XCIII.—*Organic Derivatives of Silicon. Part XXV. Saturated and Unsaturated Silicohydrocarbons,* Si_4Ph_8.

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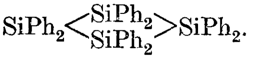
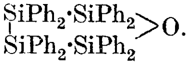
THE reactions which take place when diphenylsilicon dichloride is heated with sodium seem to be very numerous and are altogether unexpected. The halogen-free product is a complex mixture, from which, so far, three well-defined crystalline compounds have been isolated. The combined weights of these form less than 50 per cent. of the whole product and hitherto only two of them have been examined, except very superficially.

These two products are of particular interest because they seem to be isomeric and up to the present no satisfactory explanation of their relationship has suggested itself; even those constitutional formulæ which have been assigned to some of their derivatives must be taken as provisional.

The first product which will be considered is very sparingly soluble in cold benzene and in all the ordinary solvents and does not melt at 300°; it is a silicohydrocarbon, Si_nPh_{2n}, and when first investigated it was believed to be a tetraphenylsilicoethylene, $SiPh_2{:}SiPh_2$, as it combined directly with iodine at the ordinary temperature.*

Quantitative experiments showed, however, that one molecule of the supposed tetraphenylsilicoethylene united with only one atom of iodine. The main, if not the only, product of the reaction was a crystalline iodide of the molecular formula $Si_4Ph_8I_2$. The most probable explanation of the facts now seemed to be that the supposed tetraphenylsilicoethylene was in reality a closed chain compound,  $SiPh_2{<}\genfrac{}{}{0pt}{}{SiPh_2}{SiPh_2}{>}SiPh_2$. The fission of such a closed chain by the action of iodine at the ordinary temperature could not be dismissed as unlikely, because, since this would be the first known example of a molecule containing a closed chain of silicon atoms, there was no precedent which could act as a guide in the matter.

The hydrolysis of the crude iodide gave a mixture of at least four compounds; the principal product was a crystalline substance which, after a very long and careful examination, was thought to be a definite compound of the formula  $\begin{array}{l} SiPh_2\cdot SiPh_2 \\ | \\ SiPh_2\cdot SiPh_2 \end{array}{>}O$. The production of such an oxide from the di-iodide would obviously involve only normal reactions, since it is now known that even silicols of the type $SiR_3\cdot OH$ readily give the oxides $SiR_3\cdot O\cdot SiR_3$. It was not easy to decide from the results of analysis between the formulæ Si_4Ph_8O and $Si_4Ph_8(OH)_2$, but it seemed certain from a determination of its hydrogen value (p. 849) that the compound contained only one atom of oxygen (or two hydroxyl groups) combined with a chain of four directly linked silicon atoms. The fact that the compound decomposed slowly when it was heated at about 230° seemed to be incompatible with the formula Si_4Ph_8O, but otherwise the constitutions of the silicohydrocarbon, the di-iodide, and the oxide seemed to be fairly well established and represented respectively by the formulæ given above.

In the meantime, the examination of another of the crystalline products of the interaction of sodium and diphenylsilicon dichloride had made some progress. This substance differed from the "unsaturated" compound described above in very noteworthy respects. It was very readily soluble in cold benzene, and in various other

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* Schlenk and Renning have described a substance which they represent by the formula $SiPh_2{:}CH_2$ (*Annalen*, 1912, **391**, 221) and which does not react with bromine (or with potassium permanganate in aqueous solution). Their elliptical method of preparation, however, does not inspire confidence, and the nature of their supposed unsaturated compound seems to be very doubtful.

solvents it dissolved freely; it was not acted on by iodine at the ordinary temperature, although it was attacked slowly by bromine, giving apparently a mixture of products. It formed well-defined crystals, and although it did not melt at 360°, its purity seemed to be fully established by microscopic examination. It will be referred to as the saturated silicohydrocarbon.

The results of analyses and cryoscopic experiments in benzene solution agreed with those required for the formula Si_4Ph_8; in other words, the two silicohydrocarbons, which differed so widely in their solubilities and in their chemical properties, appeared to be isomeric.

The existence of isomeric compounds, Si_4Ph_8, could not of course be accepted without further evidence; conceivable alternatives were considered, but all were contrary to the facts. The results of the silicon determinations alone seemed to offer sufficient proof that the two compounds were both silicohydrocarbons, since if either contained only one atom of oxygen to four $>SiPh_2$ groups the percentage of silicon would be 15·2 instead of 15·6. Even more conclusive evidence was afforded by determinations of their hydrogen values, which showed that the molecules of both the compounds contained no oxygen combined with the silicon atoms (compare this vol., p. 849).

If it be granted that the two substances are silicohydrocarbons, Si_nPh_{2n}, and there appears to be no alternative, the next question which arises is what are their molecular formulæ? The cryoscopic results obtained with the readily soluble saturated compound were very concordant and probably trustworthy; moreover, experiments made recently with the fairly complex silicohydrocarbons, diphenyldiethyldipropylsilicoethane, and dibenzyldiethyldipropylsilicoethane (this vol., p. 647) gave values which agreed closely with the calculated molecular weights; apparently therefore the saturated compound is undoubtedly Si_4Ph_8.

