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Abstract

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INTERACTION OF SILICON HYDRIDES WITH α- AND β-CHLORONAPHTHALENES AND *p*-DICHLOROBENZENE

PYROLYSIS OF ETHYLCHLOROSILANES IN THE PRESENCE OF ARYL CHLORIDES

Recently we showed ([1,2]) that the interaction of aryl chlorides with silicon hydrides in the gas phase at high temperatures according to the scheme:

$$\mathrm{RCl} + \mathrm{HSiR'}_n\mathrm{Cl}_{3-n} \rightarrow \mathrm{RR'}_n\mathrm{SiCl}_{3-n} + \mathrm{HCl} \qquad \text{(I)}$$

(where R is an aromatic radical; R′ is an alkyl or aryl radical; $n = 0, 1, 2$) is a general method for the synthesis of arylchlorosilanes.

A. D. Petrov, V. A. Ponomarenko, and G. Odabashyan used in this reaction such silicon hydrides as dichlorosilane ([3]) and methylchlorosilane ([4]), which made it possible to synthesize, along with other substances, phenyldichlorosilane and methylphenyldichlorosilane. By this method, English investigators obtained various trifluoromethylphenylchlorosilanes in good yields ([5]).

In the present investigation the reaction of high-temperature condensation of silicon hydrides with α- and β-chloronaphthalenes has been studied in detail. In addition, for the first time the possibility has been established of the formation of *p*-bis-(trichlorosilyl)benzene and its analogs according to scheme A, as well as phenyldichlorosilane from ethyldichlorosilane and chlorobenzene according to scheme B:

$$p\text{-}\mathrm{ClC_6H_4Cl} + \mathrm{HSiCl_3} \rightarrow p\text{-}\mathrm{ClC_6H_4SiCl_3} + p\text{-}\mathrm{Cl_3SiC_6H_4SiCl_3}; \qquad \text{(A)}$$

$$\mathrm{C_2H_5HSiCl_2} \rightarrow \mathrm{C_2H_4} + [\mathrm{H_2SiCl_2}] \xrightarrow{\mathrm{C_6H_5Cl}} \mathrm{C_6H_5SiCl_2H}. \qquad \text{(B)}$$

For α-chloronaphthalene, the effect of the temperature of the reaction zone on the degree of conversion of the silicon hydride and on the yields of the reaction

products was investigated. The data obtained are presented in Figs. 1 and 2 ($\tau = 30$ sec).

In the case of chloronaphthalenes, as with other aryl chlorides, alongside the main reaction leading to the formation of naphthylsilane chlorides, a parallel reaction occurs with formation of naphthalene and silicon tetrachloride (or methyltrichlorosilane):

$$C_{10}H_7Cl + HSiR'_nCl_{3-n} \rightarrow C_{10}H_8 + R'_nSiCl_{4-n}. \quad \text{(II)}$$

It should be noted that the interaction of silicon hydrides with chloronaphthalenes begins at a lower temperature than with chlorobenzene, and, as is seen from Table 1, in this case reaction I predominates over reaction II.

When β-chloronaphthalene was used in the reaction, as in the case of α-chloronaphthalene, the maximum yields of naphthylchlorosilanes were achieved at 640° ($\tau = 30$ sec, β-$C_{10}H_7Cl : R_nSiHCl_{3-n} = 2 : 1$). The yield of β-naphthyltrichlorosilane was 51%; that of β-naphthylmethyldichlorosilane, 41%.

The naphthylchlorosilanes obtained were methylated with the aid of CH_3MgBr. α-$C_{10}H_7Si(CH_3)_3$, yield 80%, b.p. 118–119°/3 mm; n_D^{20} 1.5882; d_4^{20} 0.9880.

Found, %: C 78.10; 78.13; H 8.00; 7.88; Si 13.92; 13.75.

