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G. N. MAL’ NOVA, E. P. MIKHEEV, A. L. KLEBANSKII, S. A. GOLUBTSOV

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Abstract

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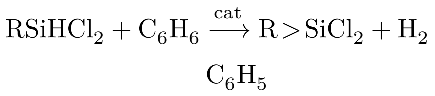
CHEMISTRY

G. N. MAL' NOVA, E. P. MIKHEEV, A. L. KLEBANSKII, S. A. GOLUBTSOV
and N. P. FILIMONOVA

ON THE CATALYTIC PHENYLATION OF HYDROGEN-CONTAINING ALKYLCHLOROSILANES WITH BENZENE

(Presented by Academician B. A. Kazanskii on 28 VI 1957)

The reaction of the catalytic interaction of hydrogen-containing alkylchlorosilanes and trichlorosilane with aromatic hydrocarbons



$$RSiHCl_2 + C_6H_6 \xrightarrow{cat} \underset{C_6H_5}{R{>}SiCl_2} + H_2$$

has been insufficiently covered in the literature. The available brief patent communications mention mainly the interaction of trichlorosilane with benzene in the presence of aluminum chloride (1,2), boron trifluoride (3,4), boron trichloride (5,3), boric acid (3), and compounds containing both boron and silicon (3).

Phenylation of methyldichlorosilane with benzene in the presence of 0.1-5% BF_3 or BCl_3, or H_3BO_3, according to the data of the patent (6), is recommended to be carried out in an autoclave at 300° for 16 hr. This gives methylphenyldichlorosilane in a yield of 6.2% of the stoichiometric amount based on methyldichlorosilane, as well as phenyltrichlorosilane, dimethyldichlorosilane, and tetrachlorodimethylphenyldisilane.

E. A. Chernyshev and A. D. Petrov, in a brief communication (7), indicate the possibility of the formation of methylphenyldichlorosilane in the presence of Raney nickel, with a yield of 17.7% based on the methyldichlorosilane that entered into the reaction; it is also noted there that in the presence of $AlCl_3$ the yield of methylphenyldichlorosilane is 23%.

The fact attracts attention that, with the exception of Raney nickel, the catalysts are compounds of elements of Group III of the periodic system.

We have investigated the phenylation reaction of methyl- and ethyldichlorosilanes with benzene.

Experimental testing showed that ferric chloride, barium chloride, benzoyl peroxide, and freshly prepared boric anhydride do not exert a catalytic effect on the reaction under study. Further investigation was carried out with boric acid, which is a sufficiently active and convenient catalyst. The experiments were conducted in autoclaves of 100 ml capacity, which were filled to half their volume with a mixture of alkyldichlorosilane with benzene, to which boric acid was added.

It was established that in the presence of 1-2% boric acid, based on the weight of the mixture, simultaneous formation of phenyltrichlorosilane occurs; separation of it from methylphenyldichlorosilane by rectification is practically impossible (difference in boiling point about 2°). By reducing the amount of catalyst to 0.1%, it is possible practically completely to eliminate the formation of phenyltrichlorosilane.

The increase in pressure in the autoclave, occurring mainly as a result of the evolution of hydrogen during the phenylation process, depending on the synthesis temperature ceases after 1 hour (at 290°) to 2 hours (at 250°). The longer heating time recommended in patents ([2–4,6]) is inadvisable, since it entails a decrease in the yield of the target substance as a result of its further transformations.

The optimum synthesis temperature in the presence of 0.1% boric acid is close to 240°. When the temperature is lowered by 5–10°, the reaction slows sharply. A considerable increase in the synthesis temperature leads to a decrease in the yield of alkylphenyldichlorosilanes and to the formation of difficultly separable by-products, mainly phenyltrichlorosilane. The latter can readily be judged from the increase in the density of the isolated methyldichlorophenylsilane fraction (see Table 1, which gives the dependence of the yield of methyldichlorophenylsilane on the synthesis temperature). The duration of heating at the indicated temperatures was 2 hours; the molar ratio $CH_3SiHCl_2 : C_6H_6$ was 1 : 1.2, and the amount of boric acid was 0.1% of the weight of the mixture.

Table 1

Synthesis temperature, °C	Maximum pressure at synthesis temperature, atm	Residual pressure at 20°, atm	Yield of $CH_3(C_6H_5)SiCl_2$ calculated as CH_3SiHCl_2, % of charged	Yield of $CH_3(C_6H_5)SiCl_2$ calculated as CH_3SiHCl_2, % of reacted	Returned CH_3SiHCl_2, %	d_4^{20} of target fraction
240	70	31	16.8	29.6	42.8	1.1778
250	100	49	13.6	14.8	13.7	1.1772
290	122	49	6.2	6.6	9.8	1.1846

The comparatively low yields of alkylphenyldichlorosilane are due mainly to the high reactivity of alkylhydrodichlorosilanes, which under the synthesis conditions are capable not only of being phenylated but also of undergoing various transformations. Among such transformations, thermal rearrangements, condensation, and reaction with alkylphenyldichlorosilane should be noted. It was therefore natural to assume that decreasing the proportion of alkylhydrodichlorosilane in the reaction mixture and increasing the proportion of benzene would entail an increase in the yield of alkylphenyldichlorosilane. The experimental results presented in Table 2 for various ratios of methyldichlorosilane and benzene, within known limits, confirm the stated assumption. The experiments were carried out at 240° with the addition of 0.1% boric acid.

When the synthesis was carried out in an autoclave of larger volume, the yield of methyldichlorophenylsilane under optimum conditions reached 40% of the reacted methyldichlorosilane.

Table 2

Molar ratio $CH_3SiHCl_2 : C_6H_6$	Maximum pressure at synthesis temperature, atm	Residual pressure at 20°, atm	Time required to reach constant pressure	Yield of $CH_3(C_6H_5)SiCl_2$ calculated as CH_3SiHCl_2, % of charged	Yield of $CH_3(C_6H_5)SiCl_2$ calculated as CH_3SiHCl_2, % of reacted
1 : 1.2	100	38	1 h 45 min	13.4	17.7
1 : 3	80	29	2 h	23.4	32.5
1 : 5	68	25	3 h 30 min	23.7	–

In the mixture after completion of the synthesis process, along with methyldichlorophenylsilane and unconverted methyldichlorosilane and benzene, by-products are present: dimethyldichlorosilane and methyltrichlorosilane (in rela-

in a ratio of 1 : 3 by weight), other products of disproportionation and condensation of methyldichlorosilane, and high-boiling substances formed in the subsequent reaction of methylphenyldichlorosilane with methyldichlorosilane.

The gaseous reaction products consist of 90–95% hydrogen and 5–10% hydrocarbons.

The synthesized methylphenyldichlorosilane was subjected to double rectification on a column with an efficiency of 25 theoretical plates, as a result of which a substance was isolated boiling at 203.1°/749 mm, with d_4^{20}1.1778; n_D^{20}1.5188; $MR_{D\ \mathrm{found}}$49.24; $MR_{D\ \mathrm{calc}}$49.24.

Found % : Cl 37.12
Calculated % : Cl 37.10

The interaction of benzene with ethyldichlorosilane in the presence of boric acid proceeds in an analogous manner. The optimum synthesis temperature is approximately 20° higher than in the case of methyldichlorosilane—close to 250°. The isolated ethylphenyldichlorosilane had b.p. 225.2°, $d_4^{20}1.1554$; $n_D^{20}1.5198$; $MR_{D\ \mathrm{found}}53.96$, $MR_{D\ \mathrm{calc}}53.87$.

Found % : Cl 34.60
Calculated % : Cl 34.57

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