The molecular formula of the "unsaturated" silicohydrocarbon seemed to have been fully established by the conversion of this compound into the iodide, $Si_4Ph_8I_2$; but in view of the existence of the supposed isomeride, it was necessary to reconsider this conclusion.

The action of iodine might perhaps be compared with a pinacone condensation or with the change which occurs in the addition of halogen to a conjugated system,

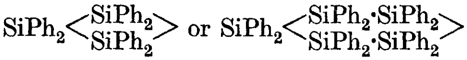
$$SiPh_2{:}SiPh_2{,}SiPh_2{:}SiPh_2 + I_2 \longrightarrow SiPh_2I{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2I;$$

further observations seemed to show, however, that such a view could not be maintained. The "unsaturated" silicohydrocarbon is very rapidly attacked by boiling tetrachloroethane,* giving apparently a dichloride, $Si_4Ph_8Cl_2$, corresponding to the di-iodide described above; at any rate, the product of the reaction is hydrolysed by water, giving the same compound as that obtained by the hydrolysis of the di-iodide, namely, the oxide, Si_4Ph_8O.

The final formation of this oxide seems to dispose of the possibility that the "unsaturated" compound might be after all a tetraphenylsilicoethylene.

At this stage determinations of the molecular weight of the "unsaturated" compound by the ebullioscopic method were made. The values obtained in benzene solution were about 700, which agreed well with the formula Si_4Ph_8, and were practically identical with those obtained by the cryoscopic method in the case of the supposed isomeric saturated compound.

Even if these results are discarded altogether as untrustworthy, it does not seem reasonable to regard the "unsaturated" compound as



$$\mathrm{SiPh_2}{<}\begin{matrix}\mathrm{SiPh_2}\\ \mathrm{SiPh_2}\end{matrix}{>} \text{ or } \mathrm{SiPh_2}{<}\begin{matrix}\mathrm{SiPh_2{\cdot}SiPh_2}\\ \mathrm{SiPh_2{\cdot}SiPh_2}\end{matrix}{>}$$

if the saturated compound is an octaphenyl*cyclo*silicotetrane, owing to the manifold differences between the two compounds.

A final and apparently an uncontrovertible piece of evidence that the "unsaturated" compound is Si_4Ph_8 is afforded by the fact that when the di-iodide, $Si_4Ph_8I_2$, is treated in boiling xylene solution with excess of sodium it is converted, although not quantitatively, into the original "unsaturated" silicohydrocarbon; the formula $SiPh_2{:}SiPh_2$, therefore, is definitely disposed of.

In addition to the important differences between the two silicohydrocarbons which have been already mentioned, there are many others; thus the "unsaturated" compound is very readily acted on by boiling nitrobenzene, whereas the saturated compound crystallises from this solvent almost if not entirely unchanged. One of the products of the action of nitrobenzene on the unsaturated silicohydrocarbon is a crystalline compound of the formula $Si_4Ph_8O_2$. This compound is also present in very small proportions in the crude oxide, Si_4Ph_8O, obtained with the aid of tetrachloroethane and also in the crude product of hydrolysis of the di-iodide. Possibly

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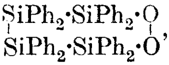
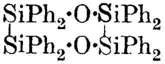
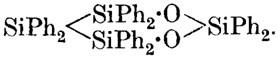
* The surprising readiness with which the silicohydrocarbon is attacked by tetrachloroethane recalls the behaviour of certain hydrides of silicon which are acted on violently by chloroform and by carbon tetrachloride: but it does not seem to be possible that the "unsaturated" compound contains the group $\cdot SiPh_2H$ for many reasons, as, for example, the non-formation of hydrogen iodide during the preparation of the di-iodide and the observed hydrogen value of the silicohydrocarbon.

it is a kind of peroxide,  $\begin{array}{l}SiPh_2{\cdot}SiPh_2{\cdot}O\\ |\qquad\qquad\qquad |\\ SiPh_2{\cdot}SiPh_2{\cdot}O\end{array}$, but so far as it has been examined its behaviour does not support this view, and it seems more probable that its constitution is represented by the formula



$$\begin{array}{l}SiPh_2{\cdot}O{\cdot}SiPh_2\\ |\qquad\quad |\\ SiPh_2{\cdot}O{\cdot}SiPh_2\end{array}$$

or



$$SiPh_2{<}\begin{array}{l}SiPh_2{\cdot}O\\ SiPh_2{\cdot}O\end{array}{>}SiPh_2.$$

Its hydrogen value shows that the molecule contains 1 atom of oxygen to every two $:SiPh_2$ groups.

One of these formulæ, however, is wanted for another compound which has been obtained in small quantities in a great many different ways and which forms well-defined, characteristic, rhomboidal prisms. This substance is produced when the saturated silicohydrocarbon is oxidised with nitric acid, or treated with bromine and the product submitted to hydrolysis; it is also produced when the oxide, Si_4Ph_8O, is oxidised with nitric acid or treated with iodine in presence of moisture. The hydrogen value of this substance seems to prove that the molecule contains one atom of oxygen to every two $:SiPh_2$ groups, and its constitution is therefore probably represented by one of the oxide formulæ just given. The principal interest which is attached to this compound at the present time is that it is a decomposition product of both the silicohydrocarbons, and its formation is therefore some indication that these two compounds are related to one another.

