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Reaction of Tetrachlorogermane with Thienyl- and Phenylchlorosilanes in Presence of Aluminum Chloride. Synthesis of Thienylchlorogermanes

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Abstract—Reaction of tetrachlorogermane with 2-thienylchlorosilane and methyl(2-thienyl)dichlorosilane in presence of $AlCl_3$ is studied. It was shown that in the reaction with 2-thienyltrichlorosilane 2-thienyltrichlorogermane mainly formed, while in the reactions with methyl(2-thienyl)dichlorosiulane aromatic germanium-containing compounds like 2-thienyltrichlorogermane and di(2-thienyl)dichlorogermane were obtained. Quantum-chemical calculations showed that the reaction of chlorine atoms exchange in $GeCl_4$ with aromatic moiety formed from arylchlorosilanes in the presence of $AlCl_3$ proceeds through a four-membered activated complex.

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One of the most simple and available methods of preparation of arylchlorogermanes is the liquid phase reaction of $GeCl_4$ with arylchlorosilanes in the presence of aluminum chloride. In this way various phenylchlorogermanes like $C_6H_5GeCl_3$, $ClC_6H_4GeCl_3$, $(C_6H_5)_2GeCl_2$, etc. are formed [1–6]. Research performed resulted in establishing some rules of the synthesis. As shown in [2] the highest yields of phenyltrichlorogermanes were obtained while using methylphenyldichlorosilane and not phenyltrichlorosilane. Note that in reactions with $MePhSiCl_2$ no organogermanium compounds with methyl groups were found. It was shown [3–6] that the concentration of $AlCl_3$ plays an important role in the formation of reaction products. At the concentration of $AlCl_3$ of 3–5% the formation of $PhGeCl_3$, Ph_2GeCl_2 and Ph_3GeCl takes place, while at the increase in its concentration to 30–40% phenyltrichlorogermane becomes the main product.

No data concerning the synthesis of another arylchlorogermanes in this way has been reported up till now. In the present study we made an attempt to use this method for the preparation of various thienylchlorogermanes exhibiting biological activity. Nowadays the information on the mechanism of the reaction of tetrachlorogermane with arylchlorosilanes in the presence of $AlCl_3$ is scarce. Therefore we also carried out quantum-chemical calculations of the reactions taking place in this process.

In this work 2-thienyltrichlorosilane **I** and di(2-thienyl)dichlorosilane **II** were used as starting substances. First of all we have studied the reaction of tetrachlorogermane with compound **I**. 2-Thienyltrichlorogermane **III** was the main reaction product.

$$\underset{\textbf{I}}{ThSiCl_3} + GeCl_4 \xrightarrow{AlCl_3} \underset{\textbf{III}}{ThGeCl_3} + SiCl_4, \qquad (1)$$

Th = 2-thienyl.

Compound **III** formed in 25–32% (Table 1). At the increase in $AlCl_3$ concentration the yield of 2-thienyltrichlorogermane decreased evidently first of all because of its decomposition. This suggestion is confirmed by the fact that the nearest analog of compound

Table 1. Reaction conditions and yields of the products in the reaction of $GeCl_4$ with 2-thienyltrichlorosilane **I** in the presence of $AlCl_3$[a]

$AlCl_3$ amount, mol %	Reaction time, h	Yield of compound **III**, %[b]	Conversion of starting compound **I**, %
10	8	32	68
20	6	30	74
30	4	28	95
40	4	25	100

[a] Reaction temperature 120°C, molar ratio of reagent **I** to $GeCl_4$ 1 : 1. [b] With respect to starting $GeCl_4$.

III, phenyltrichlorogermane, decomposes noticeably in the presence of high concentrations of $AlCl_3$. Hence, while heating $PhGeCl_3$ for 4 h at 120°C in the presence of 5 and 20 mol % of $AlCl_3$ its decomposition reached 0.4 and 13.2% respectively [3].

