

Reaction of Chloro(ethyl)silanes with Chloro(phenyl)silanes in the Presence of Aluminum Chloride. Synthesis of Chloro(ethyl)(phenyl)silanes

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Abstract—Substituent exchange at the silicon atom between chloro(phenyl)silanes (PhSiCl₃, MePhSiCl₂, Ph₂SiCl₂) and chloro(ethyl)silanes (EtSiCl₃, Et₂SiCl₂, Et₃SiCl, Et₄Si) in the presence of aluminum chloride has been studied. The examined compounds, except for PhSiCl₃ and Et₄Si, react fairly readily to give chloro(ethyl)-(phenyl)silanes in up to 48–52% yield. A probable mechanism has been proposed.

Keywords: organosilanes, aluminum chloride, disproportionation

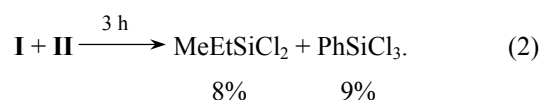
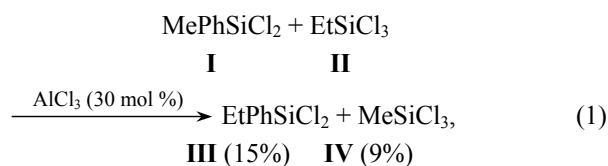
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In recent years, substituent exchange reactions at the silicon or germanium atom have been used to obtain chloro(organyl)silanes and -germanes. These reactions are usually carried out in the presence of aluminum chloride [1, 2]. However, the exchange process has been poorly studied. In particular, it remains unclear why in some cases substituent exchange occurs while in other cases does not or is difficult.

In the present work we studied substituent exchange reactions between chloro(ethyl)silanes and chloro(phenyl)silanes with a view to obtaining chloro(ethyl)(phenyl)silanes which attract interest as monomers. As substrates we used EtSiCl₃, Et₂SiCl₂, Et₃SiCl, Et₄Si, PhSiCl₃, MePhSiCl₂, and Ph₂SiCl₂.

The reactions of chloro(ethyl)silanes Et_nSiCl_{4–n} (*n* = 1–3) with trichloro(phenyl)silane were carried out at 110–130°C in the presence of 10–30 mol % of AlCl₃. No exchange of ethyl and phenyl groups was observed at 110°C in the presence of 10 mol % of AlCl₃. Raising the amount of the catalyst to 30 mol % and temperature to 130°C resulted in the formation of a small amount of EtPhSiCl₂ (2 wt %).

Dichloro(methyl(phenyl)silane reacted with EtSiCl₃, Et₂SiCl₂, and Et₃SiCl, but the results depended on the number of ethyl groups on the silicon atom. Substituent exchange in the reaction of MePhSiCl₂ (**I**) with EtSiCl₃ (**II**) followed two paths: (1) Ph/Cl and (2) Ph/Et.



Exchange of methyl and ethyl groups between compounds **I** and **II** is hardly probable. By special experiments we showed that reactions of chloro(ethyl)silanes (EtSiCl₃, Et₂SiCl₂) with chloro(methyl)silanes (MeSiCl₃, Me₂SiCl₂) do not afford substituent exchange products under the given conditions, but small amounts of Me₂SiCl₂ (6%) and Ph₂SiCl₂ (6%) are formed as a result of disproportionation [3] of MePhSiCl₂ in the presence of AlCl₃ [reaction (3)].

