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Abstract

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PREPARATION AND PROPERTIES OF HEXACHLOROCYCLOHEXYLCHLOROSILANES

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Aromatic hydrocarbons, as is known, are capable of additive halogenation. With chlorine this reaction is usually carried out under illumination ([1]) and at 0° ([2]), in the absence of substitution catalysts.

Electron-acceptor substituents usually do not hinder the formation of chlorine-addition products and, on the contrary, electron-donor substituents direct chlorination exclusively toward substitution ([3]). Thus, phenol and aniline are not capable of additive chlorination, but phenyl haloacetates and phenyl isocyanate form, in high yields, the corresponding addition products ($C_6H_5Cl_6OCOCX_3$ ([4]) and $C_6H_5Cl_6NCO$ ([5])). It could be expected that other benzene derivatives with meta-directing groups, which cause deactivation of the aromatic nucleus in substitution reactions, would also prove capable of additive chlorination. This has been confirmed by the example of aromatic chlorosilanes—phenyltrichlorosilane and phenylmethyldichlorosilane—the additive chlorination of which has been investigated for the first time in the present work.

A study of the chlorination of phenyltrichlorosilane at $0 \div 2°$ in diffused daylight showed that the only product of this reaction is the chlorine-addition product —hexachlorocyclohexyltrichlorosilane $C_6H_5Cl_6SiCl_3$ (yield 28.9% based on the silane taken and 67.4% based on the silane that entered into reaction, when 28 moles of chlorine were passed per 1 mole of $C_6H_5SiCl_3$). The interaction is noticeably accelerated under irradiation with ultraviolet light; the yield of hexachlorocyclohexyltrichlorosilane in this case (molar ratio $C_6H_5SiCl_3 : Cl_2 = 1 : 7$) reaches 90% and higher. Similar results were obtained in the photochemical chlorination of phenyltrichlorosilane at 20°. The reaction of additive chlorination of phenyltrichlorosilane proceeds relatively readily at $-20°$ (under ultraviolet irradiation); naturally, its rate in this case is lower, and to achieve a yield of $C_6H_5Cl_6SiCl_3$ of $\sim 90\%$, other conditions being equal, a larger excess of chlorine is required ($C_6H_5SiCl_3 : Cl_2 \simeq 1 : 12$).

As the temperature is raised, the yield of hexachlorocyclohexyltrichlorosilane decreases, and at 120° the photochemical chlorination of phenyltrichlorosilane already proceeds exclusively as a substitution reaction. A further increase of the temperature under these conditions to 150° leads to an increase in the rate of the substitution chlorination reaction and to the formation, as the main reaction products, of mono- and dichlorophenyltrichlorosilanes

($C_6H_5SiCl_3 : Cl_2 = 1 : 15$). In the absence of ultraviolet irradiation (in the dark), chlorination of phenyltrichlorosilane at 100° practically does not occur; at 150° it proceeds with formation of monochlorophenyltrichlorosilane, yield $\sim 50\%$ based on the silane that entered into reaction ($C_6H_5SiCl_3 : Cl_2 = 1 : 15$).

When elemental chlorine acts on phenylmethyldichlorosilane at $0 \div +5°$ in daylight ($C_6H_5(CH_3)SiCl_2 : Cl_2 = 1 : 3.7$), the only reaction product also proved to be the product of chlorine addition to the aromatic nucleus—hexachlorocyclohexyl(methyl)dichlorosilane $C_6H_5Cl_6(CH_3)SiCl_2$ (yield 78.4% based on the silane that entered into reaction, conversion of the initial silane $\sim 83\%$). Raising the reaction temperature to 20—25° ($C_6H_5(CH_3)SiCl_2 : Cl_2 = 1 : 10$) leads to a decrease in the yield of hexachlorocyclohexyl(methyl)dichlorosilane to 46% (at a conversion of $\sim 95\%$) owing to the formation of substitution products ($C_6H_3Cl_2(CH_3)SiCl_2$, yield 20.5% based on the silane that entered into reaction). Photochemical chlorination of phenylmethyldichlorosilane at 20—25° leads to the formation of a mixture of products of substitution chlorination in the methyl radical ($C_6H_5(CHCl_2)SiCl_2$ and $C_6H_5(CCl_3)SiCl_2$) and hexachlorocyclohexyl(methyl)dichlorosilane.