The reaction of $GeCl_4$ with another thienyl compound, methyl(2-thienyl)dichlorosilane **II**, was studied more thoroughly because the yields of organogermanium compounds in this case were higher those mentioned above. In the reaction of compound **II** with tetrachlorogermane two organogermanium compounds, 2-thienyltrichlorogermane **III** and di(2-thienyl)dichlorogermane **IV** are formed. It is evident that monosubstituted compound **III** is formed according to the reaction (2) at the exchange of one chlorine atom in tetrachlorogermane with 2-thienyl moiety while compound **IV** is the result of substitution of two chlorine atoms with 2-thienyl moieties.

$$\underset{\textbf{II}}{\mathrm{MeThSiCl_2}} + \mathrm{GeCl_4} \xrightarrow{\mathrm{AlCl_3}} \underset{\textbf{III}}{\mathrm{ThGeCl_3}} + \mathrm{MeSiCl_3}, \tag{2}$$

$$\textbf{II} + \textbf{III} \xrightarrow{\mathrm{AlCl_3}} \underset{\textbf{IV}}{\mathrm{Th_2GeCl_2}} + \mathrm{MeSiCl_3}, \tag{3}$$

Th = 2-thienyl.

It may be suggested that the exchange of the second chlorine atom takes place in the obtained monosubstituted compound **III**. The direct experiment of the reaction between compounds **II** and **III** confirmed the possibility of such reaction. Hence, in the presence of 10% of $AlCl_3$ at 110–120°C compound **IV** is formed in 40% yield according to reaction (3) in the course of 4 h.

Note that in the reactions (2) and (3) the exchange of chlorine atom in tetrachlorogermane and the compound **III** occurs only with the thienyl moiety. No exchange of methyl group with chlorine either in $GeCl_4$ or in the compound **III** was observed.

In Table 2 yields of compounds **III** and **IV** at varying reaction temperature from 80 to 120°C, the reaction time from 4 to 10 h, and aluminum chloride concentration from 5 to 30 mol % are presented.

Yields of compound **III** in reaction (2) are significantly higher than in reaction (1). They vary in the range of 38–62%. Temperature within the studied limits slightly affects the yield of compound **III**. Its yield most strongly depends on the concentration of aluminum chloride. At the $AlCl_3$ concentration 5 mol % yield of compound **III** is 38–41%, and at the increase in $AlCl_3$ content to 30 mol % the yield of the target substance reaches 56–62% (see Table 2).

The yield of compound **IV** also significantly depends on the concentration of $AlCl_3$, and not on the reaction temperature. Maximum yield (39–44%) of this substance was obtained in the presence of 5 mol %, and the lowest one (4–6%) is observed in the presence of 30 mol % of $AlCl_3$ (Table 2).

Table 2. Reaction conditions and yields of the products in the reaction of $GeCl_4$ with methyl(2-thienyl)dichlorosilane **II** in the presence of $AlCl_3$

$AlCl_3$ amount, mol %	T, °C	Reaction time, h	Yield, %[b]	
			III	**IV**
5	80	4	38	44
5	80	10	41	39
5	120	4	40	34
10	80	4	40	29
10	80	10	38	30
10	120	4	42	27
20	80	4	54	14
20	100	4	49	8
20	120	4	45	10
30	80	4	62	6
30	100	4	57	4
30	120	4	56	4

[a] Molar ratio of reagent **II** and $GeCl_4$ 1.5 : 1. [b] With respect to starting $GeCl_4$.

Comparison of experimental data presented in Tables 1, 2 shows that for preparative needs compound **III** must be obtained by the reaction of tetrachlorogermane with methyl(2-thienyl)dichlorosilane and not with (2-thienyl)trichlorosilane.

The availability of compound **III** permitted the preparation of organogermanium compound with two different aryl substituents according to the following reaction.

$$\mathrm{ThGeCl_3 + PhSiCl_3 \rightarrow ThPhGeCl_2 + SiCl_4.}$$

By this procedure (2-thienyl)phenyldichlorogermane was obtained in 40% yield. Detailed description of this synthesis is given in Experimental.

Note that the formation of phenylchlorogermanes proceeds according to the same type of reactions (1)–(3) [1–6].

