CCCLXIII.—*Organic Derivatives of Silicon. Part XXXIV. The Action of Sodium on Phenoxydiphenylsilicyl Chloride.*

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SINCE the product (E) of the action of sodium on diphenylsilicon dichloride may give on hydrolysis appreciable quantities of phenol (this vol., p. 2724), it was inferred that the dichloride, in spite of its constant boiling point, might be contaminated with phenoxyphenylsilicon dichloride, phenoxydiphenylsilicyl chloride, or diphenoxydiphenylsilicane. It is known that atmospheric oxidation may occur during the preparation of magnesium phenyl bromide (Porter and Steel, *J. Amer. Chem. Soc.*, 1920, **42**, 2650) and the resulting Grignard reagent, containing magnesium phenoxy-bromide, might give rise to phenoxy-derivatives if used for the preparation of diphenylsilicon dichloride from silicon tetrachloride.

The action of phenol on diphenylsilicon dichloride was therefore studied, partly in order to observe the boiling points of two of the phenoxy-derivatives just mentioned, but mainly in the hope that by the fractional distillation of the product some other unknown impurity in the dichloride might be isolated and identified.

The results gave no support to the inference that the dichloride formed a constant-boiling mixture with either of these phenoxy-derivatives, and the product—consisting of phenoxydiphenylsilicyl chloride, diphenoxydiphenylsilicane, and unchanged diphenylsilicon dichloride—could be separated into its components by fractional distillation; no fraction representing the long sought-for impurity in the dichloride (compare Kipping and Murray, this vol., p. 2734) was obtained.

The action of sodium on phenoxydiphenylsilicyl chloride was then examined in the hope that symmetrical diphenoxytetraphenylsilicoethane would be produced, just as hexaphenylsilicoethane is formed from triphenylsilicyl chloride (Kipping, P., 1911, **27**, 144); the results were quite unforeseen. The products, isolated with the aid of anhydrous solvents, were octaphenylsilicotetrane,

$$-SiPh_2\cdot SiPh_2\cdot SiPh_2\cdot SiPh_2-$$

(Kipping and Sands, J., 1921, **119**, 830; Kipping, J., 1923, **123**, 2590), diphenoxyoctaphenylsilicotetrane, $PhO\cdot[SiPh_2]_4\cdot OPh$, and diphenoxydiphenylsilicane; from the remaining material, with the use of other solvents not free from water, phenol, diphenylsilicanediol, a considerable proportion of an apparently amorphous solid, which is possibly $PhO\cdot[SiPh_2]_4\cdot OH$, and a very viscous oil, possibly $PhO\cdot SiPh_2\cdot SiPh_2\cdot OPh$, were obtained.

The formation of octaphenylsilicotetrane suggested that the phenoxy-chloride was contaminated with diphenylsilicon dichloride; but in subsequent preparations, using only material which, from its boiling point and from analyses, was the pure phenoxy-derivative, the three products named above were again obtained, apparently in the same yields as before; moreover, that of the silicohydrocarbon seemed to be about as large as if diphenylsilicon dichloride had been used instead of the phenoxy-chloride.

Now the supposed phenoxy-chloride cannot be a mixture of equal quantities of diphenylsilicon dichloride and diphenoxydiphenylsilicane. The product of the action of phenol (1 mol.) on the dichloride is not a liquid of constant boiling point, but distils over a range of about 100°. Further, the phenoxy-chloride is immediately and completely soluble in a cold 5% solution of potassium hydroxide, whereas the diphenoxy-derivative is practically insoluble in, and is only slowly hydrolysed by, such a solution; a prepared solution of the diphenoxy-compound in the dichloride gives crystals of the former when it is added to cold aqueous alkali. Another important fact, which seems to show that the phenoxy-chloride is not converted into a mixture of the dichloride and the diphenoxy-derivative at any stage of the reaction, is that, so far as can be ascertained, the other products of the action of sodium on diphenylsilicon dichloride, namely, octaphenyl*cyclo*silicotetrane (B) and the complex silicohydrocarbons (C) and (D) (Kipping, J., 1924, **125**, 2291), are not formed from the phenoxy-chloride. Finally, the production of diphenoxyoctaphenylsilicotetrane proves that a phenoxy-derivative takes part in the reaction, but apparently diphenoxydiphenylsilicane is not attacked by sodium even at temperatures above 110°.