Table 1

Starting substances: aryl chloride	Starting substances: silicon hydride	Products obtained: Ar-$SiCl_3$ or Ar-$SiCH_3Cl_2$	Yield, %	Physical properties of the chlorosilane obtained: m.p., °C	Physical properties of the chlorosilane obtained: b.p., °C/mm	Physical properties: n_D^{20}	Physical properties: d_4^{20}	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % Cl	Found, % C	Found, % H	Found, % Si	Found, % Cl
α-$C_{10}H_7Cl$	$HSiCl_3$	α-$C_{10}H_7SiCl_3$	60	54–55	126–127/1	—	—	45,98	2,67	10,82	40,73	46,07	2,63	10,80	40,82
α-$C_{10}H_7Cl$	CH_3SiHCl_2	α-$C_{10}H_7SiCH_3Cl_2$	52	—	128–129/1	1,6074	1,1428	54,77	4,24	11,63	29,46	54,47	4,28	11,82	29,37

Starting sub-stances: aryl chloride	Starting sub-stances: silicon hydride	Products obtained: Ar-$SiCl_3$ or CH_3-$SiCl_3$	Yield, %	Physical properties of the chlorosilane obtained: m.p., °C	Physical properties of the chlorosilane obtained: b.p., °C/mm	n_D^{20}	d_4^{20}	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % Cl	Found, % C	Found, % H	Found, % Si	Found, % Cl
β-$C_{10}H_7Cl$	$SiCl_4$	β-$C_{10}H_7SiCl_3$	51	51–52	183–185/1	—	—	45,98	2,67	10,82	40,73	46,12	2,63	10,98	39,28	39,48
β-$C_{10}H_7Cl$	CH_3SiHCl_2	β-$C_{10}H_7SiCl_2CH_3$	41	37–38	126–128/1	—	—	54,77	4,24	11,63	29,46	—	—	—	29,34	29,18
p-ClC_6H_4Cl + C_6H_6	$SiCl_4$*	p-$ClC_6H_4SiCl_3$	29	—	102–104/4	1,5408	1,4258	30,27	1,62	11,38	55,83	30,27	1,38	11,25	55,00	55,00
p-ClC_6H_4Cl + C_6H_6	$SiCl_4$*	p-$(Cl_3Si)_2C_6H_4$	4	76–77	114–115/2	—	—	—	—	—	61,74	—	—	—	61,38	61,52
p-ClC_6H_4Cl + C_6H_6	$SiCl_4$**	$C_6H_5SiCl_3$		—	—	—	—	—	—	—	—	—	—	—	—	—
p-ClC_6H_4Cl + C_6H_6	$SiCl_4$**	p-$ClC_6H_4SiCl_3$	30	—	101–103/4	1,5400	1,4250	—	—	—	—	—	—	—	—	—
p-ClC_6H_4Cl + C_6H_6	$SiCl_4$**	p-$(Cl_3Si)_2C_6H_4$	15	76–77	115–117/2	—	—	—	—	—	—	—	—	—	—	—
p-ClC_6H_4Cl + C_6H_6	CH_3SiHCl_2*	p-$ClC_6H_4SiCl_2CH_3$	20	—	81–83/2	1,5345	1,2855	37,25	3,12	12,69	46,94	37,38	3,14	12,35	45,29	46,24

Starting sub-stances: aryl chloride	Starting sub-stances: silicon hydride	Products obtained: Ar-$SiCl_3$ or CH_3-$SiCl_3$	Yield, %	Physical properties of the chlorosilane obtained: m.p., °C	Physical properties of the chlorosilane obtained: b.p., °C/mm	Physical properties: n_D^{20}	Physical properties: d_4^{20}	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % Cl	Found, % C	Found, % H	Found, % Si	Found, % Cl
p-ClC_6H_4Cl + C_6H_6	CH_3SiHCl_2	p-$(Cl_2CH_3Si)_2C_6H_4$	5	56–57	116–117/1	–	–	–	–	–	46,71	–	–	–	46,24 46,58
p-ClC_6H_4Cl + C_6H_6	CH_3SiHCl_2	$C_6H_5SiCl_2CH_3$	15	–	–	–	–	–	–	–	–	–	–	–	–
p-ClC_6H_4Cl + C_6H_6	CH_3SiHCl_2	p-$ClC_6H_4SiCl_2CH_3$	19	–	80–83/2	1,5348	1,2861	–	–	–	–	–	–	–	–
p-ClC_6H_4Cl + C_6H_6	CH_3SiHCl_2	p-$(CH_3Cl_2Si)_2C_6H_4$	8	56–57	116–118/1	–	–	–	–	–	–	–	–	–	–