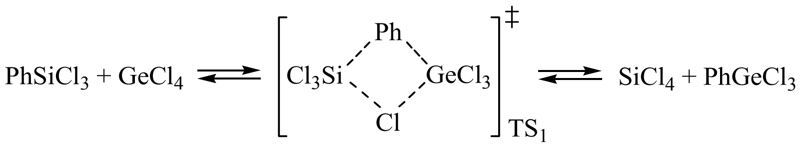
$$\mathrm{PhSiCl_3 + GeCl_4 \xrightarrow{AlCl_3} PhGeCl_3 + SiCl_4,} \qquad (4)$$

$$\mathrm{MePhSiCl_2 + GeCl_4 \xrightarrow{AlCl_3} PhGeCl_3 + Ph_2GeCl_2 + MeSiCl_3.} \qquad (5)$$

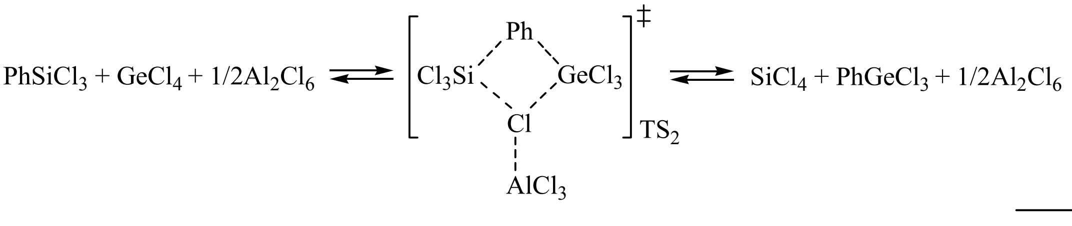
There is much in common between the syntheses of thienyl- and phenylchlorogermanes proceeding according to reactions (1)–(5). For example, the exchange between chlorine in tetrachlorogermane and organic moiety, forming from alkylarylchlorosilanes is observed only for aromatic substituents (phenyl or thienyl) but not the alkyl (methyl) ones.

For better understanding of mechanism of tetrachlorogermane reaction with arylchlorosilanes in the presence of $AlCl_3$ we have carried out quantum chemical calculations for compounds with phenyl substituents which are easier to calculate. By density functional theory [8] using the hybrid M062X *meta*-functional [9] and split valence basis set 6-31G(d,p) thermodynamic parameters of reaction (4) of substituent exchange between phenyltrichlorosilane and tetrachlorogermane were calculated. It turned out that this reaction was exothermic with the reaction enthalpy equal to –8.0 kcal/mol and Gibbs energy –7.3 kcal/mol.

For evaluation of potential barrier of reaction (4) and the effect of catalyst on its value we have found transition states of this process without the participation of aluminum chloride [reaction (6)] as well as with its participation in the formation of transition state [reaction (7)]. Non-catalytic process has the potential barrier $\Delta E^{\#}$ = 39.5 kcal/mol while coordination with aluminum chloride leads to decrease in this barrier to $\Delta E^{\#}$ = 34.8 kcal/mol.



(6)