Although, therefore, it must be concluded that octaphenylsilicotetrane and its diphenoxy-derivative are obtained from the phenoxy-chloride, the mechanism of their formation is obscure. The production of diphenoxydiphenylsilicane seems to prove that at one stage sodium phenoxide is formed, and reacts with unchanged phenoxy-chloride to give the diphenoxy-derivative; this view is confirmed by the fact that sodium phenoxide is present in the blue insoluble residue (p. 2731). It does not seem likely, however, that symmetrical diphenoxytetraphenylsilicoethane is produced and then reacts with sodium to give sodium phenoxide, because, although some ethers are attacked by the metal (Schorigin, *Ber.*, 1926, **59**, 2510), diphenoxydiphenylsilicane and diethoxydiphenylsilicane (Kipping and Murray, this vol., p. 2736) appear to be unacted on. It may be suggested, therefore, that the phenoxy-chloride is decomposed by sodium, giving first $SiPh_2Cl{\cdot}SiPh_2Cl$ and then

$$SiPh_2Cl{\cdot}[SiPh_2]_2{\cdot}SiPh_2Cl,$$

and that a part of the latter is transformed into octaphenylsilicotetrane, whilst some of it reacts with sodium phenoxide to form diphenoxyoctaphenylsilicotetrane. The absence from the reaction product of (B), (C), and (D), however, does not accord with these assumptions, since it would seem to be highly probable that (B) at any rate would also be formed from such dichlorides.

EXPERIMENTAL.

Interaction of Phenol and Diphenylsilicon Dichloride.—Phenol (1 mol.), dissolved in a little benzene, is dropped slowly into diphenylsilicon dichloride * at about 150°, hydrogen chloride being immediately evolved; the liquid is then heated at about 200° until the evolution ceases (about 3 hours). The product deposits crystals of diphenoxydiphenylsilicon when it is kept at 0°, but it is more convenient to separate the latter by distillation (40 mm.). The first fraction (15—20%) is collected at about 200—240°, a large fraction (about 45%) at 250—260°, and a second large fraction at 280—310°, leaving a small residue. The liquid collected from 200—240°, when again treated with about one-half of its weight of phenol, gave further quantities of the two phenoxy-derivatives, but no fraction having the boiling point of diethoxydiphenylsilicane, a possible impurity in the diphenylsilicon dichloride, could be isolated.

Phenoxydiphenylsilicyl chloride, $SiPh_2Cl{\cdot}OPh$, obtained by the further fractionation of the liquid, b. p. about 250—260°, is a thick oil which barely fumes in the air and is miscible with light petroleum and other anhydrous solvents; it boils at 252—254°/40 mm. [Found: Cl, 11·0, 10·9, 11·2, 11·1 (four different preparations);

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* Three samples of the dichloride (b. p. 224—226°/100 mm.) were used, containing 25·2, 24·8, and 25·7% of chlorine, respectively. (Calc. for $SiPh_2Cl_2$: Cl, 27·9%.) Compare Kipping and Murray, *loc. cit.*

Si, 9·0. $C_{18}H_{15}OClSi$ requires Cl, 11·4; Si, 9·1%]. It is immediately and completely soluble in a 5% solution of potassium hydroxide, giving the potassium derivatives of phenol and of diphenylsilicanediol. When left exposed to moist air, it is gradually converted into a solid, smelling strongly of phenol, which after recrystallisation from benzene consists of trianhydrotrisdiphenylsilicanediol.