* p-ClC_6H_4Cl : R_nSiHCl_{3-n} : C_6H_6 = 1 : 1 : 1

** p-ClC_6H_4Cl : R_nSiHCl_{3-n} : C_6H_6 = 1 : 2 : 2.

β-$C_{10}H_7Si(CH_3)_3$, yield 78%; b.p. 102–103°/1 mm; n_D^{20} 1.5725; d_4^{20} 0.9698.

Found, %:	C 78.17; 78.05;	H 8.38; 8.30;	Si 13.80; 13.96
$C_{13}H_{16}Si$. Calculated, %:	C 77.92;	H 8.04;	Si 14.04

Infrared absorption spectra were obtained for the naphthyltrimethylsilanes. It was found that when α-chloronaphthalene is used, only α-naphthylchlorosilanes are formed; when β-chloronaphthalene is used, only β-naphthylchlorosilanes are formed. Thus, isomerization of the chloronaphthalenes is not observed under the reaction conditions, and their interaction with silicon hydrides proceeds only through the C–Cl bond.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The interaction of silicon hydrides with *p*-dichlorobenzene was also carried out at 640° and with a contact time of the reacting substances of 30 sec. Since

Fig. 1. Dependence of the yields of α-$C_{10}H_7SiCl_3$ (1), $SiCl_4$ (2), and the degree of conversion of $HSiCl_3$ (3) on the temperature of the reaction zone, α-$C_{10}H_7Cl : HSiCl_3 = 2 : 1$

Fig. 2. Dependence of the yields of α-$C_{10}H_7SiCl_2CH_3$ (1), CH_3SiCl_3 (2), and the degree of conversion of CH_3SiHCl_2 (3) on the temperature of the reaction zone, α-$C_{10}H_7Cl : CH_3SiHCl_2 = 2 : 1$

p-dichlorobenzene has m.p. 53°, the reactants were introduced into the reaction zone in benzene solution at the following ratios: p-$ClC_6H_4Cl : R_nSiHCl_{3-n} : C_6H_6 = 1 : 1 : 1$ and $1 : 2 : 2$. In the case of the first ratio, for the pair of reactants p-ClC_6H_4Cl and $HSiCl_3$, the yield of *p*-chlorophenyltrichlorosilane was 29% and that of *p*-bis-(trichlorosilyl)benzene 4%; in the case of the second ratio, 30 and 15%, respectively; in addition, in this case 12% phenyltrichlorosilane was formed.

For the pair of reactants p-ClC_6H_4Cl and CH_3SiHCl_2, the yield of *p*-chlorophenylmethyldichlorosilane was 20% and that of *p*-bis-(methyldichlorosilyl)benzene 5% (first ratio), and respectively 19% and 8.5% (second ratio); in addition, in the second case 15% phenylmethyldichlorosilane was obtained. The bis(chlorosilyl)benzenes obtained both from $HSiCl_3$ and from CH_3SiHCl_2 were methylated with CH_3MgBr, and the resulting bis-(trimethylsilyl)benzenes proved to be identical.

p-$(CH_3)_3SiC_6H_4Si(CH_3)_3$, yield 80%, b.p. 116°/1 mm; m.p. 92-93°; m.p. of a mixed sample with authentic *p*-bis-(trimethylsilyl)benzene 92°.