To the question, What is this relationship? the experimental data provide no satisfactory answer.

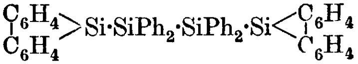
One of the compounds, of course, may be regarded as an octaphenyl*cyclo*silicotetrane, but which? To represent the one as a closed-chain compound containing in its molecule two tervalent silicon atoms, or two quadrivalent silicon atoms with a free bond each, $—SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2{\cdot}SiPh_2—$, would be one way out of the difficulty, but such a suggestion does not commend itself in view of all the facts, and indeed, seems to have little meaning.

The unsaturated compound might conceivably have the constitution $SiPh_3{\cdot}SiPh{:}SiPh{\cdot}SiPh_3$, $SiPh_3{\cdot}SiPh_2{\cdot}SiPh{:}SiPh_2$, or  $\begin{array}{l}SiPh_3\\ SiPh_3\end{array}{>}Si{:}SiPh_2$, but the formation of any one of these compounds from $SiPh_2Cl_2$ would seem to be highly improbable, even assuming the presence in the latter of $SiPh_3Cl$ and $SiPhCl_3$; further, if the " unsaturated " compound had one of these constitutions and the saturated compound was an octaphenyl*cyclo*silicotetrane, the formation of the rhomboidal oxide, $Si_4Ph_8O_2$, from both substances could not be accounted for. Direct experimental evidence against the first two of the three formulæ just given seems to be afforded by the hydrogen values of the two silicohydrocarbons (compare p. 849); even more important is the fact that, so far as can be ascertained, both compounds give on hydrolysis with wet piperidine only diphenylsilicol and its condensation products.

Owing to the readiness with which diphenylsilicol is converted by bases into a mixture of four or more condensation products (Kipping, T., 1912, **101**, 2125) and the difficulty of isolating some of these compounds, it is not possible to affirm that these are the only products of the hydrolysis of the two silicohydrocarbons. It can be stated, however, that the piperidine solutions obtained by decomposing both silicohydrocarbons have been carefully examined for triphenylsilicol, and not a trace of this compound could be found; if it had been present in any appreciable quantity it could scarcely have escaped detection. It seems therefore that all the three formulæ given above must be excluded.

The behaviour towards iodine, the observed hydrogen value, the nature of the products of hydrolysis, and other evidence also exclude from consideration any formula such as

$C_6H_4\colon SiPh\cdot SiPh_2\cdot SiPh_2\cdot SiPh\colon C_6H_4$ or



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>Si\cdot SiPh_2\cdot SiPh_2\cdot Si<\!\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$$

for either of the silicohydrocarbons, or, in fact, any formula other than Si_4Ph_8. It may be, therefore, that both compounds are octaphenyl*cyclo*silicotetranes, but that in the one the four silicon atoms are all in one plane, whilst in the other they form a tetrahedral configuration.

The further investigation of these compounds is in progress and the action of sodium on other silicon dichlorides is also being studied; it is hoped that the results will lead to definite conclusions as to the nature of the two silicohydrocarbons.

EXPERIMENTAL.

Action of Sodium on Diphenylsilicon Dichloride.

A great many experiments have been made on the interaction of these two substances under different conditions, using rather more than the quantity of sodium calculated for the proportion $2Na : SiPh_2Cl_2$.

When the two substances are heated together in the absence of any diluent, a reaction sets in as soon as the sodium begins to melt, and the metallic globules are rapidly coated with a blue crust; if the containing vessel (provided with an air condenser) is then vigorously shaken, a very considerable development of heat takes place, and the interaction seems to be completed almost immediately, with the formation of a brown, granular mass, containing bright globules of the excess of metal.

In order to prevent the sudden rise of temperature which may occur under these conditions, the dichloride was diluted with 3—10 volumes of toluene or xylene. In some experiments small portions of the metal were added to the diluted dichloride at intervals, but as a rule the whole of the sodium was covered with toluene and the diluted dichloride was added to it in small quantities at a time. In either case, the reaction started as soon as the temperature had risen to the melting point of sodium and the globules of metal were gradually transformed into a deep blue powder; the heat generated by the interaction, after each addition of dichloride, was usually sufficient to keep the liquid at its boiling point during some minutes.

Soon after the reaction has commenced, colourless six-sided crystals (substance *A*) begin to separate and gradually increase in quantity, but when the liquid has been boiled during about fifteen minutes (after all the dichloride or sodium has been added) no further change is observed.

The halogen-free, toluene or xylene solution is finally cooled and filtered and the dark blue residue of sodium chloride and unchanged metal is extracted thoroughly with boiling toluene. The extract deposits crystals of the product (*A*) and from the mother-liquors small quantities of another crystalline product (*C*) and a glue-like substance are also obtained. The dark blue powder, treated with a mixture of alcohol and acetic acid, in order to remove the sodium, changes to a pale blue solid, which, on the addition of water, gives a colourless solution; suspended in the latter is a very small proportion of a colourless, flocculent substance (*D*).

