsilyl)-2,5-dihydrofuran (IVb)

The mixture of 20.2 g (0.0878 mol) I, 10.2 g (0.0878 mol) Et_3SiH and 3×10^{-3} mol $H_2PtCl_6 \cdot 6H_2O$ (THF solution) was slowly heated to 90°C, and a strong exothermic hydrosilylation reaction began. After 30 min, the reaction mixture was cooled, 42 ml of absolute ethanol was added and the solution was heated under reflux for 30 min. The excess ethanol and trimethylethoxysilane were distilled off, 15 g (0.11 mol) $KHSO_4$ with 0.6 g (0.002 mol) dithizon were added to the residue and the mixture was heated under reflux for 15 min. The crude product obtained by distillation in vacuo was dried ($MgSO_4$) and redistilled to give IVb (12.3 g, 0.07 mol); yield 76.1% (on the basis of $HSiEt_3$); b.p. 45°C, 0.5 mmHg; $n_D^{21} = 1.4680$ [lit. b.p. 70°C/4 mmHg, $n_D^{20} = 1.4652$ [1]); MS (*m/e*, relative intensity,%): 184 (M^+, 13), 155 (54), 127 (51), 125 (11), 115 (12), 113 (15), 111 (14), 109 (10), 105 (15), 97 (17), 88 (10), 87 (100), 69 (16), 59 (49), 53 (16); ^{1}H NMR (δ, ppm) 6.02 (m, 1H, CH_2–C*H*=C), 4.66 (m, 4H, O–CH_2), 0.94 (m, 9H, $\equiv$SiCH_2CH_3) and 0.73 (m, 6H, $\equiv$Si–C$H_2$$CH_3$); IR (cm^{-1}) 1600 ($\nu$(C=C)).

2-(Dimethylphenylsilyl)-2-butene-1,4-diol (IIIc)

A mixture of 23.0 g (0.1 mol) I, 13.6 g (0.1 mol) $HSiMe_2Ph$ and 3×10^{-3} mol $H_2PtCl_6 \cdot 6H_2O$ (THF solution) was slowly heated to 50°C, and a strong exothermic hydrosilylation reaction began. After 30 min, the solution was cooled, 58 ml of absolute ethanol was added and the mixture was heated under reflux for 30 min. The excess ethanol and trimethylethoxysilane were distilled off and the residue was distilled in vacuo to give IIIc (19.3 g; 0.087 mol); yield 87%; b.p. 144–150°C, 0.4

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* Only the peaks with more than 10% intensity are given.

mmHg; $n_D^{20} = 1.5480$; ^1H NMR (δ, ppm) 7.24 (m, 5H, $\equiv Si-C_6H_5$), 6.04 (m, 1H, $CH_2-CH=C$), 4.20 (m, 4H, $O-CH_2-C=$), 0.38 (s, 6H, $\equiv Si-CH_3$); IR (cm^{-1}) 3150 (ν(OH)), 1620 (ν(C=C)).

3-(Dimethylphenylsilyl)-2,5-dihydrofuran (IVc)

IVc was prepared as described for IVa. Yield 67.8%; b.p. 75°C, 0.5 mmHg; $n_D^{24} = 1.5330$; MS (*m/e*, relative intensity,%) 204 (M^+, 21), 190 (17), 189 (100), 135 (18), 121 (19), 105 (12), 59 (12), 53 (14), 45 (11), 43 (21); ^1H NMR (δ, ppm) 7.41 (m, 5H, $\equiv Si-C_6H_5$), 6.10 (m, 1H, $CH_2-CH=C$), 4.69 (m, 4H, $O-CH_2-C=$), 0.40 (s, 6H, $\equiv Si-CH_3$); IR (cm^{-1}) 1600 (ν(C=C)).

1,4-Bis(trimethylsiloxy)-2-(trimethylgermyl)-2-butene (IId)

IId was obtained by the hydrogermylation of I using $HGeMe_3$ as described for IIa. Yield 89.2%; b.p. 90°C/1 mmHg; $n_D^{20} = 1.4465$; ^1H NMR (δ, ppm) 5.71 (m, 1H, $CH_2-CH=C$), 4.25 (m, 4H, $O-CH_2-C=$) and 0.15 (s, 9H, $\equiv Ge-CH_3$); IR (cm^{-1}) 1650 (ν(C=C)).

