

CCCLXIV.—*Organic Derivatives of Silicon. Part XXXV. The Preparation of Diphenylsilicon Dichloride: "Grignard" Ether and its Action on Silicon Tetrachloride.*

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THE analysis of the first sample of diphenylsilicon dichloride gave 28.0% of chlorine (Calc. for SiPh_2Cl_2 : Cl, 27.9%).* Large quantities of this compound were used later for the preparation of diphenylsilicanediol, and during a very careful examination of the latter and of its condensation products (J., 1912, **101**, 2108, 2125) there was no indication of unknown impurity in the dichloride. When, however, it was discovered that the product (E) contained phenoxy-compounds (this vol., p. 2720), several samples of the dichloride were examined and found to contain only 23—24% of chlorine; † they also gave 3—4% of phenol on hydrolysis.

The preparation of the magnesium phenyl bromide used in making the silicon compound was then carried out in an atmosphere of nitrogen (compare this vol., p. 2728), as was also, later on, the actual preparation of the dichloride; the samples thus obtained (b. p. 223—224° or 224—225°/100 mm.) gave inappreciable quantities of phenol, but still contained only 25.5—26% of chlorine, a proportion which could not be altered by further fractionation under various pressures. The silicon percentages in such samples agreed very closely with that required for SiPh_2Cl_2 , an indication that the

* J., 1912, **101**, 2114. The sample was prepared and purified by one of us (F. S. K.), but was analysed under direction by a senior student, ignorant of the nature of the substance.

† The purchased samples were invoiced as having a purity of 80–90%.

impurity might be $\text{SiPh}_2(\text{OEt})_2$ or $\text{SiPh}_2(\text{OEt})\text{Cl}$, formed from traces of alcohol in the large volume of ether used in their preparation; but no matter how thoroughly the Grignard ether was freed from alcohol, the purity of the dichloride could not be increased and all samples gave alcohol on hydrolysis.

The behaviour of silicon tetrachloride towards ether was then studied (the tetraiodide is known to react; Friedel, *Ber.*, 1872, 5, 27) and it was found that even at the ordinary temperature a slight action occurs, probably as follows: $\text{SiCl}_4 + \text{Et}_2\text{O} = \text{SiCl}_3\cdot\text{OEt} + \text{EtCl}$. The difficulty of preparing pure diphenylsilicon dichloride is therefore almost certainly due to the formation of ethoxydiphenylsilicyl chloride, which cannot be separated by distillation (p. 2736).

As a solution of magnesium phenyl bromide could not be obtained without the use of ether, the method of preparation of the dichloride was modified so as to limit the interaction of the ether and the tetrachloride. The results were fairly satisfactory, but the product still contained a small proportion of some ethoxy-compound.

The fact that ether reacts with silicon tetrachloride probably accounts for previous difficulties in preparing various organic derivatives of silicon. Thus from the product of the interaction of magnesium ethyl bromide and the tetrachloride, it may not be hard to obtain ethylsilicon trichloride, but the isolation of the di- and the tri-ethyl derivatives by fractional distillation is a very troublesome task (J., 1909, 95, 311); the difficulty of preparing a pure sample of phenylethylsilicon dichloride (J., 1907, 91, 217) is also possibly due to the contamination of the product with ethoxyphenylethylsilicyl chloride. In the case of a crystalline product, the formation of some ethoxy-compound would not matter so much, as the impurity would doubtless remain in the mother-liquor; this has been proved to be so in the case of dibenzylsilicon dichloride, since the liquid fractions from the crude preparation give ethyl alcohol on hydrolysis.

EXPERIMENTAL.

For the detection of phenoxy- and ethoxy-groups in an ordinary sample of diphenylsilicon dichloride, the latter is dropped into excess of a 5% solution of sodium hydroxide, and a small proportion of the liquid is then distilled and tested for alcohol; the residue is acidified and again distilled and the distillate is treated with bromine water. Samples of the dichloride prepared by the method described later do not give a recognisable quantity of tribromophenol.

