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Abstract

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COUPLING OF HALOGENATION AND ARYLATION REACTIONS OF HYDROCHLOROSILANES

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The replacement by a halogen of hydrogen bonded to silicon, expressed by the scheme

$$-\mathrm{SiH} + \mathrm{Hal}_2 \rightarrow \underset{/}{\overset{\backslash}{-}}\mathrm{SiHal} + \mathrm{HHal},$$

is accompanied by the evolution of a large amount of heat. For example, the calculated heat of chlorination of trichlorosilane

$$\mathrm{HSiCl}_{3\,\mathrm{liq}} + \mathrm{Cl}_{2\,\mathrm{gas}} \rightarrow \mathrm{SiCl}_{4\,\mathrm{liq}} + \mathrm{HCl}_{\mathrm{gas}}$$

is 62.89 kcal.

Halogenation of hydrochlorosilanes, proceeding under very mild conditions at a very high rate, is a chain homolytic reaction for which only a quite small initiating action is sufficient: weak illumination without heating, or the addition of a small amount of a substance capable of decomposing with formation of free radicals, for example, azoisobutyronitrile, etc. If special precautions are not observed, chlorination of hydrochlorosilanes assumes an explosive character.

The replacement of hydrogen bonded to silicon by an aryl group is incomparably more difficult:

$$-\mathrm{SiH} + \mathrm{HAr} \underset{/}{\overset{\backslash}{\rightarrow}} \mathrm{ArSi}- + \mathrm{H}_2,$$

According to approximate calculations, owing to the absence of experimental data on the heats of formation of arylchlorosilanes, such arylation—or, in other words, dehydrocondensation—of hydrochlorosilanes and aromatic compounds proceeds with absorption of heat, the amount of which in the dehydrocondensation of trichlorosilane and benzene

$$HSiCl_{3\,\mathrm{liq}} + C_6H_{6\,\mathrm{liq}} \to C_6H_5SiCl_{3\,\mathrm{liq}} + H_{2\,\mathrm{gas}}$$

may be roughly characterized by the value 29 ± 10 kcal.*

Neither light nor substances capable of decomposing with formation of radicals are able to initiate this reaction under relatively mild conditions. Dehydrocondensation becomes possible at high temperature and high concentration of reagents, that is, at high pressure. In the case mentioned, heating in an autoclave at 470° is required; the pressure at the end of the reaction reaches 180 atm. With the aid of catalysts (BCl_3, $AlCl_3$) the dehydrocondensation conditions are somewhat softened, but they still remain rather severe: the temperature is lowered only by 100°, and the pressure by 40 atm. Catalytic dehydrocondensation is a heterolytic reaction.

The study of both reactions prompted the supposition of the possibility of their positive coupling and, in this way, of carrying out the replacement of hydrogen in the hydrochlorosilane molecule by an aryl group under mild conditions.

* The heat of formation of phenyltrichlorosilane was taken as 72 ± 10 kcal/mole, in accordance with the calculation performed by V. V. Korobov.

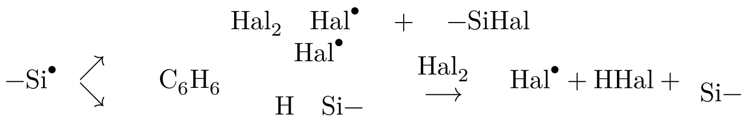
Following this assumption, the feasibility of coupling these reactions has been shown experimentally in a number of examples, some of which are given below.

The reaction of trichlorosilane, chlorine, and benzene, taken in equal molar amounts (chlorine was gradually introduced into a mixture of trichlorosilane with benzene), was initiated by light; the chlorine reacted completely. Owing to the heat of reaction and heating by the light source, the temperature rapidly reached 35°, and then, as substances boiling above the starting materials were formed, gradually rose to 51°. Separation of the reaction mixture by rectification showed that 42.7% of the trichlorosilane was converted into silicon tetrachloride, 35.4% into phenyltrichlorosilane, 8.3% remained unchanged, and 13.6% was lost (mainly with the escaping hydrogen chloride and during rectification); correspondingly, 35.4% of the benzene was also converted into phenyltrichlorosilane, 57.2% remained unchanged, and 7.4% was converted into hexachlorocyclohexanes and lost. Under the conditions of the experiment, replacement by chlorine of hydrogen in the aromatic ring was absent. The yield of phenyltrichlorosilane based on unrecovered trichlorosilane was 38.6%, and based on benzene, 82.8%. The yield of silicon tetrachloride based on unrecovered trichlorosilane reached 46.6%.

