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Abstract

Full Text

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CATALYTIC INTERACTION OF ALKYLDICHLOROSILANES WITH HALOGEN-SUBSTITUTED BENZENES

(Presented by Academician B. A. Kazanskii, July 14, 1958)

The interaction of alkyldichlorosilanes with halogen-substituted benzenes is mentioned very briefly in a few publications of a patent character. According to one patent (1), in an autoclave at 450°, without a catalyst, methyldichlorosilane and chlorobenzene give methylphenyldichlorosilane according to the scheme:

$$\mathrm{CH_3SiHCl_2 + C_6H_5Cl \rightarrow CH_3(C_6H_5)SiCl_2 + HCl.}$$

The same substances react differently in the presence of $AlCl_3$ or BCl_3 (2): in an autoclave at 150–300°, methylchlorophenyldichlorosilanes are formed in a yield of about 6% based on the charged methyldichlorosilane, according to the scheme:

$$\mathrm{CH_3SiHCl_2 + C_6H_5Cl \xrightarrow{catalyst} {}^{CH_3}SiCl_2 + H_2, \quad {}^{ClC_6H_4}}$$

We have investigated the catalytic interaction of methyldichlorosilane with chlorobenzene and fluorobenzene, and of ethyldichlorosilane with chlorobenzene.

In the present investigation, boric acid was used as the catalyst—or, more precisely, as the substance from which the catalyst is formed; before the main reaction begins, it interacts with the alkyldichlorosilane, with evolution of hydrogen chloride and formation of compounds soluble in the reaction mixture and containing $-\mathrm{Si-O-B}<$ bonds:

$$> \mathrm{Si-Cl + HO-B} < \rightarrow > \mathrm{Si-O-B} < + \mathrm{HCl.}$$

Already in studying the catalytic interaction of alkyldichlorosilanes with benzene (3), we became convinced that the use of boric acid in the arylation of $\mathrm{Si-H}$ bonds according to the scheme

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$$> \mathrm{Si} - \mathrm{H} + \mathrm{H} - \mathrm{Ar} \xrightarrow{\text{catalyst}} > \mathrm{Si} - \mathrm{Ar} + \mathrm{H}_2$$

is preferable to the use of other catalysts, owing to the greater availability of boric acid, the convenience of handling it, and the sufficient catalytic activity of the products of its interaction with chlorosilanes.

Experiments on the catalytic interaction of alkyldichlorosilanes with halogen-substituted benzenes were carried out in stainless-steel autoclaves with a capacity of 0.6 l. The autoclave was filled to 56-60% of its volume with the initial mixtures, to which boric acid was added. After sealing, the autoclave was immersed in a heated oil bath. The temperature in the autoclave reached the specified value after 20–40 min. The mixture of reacting substances was heated at the specified temperature until the pressure ceased to rise, after which heating was continued for another 15-20 min. At the end-

after heating, the autoclave was removed from the bath and allowed to cool to room temperature. The gaseous reaction products were collected in a gasometer, and the liquid mixture was rectified on a column with an efficiency of 14 theoretical plates. The low-boiling fractions were distilled off at atmospheric pressure; rectification of the high-boiling reaction products was carried out under vacuum.

Because of the greater thermal stability of the halobenzenes, charging them in an amount exceeding the stoichiometric amount favorably affects the yield of alkylhalophenyldichlorosilanes. We adopted as optimal a molar ratio of alkyldichlorosilane to halobenzene equal to 1 : 3. A series of experiments showed that addition of boric acid in an amount of 0.3% of the weight of the reaction mixture is optimal. A larger amount of boric acid greatly accelerates the disproportionation of alkyldichlorosilanes, while a smaller amount is unable to ensure a sufficient reaction rate; in both cases a decrease in the yield of alkylhalophenyldichlorosilanes is observed.

Interaction of methyl- and ethyldichlorosilane with chlorobenzene. Into the autoclave were charged 101.2 g of methyldichlorosilane, 298.8 g of chlorobenzene, and 1.2 g of boric acid, or 111 g of ethyldichlorosilane, 287 g of chlorobenzene, and 1.19 g of boric acid. The temperature required for the onset of the reaction of methyldichlorosilane with chlorobenzene is 255°. Twenty minutes after the start of the reaction it is permissible to lower the temperature by 5° without any noticeable decrease in the rate of the process. The temperature for the interaction of ethyldichlorosilane with chlorobenzene is 10° higher. The indicated temperatures are optimal.

Table 1

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Synthesis temperature, °C	Yield of C_2H_5-C_6H_4-$SiCl_2$, % based on $C_2H_5SiHCl_2$ charged	Yield of C_2H_5-C_6H_4-$SiCl_2$, % based on $C_2H_5SiHCl_2$ reacted	Did not enter into reaction, % of charged $C_2H_5SiHCl_2$	Did not enter into reaction, % of charged C_6H_5Cl
260	18.6	24.8	24.8	80.8
270	17.1	21.2	19.6	76.8
285	16.3	18.7	12.8	75.0

Table 1 gives the dependence of the yield of ethylchlorophenyldichlorosilane on the synthesis temperature.