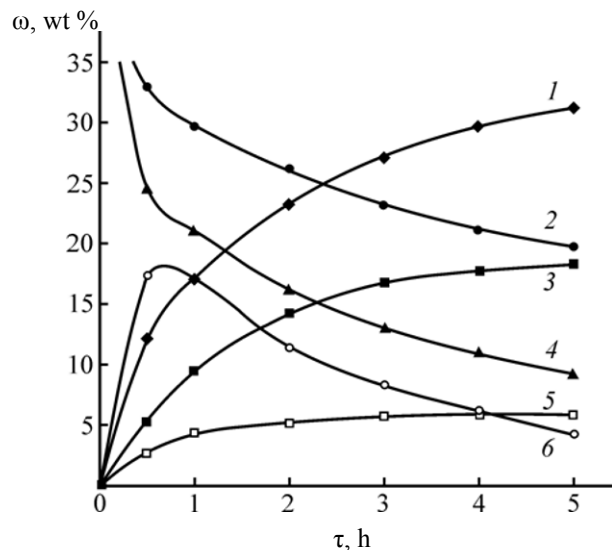


Fig. 1. Kinetic curves for the consumption of the initial reactants and accumulation of products in the reaction of MePhSiCl₂ with Et₂SiCl₂ in the presence of AlCl₃ (reactant ratio 1 : 1, 110°C, AlCl₃ 30 mol %): (1) EtPhSiCl₂, (2) Et₂SiCl₂, (3) MeEtSiCl₂, (4) MePhSiCl₂, (5) Me₂SiCl₂, (6) Ph₂SiCl₂.



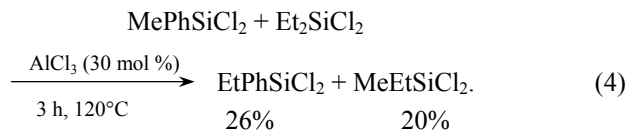
In the reactions of dichloro(methyl)(phenyl)silane with dichloro(diethyl)silane and chloro(triethyl)silane, the main pathway was phenyl/ethyl group exchange. Thus, MePhSiCl₂ reacted with Et₂SiCl₂ yielding

Table 1. Conditions and yields of the reaction of dichloro(methyl)(phenyl)silane (I) with dichloro(diethyl)silane (V) at 120°C

Molar ratio V : I	Amount of AlCl ₃ , mol %	Reaction time, h	Yield, ^a %	
			EtPhSiCl ₂	MeEtSiCl ₂
1	10	3	7	6
1	20	3	33	28
1	30	3	43	40
1	30	5	48	45
1	40	3	39	36
1.5	30	3	52	44
1.5	30	6	33	30
2	30	3	25	23
2	30	6	15	16

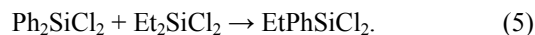
^a Calculated on the initial MePhSiCl₂.

EtPhSiCl₂ and MeEtSiCl₂ as the major products [reaction (4)].



In addition, traces of MeSiCl₃, EtSiCl₃, PhSiCl₃, Me₂SiCl₂ (6%), and Ph₂SiCl₂ (8%) were detected.

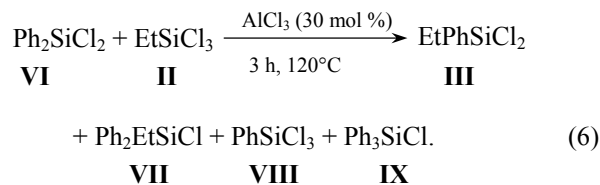
Figure 1 shows kinetic curves for the consumption of initial reactants and accumulation of major products I and V (AlCl₃, 110°C). As the reaction started, rapid increase in the concentration of three major products, EtPhSiCl₂ (curve 1), MeEtSiCl₂ (curve 3), and Ph₂SiCl₂ (curve 6) was observed due to predominance of reactions (3) and (4). However, the concentrations of EtPhSiCl₂ and MeEtSiCl₂ continuously increase until the reaction completion, whereas the concentration of dichloro(diphenyl)silane turns to decrease after 30–40 min due to reaction (5).



The concentration of dichloro(dimethyl)silane (Fig. 1, curve 5) formed via reaction (3) also rapidly increases only in the initial period, and its growth considerably slows down as the concentration of dichloro(methyl)(phenyl)silane (Fig. 1, curve 4) decreases.

The reactions conditions and yields of the major products are given in Table 1. The optimum conditions for the formation of MeEtSiCl₂ and PhEtSiCl₂ are Et₂SiCl₂-to-MePhSiCl₂ ratio 1–1.5, amount of AlCl₃ 30 mol %, reaction time ~3 h, and temperature 110–130°C.

