

ORGANOSILICON COMPOUNDS. XC.*

THE REACTION OF METHYLCHLOROSILANES WITH FREE METHYL RADICALS

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To attack the problem of the mechanism of direct synthesis of methylchlorosilanes, the interactions of free methyl radicals with trichlorosilane, methyldichlorosilane, methyltrichlorosilane and dimethyldichlorosilane have been investigated. The experiments have proved that the Si—H bond is far more reactive toward free methyl radicals than the C—H bond. In addition to the compounds that can be derived by combination of free radicals, the reaction mixtures also contained compounds formed by replacement of the hydrogen atom on silicon by a chlorine atom and organomercuric compounds of the type $(\equiv\text{SiCH}_2)_2\text{Hg}$. The results of the experiments lead to the conclusion that the direct synthesis of methylchlorosilanes proceeds very likely by a chemisorption mechanism, possibly accompanied to a very small extent by the free radical mechanism.

The mechanism of direct synthesis of methylchlorosilanes has not yet been fully elucidated¹. In the opinion of the discoverers of this synthesis, Rochow² and Müller³, the reaction of methyl chloride with silicon, catalysed by copper, is based on the formation of free methyl radicals, which bind to silicon activated by chlorine, thus giving rise to methylchlorosilanes. Other authors⁴⁻⁷ have proposed a chemisorption mechanism, according to which the reaction proceeds on the surface of a contact mass, formed by silicon and copper. The fact that under certain (optimum) conditions the direct synthesis can occur very selectively, dimethyldichlorosilane representing 80–90% of the product⁸, is an argument against the free-radical mechanism, whose selectivity is generally poor. The kinetics of the reaction of free methyl radicals generated by photolysis of azomethane with organochlorosilanes have been investigated by Kerr, Slater and Young^{9,10}. They found the Si—H bond to be much more reactive to the attack of a free methyl radical than the C—H bond, but did not isolate silanes formed by reaction of free methyl radicals with organochlorosilanes.

The direct synthesis of methylchlorosilanes, depending on the reaction conditions, yields 5 to 10% of compounds¹¹ having a higher boiling point than dimethyldichlorosilane, *i.e.* 70°C. The compounds in question are chlorosilanes with an ethyl or propyl group on silicon and compounds with the groupings $\equiv\text{SiSi}\equiv$, $\equiv\text{SiCH}_2\text{Si}\equiv$, $\equiv\text{Si}(\text{CH}_2)_2\text{Si}\equiv$, and others. The formation of these compounds can be accounted

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for either by interaction of dissociated particles on the surface of the contact mass, or by reaction of the formed methylchlorosilanes with free methyl radicals in the gaseous phase, followed by recombination or thermal decomposition of more complex free radicals, produced from the methylchlorosilanes. Since the composition of the higher-boiling fractions from the direct synthesis of methylchlorosilanes has been described in detail¹¹, we considered it worth while to identify the compounds formed by interaction of the individual methylchlorosilanes with free methyl radicals, generated by thermal decomposition of dimethylmercury, and to compare the results obtained.

EXPERIMENTAL AND RESULTS

Chemicals and procedure. Trichlorosilane, methylchlorosilane, methyltrichlorosilane and dimethylchlorosilane were commercial chemicals from VCHZ Synthesia, Kolin. After distillation through a column of 50 TP they were chromatographically pure. Dimethylmercury was obtained by the reaction of methylmagnesium chloride with mercuric chloride¹². Pyrolysis was effected at 450°C in the apparatus shown in Fig. 1. After flushing the apparatus with dry nitrogen, to remove the air, the reaction mixture of a chlorosilane and dimethylmercury was dosed by elevating the reservoir with mercury (1). The rate of the elevation was controlled with the aid of a linear-feed doser (2). After passage through the reactor (3) (length 500 mm, inner diameter 20 mm) the reaction products were condensed in a receiver (4) and a freezing trap (5) in a bath of ethanol with solid carbon dioxide. The non-condensed gases were collected over water in a Boyle-Mariotte flask (6). The mercury produced by pyrolysis of dimethylmercury was separated from the condensate and the unreacted chlorosilane was distilled off on a column of 20 TP. The residue was resolved on a microcolumn of 5 TP into rough fractions, which were analysed by gas chromatography¹³. In the compounds of the individual fractions the chlorine atoms on silicon were replaced by methyl groups (with the aid of methylmagnesium chloride) for the sake of easier work and identification. The mixtures of methylsilanes were resolved by preparative gas chromatography.

