

Reactions of trialkyl(2-furyl)germanes with electrophilic reagents

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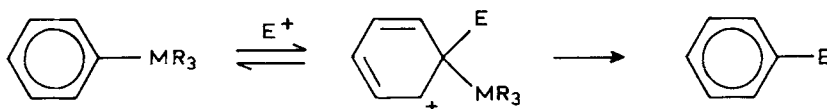
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Abstract

The metallation (n-BuLi), alkylation (t-BuOH/H⁺), nitration (NO₂⁺ BF₄[−]), bromination (NBS, dioxane dibromide (DDB)), acylation [(CF₃CO)₂O] and chlorination (chloramine T) reactions of (2-furyl)germanes were studied. Except for alkylation and bromination with DDB, the reactions involved electrophilic substitution of hydrogen atoms in position 5 or 3 of the furan ring. The alkylation reaction and bromination with DDB occur via *ipso*-substitution of the trialkylgermyl group. Dichlorocarbene generated by phase-transfer catalysis adds to the 2-germyl-substituted furan at the C₄=C₅ bond in the ring. Some of the above reactions were conducted with trimethyl(2-furyl)silane and 2-(t-butyl)furan, the silicon and carbon analogues of furylgermanes. The reactivities of the title compounds were compared.

Introduction

The first remarkable contribution by Professor Colin Eaborn to organometallic chemistry involved the discovery and detailed investigation of electrophilic aromatic *ipso*-substitution of the MR₃ group (M = Si, Ge, Sn, Pb) in compounds of the type ArMR₃:



Reactions of this kind have gained currency in organic synthesis primarily due to the fact that they provide a unique possibility for regiospecific insertion of various groups (halogen, NO₂, NO, alkyl, acyl, etc.) into the aromatic or heterocyclic ring [1,2]. In most cases, arylsilanes [3,4] and arylstananes [5,6] have been employed for *ipso*-substitution. Arylgermanes are not so commonly used for this purpose, al-

though germanium has a greater covalent radius than silicon and the energy of the Ge–C bond is lower than that of the Si–C bond [7], which would be expected to make compounds of the type ArGeR_3 more susceptible to electrophilic substitution than arylsilanes. On the other hand, the $\text{C}_{\text{Ar}}\text{--Ge}$ bond undergoes acid hydrolysis less readily than the $\text{C}_{\text{Ar}}\text{--Sn}$ bond [8], i.e. the use of arylgermanes instead of arylstannanes is more preferable in some cases. Recently, regiospecific halodegermylation of *m*- and *p*- $\text{RC}_6\text{H}_4\text{GeMe}_3$ ($\text{R} = \text{H, F, Cl, OH, OMe}$) has been reported, enabling the preparation of *m*- and *p*-disubstituted benzenes in reasonable yields, which are otherwise not easily available by other routes [9].

It must be pointed out, though, that the reactions of ArMR_3 with electrophilic reagents do not always lead to *ipso*-substitution; some reactions follow the ordinary course involving electrophilic substitution of hydrogen atoms in the aromatic ring [10,11].

The reactions of hetarylgermanes with electrophilic reagents are practically unexplored. The present communication describes the metallation, alkylation, acylation, nitration, bromination, and chlorination reactions of trialkyl(2-furyl)germanes performed in an attempt to explore the possibility of their functionalization or the possibility of *ipso*-substitution of the trialkylgermyl group in the presence of electrophiles. Some of the above reactions were also carried out with trimethyl(2-furyl)silane and 2-(*t*-butyl)furan, the appropriate silicon and carbon analogues of trialkyl(2-furyl)germanes. The role of the organoelemental substituent and its influence on heterocycle reactivity were studied in reactions of (2-furyl) MR_3 ($\text{M} = \text{Ge, Si, C}$) with the singlet electrophilic dichlorocarbene generated under phase-transfer conditions.

Results and discussion

The trimethyl- and triethyl-(2-furyl)germanes (Ia and Ib) examined in this study were prepared following the known procedure [12] using the reactions of 2-furyllithium with the corresponding trialkylchlorogermanes. The earlier unknown germane Ib was obtained in 80% yield by this method.