The residue which is obtained when the original toluene or xylene filtrate is evaporated is a yellow, glue-like or resinous mass; when treated with cold acetone, most of it (*E*) dissolves very readily, leaving a colourless powder, from which three crystalline compounds have been isolated, namely, the product (*A*), which is only very sparingly soluble in boiling toluene, a compound (*B*) which dissolves very freely in cold toluene, and traces of a substance (*C*) which is even more sparingly soluble than (*A*).

The product (*A*) is referred to as the " unsaturated " silicohydrocarbon; the yield is usually about 1—2 grams from 20 of the dichloride. The product (*B*) is called the saturated silicohydrocarbon; the yield is about the same as that of (*A*). The product (*C*) (yield about 0·1 gram) and the product (*D*) (yield about 0·5 gram) have only been very superficially examined.

The main product of the reaction, namely, the resinous portion (*E*) which is readily soluble in cold acetone, accounts for the remainder of the material. So far the evidence points to the conclusion that this resin is a mixture of saturated complex silicohydrocarbons.

Although the experimental conditions have been varied considerably as indicated above, no definite statement can yet be made as to whether such variations have any influence on the course of the reactions which occur between the metal and the dichloride.

"*Unsaturated*" *Silicohydrocarbon*, Si_4Ph_8.

The crystalline deposit (*A*) mentioned above usually consists for the most part of the "unsaturated" silicohydrocarbon, and it is principally this substance which separates from the boiling toluene solution during the treatment of the dichloride with sodium. The crude preparations invariably contain a small proportion of the much more sparingly soluble compound (*C*), which is removed only with considerable difficulty by fractional crystallisation from toluene or benzene. Since the compound (*A*) does not melt at 300°, conclusions as to its purity had to be based on the results of microscopic examination and on its behaviour towards solvents; there is little doubt, however, that preparations which were regarded as pure did in fact consist of one substance only. Silicon determinations and combustions were made with various samples (Found: Si=15·3, 15·6; C=79·0, 80·0; H=6·0, 5·7. $SiPh_2$ requires Si=15·6; C=79·0 H=5·5 per cent.). The hydrogen value (compare p. 849) agreed very well with this formula.

Cryoscopic determinations were out of the question, owing to the sparing solubility of the compound, but by the ebullioscopic method in benzene solution the values obtained were M=637, 699 (calc. for Si_4Ph_8, M=729·6). These results must only be taken as rough approximations.

The "unsaturated" silicohydrocarbon crystallises from boiling benzene in short, flat, well-defined prisms; when the crystals which have separated from a cold benzene solution are heated in a Bunsen flame on a knife blade, they burn with a series of bright flashes, and when heated on a watch glass over a small flame, they decrepitate so violently that they are scattered all over the glass.

Rough determinations gave about 335° as the melting point of the "unsaturated" silicohydrocarbon, so that it has a lower melting point than hexaphenylsilicoethane, and also than the saturated silicohydrocarbon. The fused substance crystallises when it is cooled, but if it is kept melted for a short time it solidifies to a transparent glue which is readily soluble in cold acetone and benzene.

The " unsaturated " silicohydrocarbon is almost insoluble in most of the common organic solvents at the ordinary temperature, but it is appreciably soluble in benzene and toluene; rough determinations showed that at 15·5°, 100 grams of benzene dissolved 0·21—0·22 gram of the substance and at about 80°, 1·72 grams. It is less readily soluble in benzene than hexaphenylsilicoethane, and the great differences in solubility between this " unsaturated " and the saturated silicohydrocarbon described later (p. 846) are difficult to understand in view of the supposed isomerism of the two compounds.

The " unsaturated " silicohydrocarbon dissolves comparatively easily in boiling aniline, benzyl alcohol, and phenol, but it seems to undergo some decomposition when the solutions are boiled during some time; its behaviour towards boiling tetrachloroethane and nitrobenzene is described later. It is not attacked appreciably by boiling aqueous alkalis, and only slowly by alcoholic solutions of sodium methoxide; on the other hand, it is decomposed by boiling wet piperidine with great rapidity. Aqueous oxidising agents do not seem to act on it except very slowly, doubtless owing entirely to its insolubility.

Action of Iodine on the " Unsaturated " Silicohydrocarbon.

The " unsaturated " silicohydrocarbon dissolved in benzene combines directly with iodine, and even at the ordinary temperature the reaction takes place very rapidly; hydrogen iodide is not evolved in absence of moisture. Owing to the slight solubility of the silicohydrocarbon only enough benzene was used to dissolve a small fraction of the compound, and the iodine was added in small quantities at a time until a permanent coloration was produced. In some of the experiments the solution was warmed at about 60°, merely to hasten the solution of the silicon compound; in others it was warmed only after the colour of the last portion of iodine had disappeared, and cooled again before the addition of more halogen. All the materials were dried and atmospheric moisture was excluded. At first weighed quantities of the two substances in the proportion $I_2:Si_2Ph_4$ were employed, but it was at once obvious that the iodine was in large excess; when the iodine was added much more cautiously, only about one-half of the above proportion of halogen was required to give a permanent coloration to the solution.