The reactivity of Ph₂SiCl₂ toward chloro(ethyl)silanes Et_nSiCl_{4-n} (n = 1–3) was also studied. In the reaction of Ph₂SiCl₂ with EtSiCl₃ (II) the following four products were detected: dichloro(ethyl)(phenyl)silane (III), chloro(ethyl)(diphenyl)silane (VII), trichloro(phenyl)silane (VIII), and chloro(triphenyl)silane (IX).



The major products were compounds III and VIII (19 and 45 wt %, respectively; Table 2). It should be

Table 2. Product composition in the reaction of dichloro(diphenyl)silane with chloro(ethyl)silanes in the presence of aluminum chloride^a

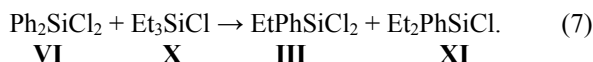
Chloro(ethyl)silane	Product fraction in the distillate, wt %					total
	PhEtSiCl ₂	Ph ₂ EtSiCl	PhSiCl ₃	Ph ₃ SiCl	PhEt ₂ SiCl	
EtSiCl ₃	19	5	45	4	—	73
Et ₂ SiCl ₂	25	4	28	7	—	64
Et ₃ SiCl ^b	29	14	3	—	14	60
Et ₄ Si	No reaction (8)					0

^a Equimolar amounts of the reactants, 30 mol % of AlCl₃, 120°C, reaction time 3 h.^b The distillate also contained 22 wt % of Et₂SiCl₂.

noted that these compounds can be formed as a result of both Ph/Cl and Ph/Et exchange.

Dichloro(diphenyl)silane reacted with Et₂SiCl₂ (**V**) to give the same products as in reaction (6) (Table 2). In the reaction with Et₃SiCl (**X**), apart from products **III**, **VII**, and **VIII**, the formation of chloro(diethyl)-(phenyl)silane (**XI**) and dichloro(diethyl)silane (**V**) was observed (Table 2).

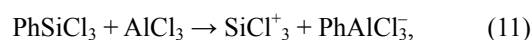
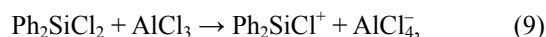
Compounds **III** and **XI** are formed via intermolecular exchange of phenyl and ethyl groups between the initial reactants [reaction (7)].



The product mixture also contained a considerable amount of dichloro(diethyl)silane (22 wt %) resulting from the reaction of initial Et₃SiCl with AlCl₃. As shown by special experiments, up to 20% of Et₂SiCl₂ is formed in the presence of 30 mol % of AlCl₃ in 10 h at 130–140°C. The conversion of the other chloro(ethyl)silanes (EtSiCl₃, Et₂SiCl₂) under analogous conditions was insignificant. Tetraethylsilane Et₄Si failed to react with Ph₂SiCl₂, and no substituent exchange was detected.

The composition of products of the AlCl₃-catalyzed reactions of Ph₂SiCl₂ with chloro(ethyl)silanes is presented in Table 2. Chloro(ethyl)silanes EtSiCl₃, Et₂SiCl₂, and Et₃SiCl react with dichloro(diphenyl)silane to give up to 60–70 wt % of substituent exchange products. We can conclude that the presence of at least one chlorine atom is necessary for substituent exchange, i.e., the role of Si–Cl bond is crucial in the examined transformations. As shown subsequently, MePhSiCl₂ also failed to react with Et₄Si.

The mechanism of the reaction under study and its thermodynamic parameters were analyzed by PBE1PBE/6-31+G(*d*) quantum chemical calculations [4]. The results obtained for reactions (8)–(13) are collected in Table 3. It is seen that reactions (8)–(10) are more probable than (11)–(13). Chloride ion transfer from chloro(organyl)silane molecule to aluminum chloride is characterized by ΔH and ΔG values of 87–105 kcal/mol [reactions (8)–(10); Table 3]. The ΔH and ΔG values for the transfer of organic phenyl anion Ph[–] [reactions (11)–(13); Table 3] are considerably higher (128–157 kcal/mol).