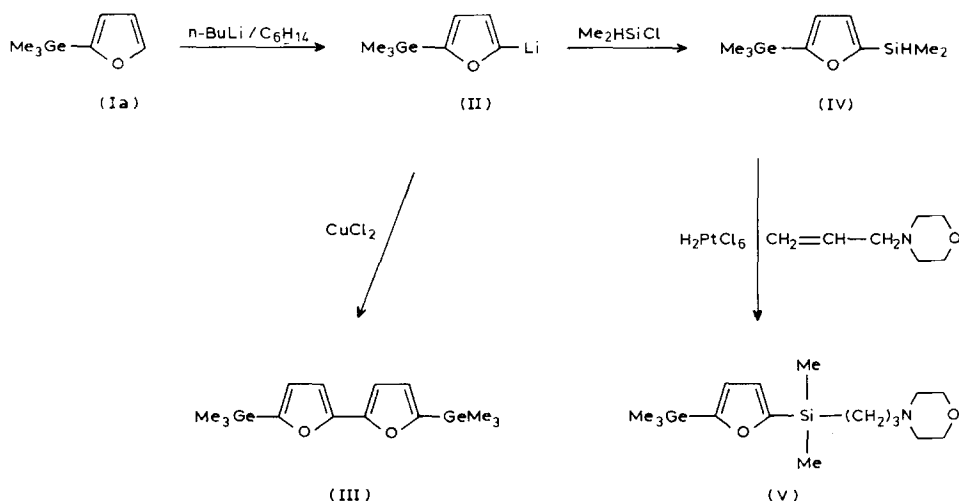
Metallation

Trimethyl(2-furyl)-silane and -germane are known to undergo metallation with *n*-butyllithium in ether to give trimethyl(5-lithium-2-furyl)-silane or -germane [13,14]. We carried out the metallation of germane Ia by treating it with *n*-BuLi in hexane, along with other reactions of the 5-lithium-substituted germane II (Scheme 1).

In the presence of CuCl_2 , germane II is converted into 5,5'-bis(trimethylgermyl)-2,2'-bifuryl (III) in 30% yield. The reaction of II with dimethylchlorosilane affords trimethyl(5-trimethylsilyl-2-furyl)germane (IV). Compound IV acts as a hydrosilylating agent, as exemplified by its reaction with *N*-allylmorpholine. In the presence of Speier's catalyst ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), a β -addition product V is formed in 82% yield.

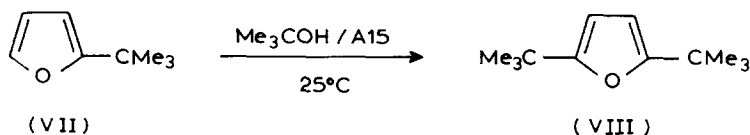
Alkylation and acylation

The alkylation of furylgermane Ia and its analogues, viz. trimethyl(2-furyl)silane (VI) [12] and 2-(*t*-butyl)furan (VII), with *t*-butanol was performed using a strongly acidic cation exchanger, Amberlyst 15 (A15), for carbocation generation. It has been

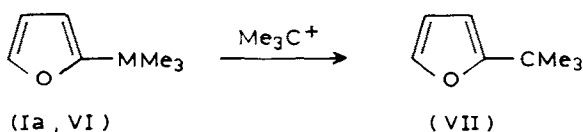


Scheme 1

demonstrated earlier that the system *t*-BuOH/A15 is extremely effective for the alkylation of furan to 2-(*t*-butyl)furan [15]. As expected, under similar conditions alkylfuran (VII) gives 2,5-di(*t*-butyl)furan (VIII).



*Ips*o-substitution affecting the organoelemental group was observed for germane Ia and silane VI, leading to VII as the sole product.



M = Ge (Ia) , Si (VI)

A comparison of the reactivities of furan, furysilane VI and furylgermane Ia (Table 1) indicates that with respect to the ease of substitution the leaving groups can be arranged as follows: $\text{Me}_3\text{Si} > \text{Me}_3\text{Ge} > \text{H}$.

Upon acylation of germane Ib with trifluoroacetic acid anhydride, degermylation fails to occur, and the reaction follows the ordinary course via electrophilic substitution resulting in (5-trifluoroacetyl-2-furyl)triethylgermane (IX) in 64% yield.

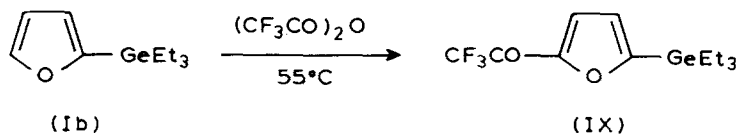


Table 1

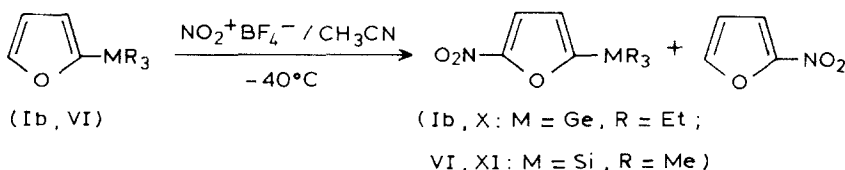
Alkylation of furan and its derivatives with *t*-butanol in the presence of the cation exchanger Amberlyst 15 (25°C, 1 ml of substrate, 2.3 mmol SO₃H groups, 2 mmol of *t*-BuOH)

Substrate	Reaction time	2-(<i>t</i> -butyl)furan yield (%) (based on <i>t</i> -butanol) ^a
Furan	24	80 [15]
Ia	2.5	70
VI	0.5	75 ^b

^a GLC data. ^b ca. 10% of 2,5-di(*t*-butyl)furan is present in the reaction mixture.