As examples of the accuracy with which such titrations can be carried out, the following data may be given : 1·1 grams of substance required 0·36 gram of iodine; 0·38 gram is the theoretical quantity for the equation $2Si_2Ph_4+I_2=Si_4Ph_8I_2$. 1·17 Grams of silicohydrocarbon required 0·397 gram of iodine, the quantity calculated on the same basis being 0·41 gram. The silicohydrocarbon passes into solution in the form of its iodide and the complete disappearance of the sparingly soluble substance should coincide with the production of a permanent coloration. If the silicohydrocarbon has been incompletely purified and contains even a very small proportion of the product (*C*) referred to above, the latter remains undissolved, as it is not acted on by iodine and is almost insoluble in cold benzene.

Octaphenyldi-iodosilicotetrane, $Si_4Ph_8I_2$.

The benzene solution of the preceding iodide, evaporated to dryness under reduced pressure, gave a colourless or pale yellow, crystalline residue, which dissolved freely in warm chloroform; from this solution the iodide was precipitated on the addition of dry ether in colourless crystals, which were rapidly washed well with ether on a filter and then heated for a few minutes at 100° in a dry atmosphere. For analysis, a weighed quantity of the substance was hydrolysed with aqueous acetone containing a small quantity of ammonium hydroxide solution, and the iodide in the aqueous solution was estimated; a silicon estimation was also made with a sample of the pure iodide (Found: I=25·2, 25·7; Si=11·5. $Si_4Ph_8I_2$ requires I=25·8; Si=11·5 per cent.). A molecular weight determination in benzene solution by the cryoscopic method gave M about 900, the calculated value being 983.

Octaphenyldi-iodosilicotetrane turns pink and then yellowish-brown on exposure to light and moist air. It crystallises well from a mixture of ether and benzene in highly lustrous, very acute rhomboidal plates, which do not melt or undergo any visible change even at 250°. It is only very sparingly soluble in cold ether, but dissolves rather freely in cold benzene. When a sufficiently small proportion of benzene is used in preparing the di-iodide, massive crystals of the latter are deposited. Although relatively stable in the solid state, its solutions in benzene and ether soon turn brown on exposure to air and light, and when dissolved in acetone it gives a yellowish-brown solution immediately; even crystals left in the dark in a saturated solution in benzene undergo gradual decomposition.

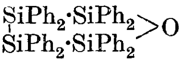
Products of Hydrolysis of the Di-iodide.

For the study of its products of hydrolysis, the crude iodide was treated with an ammoniacal solution of acetone. No particular attention was paid at the time to the duration of this treatment, or to the concentration of the ammonium hydroxide; these factors, however, possibly had an important influence on the nature of the results.

The solid, halogen-free, colourless material thus obtained was usually somewhat pasty at first, but it soon became hard and friable; when roughly dried and extracted with cold acetone, about 10—15 per cent. of some very soluble glue-like matter dissolved. The rest of the material—a crystalline powder, only very sparingly soluble in cold acetone—was submitted to fractional crystallisation from nearly all the common solvents, including mixtures of them in various proportions. The first definite result of such operations was the isolation of a relatively very small quantity of a compound which crystallised in well-defined, rhomboidal prisms, melting sharply at 221—222° (p. 844), and later on a second well-defined by-product was identified in the final mother-liquors (p. 844).

The main product of hydrolysis which then remained crystallised from nearly all solvents in microscopic needles; to the unaided eye, the preparations had that white, opaque appearance which is common to mixtures, but under the microscope they looked quite homogeneous. The melting points of such preparations were most indefinite and irregular; some samples sintered at 205—210° and melted completely at about 220°; others did not sinter until about 220° and melted gradually up to about 245° or occasionally as high as 250—260°. Further, the melted material was rather a jelly than a liquid, and stuck to the sides of the tube; when cooled it did not solidify readily, but slowly gave a white solid which melted at a much lower temperature than the original substance, in some cases below 190°, but not sharply.

The ill-defined melting point of any given sample varied with the rate of heating and with the coarseness of the crystals; a sample, for example, which did not melt at 225° would do so as the temperature slowly fell to 210°, and one and the same sample would melt at 210—220° or at 230—245°, according to the rate at which it was heated. It seemed possible from these observations that the material was a mixture of the oxide and the dihydroxide, or even of these two substances and open-chain condensation products of the latter. Whether it was or was not a pure substance, it was very difficult to say, but the results of analysis seemed to show that it was an octaphenylsilicanetetrane oxide of the constitution



$\begin{matrix}\mathrm{SiPh_2{\cdot}SiPh_2}\\ \mathrm{SiPh_2{\cdot}SiPh_2}\end{matrix}\!>\!\mathrm{O}$ (Found: Si=15·5. Calc., Si=15·2 per cent.). Combustions of the substance were not attempted, as it was so difficult to burn it, even over the blowpipe flame. Cryoscopic determinations in benzene solution gave M 692, 817, and 706 (calc., M=744). Of more importance than these results were those obtained for the hydrogen value of the compound, which seemed to prove conclusively that the molecule contains four $SiPh_2$ groups to one atom of oxygen, or to two hydroxyl groups. The formula $Si_4Ph_8(OH)_2$, which requires Si=14·9 per cent. and a hydrogen value of 88·2 (p. 849), seems to be excluded, because the substance crystallises unchanged from boiling acetic anhydride and does not lose water when it is heated at 220° during ten minutes or so. The readiness with which the di-iodide undergoes hydrolysis seems to show definitely that the two iodine atoms, and therefore the two hydroxyl groups in the primary product of hydrolysis, are directly united to silicon; the constitution of the substance in question seems therefore to be fairly well settled.