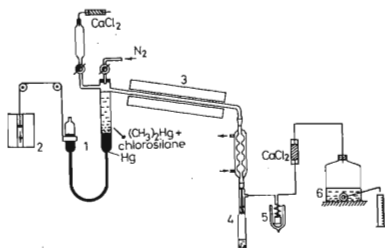


FIG. 1
Apparatus for Pyrolysis

Pyrolysis of trichlorosilane. A mixture of trichlorosilane (1030 g, 7.6 mol) and dimethylmercury (97 g, 0.42 mol) was introduced into a reactor at a rate of 44.5 g/h and a temperature of 450°C. After distilling off the unreacted trichlorosilane the higher-boiling fraction (92.7 g) was composed of tetrachlorosilane (21.4%), methyltrichlorosilane (1.5%), hexachlorodisilane (68%) and non-identified products (9%). Methyltrichlorosilane was determined on the basis of the elution volume, hexachlorodisilane, b.p. 141–144°C, was methylated to hexamethyldisilane, b.p. 111–112°C. The conversion of dimethylmercury into methyltrichlorosilane and hexachlorodisilane was 58.4%. For the sake of comparison trichlorosilane alone was pyrolysed under similar conditions, i.e. at 450°C and a feeding rate of 42 g/h. It was found that the amount of tetrachlorosilane was $\frac{1}{8}$ of that formed in the presence of dimethylmercury.

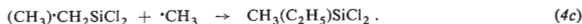
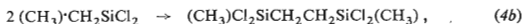
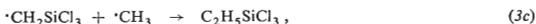
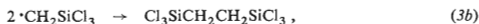
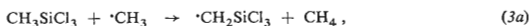
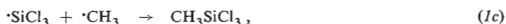
Pyrolysis of methyldichlorosilane. The reactor was fed with a mixture of methyldichlorosilane (990 g, 8.6 mol) and dimethylmercury (110 g, 0.477 mol) at a rate of 40 g/h. There was obtained 94.2 g of a higher-boiling mixture, which was resolved into fractions by distillation through a column. Gas chromatography of the fractions showed that the mixture had the following composition: methyltrichlorosilane (15%), dimethyldichlorosilane (7.5%), dimethyltetrachlorodisilane (60%) and non-identified products (17.5%). Methyltrichlorosilane and dimethyldichlorosilane were identified by their elution volumes, dimethyltetrachlorodisilane, b.p. 150–155°C, was converted by methylation into hexamethyldisilane, b.p. 112°C. The utilization of dimethylmercury for the formation of dimethyldichlorosilane and dimethyltetrachlorodisilane was 63.5%.

Pyrolysis of methyltrichlorosilane. The reactor was fed with a mixture of methyltrichlorosilane (3580 g, 23.9 mol) and dimethylmercury (340 g, 1.475 mol) at a rate of 41.5 g/h. There was obtained a liquid mixture (149.5 g), from which 2.8 g of a crystalline substance was removed by filtration; this was sublimed *in vacuo* and identified as methylmercuric chloride (found: 79.42% Hg; calculated: 79.89% Hg). The filtrate was methylated with methylmagnesium chloride. The product, 87.6 g, had the following composition: ethyltrimethylsilane (6%), hexamethyldisiloxane (4%), 1,2-bis(trimethylsilyl)ethane (7%), bis(trimethylsilylmethyl)mercury (63%) and non-identified compounds (20%). Ethyltrimethylsilane, hexamethyldisiloxane and 1,2-bis(trimethylsilyl)ethane were identified by their elution volumes. Bis(trimethylsilylmethyl)mercury boiled at 63.5–64°C at 1.6 Torr and had n_D^{20} 1.4878 (found: 25.55% C, 5.74% H, 53.07% Hg; calculated: 25.61% C, 5.92% H, 53.51% Hg). The sample for analysis was purified by percolation through a column of alumina, activity I. To prove the identity of bis(trimethylsilylmethyl)mercury an authentic sample was prepared by the reaction of chloromagnesiummethyltrimethylsilane with mercuric chloride¹⁴. Both substances had identical infrared spectra. The conversion of dimethylmercury into ethyltrichlorosilane, 1,2-bis(trichlorosilyl)ethane and bis(trichlorosilylmethyl)mercury was 15.8%.

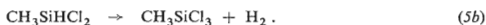
Pyrolysis of dimethyldichlorosilane. The reactor was fed at a rate of 38.5 g/h with a mixture of dimethyldichlorosilane (2340 g, 18.2 mol) and dimethylmercury (250 g, 1.08 mol). There was obtained 96.2 g of a higher-boiling liquid, from which 1.4 g of methylmercuric chloride was removed by filtration. Methylation of the filtrate afforded 67.4 g of a mixture composed of trimethylsilylsilane (5%), hexamethyldisiloxane (3%), 1,2-bis(trimethylsilyl)ethane (10%), bis(trimethylsilylmethyl)mercury (67%) and non-identified substances (15%). The identification tests were the same as with the methylated compounds obtained by pyrolysis of dimethylmercury and methyltrichlorosilane. The conversion of dimethylmercury into methylethyldichlorosilane, 1,2-bis(methyldichlorosilyl)ethane and bis(methyldichlorosilylmethyl)mercury was 17.8%. The composition of the gas from pyrolysis of methyltrichlorosilane and dimethylmercury, not condensing at –78°C, was determined chromatographically: 96% CH₄, 3.6% H and 0.4% C₂H₆.