Nitration

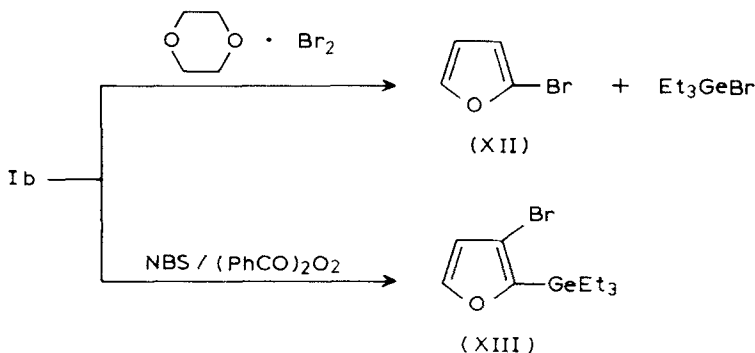
The general method for introduction of a nitro group into the molecule of furan or its derivatives is nitration with acetyl nitrate [16]. Application of this method to furylgermane Ib failed because of strong reaction mixture resinification. Intensive resin formation also occurs in the presence of neutral nitrating agents; nonetheless, ~ 10% of (5-nitro-2-furyl)germane (X) could be isolated from the reaction mixture.

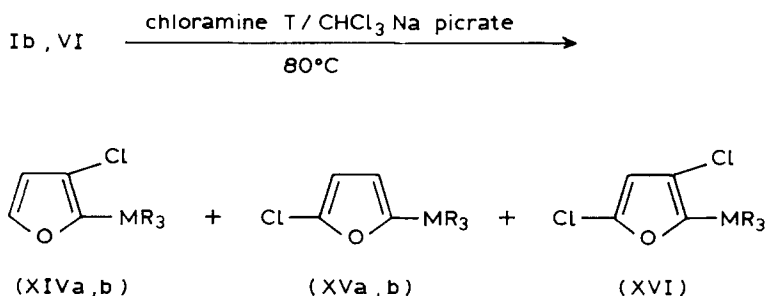


Silane VI reacts similarly, the yield of compound XI amounting to only 3–4%. According to GLC/MS data, small amounts of 2-nitrofuran are also formed in both cases, i.e. electrophilic substitution of the germyl (silyl) group and hydrogen in the ring proceed in parallel. The low selectivity of nitration with NO₂⁺ BF₄⁻ has been demonstrated by Olah et al. [17] for unsubstituted furan (the yield of 2-nitrofuran was 15%). Compounds X and XI, the first representatives of germanium-, and silicon-containing nitrofurans, were isolated by preparative GLC.

Halogenation

The bromination of (2-furyl)germane (Ib) was carried out with the aid of brominating agents commonly applied to achieve the insertion of bromine into the





(Ib, XIVa, XVa, XVI : M = Ge, R = Et ;

VI, XIVb, XVB : M = Si, R = Me)

molecule of heteroaromatic compounds. *Ips*o-substitution leading to 2-bromofuran (XII) and triethylbromogermene occurs exclusively in the case of dioxane dibromide, which has been used earlier to prepare 2-bromofuran from furan [18].

The radical bromination of germane Ib with *N*-bromosuccinimide in the presence of benzoyl peroxide (i.e. under the conditions described for the bromination of trimethyl(2-alkyl-4-furyl)silane [18]) gives trimethyl(3-bromo-2-furyl)germane (XIII) in 43% yield.

The chlorination of furylgermane Ib was performed with chloramine T [20] in the two-phase system $\text{CHCl}_3/\text{H}_2\text{O}$ at 80°C in the presence of sodium picrate as catalyst. The catalyst apparently serves to transfer chloronium ions from the aqueous phase containing chloramine T to the organic one as the $[\text{picrate}]^- [\text{Cl}]^+$ ion pair. According to our findings, the major product formed in the reaction under these conditions is (3-chloro-2-furyl)triethylgermane (XIVa). Isomeric germane XVa and dichloro-substituted furylgermane XVI are also formed in small amounts. Upon 100% conversion of Ib, the yield of germane XIVa is 35% (GLC data).