The coupling of the reactions of halogenation and arylation of hydrochlorosilanes apparently may be expressed by the following schemes:

$$\mathrm{Hal_2} \rightarrow \mathrm{Hal}^{\bullet} + \mathrm{Hal}^{\bullet},$$

$$\mathrm{Hal}^{\bullet} + \mathrm{HSi} \longrightarrow -\mathrm{Si}^{\bullet} + \mathrm{HHal},$$



$$-\mathrm{Si}^{\bullet} \begin{array}{l} \nearrow \\ \searrow \end{array} \quad \mathrm{C_6H_6} \quad \begin{array}{c} \mathrm{Hal_2} \quad \mathrm{Hal}^{\bullet} \quad + \quad -\mathrm{SiHal} \\ \mathrm{Hal}^{\bullet} \\ \\ \mathrm{H} \quad \mathrm{Si}- \end{array} \xrightarrow{\mathrm{Hal_2}} \mathrm{Hal}^{\bullet} + \mathrm{HHal} + \mathrm{Si}-$$

The formation of hydrogen halide at the last stage of the reaction, accompanied by the liberation of a considerable amount of heat, stimulates abstraction of a hydrogen atom from the six-membered cyclic radical, i.e., conversion of the latter into an arylchlorosilane.

The ratio of the rates of halogenation and arylation, and consequently the yields of halogenchlorosilanes and arylchlorosilanes, is determined mainly by the relative reactivity of the hydrochlorosilane, the aromatic compound, and the halogen; to some extent it also depends on the temperature and the relative concentration of the reactants.

Chlorobenzene, for example, is less reactive than benzene. Under analogous conditions only 27.1% of it was converted into chlorophenyltrichlorosilane, 68.7% remained unchanged, and 4.2% was converted into heptachlorocyclohexanes and lost; correspondingly, 57% of the trichlorosilane was converted into $\mathrm{SiCl_4}$, 27.1% into chlorophenyltrichlorosilane, 2.1% remained unchanged, and 13.8% was lost. The arylating ability of benzonitrile under similar conditions proved to be practically equal to zero. Methyldichlorosilane is arylated with more difficulty and is chlorinated more readily (at the hydrogen attached to silicon) than trichlorosilane. At 60–65°, with gradual addition of methyldichlorosilane to the reaction zone, only 15.5% of it was converted into methylphenyldichlorosilane, and at 22° only 5%. Under the conditions of the experiments, replacement by chlorine of hydrogen in the methyl group and in the aromatic ring was absent.

A silicon hydride such as triethoxysilane, in benzene, is chlorinated at a very high rate (at the hydrogen attached to silicon) and is not arylated at all.

It should be noted that coupling of the reactions of halogenation of aromatic compounds and arylation of hydrochlorosilanes by aromatic compounds,

$$\mathrm{ArH} + \mathrm{Hal_2} \rightarrow \mathrm{ArHal} + \mathrm{HHal} \quad \text{and} \quad \left(-\!\!\rangle\mathrm{SiH} \right) + \mathrm{HAr} \rightarrow \mathrm{ArSi}\left(\langle \right) - \mathrm{H_2},$$

is absent.

When chlorine acts on a mixture of benzene with trichlorosilane in the presence of 0.1% ferric chloride, only chlorination of benzene occurs; the trichlorosilane remains unchanged. This should be explained by the fact that, on the one hand, in the presence of silicon hydrides only heterolytic chlorination of the aromatic ring is possible, in which no free aryls are formed; on the other hand, silicon hydrides under mild conditions are not capable of heterolytic chlorination, while catalysts of heterolytic chlorination ($FeCl_3$, $AlCl_3$) are inhibitors of homolytic processes, as a result of which, in the case under consideration, free silyl groups are not formed either.

At present, the study is continuing of the arylating ability of various aromatic compounds, the behavior of other silicon hydrides, and the influence of conditions on the course of the reactions.

Table 1

Formula	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calculated	Hydrolyzable Cl content, %, found	Hydrolyzable Cl content, %, calculated
$C_6H_5SiCl_3$	1.3227	1.5230	48.86	48.78	50.65	50.28
$ClC_6H_4SiCl_3$	1.4509	1.5460	53.69	53.61	43.52	43.06
$CH_3(C_6H_5)SiCl_2$	1.1771	1.5183	49.23	49.22	37.16	37.10

Experimental procedure. Into a four-necked flask of 0.6 l capacity, fitted with a tube for introducing chlorine, a thermometer, and a water-cooled reflux condenser with a trap for additional condensation of vapors by solid carbon dioxide with acetone, were placed 2 g-mol of hydrochlorosilane and 2 g-mol of the aromatic substance. The outlet of the condenser was protected from atmospheric moisture by a calcium chloride tube. The liquid in the flask was illuminated with an electric incandescent lamp of 109 W, located at a distance of ~ 100 mm from the flask. After the consumption of chlorine had reached 2 g-mol (determined by weighing the cylinder), the reaction mixture was rectified on a column with an efficiency of 15 theoretical plates. The composition of the intermediate fractions was calculated from the densities. The characteristics of the isolated arylchlorosilanes are given in Table 1.

As a result of the study it was found that in a number of cases there is positive coupling of the halogenation and arylation reactions of silicon hydrides, making it possible to carry out the latter reaction under mild conditions (^{1}).

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

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