Octaphenylsilicotetrane oxide is very sparingly soluble in cold alcohol, acetone, glacial acetic acid, ether, and light petroleum, but it dissolves freely in cold benzene and chloroform. It may be conveniently recrystallised from mixtures of chloroform or benzene and acetone, from which it separates in microscopic needles.

From hot ethyl acetoacetate, nitrobenzene, or aniline, the compound crystallises in a much more satisfactory manner, in long, transparent prisms, which seem to be hexagonal in section and are often aggregated together, forming beautiful, lustrous rosettes. These crystals become opaque when they are warmed with acetone.

The oxide is slowly acted on by an acetone solution of sodium hydroxide with evolution of hydrogen. It is oxidised by nitric acid in glacial acetic acid solution, giving the rhomboidal oxide described later, and it is attacked by hydrogen bromide in acetic acid solution, giving this same compound. It is not acted on appreciably by boiling nitrobenzene or by tetrachloroethane, in which respects it differs markedly from the parent hydrocarbon.

The glue-like substance which is extracted from the products of hydrolysis of the iodide (see above), and which is readily soluble in cold acetone, can be obtained as a colourless powder which does not melt at 250°; it has not been further examined.

Hydrolysis of the Di-iodide with Aniline and Water.

The complex character of the material obtained by hydrolysing the iodide with aqueous ammoniacal acetone was probably due either to the use of excess of iodine in the preparation of the iodide or to some action of ammonia on the original product of hydrolysis.

A much less impure product was obtained by warming the pure iodide with an aqueous alcoholic solution of aniline, or by leaving it in contact with acetone during some hours and then adding a slight excess of sulphurous acid. These preparations, when fractionally crystallised from various solvents, gave deposits which, excluding the most soluble fraction (compare p. 844), seemed to be homogeneous, although they showed the same irregular behaviour as the oxide described above, with which they seemed to be identical; it may therefore be concluded that the normal product of hydrolysis of the di-iodide is that compound of indefinite melting point having the composition Si_4Ph_8O.

Action of Tetrachloroethane on the "Unsaturated" Silicohydrocarbon.

The "unsaturated" silicohydrocarbon dissolves freely in hot tetrachloroethane, and when a sufficiently concentrated solution is immediately cooled again the silicon compound is deposited in ill-defined, microscopic prisms; when, however, such a solution is heated at its boiling point for a minute or two, there is no separation of crystals when the solution is afterwards cooled. Solutions which have boiled during about three to five minutes give, when evaporated under reduced pressure, a colourless residue which is soluble in dry ether; the ethereal solution slowly deposits a small proportion of a crystalline product which melts at about 180° and is probably the dichloride, $Si_4Ph_8Cl_2$. The addition of a little water to the ethereal solution causes the gradual deposition of a colourless product of hydrolysis, and aqueous washings of the solution give an immediate and heavy precipitate on the addition of a solution of silver nitrate. When the product is fractionally crystallised, it gives fractions which, except the most soluble one, seem to be all the same, and identical with the product of hydrolysis of the di-iodide. It has the same highly indefinite melting point as the latter, and the evidence of the identity of the two preparations is that derived from a direct comparison of their crystals as deposited from various solvents; also from observations of the melting points of mixtures heated simultaneously with the separate substances.

Action of Boiling Nitrobenzene on the "Unsaturated" Silicohydrocarbon.

Apparently the relative stability of the "unsaturated" silicohydrocarbon towards aqueous oxidising agents is due entirely to its insolubility, as it is readily attacked by boiling nitrobenzene. When a small quantity of the compound is dissolved in about five times its weight of hot nitrobenzene and the solution is immediately cooled, microscopic prisms, apparently those of the original substance, are deposited; but if the solution is boiled during a minute or so, crystals do not separate from the cooled solution. The reaction occurs with a considerable development of heat, and even when only about 0·5 gram of the substance is used the solution will continue to boil for a few moments without the further external application of heat; the liquid turns dark brown and a faint odour of carbylamine is noticeable.

The addition of 6—8 volumes of alcohol to the cold solution causes the slow deposition of lustrous crystals, but precipitation is very incomplete. The solution is therefore submitted to steam distillation; the distillate has a marked green colour, possibly due to the presence of nitrosobenzene. When all the nitrobenzene has passed over, the water is decanted and the viscous, brown residue is dissolved in boiling acetone; this solution gives first a crystalline deposit and then a brown resin which is freely soluble in cold acetone. The crude crystalline substance is very easily purified. The yield is only poor and barely amounts to 50 per cent. of the material taken; as the product seems to be unchanged by boiling nitrobenzene, it seems likely that the poor yield is due, not to the result of heating the solutions during too long a period (two to ten minutes), but to the simultaneous occurrence of two or more reactions. The by-products have not yet been examined, but judging from their solubility in cold acetone, it seems probable that they consist mainly of condensation products of diphenyl silicanediol.