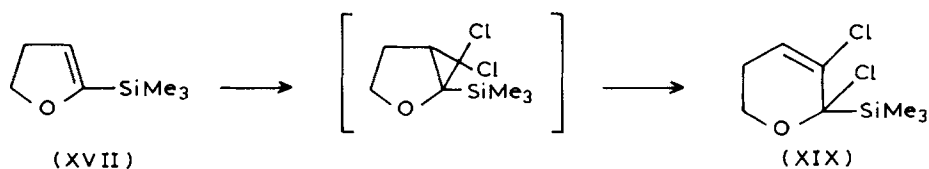
Without sodium picrate the conversion yield does not exceed 20%.

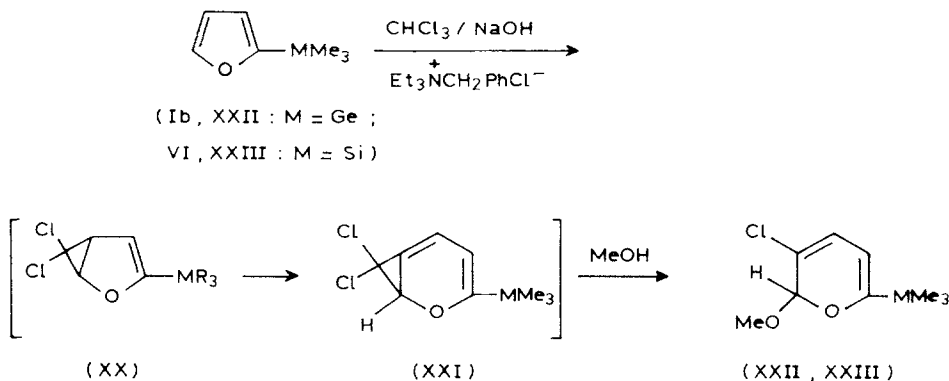
No definite conclusions as to the halodegermylation of germane Ib under the above conditions can be made, because the possible product of germane Ib halodegermylation (2-chlorofuran) was not detected.

Furylsilane VI undergoes chlorination similarly to germane Ib, a mixture of two monochloro-substituted furylsilanes (XIVb and XVB) being formed at room temperature.

Reactions of trimethyl(2-furyl)germane (Ia) and its analogues (VI and VII) with dichlorocarbene

It has been reported earlier [21] that [2-(4,5-dihydrofuryl)]trimethylsilane (XVII) adds dichlorocarbene at the C=C bond in the dihydrofuran cycle with subsequent isomerization to 2,3-dichloro-2-trimethylsilyl-5,6-dihydro-2*H*-pyran (XIX).

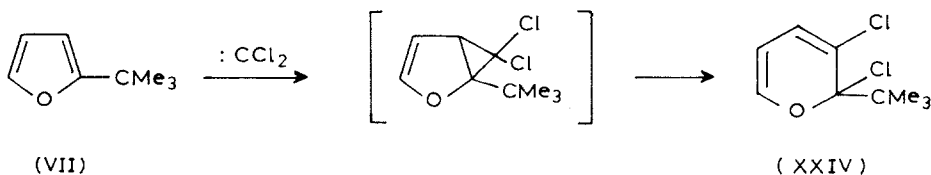




We examined the reactions of Ib, VI and VII with dichlorocarbene generated by treating chloroform with solid NaOH in the presence of a phase-transfer catalyst [22]. Here, unlike the case of silane XVII, alternative pathways of :CCl_2 addition to the $\text{C}(2)=\text{C}(3)$ or $\text{C}(4)=\text{C}(5)$ bond in the furan ring are possible. Furylgermane Ib and furylsilane VI react with dichlorocarbene in methanol-containing chloroform to afford 6-trimethylgermyl- and 6-trimethylsilyl-3-chloro-2-methoxy-2*H*-pyrans (XX and XXI), respectively, in 28–36% yield (resinification is conspicuous).

Thus, the reaction involves the addition of :CCl_2 at the $\text{C}(4)=\text{C}(5)$ bond with subsequent isomerization of adduct XX to the 2,3-dichloro-2*H*-pyran derivative XXI and nucleophilic substitution of the chlorine atom in position 2 for a methoxy group. We failed to obtain compound XXI in alcohol-free chloroform, possibly due to gradual β -elimination of HCl from XXI in the presence of alkali.

2-Alkylfuran (VII), unlike its organoelemental analogues Ib and VI, reacts with dichlorocarbene generated under liquid-solid phase transfer conditions in alcohol-free CHCl_3 . The reaction affects the $\text{C}(2)=\text{C}(3)$ bond in the ring to give 2,3-dichloro-2-(*t*-butyl)-2*H*-pyran (XXIV) in 16% yield.



Compounds XXII, XXIII and XXIV were isolated from the reaction mixture using preparative GLC and assigned by ^1H NMR and mass spectra.