2-(Trimethylgermyl)-2-butene-1,4-diol (IIId)

IIId was prepared as described for IIIa. Yield 62%; b.p. 140°C, 1 mmHg; $n_D^{20} = 1.4950$; ^1H NMR (δ, ppm) 5,92 (t, 1H, $CH_2-CH=C$), 4.25 (m, 4H, $O-CH_2=C$) and 0.22 (s, 9H, $\equiv Ge-CH_3$); IR (cm^{-1}) 3360 (ν(OH)), 1626 (ν(C=C)).

3-(Trimethylgermyl)-2,5-dihydrofuran (IVd)

To a solution of 12.4 g (0.05 mol) IIId and 16.5 g (0.06 mol) of PPh_3 in 75 ml of dry chloroform, 10 g (0.06 mol) of diethyl azodicarboxylate was added dropwise at 10–15°C and then stirred for 2 h at the same temperature. After evaporation of chloroform the residue was distilled in vacuo to give IVd (5.6 g, 0.03 mol); yield 60%; b.p. 52°C, 7 mmHg; $n_D^{22} = 1.4672$; MS (*m/e*, relative intensity,%) 188 (M^+, 4) 173 $(M-CH_3)^+$ (19), 171 (12), 143 (20), 141 (14), 121 (22), 119 (100), 118 (25), 117 (74), 115 (57), 105 (43), 104 (16), 103 (35), 101 (27), 91 (12), 89 (31), 87 (27), 85 (16); ^1H NMR (δ, ppm) 5.91 (m, 1H, $CH_2-CH=C$), 4.66 (m, 4H, $O-CH_2-C=$), 0.25 (s, 9H, $\equiv Ge-CH_3$); IR (cm^{-1}) 1605 (ν(C=C)).

IVa–IVd hydrogenation (general procedure)

10–20 ml of 0.1 *M* IVa–IVd solution (in an appropriate solvent) and 25–50 mg of catalyst (Pd/C or Pd/Al_2O_3) were placed in a thermostatically-controlled glass reactor provided with a tapping device for sampling by means of a microsyringe. The mixture was stirred at r.t. under hydrogen (1 atm.). The reaction was controlled by GLC using a Chrom-42 instrument with flame-ionization detector, glass column with 3 mm internal diameter and He as carrier-gas (50 ml/min). The other GLC parameters were varied depending on the composition of the mixture to be analyzed (Table 7). Tetrahydrofuryl derivatives (VI) were prepared by hydrogenation until the starting compound IV and its isomers disappeared from the reaction mixtures (see Tables 2–5). The catalyst was separated by filtration through alumina. The solvent was distilled off and the mixture containing V and VI was separated by preparative GLC using a stainless column (1 m × 10 mm) packed with 20% dinonyl phthalate/Chromosorb W-AW at the temperature of GLC analysis (see Table 7). Only VId was isolated by vacuum-distillation. To prepare isomers VIIa–VIIc the hydrogenation in

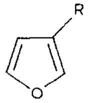
TABLE 7

GLC PARAMETERS

Components of analyzed mixture	Stationary phase (wt.%)	Sorbent	Column length (m)	Analysis temperature (°C)
IVa,Va,VIa,VIIa	dinonyl phthalate (20)	Chromosorb W-AW (60–80 mesh)	3.6	120
IVb,Vb,VIb,VIIb	SE-30 (10)+ Reoplex-400 (2.5)	Chromosorb W-AW (60–80 mesh)	2.4	130
IVc,Vc,VIc,VIIc	SE-30 (10)+ Reoplex-400 (2.5)	Chromosorb W-AW (60–80 mesh)	2.4	160
IVd,Vd,VId,VIId VIIId	Poropak Q (80–100 mesh)	–	1.2	230

TABLE 8

^{1}H NMR SPECTRAL DATA FOR

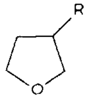


R	Chemical shift (δ, ppm)						
	H(2)	H(4)	H(5)	CH_3	C_6H_5	C_2H_5	
						CH_2	CH_3
$Si(CH_3)_3$[a]	7.39(m)	6.41(m)	7.52(m)	0.23(s)	–	–	–
$Si(CH_2CH_3)_3$	7.39(m)	6.40(m)	7.53(m)	–	–	0.65(m)	0.95(m)
$Si(CH_3)_2C_6H_5$	7.31–7.46(m)	6.41(m)	7.31–7.46(m)	0.46(s)	7.31–7.68(m)	–	–
$Ge(CH_3)_3$[a]	7.30(m)	6.37(m)	7.51(m)	0.16(s)	–	–	–

[a] The spectral data are in accord with the data described in [16].

