

## PREPARATION OF DIPHENYLALKOXYCHLOROSILANES AND DIPHENYLDIALKOXYSILANES

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Received January 30th, 1975

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Formation of diphenylmethoxychlorosilane and diphenylethoxychlorosilane by reaction of diphenyldichlorosilane with the corresponding alcohols was examined. In the presence of pyridine the reaction produces exclusively diphenyldialkoxysilanes.

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Previous works of this series concerned with synthesis of *p*-bis(diphenylalkoxysilyl)benzenes<sup>1,2</sup>, *p*-chlorophenyldiphenylalkoxysilanes<sup>3</sup>, (phenoxyphenyl)diphenylalkoxysilanes<sup>4</sup> and some bis-(diphenylalkoxysilyl)-substituted biphenyl and diphenyl ether derivatives<sup>5</sup> by Grignard reaction of corresponding dihalogenoarenes with diphenylethoxychlorosilane or diphenylmethoxychlorosilane. Some of these reactions gave nearly 90% yields. Little attention has so far been, however, paid to these very reactive compounds. Its reliable synthesis has not yet been reported.

Breed and Elliot<sup>6</sup> have described preparation of diphenylethoxychlorosilane by reaction of diphenyldichlorosilane with ethanol in the presence of pyridine. When repeating this reaction we have found by gas chromatography that instead of the required diphenylethoxychlorosilane a mixture of the unreacted diphenyldichlorosilane and diphenyldiethoxysilane is formed under the conditions given. A detailed examination of the course of this reaction showed that the reaction of ethanol with diphenyldichlorosilane in the presence of pyridine produces the corresponding diethoxy derivative as a sole product, irrespective of the reaction temperature (experiments were carried out at 20°C, 0°C and -80°C). We were not able to prove the presence of diphenylethoxychlorosilane in the reaction mixture. In contrast to this, in the absence of pyridine and if ethanol is slowly added to diphenyldichlorosilane, diphenylethoxychlorosilane is not only formed but it can be isolated in good yields from the reaction mixture by distillation. The distillate contains diphenyldichlorosilane and diphenyldiethoxysilane as further components. The product cannot be freed of these components by distillation, owing to their very similar boiling points. Their presence was not prejudicial to further application of the product in our case. On heating a mixture of alkylchlorosilane with alkylalkoxysilanes, the compounds disproportionate to give corresponding alkylalkoxychlorosilanes<sup>7</sup>; one can expect that this reaction proceeds to a small extent also with the corresponding diphenyl derivatives.

Further addition of ethanol leads to proportional formation of diphenyldiethoxysilane which can be obtained in a yield of max. 95%. The higher yields cannot be achieved either by heating or by the excess alcohol. We found that the addition of a small amount of pyridine to this reaction mixture increases immediately conversion of the reaction to 100%. In order to obtain the pure diethoxy derivative, the presence of equivalent amount of pyridine (which acts as an acceptor of the hydrogen chloride formed) is not therefore prerequisite; the addition of pyridine in small amounts towards the end of the reaction is quite sufficient.

The reaction of diphenyldichlorosilane with methanol proceeds in a similar way (Fig. 1). The addition of 1 mol of methanol leads to formation of a mixture consisting of 87% diphenylmethoxychlorosilane, 8.6% of the unreacted chlorosilane, and 4.4% of the dimethoxy derivative. Further addition of methanol results in proportional increase the amount of the diphenyldimethoxysilane formed. Also in this case the esterification is not quantitative, and the pure dimethoxy derivative is obtained only after pyridine is added to the reaction mixture towards the end of the reaction. When compared to the procedures using pyridine as an acceptor of all the hydrogen chloride formed, the method described in this work is advantageous in that the required alkoxy derivatives are obtained in the higher yields and that pyridine is used in the substantially smaller amounts.

## EXPERIMENTAL

Composition of the final reaction mixtures and the purity of the compounds were determined on a gas chromatograph equipped with a thermal conductivity detector (Vývojové dílny ČSAV, Prague). The 3 m-column was filled with 16 or 22% poly(trifluoropropylmethylsiloxane) on Chromosorb W and nitrogen or hydrogen were used as a carrier gas.

*Reaction of diphenyldichlorosilane with ethanol in the presence of pyridine.* A solution of 23.04 g (0.5 mol) of absolute ethanol and 39.56 g (0.5 mol) of pyridine was added to a solution of 50.64 g (0.5 mol) of diphenyldichlorosilane in 250 ml of light petroleum ether with stirring and external cooling with ice. As found by gas chromatography, the reaction mixture contained diphenyldiethoxysilane and the unreacted diphenyldichlorosilane in approx. 1:1 molar ratio. Similar results were also obtained at  $-80^{\circ}\text{C}$  and  $20^{\circ}\text{C}$ .

*Preparation of diphenylethoxychlorosilane.* A mixture of 241.5 g (5.25 mol) of absolute ethanol and the same volume of light petroleum was added under stirring during 4.5 h to 1266 g (5 mol) of diphenyldichlorosilane. The alcohol solution was introduced below the level of the reaction mixture. The reaction was carried out under nitrogen. A distillation gave the following fractions: b.p.  $119-120^{\circ}\text{C}/1.5$  Torr, 32.55 g, 12.1% diphenyldiethoxysilane; b.p.  $120-125^{\circ}\text{C}/1.5$  Torr, 1160.2 g, 11.5% the diethoxy derivative; b.p.  $125^{\circ}\text{C}/1.5$  Torr, 125.0 g, 9.35% diphenyldiethoxysilane. The unreacted diphenyldichlorosilane and the diphenylethoxychlorosilane formed were determined jointly by gas chromatographic analysis, since they had identical retention times.