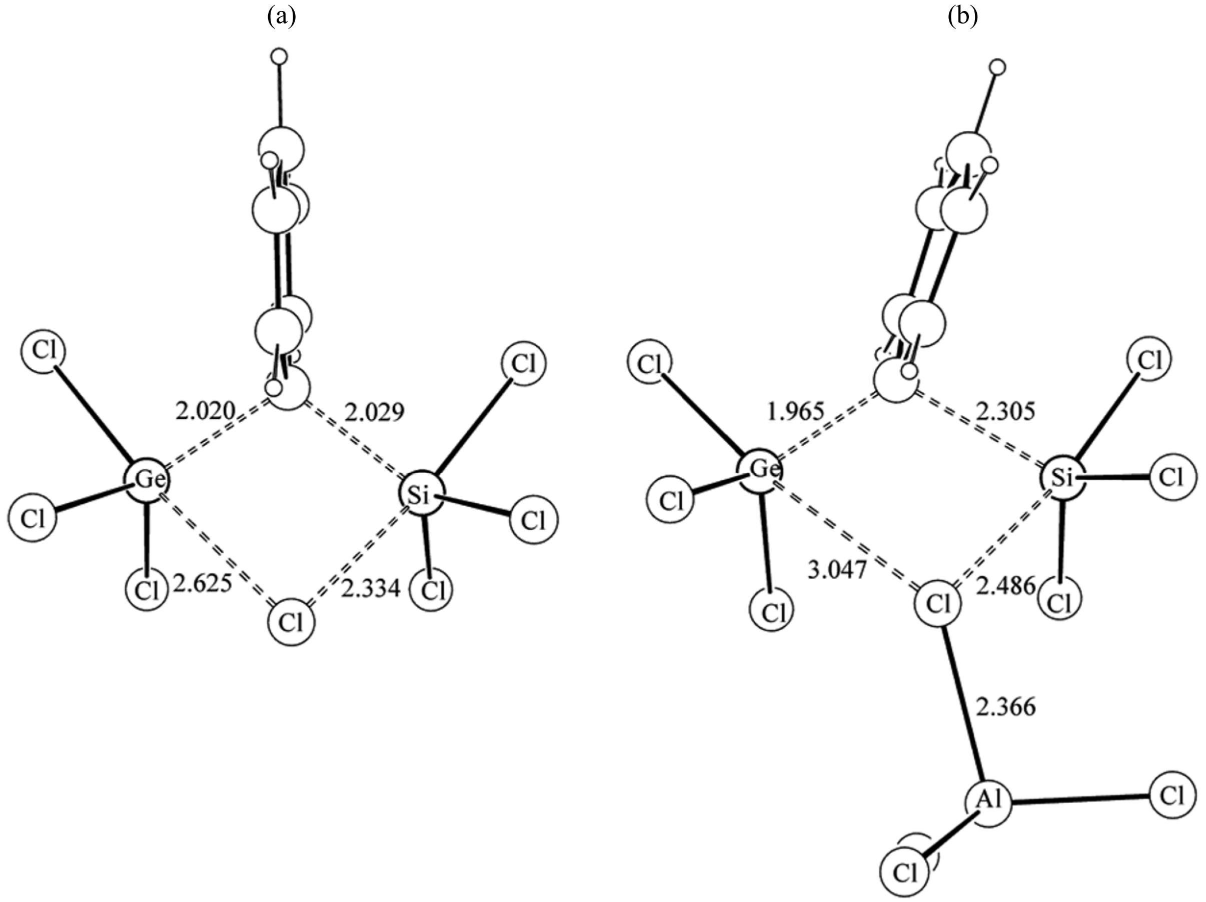


(7)

Transition states (see the figure) have four-membered structure and possess one imaginary frequency in the vibration spectrum corresponding to the motion of atoms along the reaction coordinate. In the transition states interatomic distances are shown in Å.

Note that reaction (6) without the catalyst practically does not go to completion. It evidently finishes on the stage of the formation of activated complex TS_1 which then decomposes to starting substances. But reaction (6) is useful for considering specific features of formation of activated complex TS_2 in the presence of aluminum chloride.

From the comparison of the transition states TS_1 and TS_2 if follows that coordination with $AlCl_3$ leads to the increase in the interatomic distance from 2.625 to 3.047 Å between the migrating chlorine atom and

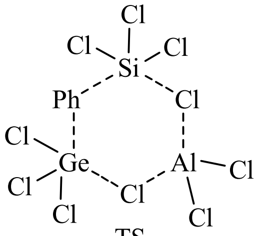


Molecular structure of the transition states of reaction (4) without (a) and with the catalyst(b) (interatomic distances are given in Å).

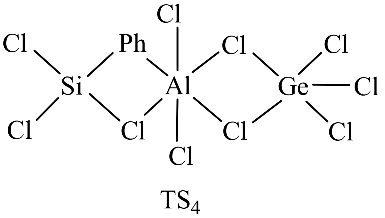
the germanium atom. The bond length between the phenyl group and the silicon atom increases from 2.029 to 2.305 Å while the bond between the phenyl group and germanium atom decreases from 2.020 to 1.965 Å. It evidently creates good conditions for migration of phenyl group from silicon to germanium, and of chlorine atom from germanium to silicon.