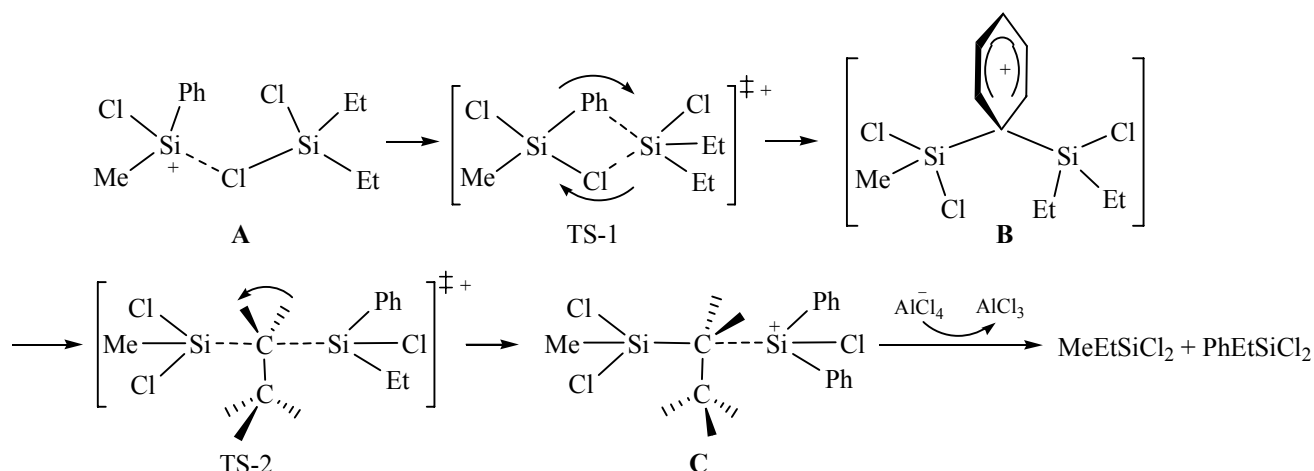


It should be noted that the chloride ion transfer from PhSiCl₃ to AlCl₃ [reaction (8)] is less energetically favorable ($\Delta H = 105.1$, $\Delta G = 105.5$ kcal/mol)

Table 3. Total energies and thermodynamic parameters of reactions (8)–(13) according to PBE1PBE/6-31+G(*d*) calculations

Reaction no.	ΔE , kcal/mol	ΔH , kcal/mol	ΔG , kcal/mol
8	105.2	105.1	105.5
9	88.4	89.1	87.2
10	95.8	95.5	94.8
11	157.4	156.7	156.5
12	127.9	127.8	124.7
13	141.0	140.2	138.2

Scheme 1.



than the transfer of Cl^- from Ph_2SiCl_2 and MePhSiCl_2 [reactions (9) and (10); ΔH and ΔG do not exceed 95 kcal/mol]. This is consistent with the experimental data according to which PhSiCl_3 is weakly reactive in substituent exchange reactions with chloro(ethyl)silanes.

The role of aluminum chloride consists of initial generation of chloro(diorganyl)silyl cations which exchange organic substituents more readily than do neutral molecules. Insofar as both reactants in (4)

possess chlorine atoms, elimination of chloride ion by the action of AlCl_3 is possible from both of them.



However, on the basis of the calculated energies of reactions (10) and (14) we presumed the formation of MePhSiCl^+ cation to be more favorable: the ΔG value for reaction (10) 94.8 kcal/mol against $\Delta G = 103.2$ kcal/mol for reaction (14) [PBE1PBE/6-31+G(d) calculations].

A probable scheme of the examined substituent exchange reactions is shown in Scheme 1 for the reaction of MePhSiCl^+ with dichloro(diethyl)silane as example.