Analyses of the crystalline substance gave Si=14·7 and 14·8 per cent., and cryoscopic determinations in benzene solution gave M=720. These results agree with those required for a compound $Si_4Ph_8O_2$ (Si=14·9; M=761) or $Si_4Ph_8(OH)_2$ (Si=14·9; M=763), but they are not very different from those required for a compound of the composition Si_4Ph_8O (Si=15·2 per cent.).

A distinction between the formulæ $Si_4Ph_8O_2$ and Si_4Ph_8O is, however, easily arrived at from measurements of the hydrogen value of the compound (p. 849), which show that if the molecule contains four $\colon SiPh_2$ groups, as indicated by the cryoscopic determinations, it also contains two atoms of oxygen directly linked to silicon; as there is no evidence that the molecule contains hydroxyl groups, its constitution may be represented by one of the formulæ already given (p. 833), but it is not easy to decide which.

The compound crystallises from cold acetone containing a little nitrobenzene in massive lustrous forms, which appear to be almost cubes to the unaided eye; from the same mixture it is also deposited in small pyramidal crystals which have a six-sided base, usually somewhat rounded at the opposite obtuse angles; under the microscope, some of these crystals look exactly like a longitudinal section through a thick-walled barrel. Long, highly lustrous prisms, hexagonal in section, are also formed, and from warm acetone the compound separates in slender needles. The crystals become opaque when cold acetone is poured on to them or when they are warmed gently with their mother-liquor; this appears to be due to the very unequal corrosion of the crystal faces. The compound is readily soluble in cold benzene and chloroform, less so in ethyl acetate, rather sparingly in cold acetone and very sparingly in alcohol.

When heated rather quickly, the compound generally melted at about 245—246° fairly sharply, but the temperature depended on the rate of heating, and if the sample were first kept at about 220° during some minutes it then melted at about 235°; the liquefied substance crystallised very readily when it was cooled and then melted at about 190°, but not completely; this second melting point seems to be a constant and fairly definite one, which can be observed over and over again with one and the same sample. These observations indicate dimorphism; further, samples crystallised from a cold mixture of benzene and acetone, if plunged into a bath heated at 220°, immediately melted, then generally solidified again at once and melted for a second time at about 242—245° and for a third time at about 190°, as stated above. This oxide, $Si_4Ph_8O_2$, is present in small proportions in the final, most soluble fractions of the oxide, Si_4Ph_8O, whether the latter has been produced by the hydrolysis of the iodide in various ways (p. 842) or by the action of tetrachloroethane, followed by that of water, on the "unsaturated" silicohydrocarbon. It differs from octaphenylsilicotetrane oxide in one noteworthy respect; although it is oxidised by nitric acid in acetic acid solution, it does not seem to give the rhomboidal oxide described later. It does not behave like a peroxide and does not liberate halogen from a solution of hydrogen iodide in acetic acid.

The Rhomboidal Oxide, $Si_4Ph_8O_2$.

This substance was first observed during the examination of the earlier preparations of the oxide, Si_4Ph_8O (p. 840). It is easily recognised by its appearance under the microscope and it is readily separated from the oxide Si_4Ph_8O, because it is so much less soluble than the latter in chloroform, benzene, and other solvents.

The compound usually separates from ethyl acetate, chloroform, and benzene in rhomboidal crystals, but from these and other solvents it is also deposited in fern-like masses or in well-defined pyramidal crystals, having a rhomboidal base and often a truncated apex. It is apparently dimorphous; when precipitated from a warm benzene solution by the addition of acetone, it sometimes separates in long needles, which form a bulky mass, but if left at the ordinary temperature in contact with their mother-liquor, these bulky needles give place to a compact deposit of the small rhomboidal prisms. The latter often become translucent or opaque when warmed with their mother-liquor, but sometimes remain quite transparent.

The rhomboidal oxide melts sharply at 221—222° to a clear liquid which solidifies immediately when it is cooled and melts again at 221—222°. The formula assigned to this substance is based chiefly on the results of silicon estimations and the hydrogen value; molecular-weight determinations were made by the ebullioscopic method, but very little weight can be attached to the results (Found: $Si=15·1$. Hydrogen value$=59·7$. $M=800—900$. $Si_4Ph_8O_2$ requires $Si=14·9$ per cent. Hydrogen value$=58·3$. $M=761$).

The hydrogen value alone does not exclude the formula $HO·SiPh_2·SiPh_2·OH$ (p. 849), but all the other evidence available points to one of the alternative closed-chain formulæ already given (p. 834). It is obvious that certain objections might be raised to all these formulæ, but it would not be profitable to discuss such matters at the present juncture.

