CLVI.—*Organic Derivatives of Silicon. Part XXXIX. The Action of Sodium on Phenoxychlorosilicanes.*

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A very few silicon compounds of the type SiR_3Cl are known to be converted into derivatives of silicoethane when they are heated with sodium (Kipping, J., 1921, **117**, 647), but diphenylsilicon dichloride, instead of yielding a derivative of silicoethylene, is transformed into closed- and open-chain compounds $(SiPh_2)_n$ in which n is not less than 4 (Kipping and Sands, *ibid.*, p. 830).

In an attempt to obtain some silicoethane derivatives from which silicoglycols might be prepared, the action of sodium on diphenylphenoxysilicon chloride was recently studied (Kipping, J., 1927, 2728); here again, instead of the desired product

$$OPh{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}OPh,$$

octaphenylsilicotetrane and diphenyldiphenoxysilicane were formed, together with a small proportion of octaphenyldiphenoxysilicotetrane and other substances.

It was therefore of interest to study the action of sodium on various phenoxychlorosilicanes and for this purpose the mono-, di-, and tri-phenoxy-chlorides were prepared by treating silicon tetrachloride with phenol; they are all colourless liquids and are readily hydrolysed by water. When they are heated with excess of sodium in boiling xylene solution, they are all slowly attacked, giving a dark bluish-black deposit, and the whole of their chlorine is finally eliminated as sodium chloride. The filtered solution contains in all cases phenyl orthosilicate, $Si(OPh)_4$, the yield of which shows that practically all the phenoxy-groups in the original halogen compound are obtained in the form of the ortho-ester, as, for example,

$$2Si(OPh)_2Cl_2 + 4Na = Si(OPh)_4 + Si + 4NaCl.$$

Now the phenoxy-chloride when heated alone does not undergo any change, so the production of the ortho-ester is not due to interactions such as $2Si(OPh)_2Cl_2 = Si(OPh)_4 + SiCl_4$; it must be concluded, therefore, that the metal attacks some of the halogen compound, forming sodium phenoxide, which then reacts with the remainder to give the ortho-ester.

The insoluble product, freed from sodium and sodium chloride, is in all cases a grey powder, insoluble in all organic solvents. Different preparations from the different phenoxy-chlorides contain 38—40% of silicon; they give hydrogen with an aqueous solution of sodium hydroxide, and the same quantity also when warmed with water, but this quantity varies greatly with different samples from a given phenoxy-chloride. These facts seem to show that the original insoluble material may consist largely of silicon, most of which is converted into silica or silicoformic acid by the action of water during its separation from the sodium and sodium chloride.

EXPERIMENTAL.

Interaction of Phenol and Silicon Tetrachloride.—Phenol ($2\frac{1}{4}$ mols.), dissolved in an approximately equal volume of benzene, is dropped slowly into boiling silicon tetrachloride (1 mol.). Hydrogen chloride is immediately evolved, but the reaction gradually slows down, and after all the phenol has been added the mixture is heated to, and kept at, 200° during 3 to 4 hours. The liquid is distilled (60 mm.) and the following products are collected: I, b. p. 170—195° (about 20%); II, b. p. 195—230° (35—40%); III, b. p. 230—265° (about 35%). The residue (2—5%) solidifies when cooled and consists principally of phenyl orthosilicate.

Phenoxytrichlorosilicane, $Si(OPh)Cl_3$, is isolated by systematically fractionating the crude product (I) through a 12″ rod and disc column. It is a somewhat viscous liquid of high density, b. p. 183—186°/60 mm.; it fumes strongly in moist air, is miscible with most anhydrous solvents, and is readily hydrolysed by water (Found in two different preparations: Cl, 46·6, 46·7. $C_6H_5OCl_3Si$ requires Cl, 46·8%).

Diphenoxydichlorosilicane, $Si(OPh)_2Cl_2$, is obtained by the further fractionation of the crude product (II) in a similar manner. It is a viscous fuming liquid, b. p. 215—218°/60 mm. and 199·5—202°/40 mm., similar in properties to the monophenoxy-derivative (Found in three different preparations: Cl, 24·6, 24·9, 25·0. $C_{12}H_{10}O_2Cl_2Si$ requires Cl, 24·9%).

Triphenoxychlorosilicane, $Si(OPh)_3Cl$, isolated from the fraction (III) in like manner, boils at 252—256°/60 mm. and at 235—239°/25 mm. It is very viscous, miscible with most anhydrous solvents, and fumes only slightly in moist air (Found in two different samples: Cl, 10·3, 10·2. $C_{18}H_{15}O_3ClSi$ requires Cl, 10·3%).

The solid residue from the first distillation crystallises from light petroleum in long colourless prisms, m. p. 48°. It was identified as phenyl orthosilicate by analysis and by its properties.