When methyldichlorosilane is reacted with chlorobenzene under the described conditions, reaction mixtures of the following composition are obtained: ~6% unchanged methyldichlorosilane, ~7% methyltrichlorosilane, ~5% dimethyldichlorosilane, ~60% unchanged chlorobenzene, ~4% intermediate fraction with b.p. 44-128°/29 mm, ~10% methylchlorophenyldichlorosilane, and ~5% products constituting the still residue. The gaseous reaction products, formed in an amount of 0.32 g-mol per 1 g-mol of charged methyldichlorosilane, contain 86.5-87.5% hydrogen, 9-10% methane, and 0.7-1% hydrogen chloride. Rectification of the reaction mixtures gives fractions of methylchlorophenyldichlorosilane, which are mixtures of the *o*-, *m*-, and *p*-isomers, having b.p. 232-238°; d_4^{20} 1.2920-1.2965; n_D^{20} 1.5338-1.5342; MR_D found: 54.09-54.26, calculated 54.08.

Found, %: hydrolysis Cl 31.21-31.97
Calculated, %: hydrolysis Cl 31.43

The isomers of methylchlorophenyldichlorosilane are contained in the separated fractions in the following ratio: ortho ~20%, meta ~45%, and para ~35%*. The yield of methylchlorophenyldichlorosilanes is 24% based on reacted methyldichlorosilane; in autoclaves of larger capacity the yield reaches 27%.

* The ratio of isomers in the fractions of methylhalophenyldichlorosilanes was determined by the method of combinational light scattering by K. K. Popkov, for which we express our deep gratitude to him.

In the interaction of ethyldichlorosilane with chlorobenzene under optimum conditions, mixtures are obtained containing: ~7% unchanged ethyldichlorosilane, ~5% ethyltrichlorosilane, ~2% diethyldichlorosilane, ~60% chlorobenzene, ~4% of an intermediate fraction with b.p. 37.5-135.5°/18 mm, 9.6% ethylchlorophenyldichlorosilane, and ~6% of products remaining in the flask of the rectification column. The gaseous reaction products, formed in an amount of 0.32 g-mol per 1 g-mol of charged ethyldichlorosilane, contain 90% hydrogen and 5% ethane. The fractions isolated by rectification from the reaction mixtures, which are mixtures of the *o*-, *m*-, and *p*-isomers of

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ethylchlorophenyldichlorosilane, have b.p. 255-258°; d_4^{20} 1.2592-1.2621; n_D^{20} 1.5298-1.5317; MR_D found 58.76-58.83, calculated 58.71.

Found, %: hydrolyzable Cl 29.91-30.36
Calculated, %: hydrolyzable Cl 29.59

The yield of ethylchlorophenyldichlorosilanes reaches 25% based on the ethyldichlorosilane that has reacted.

Interaction of methyldichlorosilane with fluorobenzene. Into an autoclave were charged 100 g of methyldichlorosilane, 250 g of fluorobenzene, and 1.05 g of boric acid. The minimum temperature required for the start of the reaction proved to be 255-260°; it is also the optimum temperature. As a result of the interaction under the above-indicated conditions, there are formed: a mixture of liquid substances containing ~8% methylfluorophenyldichlorosilanes, and gaseous products in an amount of 0.35 g-mol per 1 g-mol of charged methyldichlorosilane, containing 83-86% hydrogen and 12-14% methane.

On rectification of the liquid reaction products, fractions are isolated which are mixtures of the *o*-, *m*-, and *p*-isomers of methylfluorophenyldichlorosilane, with b.p. 196-199.7°; d_4^{20} 1.2438-1.2492; n_D^{20} 1.4960-1.4998; MR_D found 49.06-49.32, calculated 49.27.

Found, %: Cl 33.66-34.20
Calculated, %: Cl 33.91

The ratio of the isomers of methylfluorophenyldichlorosilane in the isolated fractions is as follows: ortho ~25%, meta ~60%, and para ~15%. The yield of methylfluorophenyldichlorosilanes is 18% based on the methyldichlorosilane that has reacted.

Table 2

Starting aromatic compound	Minimum synthesis temperature, °C	Optimum amount of boric acid, % by weight of mixture	Yield $CH_3(XC_6H_4)SiCl_2$, % based on CH_3SiHCl_2
Benzene	240 ± 5	0.1	40
Chlorobenzene	250 ± 5	0.3	24
Fluorobenzene	255 ± 5	0.3	18

The conditions for the interaction of methyldichlorosilane with benzene and its halogen-substituted derivatives, as well as the yields of the reaction products, compared in Table 2, indicate that in the reaction under consideration there is also a regular decrease in the reactivity of the benzene ring when a hydrogen atom in it is replaced by a halogen atom. The tendency toward a decrease in reactivity is the stronger, the greater the polarity of the halogen.

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CITED LITERATURE

1. Brit. Pat. 635645 (1950); *Chem. Abstr.*, **44**, 6882 (1950).
2. US Pat. 2499561 (1950); *Chem. Abstr.*, **44**, 5907 (1950).
3. G. N. Mal' kova, E. P. Mikheev et al., *DAN*, **117**, No. 4, 623 (1957).

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

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