Diphenoxydiphenylsilicane, $SiPh_2(OPh)_2$, separates in crystals from the fraction collected above 280°, but as it is always mixed with a considerable proportion of the oily phenoxy-chloride the crude product is fractionated again; it then crystallises from light petroleum in massive, colourless prisms and octahedra, m. p. 70—71° (Found: Si, 7·7, 7·8. $C_{24}H_{20}O_2Si$ requires Si, 7·7%). It is very readily soluble in ether, chloroform, benzene, or acetone, but only moderately soluble in cold alcohol. It can be recrystallised from the last-named solvent, but the crystals seem rather sticky and melt at 65—69°, doubtless owing to some very slight hydrolysis having occurred; if attempts are made to recrystallise the impure substance, containing phenoxy-chloride, from alcohol, complete decomposition results, and trianhydrotrisdiphenylsilicanediol may separate. When boiled with water for a short time, the diphenoxy-derivative is not appreciably hydrolysed, owing to its insolubility; it is also relatively stable towards a 5% solution of sodium hydroxide, but it is very readily hydrolysed in presence of acetone or alcohol with separation of trianhydrotrisdiphenylsilicanediol, whilst sodium phenoxide remains in solution. The fact that diphenoxydiphenylsilicane is present in a toluene solution which has been boiled during several hours with excess of sodium, is conclusive evidence of its stability under such conditions, and yet when an apparently pure specimen, recrystallised from light petroleum and melting sharply at 70—71°, is heated with sodium and a little toluene a distinct effervescence occurs and the metal is coated with a white powder. The reaction, however, soon ceases and the rest of the phenoxy-compound is unaltered. It would seem from these observations, repeated several times, that the recrystallised substance contains a small proportion of diphenylsilicanediol or phenoxyhydroxydiphenylsilicane.

Action of Sodium on Phenoxydiphenylsilicyl Chloride.—Freshly distilled phenoxy-chloride is dissolved in dry toluene (about 4 vols.), excess of sodium added, and the whole heated; an exothermic reaction soon sets in and the metal becomes coated with a blue crust similar to that obtained with diphenylsilicon dichloride under the same conditions. After the solution has boiled during 2—3 hours it contains some colourless crystals and seems to be free from phenoxy-chloride when tested with a copper wire. The hot solution is filtered, the blue residue (I) washed with toluene, and the combined filtrate and washings are evaporated under reduced pressure. The almost colourless, oily product, when mixed with a little light petroleum (b. p. 50—60°), gives a crystalline precipitate (II), and the filtered solution, diluted with more petroleum, gives an oily separation (III); the clear petroleum solution, decanted from the oil, gives a further oily deposit (IV) when it is kept at 0°, but even then it contains a considerable quantity of product (V).

Isolation of octaphenylsilicotetrane. The blue residue (I) of sodium, sodium chloride, and sodium phenoxide is added in small portions to alcohol–acetic acid, the solution being kept acid; the insoluble matter, after being well washed with water, consists of almost pure octaphenylsilicotetrane, which was fully identified by a mixed melting-point determination, by its characteristic action with nitrobenzene and with iodine (compare Kipping and Sands, *loc. cit.*), and in other ways. So far as could be ascertained, the silicohydrocarbons (C) and (D) which are formed together with octaphenylsilicotetrane by the action of sodium on diphenylsilicon dichloride are not produced from the phenoxy-chloride; all the organic matter from the blue residue is soluble in boiling benzene, and although the final mother-liquors and the deposits were carefully examined, not a single crystal of (C) could be detected (compare Kipping, J., 1924, **125**, 2294).

Diphenoxyoctaphenylsilicotetrane, $PhO\cdot[SiPh_2]_4\cdot OPh$. The precipitate (II) consists of diphenoxyoctaphenylsilicotetrane and octaphenylsilicotetrane. The former is extracted with boiling benzene, in which it is much the more soluble, and is then recrystallised from boiling chloroform and again from benzene, from which it separates in well-defined, rhomboidal pyramids and in prisms, m. p. 215—216° (Found: Si, 12·3; C, 78·1; H, 5·2; *M*, in camphor, 1083, 1040. $C_{60}H_{50}O_2Si_4$ requires Si, 12·3; C, 78·7; H, 5·5%; *M*, 915). The diphenoxy-compound is decomposed when it is heated with piperidine and a concentrated solution of sodium hydroxide, giving the sodium derivatives of phenol and diphenylsilicanediol, with evolution of hydrogen. [Hydrogen value (compare Kipping and Sands, J., 1921, **119**, 848) found, 69·0, 67·4, 70·5; calc. for $PhO\cdot[SiPh_2]_4\cdot OPh + 10NaOH = 2PhONa + 4SiPh_2(ONa)_2 + 2H_2O + 3H_2$, 73·1].