The correspondence of transition states to the reaction of phenyl substituent transfer is confirmed by the calculation of intrinsic reaction coordinate of the (IRC calculations).

Six-membered activated complex TS_3 that we suggested before quantum-chemical studies and fairly intricate activated complex TS_4 assumed in [5, 6] for reactions catalyzed with $AlCl_3$ were not localized within the frames of chosen M062X/6-31G(d,p) approximation. In particular, TS_3 state during the optimization transforms to TS_2.



TS_3



TS_4

Hence, proceeding of the exchange reaction (4) through the formation of four-membered transition complex TS_2 is the most probable.

EXPERIMENTAL

Starting substances and reaction products were analyzed by GLC on an LKhM-80 chromatograph equipped with a katharometer, helium carrier gas, 30 mL/min. Analysis was carried out on a 0.3×200 cm stainless steel column filled with Chromaton N-AW-

DMCS solid carrier with the particle size 0.25–0.31 mm, stationary phase SE-30 silicon elastomer (5% mass), ramp from 30 to 250°C at a rate 12°C/min.

^{1}H NMR spectra were registered on a Bruker AM-360 (360 MHz) Fourier spectrometer. Liquid substances were analyzed as 15–30% solutions in $CDCl_3$. Chemical shifts are measured with respect to TMS.

Reaction of 2-thienyltrichlorosilane I with tetrachlorogermane in the presence of $AlCl_3$. The mixture of 19.6 g of 2-thienyltrichlorosilane, 19.3 g of germanium tetrachloride, and 2.67 g of $AlCl_3$ was stirred for 8 h at 120°C and then cooled. The mixture obtained was treated with 3.10 g of $POCl_3$, and the obtained complex was filtered off. The filtrate was distilled in a vacuum to give 7.55 g of 2-thienyltrichlorogermane **III**, bp 73°C (3–4 mm Hg), n_D^{20} 1.5650. ^{1}H NMR spectrum, δ, ppm: 7.60 d (H^5, $^3J_{HH}$ 4.7 Hz), 7.47 d (H^3, $^3J_{HH}$ 3.2 Hz), 7.11 d.d (H^4, $^3J_{HH}$ 4.7 Hz, $^3J_{HH}$ 3.2 Hz). Yield of compound **III** basing on starting tetrachlorogermane 32%.

Reaction of methyl(2-thienyl)dichlorosilane II with tetrachlorogermane in the presence of $AlCl_3$. The mixture of 23.6 g of methyl(2-thienyl)dichlorosilane, 17.2 g of $GeCl_4$, and 2.91 g of $AlCl_3$ was stirred at 80°C for 4 h and then cooled. Resulting mixture was treated with 3.37 g of $POCl_3$ and filtered. The filtrate was distilled in a vacuum to give 8.39 g (40%) of 2-thienyltrichlorogermane **III** and 7.20 g (29%) of di(2-thienyl)dichlorogermane of bp 165–167°C (1–2 mm Hg), n_D^{20} 1.6182. ^{1}H NMR spectrum, δ, ppm: 7.50 d (H^5, $^3J_{HH}$ 4.6 Hz); 7.43 d (H^3, $^3J_{HH}$ 3.4 Hz); 7.05 d.d (H^4, $^3J_{HH}$ 4.6 Hz, 3.4 Hz).

Reaction of methylphenyldichlorosilane with 2-thienyltrichlorogermane in the presence of $AlCl_3$. The mixture of 17.2 g of methylphenyldichlorosilane, 23.6 g of 2-thienyltrichlorogermane, and 2.67 g of $AlCl_3$ was stirred at 60°C for 6 h and then cooled. The mixture obtained was treated with 3.07 g of $POCl_3$ and filtered. The filtrate was distilled in a vacuum to give 8.48 g of (2-thienyl)phenyldichlorogermane **V**, bp 152°C (2–3 mm Hg), n_D^{20} 1.6075. ^{1}H NMR spectrum, δ, ppm: 7.44, 7.36, 7.00.

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