The rhomboidal oxide is apparently isomeric with the compound formed from the " unsaturated " silicohydrocarbon by the action of nitrobenzene; it is certainly much less soluble than the latter in chloroform, benzene, and most other common solvents, but perhaps the difference is not greater than might be expected in the case of isomerides having the suggested relationship; the rhomboidal oxide is very prone to form supersaturated solutions, whereby a false impression of its solubility might be created. The rhomboidal oxide has been obtained, but always in relatively small quantities, both from the saturated and the " unsaturated " silicohydrocarbons. Thus, it is formed when the saturated compound is heated with glacial acetic acid containing a small proportion of nitric acid; also when the saturated silicohydrocarbon is treated with bromine at the ordinary temperature and the product submitted to hydrolysis. It has not been obtained directly from the " unsaturated " silicohydrocarbon, but it is formed when the oxide, Si_4Ph_8O, is cautiously oxidised with nitric acid in glacial acetic acid solution, or very carefully treated with piperidine in acetone solution. It is also produced by the decomposition of the iodide in benzene solution, probably owing to the combined action of atmospheric oxygen and hydrogen iodide.

None of these methods of formation throws much light on the structure of the oxide or on the relationship between the saturated and the " unsaturated " silicohydrocarbons; so far a good method for its preparation has not been elaborated. Except for its decomposition under the influence of aqueous piperidine or methyl-alcoholic solutions of alkali hydroxides, the oxide seems to be relatively very stable; it crystallises unchanged from boiling acetic anhydride and it is only very slowly oxidised by an acetic acid solution of nitric acid.

Saturated Silicohydrocarbon, Si_4Ph_8.

The product (*B*) of the interaction of diphenylsilicon dichloride and sodium (compare p. 836) is easily obtained in a pure state by recrystallisation from ethyl acetate. It does not melt at 400°, but if kept at this temperature during a short time it is changed into a glue-like mass. As it crystallises in short, well-defined, rectangular prisms which are fairly characteristic, its purity could be relied on with practical certainty from its appearance under the microscope. Many different samples were analysed (Found: Si=15·5, 15·6, 15·8, 15·7, 15·8; C=78·3; H=5·6. $SiPh_2$ requires Si=15·6; C=79·0; H=5·5 per cent.). The hydrogen value showed clearly that the substance was a silicohydrocarbon (compare this vol., p. 849) and cryoscopic results in benzene solution gave M=734, 718, 718 (calc. for Si_4Ph_8, M=729·6).

This saturated silicohydrocarbon dissolves very readily in cold benzene; it is also readily soluble in cold chloroform and hot ethyl acetate, but only sparingly in boiling acetic acid and almost insoluble in cold acetone, ether, and ethyl alcohol. Compared with the "unsaturated" silicohydrocarbon, it is a very inert substance. It is not attacked appreciably by iodine in benzene solution at the ordinary temperature, and even bromine acts on it very slowly. It may be repeatedly recrystallised from boiling tetrachloroethane or boiling nitrobenzene without its undergoing any appreciable decomposition, and it may also be recrystallised from boiling piperidine several times without any notable change. When, however, its solution in wet piperidine is heated at about 90° during some hours, the silicohydrocarbon is completely decomposed; from the solution it is possible to isolate diphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol (T., 1912, **101**, 2125), but no substances other than diphenylsilicanediol and its condensation products seem to be formed in this reaction. The silicohydrocarbon is also acted on, but relatively slowly, by aqueous methyl alcohol or acetone solutions of alkali hydroxides; from these solutions after the expulsion of the organic solvent, acetic acid precipitates long, colourless needles which have the (somewhat indefinite) properties of diphenylsilicanediol.

The action of bromine on a carbon tetrachloride solution of the saturated silicohydrocarbon at the ordinary temperature does not result in the separation of any silica; so far the only products which have been identified are the rhomboidal oxide and condensation products of diphenylsilicanediol. When the saturated silicohydrocarbon, partly dissolved and partly suspended in boiling acetic acid, is treated with a small proportion of nitric acid, a vigorous action sets in, but soon subsides; after some time the crystalline deposit consists of the rhomboidal oxide either alone or mixed with a certain proportion of the unchanged silicohydrocarbon.

Formation of the " Unsaturated " Silicohydrocarbon from the Di-iodide.

A freshly-prepared benzene solution of the di-iodide was evaporated under reduced pressure and the residue dissolved in xylene; a considerable excess of sodium was then added and the solution was boiled during about nine hours until the separation of sodium iodide seemed to be at an end and a portion of the filtered liquid seemed to be free from halogen. When cold, the xylene solution was filtered and the residue extracted with boiling benzene; from the extract there was obtained a compound which, judging from its appearance under the microscope and its slight solubility in benzene, was identical with the " unsaturated " silicohydrocarbon; like the latter, moreover, it combined with iodine in benzene solution at the ordinary temperature and the iodide, on hydrolysis, gave a product which was indistinguishable from the oxide, Si_4Ph_8O, already described. The original xylene filtrate gave on evaporation a residue, which was treated with cold acetone; the insoluble portion consisted of the " unsaturated " silicohydrocarbon, whereas the soluble matter was a glue-like or resinous substance similar in character to the main product of the action of sodium on diphenylsilicon dichloride. As it seemed impossible that this glue contained any of the saturated silicohydrocarbon, it was not further examined. The yield of the " unsaturated " silicohydrocarbon was not more than 60—70 per cent. of the theoretical and the conversion of the iodide into this substance seemed to require a higher temperature and far more prolonged heating than are necessary in the preparation of the " unsaturated " compound from diphenylsilicon dichloride.

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