*Preparation of diphenyldiethoxysilane.* A total of 50.6 g (1.1 mol) of absolute ethanol were added during 40 min to 126.6 g (0.5 mol) of diphenyldichlorosilane under nitrogen, while stirring the mixture and cooling it externally with ice. The two layers formed, the upper containing 65%

of diphenyldiethoxysilane and the lower one 45% of this compound. Then, 4.6 g (0.1 mol) of ethanol were added and the reaction mixture was heated at 80°C. The content of the diethoxy derivative after 60, 100, and 150 min heating was respectively 75.0, 87.5, and 90%. Then, another 20 ml of ethanol were added. After 20, 60, 180, and 320 min heating at 80°C the mixture contained respectively 94.0, 94.0, 94.6, and 95.0% of the diethoxy derivative. After addition of 5 g of pyridine, the content of the diethoxy derivative increased to 100%. The reaction mixture was washed with water and the product was dried over sodium sulphate. The yields of the undistilled derivative were nearly quantitative.

Diphenyldiethoxysilane has so far been reported to be prepared by reaction of diphenyldichlorosilane with ethanol under normal pressure<sup>8,9</sup> (the product was contaminated with little chlorine<sup>8</sup>) and reduced pressure<sup>10,11</sup> (the yields 86.2 and 86%, respectively), and further in the presence of pyridine which was used as an acceptor of all the hydrogen chloride formed<sup>12,13</sup> (the yields 54 and 84.8%). On repeating the reported procedure<sup>13</sup>, the pure product was obtained in 59.5% yield.

*Reaction of diphenyldichlorosilane with methanol.* Diphenyldichlorosilane (126.6 g, 0.5 mol) was placed into a three-necked flask equipped with a stirrer and a nitrogen inlet and then a solution of 32.0 g (1 mol) of absolute methanol in 100 ml of light petroleum was added dropwise from the burette under stirring. At fixed time intervals the samples of the reaction mixture were withdrawn and analysed by gas chromatography. After the addition was completed, 3.2 g (0.1 mol) of methanol were added and the mixture was refluxed for 30 min. After removal of the sample, another 3.2 g of the alcohol and 2 ml of pyridine were added, and the mixture was refluxed for 15 min. The addition of 0.6, 0.9, 1.0, 1.15, 1.55, 2.0, 2.2, and 2.4 mol of methanol gave the following results (calculated per 1 mol of the starting diphenyldichlorosilane): the mixtures contained respectively 48, 17.1, 8.6, 4.1, 1.7, 0, 0, and 0% of diphenyldichlorosilane, 52, 81.0, 87.7, 83.7, 65.4, 32.2, 5.6, and 0% of diphenylmethoxychlorosilane and 0, 1.9, 4.4, 12.2, 32.9, 67.8, 94.4, and 100% of diphenyldimethoxysilane. The literature<sup>14,15</sup> reports on the use of diphenylmethoxychlorosilane, without mentioning the method used for its preparation. When calibrating the chromatograms, we have found that on injecting a mixture of the pure diphenyldichlorosilane and diphenyldimethoxysilane (1:1), the chromatogram shows 48.9% of the dimethoxy derivative 48.9% of the dichlorosilane, and 2.2% of the diphenylmethoxychlorosilane formed by disproportionation<sup>7</sup>.

*Diphenylmethoxychlorosilane.* A reaction flask was charged with 189.9 g (0.75 mol) of diphenyldichlorosilane and then a solution of 25.2 g (0.786 mol) of absolute methanol in 70 ml

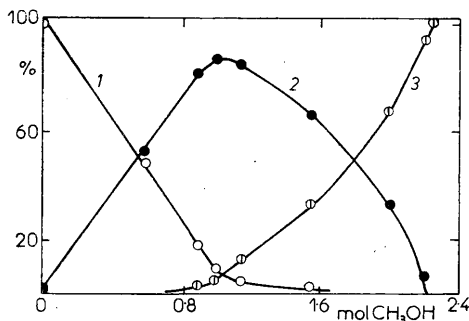


FIG. 1  
The Course of the Reaction of 1 mol of Diphenyldichlorosilane with Methanol  
1 Diphenyldichlorosilane, 2 diphenylmethoxychlorosilane, 3 diphenyldimethoxysilane.

of light petroleum was added during 40 min under stirring the reaction mixture and simultaneous passing nitrogen through it. After the addition was completed, the mixture was allowed to stir for another 15 min and then distilled; first, the light petroleum was removed by distillation under a pressure of a water pump and then the product was distilled under vacuum of an oil vacuum pump to give 182.0 of the silane, b.p. 94–97°C/0.3 Torr.

*Diphenyldimethoxysilane.* Absolute methanol (192.3 g, 6 mol) was added dropwise during 4 h under nitrogen to 506.4 g (2 mol) of diphenyldichlorosilane. As the reaction mixture still contained diphenylmethoxychlorosilane, 60 ml of pyridine were added in three portions. The reaction mixture was diluted with light petroleum and decomposed by ice water. A distillation of the organic layer gave the pure product in 95% yield. When a solution of 126.5 g (0.5 mol) of diphenyldichlorosilane in 300 ml of benzene was added to a mixture of 33.6 g (1.05 mol) of methanol and 82.9 g (1.05 mol) of pyridine, filtering-off the pyridine hydrochloride and its washing with light petroleum, followed by distillation, afforded 106.4 g (87%) of the dimethoxysilane, b.p. 150°C/10 Torr.

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Translated by J. Hetflejš.