The observed differences in the direction of electrophilic attack by dichlorocarbene in its reactions with furyl-germane Ib and -silane VI, on the one hand, and with 2-(*t*-butyl)furan VII, on the other, can evidently be explained by the π -acceptor properties of the organoelemental substituents [23–25] causing a decrease in the nucleophilicity of the $\text{C}(2)=\text{C}(3)$ bond, as compared with the $\text{C}(4)=\text{C}(5)$ bond. 2-Alkyl-substituted furan VII, owing to the presence of an electron-donating group (as in the case of 2-methylfuran [26]), reacts with :CCl_2 at the $\text{C}(2)=\text{C}(3)$ bond.

Experimental

^1H NMR spectra were recorded on a Bruker WH-90/DS spectrometer (90 MHz) in CDCl_3 and C_6D_6 using tetramethylsilane and cyclohexane as internal standards. Mass spectra were recorded on Kratos MS-25 (70 eV) and MS-50 (70 eV) instruments. GLC analysis was conducted on a Chrom-5 chromatograph supplied with a flame-ionization detector and glass columns packed with 10% SE-30 + 25% Reoplex-400 on Chromosorb W-AW (60–80 mesh) or 5% OV-17 on Chromosorb W-HP (80–100 mesh) with helium ($60\text{ cm}^3/\text{min}$) used as carrier gas. Preparative GLC runs were carried out on a Pye Unicam 105 chromatograph with a $2.1\text{ m} \times 7\text{ mm}$ column packed with 10% SE-30 on Chromatone NAW-DMCS (60–80 mesh).

The starting compounds, germane Ia [12], silane VI [12] and 2-(*t*-butyl)furan [15] were prepared following known procedures. Commercially available reagents, nitronium tetrafluoroborate, chloramine T, Amberlyst 15 and triethylbenzylammonium chloride, were purchased from Fluka.

Triethyl(2-furyl)germane (Ib)

65 ml of 1.5 *N* *n*-butyllithium in hexane was added dropwise to a solution of freshly distilled furan (6.8 g, 0.1 mol) in 100 ml of absolute ether cooled to -30°C . After the addition of butyllithium, the temperature was raised to 15°C and the reaction mixture was stirred at this temperature for 4 h. After cooling to -15°C , a solution of triethylchlorogermane (19.5 g, 0.1 mol) in 100 ml of absolute ether was added dropwise. The mixture was allowed to stand overnight at room temperature and lithium chloride was filtered off. The solvent was removed by distillation and the residue was distilled in vacuum. A fraction with b.p. $84\text{--}85^\circ\text{C}/2\text{ mmHg}$ was collected giving 18.0 g (80%) of compound Ib, $n_{\text{D}}^{20} = 1.4720$; the ^1H NMR and mass spectral data of Ib are presented in Table 2.

5,5'-Bis(trimethylgermyl)-2,2'-bifuryl (III)

32 ml of 1.5 *N* *n*-BuLi in hexane was added dropwise to 9.2 g (0.05 ml) of (2-furyl)germane (Ia) dissolved in an ether/THF (3/1) mixture (20 ml) cooled to -25°C . The temperature was raised to 0°C and the reaction mixture was stirred for 4 h. It was then cooled to -60°C and a solution of CuCl_2 (5.4 g, 0.04 mol) in 20 ml of ether/THF (3/1) was added in small portions. The mixture was stirred for 1 h at -10°C , supplemented with 4 ml of methanol and 30 ml of saturated glycine solution followed by stirring for 30 min. The organic layer was removed and the aqueous layer extracted with ether ($30\text{ ml} \times 3$). The combined organic layer was dried with anhydrous magnesium sulphate. The solvent was removed by distillation, and the residue was dissolved in 30 ml of petroleum ether and run through a column with neutral Al_2O_3 . The solvent was removed by distillation and the residue was crystallized to give 2.62 g (29%) of compound III, m.p. $92\text{--}94^\circ\text{C}$; the ^1H NMR and mass spectral data for III are presented in Table 2.

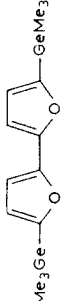
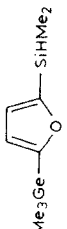
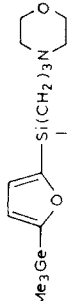
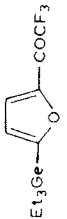
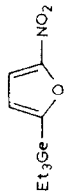
Trimethyl(5-dimethylsilyl-2-furyl)germane (IV)

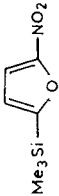
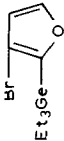
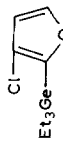
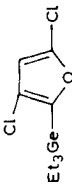
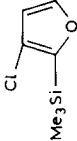
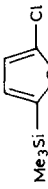
6.7 ml of 1.5 *N* *n*-butyllithium solution in hexane was added dropwise to a solution of germane Ia (1.85 g, 0.01 mol) in absolute ether cooled to between -25 and -30°C . After the addition of butyllithium, the temperature was raised to 20°C and the mixture was stirred for 2 h. After cooling to -15°C , a solution of