Diphenoxyoctaphenylsilicotetrane is practically insoluble in ether, acetone, alcohol, and glacial acetic acid, and is far less soluble in cold benzene and chloroform than octaphenyl*cyclo*silicotetrane (B): it is so like the rhomboidal oxide (Kipping and Sands, J., 1921, **119**, 844) in crystalline form, solubilities, and melting point that it might well be mistaken for the latter, but its mixture with the rhomboidal oxide melts at 208—211°. It is very readily soluble in boiling aniline, from which it separates on cooling in small prisms. It seems to be unchanged when it is heated during 1—2 hours with a glacial acetic acid solution of nitric acid, and it is so slowly hydrolysed when it is boiled with an alcoholic solution of hydrochloric acid that after about 20 hours' heating most of the substance remains undissolved and unchanged; the presence of phenol in the resulting pink solution can, however, be proved. The stability of the compound may be attributed to steric hindrance; its formation from the phenoxy-chloride under the above-described conditions is all the more noteworthy in view of the non-production of decaphenylsilicotetrane by the action of magnesium phenyl bromide on octaphenylsilicotetrane di-iodide (Kipping, J., 1923, **123**, 2602).

Other products from the phenoxy-chloride. From the combined oily separations (III) and (IV), by fractional extraction with light petroleum, diphenoxydiphenylsilicane was isolated and then, with the aid of a mixture of acetone and light petroleum, some diphenylsilicanediol, which had no doubt been formed by the hydrolysis of the diphenoxy-derivative during the prolonged fractionation with undried solvents. The mother-liquors from the diol gave on evaporation a glue-like mass, smelling strongly of phenol, which did not crystallise in the course of some weeks; after being washed with water and dissolved in acetone, this glue was precipitated by alcohol as a white curd, very similar in properties to the precipitates of (E_1) obtained in like manner (this vol., p. 2723). This product was redissolved and reprecipitated many times and then repeatedly extracted with warm alcohol, in which it was only very sparingly soluble; the warm glue was then drawn into threads and when cold the brittle mass was powdered and freed from solvent. Two different preparations gave Si, 13·3 and 13·6%, respectively; when hydrolysed with piperidine and sodium hydroxide, they gave hydrogen, sodium phenoxide, and the sodium derivative of diphenylsilicanediol, and the following hydrogen values: 82·7, 80·3, 81·1. These results agree with those required for

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

but the physical properties of the material do not seem to correspond with such a formula; possibly the substance is an oxide, $(PhO{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot})_2O$.

The light petroleum solution of the product (V) gave on evaporation a very thick, colourless oil, which in the course of some months deposited a considerable proportion of diphenoxydiphenylsilicane; this was removed by repeated extraction with warm alcohol. The residue was then completely and readily soluble in cold light petroleum (b. p. 40—50°), from which it separated as an oil. This product contained 10·9% of silicon and is possibly impure symmetrical diphenoxytetraphenylsilicoethane, $PhO\cdot SiPh_2\cdot SiPh_2\cdot OPh$, which requires Si, 10·3%; it gave hydrogen with acetone and sodium hydroxide, and the alkaline solution then contained sodium phenoxide and the sodium derivative of diphenylsilicanediol.

The author wishes to express his indebtedness to Mr. R. Vyle, M.Sc., who rendered very efficient assistance during this work, and to the Government Grant Committee of The Royal Society for funds from which to buy diphenylsilicon dichloride from Boots' Pure Drug Co.

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