

CXXVIII.—*Organic Derivatives of Silicon. Part XLIII. The Formation of Tri- and Tetra-phenylsilicane by the Action of Sodium on Triphenylsilyl Chloride.*

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THE action of sodium on phenylsilicon trichloride in boiling xylene solution in an atmosphere of nitrogen results in the production of a very complex mixture, the soluble components of which contain from 6 to 50 atoms of silicon in their molecules; some of these components, submitted to fission with alkalis, give diphenylsilicanediol and therefore contain $>\text{SiPh}_2$ groups (Kipping, Murray, and Maltby, J., 1929, 1180). In the absence of a solvent in the presence of dry air the trichloride is almost entirely converted at about 180° into a product which is insoluble in all ordinary solvents; but in the absence of air the reaction seemed to proceed differently (*loc. cit.*, footnote, p. 1184).

In the course of further experiments in which the trichloride was heated with the metal in a stream of pure nitrogen, tri- and tetraphenylsilicane were obtained.

The formation of the last-named compound is probably due to the prior production of sodium phenyl, which then reacts with the unchanged trichloride; the same suggestion was made to account for the presence of $>\text{SiPh}_2$ groups in some of the compounds obtained in xylene solution (*loc. cit.*, p. 1183). The related observations on the formation of tri- and tetra-benzyl derivatives from dibenzylsilicon dichloride and sodium (Steele and Kipping, J., 1928, 1431) seem to show that aryl groups generally, directly combined with silicon, may give sodium aryl compounds; the alternative view that aryl chloride separates and then reacts with the unchanged silicon halide in the presence of sodium seems to be less probable; but, however produced, the unexpected formation of tetraphenylsilicane in this and other reactions (Kipping and Murray, J., 1929, 360) affords an interesting contrast to the non-formation of tetraphenylmethane under conditions which might be expected to give it.

The production of triphenylsilicane from the trichloride is difficult to explain. It was at first thought that the hydrogen in this compound might be derived from sodium hydride, which is present in the metal in very small proportion; but when the trichloride is heated at its boiling point with sodium hydride in the absence of air during many hours there is no sign of any reaction. As it also seems impossible that the hydrogen can be derived from any phenyl-

ethoxysilicon dichloride present in the purified trichloride (J., 1929, 1184), it is necessary to assume that it is formed from phenyl groups by changes such as $2 >SiPh_2 \longrightarrow >SiPh \cdot C_6H_4 \cdot SiPh_2 + H$. This assumption was made in order to account for the production of triphenylsilicane from octaphenylcyclosilicotetrane (Kipping and Murray, *loc. cit.*) and considering the high temperature at which that change occurred it seemed to be a reasonable one; there was also some collateral evidence of the presence of phenylene groups in some of the products. In the experiments with the trichloride the temperature hardly exceeds 200° , unless locally, and such an explanation of the origin of the hydrogen is less probable, but there seems to be no alternative.

The yields of the tri- and tetra-phenyl derivatives cannot be given exactly; they both seem, however, to be less than 3% of the weight of the chloride.

EXPERIMENTAL.

To freshly distilled phenylsilicon trichloride (10—15 g.) contained in a 400 c.c. flask, large clean blocks of sodium ($4-4\frac{1}{2}$ atoms) are added and a stream of oxygen-free nitrogen, dried finally with phosphoric oxide and sodium wire, is passed through the apparatus, which is provided with an upright quill-tube air-condenser about 30" long. The escaping gas is led through two wash-bottles containing benzene (or xylene) and after passing a mercury seal is bubbled through water. When all the air has been expelled, the flask is heated in an oil-bath and the nitrogen stream is reduced to about 1 bubble per second. Just below the boiling point of the trichloride the bright metal becomes coated with a brown crust and appears to increase considerably in volume. Gentle agitation releases the molten metal, which then becomes encrusted as before, and in the course of an hour or so a film of oil is usually visible in the condenser; the heating at about 190° is continued until the contents of the flask have become almost solid (about 10—20 hours). In some experiments, in which the temperature was finally raised to about 230° , crystals of tetraphenylsilicane were deposited on the upper portions of the flask and drops of oil, collected from the lower end of the air-condenser, were found to consist almost entirely of triphenylsilicane. If the flask is very vigorously shaken when the reaction has well started and the temperature has risen to about 160° , a great development of heat occurs and the contents of the flask are rapidly transformed into a granular brown solid.

In an experiment in which sublimed sodium hydride was used instead of sodium there was no sign of any reaction and the surface of the hydride was not coated with any crust even when the contents of the flask had been gently boiled during some 8—10 hours.

The oily film which, when sodium was used, coated the whole length of the condenser, and in which six-sided prisms were sometimes detected, was readily soluble in cold acetone, most of the crystalline matter being undissolved; this solution was practically free from chlorine and on evaporation yielded about 0.2 g. of a colourless viscous residue which did not crystallise at 0°. This product had the properties of triphenylsilicane (J., 1929, 364); when treated with aqueous alkali and a little acetone, it was rapidly attacked at the ordinary temperature with the evolution of hydrogen and formation of triphenylsilicol. The latter was fully identified by converting it into triphenylsilicyl oxide and crystallising the product from benzene; the highly characteristic rhomboidal crystals, m. p. 222°, of the oxide, which became opaque at 100°, were obtained. Small additional quantities of crude triphenylsilicane may be extracted from the main product with light petroleum (b. p. 30—40°).

The crystals sparingly soluble in acetone from the air-condenser and those forming a sublimate in the reaction flask were recrystallised from boiling acetone; the product, usually less than 0.1 g., was thus obtained in highly lustrous needles which were proved to be those of tetraphenylsilicane by direct comparison and by mixed melting-point determinations.

The products which were collected in the benzene wash-bottle are still under investigation; it seems that they contain either silicochloroform or silicon dichloride; and the water with which the escaping nitrogen was finally washed contains hydrochloric acid.

The main product of the reaction has not been thoroughly investigated, as it is no doubt a very complex mixture similar to that formed from the trichloride in boiling xylene solution; further, it is very difficult to decompose completely all the silicon halide and after 15—20 hours' heating the mixture still contains halogen compounds soluble in benzene which would make its investigation even more troublesome than that of the halogen-free products previously described. In order, however, to try to ascertain the approximate yield of the tetraphenyl derivative the products soluble in cold benzene were fractionally crystallised from that solvent and then from acetone; most of the fractions thus obtained were glue-like in consistency, but some of the more soluble portions seemed to be partly crystalline and from these after many operations there was isolated about 0.2 g. of crystalline matter. This product melted at 229—230° and gave with pure silicon tetraphenyl a mixture which melted from 230—232°, but it separated from solvents, including acetone, in microscopic nodules, whereas tetraphenylsilicane always crystallises from that solvent in highly lustrous needles; when warmed with acetone and aqueous alkali, it gave a little hydrogen

and therefore contained some linked silicon atoms, but after this impurity had been eliminated almost the whole of the substance was recovered apparently unchanged in crystalline form and in melting point. Since it had been found that tetraphenylsilicane sublimed readily, this nodular material was heated at about 220°; pure tetraphenylsilicane sublimed in lustrous needles, leaving only a very small proportion of gelatinous matter. Several of the more soluble fractions of the main products were treated with acetone and aqueous alkali until the hydrogen evolution ceased and after evaporation of the acetone the insoluble matter was again fractionated, but only very small quantities of tetraphenylsilicane were thus obtained. It seems, therefore, that the total yield of this compound is not very much greater than that of the triphenyl derivative.

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