Found, %:	C 65.52; 65.40;	H 10.07; 10.00;	Si 24.68; 24.80
$C_{12}H_{22}Si_2$. Calculated, %:	C 65.05;	H 9.91;	Si 25.04

The infrared spectrum of the synthesized bis-(trimethylsilyl)benzene confirmed the structure of *p*-disubstituted benzene. Thus, under the reaction conditions, isomerization of *p*-dichlorobenzene is likewise not observed, and its interaction with silicon hydrides proceeds only through the C—Cl bonds.

The results of the experiments are presented in Table 1 (reaction-zone temperature 640°, contact time 30 sec; ratio $ArCl : R_nSiHCl_{3-n} = 2 : 1$).

Interesting results were obtained in studying the reaction of high-temperature condensation of ethyldichlorosilane with various aryl chlorides.

At temperatures above 550°, ethyldichlorosilane undergoes pyrolytic decomposition with liberation of ethylene and ethane. As intermediate particles, silyl radicals are probably formed, which enter into reaction with the aryl chloride. Along with the formation of silyl radicals directly, it is possible that an Si–H bond is formed instead of an Si–C bond. Analysis of the composition of the reaction products speaks in favor of this assumption. Thus, in the interaction of chlorobenzene and ethyldichlorosilane (ratio 2 : 1) at 560° ($\tau = 40$ sec) and 700° ($\tau = 30$ sec), alkyl- and arylchlorosilanes, presented in Table 2, were found in the reaction products.

Table 2

At 560°	Yield, %	At 700°	Yield, %	At 560°	Yield, %	At 700°	Yield, %
$C_2H_5SiHCl_2$	27	$HSiCl_3$	5	$C_6H_5SiCl_3$	12	$C_6H_5SiCl_3$	23
$C_2H_5SiCl_3$	21	$SiCl_4$	9	$C_6H_5SiC_2H_5Cl_2$	8	$C_6H_5SiC_2H_5Cl_2$	3
$C_6H_5SiHCl_2$	9	$C_2H_5SiCl_3$	15	$(C_6H_5)_2SiCl_2$	3	$(C_6H_5)_2SiCl_2$	7

A considerable amount of ethylene was found in the gaseous reaction products. At higher temperature the pyrolysis proceeds more deeply; moreover, phenyldichlorosilane, reacting with chlorobenzene, is converted completely into phenyltrichlorosilane and diphenyldichlorosilane. Even at a reaction-zone temperature of 600°, phenyldichlorosilane can no longer be detected in the reaction products.

It proved possible to carry out the reaction of chlorobenzene not only with ethyldichlorosilane, but also with ethyltrichlorosilane and diethyldichlorosilane. In the interaction of $C_2H_5SiCl_3$ and C_6H_5Cl (ratio 1 : 1, at 620°, $\tau = 30$ sec), only 20% of the initial ethyltrichlorosilane was recovered. Phenyltrichlorosilane was isolated in 29% yield. Analysis of the gaseous reaction products showed that they contained (in vol. %): ethylene 71; ethane 14.2; hydrogen 7.3; methane 4.2. In the case of the interaction of chlorobenzene with diethyldichlorosilane (ratio 1 : 1, at 550°; $\tau = 30$ sec), 5% phenyldichlorosilane, 6% phenylethyldichlorosilane, and 5% diphenyldichlorosilane were found in the reaction products.

The reaction of ethyldichlorosilane with α-chloronaphthalene was carried out at 560° and a contact time of 30 sec (α-$C_{10}H_7Cl$: $C_2H_5SiHCl_2$ = 2 : 1). Whereas under similar conditions in the reaction with chlorobenzene only 8% phenylethyldichlorosilane was obtained, the yield of α-naphthylethyldichlorosilane reached 21% (b.p. 176–177/5; n_D^{20} 1.5995; d_4^{20} 1.2224). At the same time, about 30% α-naphthyltrichlorosilane was formed.

In this work we used the procedure for carrying out the experiments and for analyzing the mixture of substances obtained that was described earlier ([2]).

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Note: Figure translations are in progress. See original paper for figures.