DISCUSSION

To study the reaction of free methyl radicals with chlorosilanes three types of chlorosilane have been selected: 1) trichlorosilane, in which only the Si—H bond can react; 2) methyltrichlorosilane and dimethyldichlorosilane, where the only reactive bond is C—H; 3) methyldichlorosilane, which contains both these bonds. Analysis of the reaction mixtures gave some idea on the course of the reactions. Pyrolysis of dimethylmercury yields methyl radicals, which abstract hydrogen from the bond Si—H or C—H in the molecule of chlorosilane. There is formed methane and a more complex radical, which combines either with another radical of the same kind or with a methyl radical. The reactions can be expressed by the equations:



The Si—H bond has proved to be much more sensitive to the action of a methyl radical than the bond C—H, which finding accords with the papers of Kerr, Slater and Young^{9,10}. These authors measured the activation energies of the reactions of free methyl radicals with trichlorosilane methyldichlorosilane, obtaining values 8.5 and 7.2 kcal/mol respectively, whereas with methyltrichlorosilane and dimethyldichlorosilane they determined values 11.5 and 11.6 kcal/mol. This difference was expressed in our experiments by the fact that 60% of dimethylmercury was converted to the reaction of methyl radicals with Si—H bonds in the case of methyldichlorosilane and trichlorosilane, whereas only 15 to 18% to the reaction with C—H bonds in methyltrichlorosilane and dimethyldichlorosilane. The expected free-radical reactions were found to be accompanied by chlorination of the Si—H bond, trichlorosilane and methyldichlorosilane yielding tetrachlorosilane and methyltrichlorosilane, respectively:

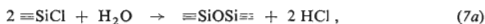


These reactions occur to a small extent even in the absence dimethylmercury. Why the formation of tetrachlorosilane from trichlorosilane increases eight times in the presence of dimethylmercury is not quite clear. A catalytic effect of mercury vapour may be the cause.

A striking observation was the formation of organomercuric compounds in the pyrolysis of methyltrichlorosilane and dimethyldichlorosilane with dimethylmercury. The formed bis(trichlorosilylmethyl)mercury and bis(dichloromethylsilylmethyl)mercury were isolated after replacement of the chlorine atoms on silicon by methyl groups, *i.e.* in the form of bis(trimethylsilylmethyl)mercury. These reactions can be expressed by the equations:



The formation of hexamethyldisiloxane and methylmercuric chloride is probably due to the moisture in the apparatus:



Apart from the organomercurials, the compounds formed by the reaction of free methyl radicals with chlorosilanes were also isolated from the higher-boiling fractions after removing methylchlorosilanes. In respect to this fact our results are not at variance with the free radical theory of the direct synthesis of methylchlorosilanes. Inconsistent with this theory is the high reactivity of the Si—H bond to free methyl radicals. This high reactivity would exclude the possibility of trichlorosilane and methyldichlorosilane formation in the direct synthesis of methylchlorosilanes. This circumstance is especially significant in the direct synthesis of ethylchlorosilanes, where the yield of ethyldichlorosilane was reported¹⁵ to be as high as 30%. Proportion of the products from the reaction of free methyl radicals with chlorosilanes, compared with that of the compounds isolated by Čermák and Franc¹¹ from the higher-boiling fractions in the direct synthesis of methylchlorosilanes, reveals one essential difference. The cited authors report that the higher-boiling products of the direct synthesis of methylchlorosilanes contained 10 to 35% of compounds $\equiv\text{SiCH}_2\text{Si}\equiv$, which, consequently, was the predominant type in the fraction. In our experiments no compound of this type was detected in the reaction products of free methyl radicals with chlorosilanes. From this fact we assume that the compounds contained in the higher-boiling products of the direct synthesis of methylchloro-

silanes are formed by a mechanism different from that operative in the reaction of free methyl radicals with chlorosilanes. On the basis of these and earlier⁶ results, as well as the data reported by other authors^{4,5,7}, we believe that direct synthesis of methylchlorosilanes is a heterogeneously catalysed reaction, possibly accompanied, to a small extent, by the reaction with a free-radical mechanism.

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