Interaction of Ether and Silicon Tetrachloride.—Very carefully

purified ether was heated under reflux during about 4 hours with an equal volume of silicon tetrachloride; about one-half of the liquid was then distilled and the residue was treated with an excess of sodium hydroxide solution and again distilled; the first small portion of the aqueous distillate gave a distinct but very slight iodoform reaction. By heating the recovered ether (20 c.c.) with about 5% of silicon tetrachloride in a sealed tube during about 8 hours at 100° and then proceeding as before, about four times as much iodoform was obtained, but even under these conditions the quantity was only about 5 mg. The interaction also occurs at the ordinary temperature; after 30 c.c. of ether had been left with about 5 c.c. of silicon tetrachloride during 3 days and most of the ether then distilled off, the residue, on hydrolysis, gave enough alcohol to afford a very slight precipitate of iodoform, and the ether which had been distilled from the mixture, treated again with the tetrachloride, gave a further quantity of the product which yielded alcohol; these processes were repeated four times, with the ether recovered from each previous treatment, and iodoform was obtained, apparently in much the same quantity, after each set of operations.* As the precipitate of iodoform was not appreciably larger than usual when the mixture had been kept during several weeks, it would seem that the reaction is reversible.

Diethoxydiphenylsilicane, $\text{SiPh}_2(\text{OEt})_2$, was prepared in order to compare its boiling point with that of diphenylsilicon dichloride. Carefully dehydrated alcohol, in slight excess, was added to the dichloride; only a feeble evolution of hydrogen chloride occurred and two layers were formed, but after having been heated under reflux during 6—8 hours the liquid became homogeneous and was then distilled (100 mm.). The product still contained a little chlorine, and was therefore heated again with a small proportion of alcohol and then fractionated; practically the whole passed over at 217—218°, and a considerable quantity of the preparation gave only an insignificant reaction with an aqueous solution of silver nitrate [Found: Si, 10.4. $\text{SiPh}_2(\text{OEt})_2$ requires Si, 10.4%]. The b. p. of the diethoxy-compound differs only very little from that of the dichloride,

$\text{SiPh}_2(\text{OEt})_2$	197—198°/50 mm.	217—218°/100 mm.	302—304°/767 mm.
SiPh_2Cl_2	199—202°/50 mm.	222—224°/100 mm.	302—305°/757 mm.

* A blank experiment in which ether alone was heated under reflux with a solution of sodium hydroxide during 4 hours, and the alkaline solution was then tested for alcohol, gave a negative result and did not confirm the statement in Allen's "Commercial Organic Analysis" (vol. I, p. 179) that ether kept in presence of moisture generates traces of alcohol.

and it may therefore be deduced that that of the ethoxy-chloride, $\text{SiPh}_2\text{Cl}\cdot\text{OEt}$, would differ even less, so that its separation from the dichloride by distillation would be impossible.

Diethoxydiphenylsilicane is specifically heavier than water and is miscible with the common solvents; it seems to be unchanged when it is left during some hours with a 5% solution of potassium hydroxide, but it is quickly hydrolysed by an alcoholic solution and when only a little alkali is present trihydrotris(diphenylsilicanediol) may separate in crystals; it is also slowly hydrolysed by dilute sulphuric acid. It appears to be unchanged by sodium at 100° .

Preparation of Diphenylsilicon Dichloride.—Silicon tetrachloride (170 g.), diluted with benzene (3 vols.), is placed in a bulb provided with three tubulures, which is fitted with a stirrer and a reflux condenser and is connected through a dropping-funnel with the apparatus for the preparation of magnesium phenyl bromide ($2\frac{1}{2}$ mols.). The air in the whole apparatus is displaced with dry nitrogen and the Grignard reagent is then prepared at 0° , the minimum quantity of ether being used. When about one-half of the magnesium has been dissolved, the ethereal solution is drawn into the exhausted dropping-funnel and is then slowly added to the well-cooled and stirred tetrachloride while the remainder of the Grignard reagent is being made. This portion is then drawn into the funnel as before and added to the tetrachloride, so that at no stage is there any possibility of oxidation. After the product has been stirred during a further period of about 30 minutes, as much ether as possible is distilled off on a water-bath, the operation lasting about 3 hours. More benzene (2 vols.) is then added and the magnesium salts are separated in the usual apparatus (J., 1907, 91, 216) and well washed with benzene. The combined filtrate and washings give on evaporation such a small deposit of magnesium salt that a second filtration is unnecessary (J., 1912, 101, 2114) and the product can be directly fractionated. Samples thus obtained contain 27.2—27.3% of chlorine.

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