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Abstract

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INTERACTION AT HIGH TEMPERATURES OF TRIARYLSILANES WITH ALLYL CHLORIDE, CHLORO- AND *p*-DICHLOROBENZENES

The recently discovered reaction involving formation of a new bond, Si—C, was studied using as an example the high-temperature condensation of alkenyl chlorides and chlorobenzene with aliphatic monohydrosilanes (^{1}). It was shown that, in the condensation of vinyl chloride with $HSiCl_3$, the yields reach 60–80%; they decrease to 40–50% in the case of CH_3HSiCl_2 and fall to 0 in the case of $(C_2H_5)_3SiH$ (^{2}). Usually the reaction proceeds according to scheme (I):

$$CH_3HSiCl_2 + CH_2{=}CHCl \begin{cases} \longrightarrow CH_3(CH_2{=}CH)SiCl_2 + HCl \quad (1) \\ \longrightarrow CH_3SiCl_3 + CH_2{=}CH_2 \quad (2) \end{cases} \tag{I}$$

i.e., simultaneously with condensation there also occurs a side reduction reaction, which in the case of $(C_2H_5)_3SiH$ becomes the principal one.

The reaction with chlorobenzene also proceeds according to an analogous scheme (II):

$$HSiCl_3 + C_6H_5Cl \begin{cases} \longrightarrow C_6H_5SiCl_3 + HCl \quad (1) \\ \longrightarrow SiCl_4 + C_6H_6 \quad (2) \end{cases} \tag{II}$$

In direction 1 (condensation) this reaction proceeds to the extent of 40–50%.

On the basis of the results cited, it could be assumed that, for formation of the Si—C bond, the presence of an electronegative substituent at the silicon atom is necessary. In their electronegativity, aryl radicals occupy an intermediate position between alkyls and halogen atoms. Therefore, in the present investigation we decided to study the possibilities of high-temperature condensation, both with allyl chloride and with phenyl chlorides, of triarylsilanes. If, for example, the latter reaction were successful, the route to the synthesis of tetraarylsilanes would be considerably simplified. Until now the latter have been obtained only by schemes of organometallic synthesis, for example by the Gilman and Miller scheme (^{3}):

$$4ClC_6H_4Li + Si(OC_2H_5)_4 \rightarrow Si(C_6H_4Cl)_4 + 4C_2H_5OLi. \qquad \text{(III)}$$

As shown below, in the experimental part, our expectations were to a considerable extent justified. In contrast to trialkylsilanes, which do not enter into the condensation reaction at all, triarylsilanes enter into the condensation reaction according to the same scheme indicated above:

$$Ar_3SiH + CH_2{=}CH{-}CH_2Cl \begin{cases} \longrightarrow Ar_3SiCH{-}CH{=}CH_2 + HCl \\ \longrightarrow Ar_3SiCl + CH_3CH{=}CH_2 \end{cases} \qquad \text{(IV)}$$

The triarylsilanes investigated, in the order of increasing yields of the products of their condensation with alkenyl halides, were arranged in the series:

$$(CH_3C_6H_4)_3SiH < (C_6H_5)_3SiH < (ClC_6H_4)_3SiH.$$

The data in Table 1 indicate that, in terms of the electronegativity of the X_3Si groups, the triarylsilanes we studied do indeed lie between $HSiCl_3$, which gives the highest yields of condensation products, and $HSi(C_2H_5)_3$, which does not form them at all. However, the electronegativity values for all the arylsilanes studied are very close, whereas the yields of the condensation products differ sharply. It is evident that, in addition to the electronegativity of the X_3Si groups, the yield of condensation products is also determined by other factors, the evaluation of which should be the subject of further investigations.

Table 1

Electronegativity of the X_3Si groups in X_3SiH $(X = Cl,\ Alk,\ Ar)$

Hydridosilane	Bond vibrational frequencies	Electronegativity (4)
$(ClC_6H_4)_3SiH$	2138	2.12
$(C_6H_5)_3SiH$	2126	2.10
$(CH_3{—}C_6H_4)_3SiH$	2135	2.11
Cl_3SiH (5)	2257	2.24
$(C_2H_5)_3SiH$ (5)	2098	2.07

Interesting results were obtained in the high-temperature condensation reaction of tri-(*chlorophenyl*)silane with *p*-dichlorobenzene, carried out at 630°. Here the reaction proceeded according to a more complex scheme (V), which may be represented by the following equations:

$$(ClC_6H_4)_3SiH + ClC_6H_4Cl \begin{cases} \to \text{a) } (ClC_6H_4)_4Si + HCl \quad 17\% \\ \to \text{b) } (ClC_6H_4)_3SiCl + ClC_6H_5 \quad 12\% \\ \to \text{c) } [(ClC_6H_4)_3Si]_2C_6H_4 + 2HCl > 20\% \end{cases} \tag{V}$$

The synthesis was carried out in a quartz tube 20 mm in diameter, placed in an electric furnace. Before the beginning of the experiment the tube was filled with nitrogen, which was also passed through during the experiment at a rate of 2 cm^3/sec. The reaction products were collected in a trap cooled to −20°. After the trap an absorber with 0.1 N NaOH was placed. After each experiment the amount of liberated HCl was determined by titration.