(Continued on p. 21)

Table 2

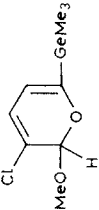
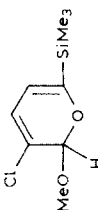
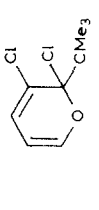
¹H NMR and mass spectral data for the new compounds

Compound	Chemical shift, δ (ppm), J (Hz)	m/z (rel. abundance, %) ^{a,b}
 (Ib)	1.09 (m, 15H, GeEt ₃), 6.43 (dd, 1H, H ⁵), 6.55 (dd, 1H, H ³), 7.68 (dd, 1H, H ⁵); $J_{4,5}$ 0.6; $J_{4,5}$ 1.6	228 (M^+ , 12), 199 ($M^+ - Et$, 100), 171 (49), 143 (42), 113 (13)
 (III)	0.43 (s, 9H, GeMe ₃), 6.56 (s, 2H, H ³ , H ⁴)	370 (M^+ , 63), 355 ($M^+ - Me$, 100), 340 (30), 289 (52), 119 (82), 60 (19), 57 (22), 44 (18)
 (IV)	0.22 (s, 6H, SiMe ₂), 0.29 (c, 9H, GeMe ₃), 4.32 (s, 1H, Si-H), 6.58 (d, 1H, H ³), 6.42 (d, 1H, H ⁴); $J_{3,4}$ 3.1	244 (M^+ , 14), 229 ($M^+ - Me$, 100), 179 (27), 163 (5), 119 (17), 89 (17), 73 (29), 59 (14), 51 (29)
 (V)	0.25 (s, 6H, SiMe ₂), 0.40 (c, 9H, GeMe ₃), 0.72 (m, 2H, CH ₂ Si), 1.56 (m, 2H, C-CH ₂ -C), 2.41 (m, 4H, N-CH ₂), 3.71 (m, 4H, O-CH ₂), 6.51 (d, 1H, H ⁴), 6.62 (d, 1H, H ³); $J_{3,4}$ 3.2	
 (IX)	0.89–1.05 (m, 15H, GeEt ₃), 6.76 (d, 1H, H ⁴), 7.52 (d, 1H, H ³); $J_{3,4}$ 3.9	324 (M^+ , 5), 295 ($M^+ - Et$, 100), 267 (50), 239 (66), 103 (15), 97 (20), 75 (15)
 (X)	1.08 (m, 15H, GeEt ₃), 6.67 (d, 1H, H ³), 7.27 (d, 1H, H ⁴), $J_{3,4} = 3.5$	244 ($M^+ - Et$, 29), 212(15), 186 (13), 161 (35), 133 (100), 105 (73), 101 (60), 75 (31)

 (XI)	0.41 (s, 9H, SiMe₃), 6.81 (d, 1H, H³), 7.33 (d, 1H, H⁴); <i>J</i>_{3,4} 3.4	185 (<i>M</i>⁺, 14), 170 (<i>M</i>⁺ – Me, 73), 104 (100), 73 (39), 55 (14), 53 (17), 43 (38)
 (XII)	1.04–1.19 (m, 15H, GeEt₃), 6.31 (d, 1H, H⁴), 7.48 (d, 1H, H⁵); <i>J</i>_{4,5} 1.8	306 (<i>M</i>⁺, 14), 277 (<i>M</i>⁺ – Et, 100), 249 (969), 221 (77), 153 (30), 99 (16)
 (XIII)	1.03 (m, 15H, GeEt₃), 6.30 (d, 1H, H⁴); 7.39 (d, 1H, H⁵), <i>J</i>_{4,5} 2.1	262 (<i>M</i>⁺, 18), 233 (<i>M</i>⁺ – Et, 100), 205 (74), 177 (84), 109 (40)
 (XIVa)	1.10 (m, 15H, GeEt₃), 6.13 (d, 1H, H³), 6.51 (d, 1H, H⁴); <i>J</i>_{3,4} 3.3	262 (<i>M</i>⁺, 20), 233 (<i>M</i>⁺ – Et, 100), 205 (68), 177 (35), 109 (44), 67 (18)
 (XVa)	1.03–1.15 (m, 15H, GeEt₃), 6.10 (s, 1H, H⁴)	296 (<i>M</i>⁺, 16), 276 (<i>M</i> – Et, 80), 239 (72), 109 (84), 73 (44), 28 (100)
 (XVI)	0.24 (s, 9H, SiMe₃), 6.32 (d, 1H, H⁴), 7.32 (d, 1H, H⁵), <i>J</i>_{4,5} 2.1	174 (<i>M</i>⁺, 28), 159 (<i>M</i>⁺ – Me, 56), 103 (10), 93 (100), 65 (10)
 (XIVb)	0.14 (s, 9H, SiMe₃), 6.01 (d, 1H, H³), 6.57 (d, 1H, H⁴); <i>J</i>_{3,4} 3.3	174 (<i>M</i>⁺, 18), 159 (<i>M</i>⁺ – Me, 100), 93 (100)

continued

Table 2 (continued)