A study of the composition of the products of chlorination of phenyltrichlorosilane and phenylmethyldichlorosilane under irradiation (daylight or ultraviolet) under ordinary conditions (20–25°) shows that addition and substitution chlorination take place simultaneously, but at different rates; here the rate of addition of chlorine to the aromatic nucleus exceeds the rate of substitution of hydrogen atoms in it. With an increase in the chlorination temperature, the rate of substitution increases, and chlorination of phenyltrichlorosilane at 120° and of phenylmethyldichlorosilane at 50° proceeds already exclusively as substitution. Conversely, with a decrease in temperature, the reaction of addition of chlorine to the aromatic nucleus becomes predominant, and at 0–5° it becomes the only possible one.

As follows from the above, addition chlorination of aromatic chlorosilanes, especially phenylmethyldichlorosilane, proceeds considerably more readily than such chlorination of benzene. This is probably a consequence both of some disturbance of the symmetry of the π-electron cloud of the benzene ring under the influence of the electrophilic substituent, and of deactivation of the phenyl radical by the silyl chloride group toward substitution reactions.

The clearly expressed greater tendency of phenylmethyldichlorosilane, in comparison with phenyltrichlorosilane, toward addition chlorination is evidently associated with some decrease in the electrophilicity of the silicon atom when chlorine is replaced by a methyl group. Apparently, there is a relationship between the electrophilicity of the substituent and the rate of addition chlorination of substituted aromatic compounds. This follows from comparison of the above with the known difficulty of addition of chlorine to nitrobenzene ([3]) and the ease of addition chlorination of phenyl isocyanate and phenyl trihaloacetates. Kinetic studies of these reactions to clarify the indicated relationship remain very desirable.

Table 1

Substance	B.p., °C	Pressure, mm	d_4^{20}	n_D^{20}	C, % calc.	C, % found	H, % calc.	H, % found	Si, % calc.	Si, % found	Cl, % calc.	Cl, % found
$C_6H_5Cl_6SiCl_3$	175–182	3	1.7968	1.5708	16.96	16.65	1.17	1.05	6.59	6.21	75.26	74.99
$C_6H_5Cl_6(CH_3)SiCl_2$	175–179	5	1.6921	1.5690	20.79	20.92	1.98	1.99	6.93	6.23	70.30	69.96
$C_6H_5Cl_6Si(OC_2H_5)_3$	184–187	3	1.4200	1.5065	31.78	31.49	4.41	4.17	6.18	5.89	47.02	47.40
$C_6H_5Cl_6(CH_3)Si(OC_2H_5)_2$	187–190	5	1.4352	1.5200	31.20	30.87	4.25	3.99	6.62	6.60	50.35	50.09

Hexachlorocyclohexyltrichlorosilane and hexachlorocyclohexyl(methyl)dichlorosilane (see Table 1) are colorless viscous liquids, fuming slightly in air; they distill in vacuum without decomposition and dissolve well in organic solvents; on prolonged standing they crystallize (needles), m.p. 90–93° (from petroleum ether). The broad boiling-temperature ranges of these compounds are apparently explained by the formation in the reaction of a mixture of stereoisomers. Under the action of water they are hydrolyzed to siloxanes, the Si–C bond not being affected. Under the action of aqueous alkali solutions, hydrolysis proceeds more deeply—with cleavage of the hexachlorocyclohexyl radical from the silicon atom. The intermediate hexachlorocyclohexane formed, undergoing dehydrochlorination, is converted into trichlorobenzene (yield 90.6%), which was isolated from this reaction. On interaction with ethyl alcohol, the corresponding hexachlorocyclohexylethoxysilanes are formed (see Table 1).

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