The above results seem to prove that the three phenoxy-chlorides do not interchange chlorine atoms and phenoxy-groups at the given temperatures; the compounds are also stable at higher temperatures. Samples of the mono- and of the di-chloro-derivative were heated almost to ebullition under atmospheric pressure during about 6 hours and then distilled under 60 mm.; the boiling points of the original samples had undergone no change.

Action of Sodium on Phenoxytrichlorosilicane.—Phenoxytrichlorosilicane (15 g.) is dissolved in pure xylene (3—4 vols.), sodium (5 g.) added, and heat applied. A reaction soon sets in and a bluish-black crust is formed on the metal. The flask is vigorously shaken at intervals and the heating is continued until, at the end of about 15 hours, a few drops of the filtered liquid treated with aqueous acetone give a neutral extract. Hydrogen chloride is evolved during the operation, but apparently the gas is free from any silicon compound.

The solution is filtered in a dry atmosphere, and the black residue washed with dry xylene two or three times; the combined filtrate and washings are then evaporated under reduced pressure. The product is a brown syrup, the weight of which (6·5 g.) corresponds almost exactly with that calculated for $4Si(OPh)Cl_3 + 12Na = Si(OPh)_4 + 12NaCl + 3Si$. When cooled, it solidifies almost completely, and after recrystallisation from light petroleum it melts at 47—48° and does not depress the melting point of phenyl orthosilicate. The oily mother-liquor from the crystalline ortho-ester gives a further crop of this compound when cooled in ice; the oil which then remains seems to be merely phenyl orthosilicate mixed with a very small proportion of some impurity; it is completely hydrolysed by aqueous alkali [Found : Si, 7·3. Calc. for $Si(OPh)_4$: Si, 7·0%].

The almost black residue (see above) is added in small portions at a time to a mixture of alcohol and excess of glacial acetic acid, and the whole is then poured into a large volume of water. The insoluble matter, which rises to the surface of the aqueous solution as a dark grey curdy precipitate, continually gives off bubbles of gas. It is separated, washed with water, alcohol, and ether successively, and dried over sulphuric acid under reduced pressure. The product, light grey in colour, does not lose in weight at 150°, and contains 38·5% of silicon. It is attacked by a solution of sodium hydroxide, but 1 g. gives only 50·1 c.c. of hydrogen at N.T.P.,* a fact which shows that it consists principally of silica. An equal volume of hydrogen is obtained when hot water is used instead of sodium hydroxide solution.

The Action of Sodium on Diphenoxydichlorosilicane.—The diphenoxy-derivative (35·9 g.) is heated with excess of sodium in exactly the same way as the monophenoxy-compound; the products are isolated as already described. The weight of the crude soluble matter is 20 g., which agrees with that calculated for $2Si(OPh)_2Cl_2 + 4Na = Si(OPh)_4 + 4NaCl + Si$, and this product, which crystallises

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* The volume of hydrogen given by 1 g. of silicon, silicoformic acid, and silico-oxalic acid would be 1584, 358, and 183 c.c., respectively.

when cooled, is practically pure phenyl orthosilicate. The insoluble residue contained 38·1% of silicon, and 1 g. gave 139 c.c. of hydrogen with sodium hydroxide solution and 146 c.c. with hot water, so that the proportion of silicon or other hydrogen-giving substance in this preparation was much larger than in the previous insoluble product.

A totally different sample gave Si = 38% and 1 g. gave 89·1 c.c. of hydrogen. A third sample, in the isolation of which care had been taken to keep the alcohol–acid mixture very cold and the contact of the product with water as short as possible, gave a hydrogen value of 209·3; another portion of the same preparation, during the isolation of which the acid–alcohol mixture was allowed to get hot, but which had been kept in contact with water during the same length of time as the first portion, gave a hydrogen value of 177 and contained 37·8% of silicon. The fact that the hydrogen values of different samples containing practically the same percentage of silicon vary from 50·1 c.c. to 209 c.c. seems to show that the hydrogen-giving compound is mainly silicoformic acid.

Two different samples of the insoluble matter were submitted to combustion [Found: (sample I) C, 7·8, 7·7; H, 1·8, 1·8; (sample II) C, 7·7; H, 1·7%]. When heated with alkali, these samples gave quantities of sodium phenoxide corresponding with about one-quarter of the carbon present; this phenoxide was possibly formed from occluded phenyl orthosilicate. The alkaline solutions gave with acids gelatinous precipitates which, when thoroughly washed and dried, charred when warmed with concentrated sulphuric acid and contained 30·6—30·8% of silicon. As the organic matter in these precipitates seems to consist of phenyl groups directly combined with silicon, it may be surmised that the original grey insoluble matter contains some complex condensation product of phenylsiliconic acid and silicic acid.

The Action of Sodium on Triphenoxychlorosilicane.—The procedure was identical with that described in previous cases; 21 g. of the compound gave after 12 hours 16·6 g. of crude phenyl orthosilicate and 0·6 g. of a grey insoluble residue, which contained 39·1% of silicon and had a hydrogen value of 120.

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