Compound	Chemical shift, δ (ppm), J (Hz)	m/z (rel. abundance, %) ^{a,b}
 (XXII)	0.27 (s, 9H, GeMe ₃), 3.20 (s, 3H, OMe), 5.24 (d, 1H, H ⁵), 5.49 (s, 1H, OCHOMe), 6.04 (d, 1H, H ⁴), $J_{4,5}$ 6,6	264 (M^+ , 8), 249 (M^+ - Me, 3), 233 (M^+ - OMe, 12), 145 (33), 119 (100), 87 (24), 82 (54), 69 (21)
 (XXIII)	0.10 (s, 9H, SiMe ₃), 3.16 (s, 3H, OMe), 5.31 (d, 1H, H ⁵), 5.47 (s, 1H, OCHOMe), 6.04 (d, 1H, H ⁴), $J_{4,5}$ 6,6	218 (M^+ , 4), 203 (M^+ - Me, 3), 187 (M^+ - OMe, 13), 183 (M^+ - Cl, 14), 93 (19), 89 (31), 73 (100), 66 (12)
 (XXIV)	0.92 (s, 9H, CMe ₃), 5.84 (1H, H ⁴), 6.45 (1H, H ⁵) and 8.16 (1H, H ⁶); ABX system, $J_{4,5}$ 11.7, $J_{5,6}$ 10.7, $J_{4,6}$ 0.6	171 (M^+ - Cl, 16), 149 (M^+ - CMe ₃ , 22), 57 (100), 41 (30)

^a The peaks of characteristic ions and peaks with intensity $\geq 10\%$ are indicated. ^b The peaks of halogen- and germanium-containing ions are indicated for the isotopes ³⁵Cl, ⁷⁹Br and ⁷⁴Ge.

dimethylchlorosilane (0.96 g, 0.01 mol) in 5 ml of absolute ether was added dropwise. The reaction mixture was allowed to stand overnight at room temperature. Lithium chloride was filtered off, the solvent was removed by distillation and the residue was fractionated in vacuum to give 0.75 g (31%) of IV, b.p. 58–60 °C/2 mmHg, $n_D^{20} = 1.4697$; the ^1H NMR and mass spectral data for IV are given in Table 2.

Reaction of trimethyl(5-dimethylsilyl-2-furyl)germane (IV) with N-allylmorpholine

Allylmorpholine (0.4 g, 0.003 mol) and one drop of 0.1 M chloroplatinic acid solution in THF were added to compound IV (0.7 g, 0.003 mol). The mixture was heated on a water bath for 1 h. Fractionation in vacuum yielded 0.9 g (82%) of 5-trimethylgermyl-2-((dimethyl)[3-(morpholino)propyl]silyl)furan (V), b.p. 182–184 °C/1 mmHg; for ^1H NMR spectral data, see Table 2.

Alkylation of germane Ia and silane VI (general procedure)

0.5 g (2.3 mmol in terms of the SO_3H groups) of Amberlyst 15 (exchange capacity 4.6 mg-equiv./g, moisture content < 3%) was added to a solution of t-butanol (0.152 g, 2 mmol) in 1 ml of Ia or VI and stirred at room temperature. The reaction course was monitored by GLC analysis. The results are summarized in Table 1.

Triethyl(5-trifluoroacetyl-2-furyl)germane (IX)

Trifluoroacetic acid anhydride (6.0 g, 0.03 mol) was added to 2-furylgermane Ib (5.6 g, 0.025 mol), heated to 55 °C and kept at this temperature for 1 h. The mixture was cooled, supplemented with 3 ml of distilled water, stirred for 10 min and titrated with 10% KOH to pH 7. After washing with water, it was dried with anhydrous magnesium sulphate. The solvent was removed by distillation and the residue was fractionated in vacuum. A fraction boiling at 84–85 °C/1 mmHg was collected giving 5.1 g (64%) of compound IX; $n_D^{20} = 1.4670$; ^1H NMR spectral data are presented in Table 2.

Triethyl(5-nitro-2-furyl)germane (X)

A solution of nitronium tetrafluoroborate (133 mg, 1 mmol) in 40 ml of anhydrous acetonitrile was added dropwise to a germane Ib solution (228 mg, 1 mmol) cooled to –40 °C for 0.5 h. The temperature of the solution must not rise above –35 °C. The reaction mixture was then stirred for 1 h at room temperature. According to GLC data, the dark brown solution contained 10% of compound X. The mass spectral data obtained by GLC/MS analysis of the reaction mixture and the ^1H NMR spectral data of X after its preparative isolation are presented in Table 2.