TABLE 9

^{1}H NMR SPECTRAL DATA FOR

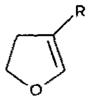


R	Chemical shift (δ, ppm)					
	4H(H(2),H(5))	3H(H(3),H(4))	CH_3	C_6H_5	C_2H_5	
					CH_2	CH_3
$Si(CH_3)_3$	3.40–4.13(m)	1.22–2.04(m)	0.03(s)	–	–	–
$Si(C_2H_5)_3$	3.41–4.11(m)	1.20–2.05(m)	–	–	0.61(m)	0.96(m)
$Si(CH_3)_2C_6H_5$	3.40–4.09(m)	1.41–2.09(m)	0.32(s)	7.27–7.67(m)		
$Ge(CH_3)_3$	3.34–4.10(m)	1.34–2.18(m)	0.16(s)	–	–	–

the appropriate solvent was continued until their concentration in the reaction mixture reached maximum (see Tables 2–5). After that, VIIa–VIIc were isolated by preparative GLC, as described above. The mass and ^{1}H NMR spectral data of the catalytically-obtained compounds are presented in Tables 8–11.

The catalytic reactions of IVa–IVd in the absence of hydrogen were carried out in

TABLE 10

^{1}H NMR SPECTRAL DATA FOR 

R	Chemical shifts δ(ppm) (J, Hz)						
	H(2)	H(4)	H(5)	CH_3	C_6H_5	C_2H_5	
						CH_2	CH_3
$Si(CH_3)_3$	6.24 (t, $^4J(2,4) = 3.0$)	2.54 (dt, $J(4,5) = 9.8$)	4.29(t)	0.13(s)	–	–	–
$Si(CH_2CH_3)_3$	6.24 (t, $^4J(2,4) = 2.1$)	2.59 (dt, $J(4,5) = 9.4$)	4.26(t)	–	–	0.69(m)	1.13(m)
$Si(C_6H_5)(CH_3)_2$	6.29(m)	2.47 (t, $J(4,5) = 10.0$)	4.31(t)	0.36(s)	7.31–7.40(m)	–	–

TABLE 11

MASS SPECTRAL DATA FOR CATALYTICALLY-OBTAINED COMPOUNDS

Compound	m/e (rel.intensity, % [a])
Va	140(M^+,15), 126(13), 125($M^+ - CH_3$,100), 45(15), 43(18)
Vb	182(M^+,10), 154(13), 153($M^+ - C_2H_5$,74), 126(12), 125(100), 97(77), 53(11), 45(18)
Vc	202(M^+,19), 188(17), 187($M^+ - CH_3$,100), 43(12)
Vd	186(M^+,11), 173(22), 171($M^+ - CH_3$,100), 170(26), 169(74), 167(55), 119(11), 115(10), 105(19), 103(16), 101(14), 89(20), 87(16), 85(16)
VIa	129($M^+ - CH_3$,10), 103(72), 101(58), 99(49), 75(40), 73(100), 70(20), 59(10), 45(40), 43(38)
VIb	157($M^+ - C_2H_5$,25), 130(12), 129(100), 127(23), 115(24), 101(13), 99(57), 87(62), 75(23), 71(20), 70(11), 59(63), 58(11), 57(15), 45(14), 43(14)
VIc	206(M^+,1), 165(24), 161(13), 136(19), 135(100), 128(17), 121(16), 105(11), 43(17)
VId	175($M^+ - CH_3$,8), 149(25), 147(21), 145(22), 121(27), 119(100), 118(24), 117(75), 115(54), 105(44), 104(15), 103(34), 101(26), 91(11), 89(27), 87(21), 85(13), 70(13), 69(18)
VIIa	142(M^+,27), 128(20), 127($M^+ - CH_3$,100), 97(10), 75(25), 73(37), 59(53), 53(11), 45(23), 43(28)
VIIb	184(M^+,16), 156(14), 155($M^+ - C_2H_5$,100), 127(83), 99(78), 87(19), 59(26), 53(12), 47(12), 43(13)
VIIc	204(M^+,22), 190(18), 189($M^+ - CH_3$,100), 135(16), 121(17), 43(13)
VIId	188(M^+,13), 175(19), 173($M^+ - CH_3$,89), 172(24), 171(65), 169(48), 119(10), 107(11), 105(50), 104(15), 103(39), 101(30), 91(13), 89(29), 87(22), 85(14)
VIIId	188(M^+,10), 121(23), 119(100), 118(25), 117(74), 115(54), 105(10), 89(16), 87(10), 69(44)

[a] Only the peaks with more than 10% intensity are given (except for the peaks of molecular ions).

a 5 cm^3 glass microautoclave (Pierce). The experimental conditions are presented in Tables 1 and 6. These processes were also controlled by GLC (see Table 7).

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