According to the proposed scheme, attack by MePhSiCl^+ cation on neutral Et_2SiCl_2 molecule gives intermediate complex **A** where the silicon atom of the cation is coordinated to one chlorine atom of the neutral molecule. Complex **A** is then converted into intermediate **B** through transition state TS-1 whose structure is shown in Fig. 2. In the next step, transfer of the ethyl group is mediated by transition state TS-2 in which both silicon atoms are linked to the methylene carbon atom of the migrating ethyl group. Further movement along the reaction coordinate leads to intermediate **C** whose reaction with AlCl_4^- anion yields final disproportionation products.

This scheme rationalizes the fact that no substituent exchange reaction occurs with SiEt_4 . First, SiEt_4 molecule lacks chlorine atoms and is therefore incapable of forming cationic species in reaction with AlCl_3 . Second, tetraethylsilane is less prone to coordination with already generated cations with formation of

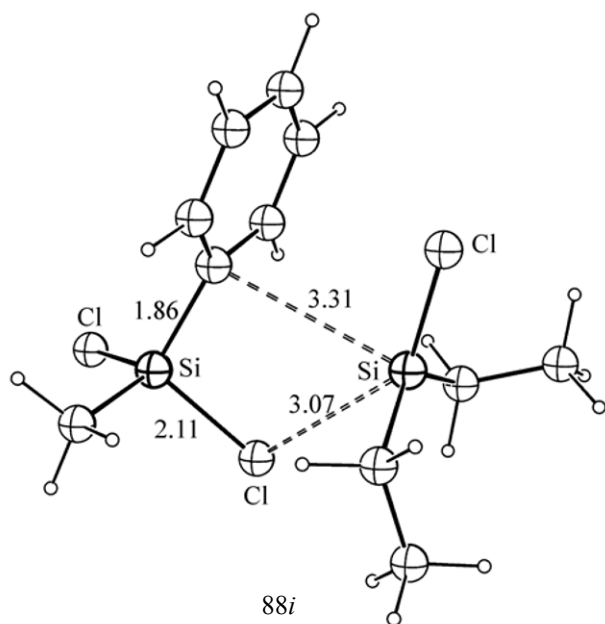


Fig. 2. Structure of transition state TS-1 in the reaction of MePhSiCl^+ with Et_2SiCl_2 according to PBE1PBE/6-31+G(d) calculations. Interatomic distances (Å) are given; imaginary frequency 88i.

complex **A** since this coordination also involves chlorine atom.

EXPERIMENTAL

The initial reactants and reaction products were analyzed by GLC on an LKhM-80 chromatograph equipped with a thermal conductivity detector (stainless steel column, 0.3×200 cm, packed with 5 wt % of SE-30 on Chromaton N-AW-DMCS, grain size 0.25–0.31 mm; carrier gas helium, flow rate 30 mL/min; oven temperature programming from 30 to 250°C at a rate of 12 deg/min).

Reaction of dichloro(methyl)(phenyl)silane with dichloro(diethyl)silane in the presence of aluminum chloride. A round-bottom flask equipped with a stirrer, thermometer, and reflux condenser was charged with 47.8 g (0.25 mol) of dichloro(methyl)(phenyl)silane, 39.2 g (0.25 mol) of dichloro(diethyl)silane, and 28.0 g (0.21 molya) of AlCl_3 . The mixture was stirred for 3 h at 120°C and cooled, 32.5 g (0.21 molya) of POCl_3 was added, and the precipitate was filtered off. The filtrate was distilled first under atmospheric pressure at 70–130°C and then under reduced pressure (10–12 mmHg) at 90–170°C. The distillate, 75.5 g, contained 4.7 g of Me_2SiCl_2 , 14.3 g of MeEtSiCl_2 , 19.5 g of Et_2SiCl_2 , 11.0 g of MePhSiCl_2 , 22.1 g of EtPhSiCl_2 , and 3.9 g of Ph_2SiCl_2 . The yields of EtPhSiCl_2 and MeEtSiCl_2 , calculated on the initial MePhSiCl_2 , were 43 and 40%, respectively.

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