Trimethyl(5-nitro-2-furyl)silane (XI)

A solution of nitronium tetrafluoroborate (1.33 g, 10 mmol) in 30 ml of acetonitrile was added dropwise for 1 h with stirring to a solution of silane VI (1.4 g, 10 mmol) in 20 ml of anhydrous acetonitrile cooled to –40 °C (the temperature must not rise above –35 °C) and the mixture was stirred for another hour to room temperature. The resultant dark-brown solution contained 3% of compound XI and 10% of 2-nitrofurane (GLC data). Silane XI was isolated from the mixture by preparative GLC. The ^1H NMR and mass spectral data of XI are given in Table 2.

Triethyl(3-bromo-2-furyl)germane (XIII)

N-Bromosuccinimide (1.78 g, 0.01 mol) and a few crystals of benzoyl peroxide were added to a solution of germane Ib (2.2 g, 0.01 mol) in 10 ml of carbon tetrachloride and the mixture was boiled for 1 h. The succinimide was filtered off, the solvent was removed by distillation and the residue was fractionated in vacuum. A fraction boiling at 130 °C/2 mmHg was collected giving 1.3 g (43%) of compound XIII; $n_D^{20} = 1.4810$. The ^1H NMR and mass spectral data of XIII are presented in Table 2.

Bromination of triethyl(2-furyl)germane (Ib) with dioxane dibromide

Dioxane dibromide (0.62 g, 2.5 mmol) in 12 ml of dioxane was added to a solution of germane Ib (0.57 g, 2.5 mmol) in 12 ml of dioxane cooled to 0 °C (the temperature must not rise above 0 °C) and the mixture was stirred for another 10 min, allowing the temperature to reach 10 °C. According to GLC/MS data, the resultant dark brown solution contained 2-bromofuran and triethylbromogermane. No products of germane Ib bromination could be detected.

Reaction of germane Ib and silane VI with chloramine T in a two-phase catalytic system

2 ml of a saturated aqueous solution of chloramine T and 5 mg (0.02 mmol) of sodium picrate were added to a solution of germane Ib (0.2 mmol) in chloroform (0.6 ml) in a 5 cm³ Pierce reaction vial. The reaction mixture was stirred for 2 h at 80 °C, cooled and the organic layer was removed. According to GLC/MS data, the reaction mixture contained two triethyl(monochlorofuryl)germanes and triethyl(dichlorofuryl)germane. A mixture of the two monochloro derivatives and the individual dichlorofurylgermane were isolated by preparative GLC. According to ^1H NMR spectroscopic evidence, the reaction yields triethyl(3-chloro-2-furyl)germane (XIV, 35%), triethyl(5-chloro-2-furyl)germane (XVa, 1%) and triethyl(3,5-dichloro-2-furyl)germane (XVI, 4%).

The chlorination of furylsilane Ia was carried out similarly, but the reaction was conducted at room temperature. After stirring the reaction mixture for 24 h, it contained 7% of two products (100% selectivity) which, according to GLC/MS analysis, were trimethyl(monochlorofuryl)silanes. The ^1H NMR spectra of the mixture isolated by preparative GLC are indicative of trimethyl(3-chloro-2-furyl)silane (XIVb) and trimethyl(5-chloro-2-furyl)silane (XVb) present in the ratio 4/1. The ^1H NMR and mass spectral data for the chlorination products are given in Table 2.

Reactions of furylgermane (Ia), furylsilane (VI) and alkylfuran (VIII) with dichlorocarbene under phase-transfer conditions (general procedure)

Methanol (2 g) and triethylbenzylammonium chloride (0.23 g, 1 mmol) were added to the starting compound (0.01 mmol) dissolved in ethanol-free chloroform. Finely ground NaOH was gradually added to the resulting mixture to prevent its heating above 35–40 °C. After the addition of alkali, the reaction mixture was stirred for 24 h at room temperature and the reaction course was monitored by GLC. In the case of germane Ia, the yield of 6-trimethylgermyl-3-chloro-2-methoxy-2*H*-pyran (XXII) amounted to 28%, while 6-trimethylsilyl-3-chloro-2-methoxy-2*H*-pyran (XXIII) was formed from silane VI in 36% yield.

The reaction of 2-(*t*-butyl)furan with dichlorocarbene was similarly conducted, except for the addition of methanol. The yield of 2-(*t*-butyl)-2,3-dichloro-2*H*-pyran (XXIV) amounted to 16% (GLC data). The ^1H NMR and mass spectral data for compounds XXII–XXIV are summarized in Table 2.

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