The initial triarylsilanes were synthesized by the Grignard reactions.

A. **Reaction of tri-*p*-chlorophenylsilane with allyl chloride.** At the optimal reaction temperature, which in this case proved to be 580°, it was possible to isolate, in 42% yield, only one crystalline product with m.p. 112°.

$$(ClC_6H_4)_3SiCH_2—CH = CH_2.$$

Found, %: C 62.18; H 4.29; Si 7.01; Cl 26.38
Calculated, %: C 62.42; H 4.24; Si 6.95; Cl 26.33

By titration of HCl, the content of $(ClC_6H_4)_3SiCl$ in the reaction products was determined to be 6%.

B. **Reaction of tri-*p*-tolylsilane with allyl chloride.** At 580°, two crystalline products were isolated. From petroleum ether, a crystalline product with m.p. 116—117° was isolated in an amount of 32%.

$$(CH_3C_6H_4)_3SiCl.$$

Found, %: C 74.68; H 6.22; Si 8.4; Cl 10.38
Calculated, %: C 74.85; H 6.25; Si 8.33; Cl 10.52

Tritolylallylsilane (in an amount of about 5%) was initially isolated in the form of a difficultly crystallizing oil, which was subjected to distillation. After treatment with petroleum ether with b.p. 30—50°, it was converted into transparent octahedra with m.p. 114°.

$$(CH_3C_6H_4)_3SiCH_2—CH = CH_2.$$

Found, %: C 84.12; H 7.69; Si 8.2
Calculated, %: C 84.14; H 7.65; Si 8.2

B. Interaction of triarylsilanes with halobenzenes.

a) Reaction with chlorobenzene. As in the case of alkenyl halides, the reaction, as expected, should have proceeded to one degree or another both in the direction of condensation and in the direction of reduction,

$$\mathrm{R_3SiH + C_6H_5Cl} \begin{array}{l} \nearrow \; \mathrm{R_3SiC_6H_5 + HCl} \\ \searrow \; \mathrm{R_3SiCl + C_6H_6} \end{array} \tag{VI}$$

The optimum condensation temperature in the case of aryl halides proved to be 630°. In the condensation of tritolylsilane, tritolylphenylsilane was formed in an amount of only 2%. Tritolylchlorosilane was obtained in a yield of 42%. In the condensation of tri-*n*-chlorophenylsilane, tri-*n*-chlorophenylchlorosilane, m.p. 108–112°, was obtained in a yield of 14% (by extraction with petroleum ether), and tri-*n*-chlorophenylphenylsilane, m.p. 134°, in a yield of 19% (by extraction with benzene). After separation of the two indicated compounds there still remained a high-melting product, m.p. 258–262° (recrystallization from hot benzene). By molecular weight (found 710–730, calculated 732) and elemental analysis it corresponded to a product of composition $\mathrm{Si_2Cl_4C_{42}H_{30}}$. We assume that this product was formed as a result of twofold condensation and reduction according to the scheme:

$$\mathrm{(ClC_6H_4)_3SiH + ClC_6H_4Si(C_6H_4Cl)_2 \rightarrow HCl + (ClC_6H_4)_3Si{-}C_6H_4Si(C_6H_4Cl)_2} \quad (A)$$

H H

$$\mathrm{A + C_6H_5Cl \rightarrow (ClC_6H_4)_3SiC_6H_4Si(C_6H_5)(C_6H_4Cl)_2B + HCl}$$

$$\mathrm{B + HSi(C_6H_4Cl)_3 \rightarrow ClSi(C_6H_4Cl)_3 + (ClC_6H_4)_2(C_6H_5)Si{-}C_6H_4Si(C_6H_5)(C_6H_4Cl)_2}$$

b) Reaction with *n*-dichlorobenzene. From the products of the reaction that proceeded according to the scheme given above (V), tri-*n*-chlorophenylchlorosilane, m.p. 110–112°, in a yield of 12%, was isolated by extraction with petroleum ether. After this, tetra-*n*-chlorophenylsilane, m.p. 180°, in a yield of 17%, was isolated by extraction with benzene. In this reaction, three times as much HCl was evolved as was expected according to reaction a). In addition, after extraction of tetra-*n*-chlorophenylsilane, a high-molecular product remained, m.p. 263–269°. This product consisted mainly of bis-(tri-*n*-chlorophenylsilyl)-benzene, obtained according to equation **c)**. This is indicated by the analysis. For $\mathrm{Si_2Cl_6C_{42}H_{28}}$, molecular weight calculated 801, found 780.

Found, %: C 63.48; H 4.14; Si 7.8; Cl 24.2
Calculated, %: C 62.90; H 3.52; Si 7.1; Cl 26.5

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