CLXXXVIII.—*Organic Derivatives of Silicon. Part XXXVII. The Production of Tetrabenzylsilicane, Tribenzylsilicyl Oxide, and Other Products by the Action of Sodium on Dibenzylsilicon Dichloride.*

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THE reactions which occur when dibenzylsilicon dichloride in toluene solution is treated with sodium and potassium in absence of oxygen are very complex and the final results are quite different from those obtained with diphenylsilicon dichloride (Kipping and Sands, J., 1921, **119**, 830, 848; Kipping, J., 1923, **123**, 2590, 2598; 1924, **125**, 2291; 1927, 2719). No silicohydrocarbon corresponding with one or other of the four (A, B, C, D) diphenyl compounds $(SiPh_2)_n$ has been isolated; the soluble product contains a very small proportion of tribenzylsilicyl oxide, $[Si(CH_2Ph)_3]_2O$, and about 15% of tetrabenzylsilicane, the rest consisting of a glue-like or resinous substance.

The formation of the tri- and tetra-benzyl derivatives involves that of a corresponding quantity of material rich in silicon, which is insoluble in toluene and other solvents; this product is variable in composition and seems to be composed of compounds which contain less than one benzyl group for each silicon atom.

The synthesis of the tri- and tetra-benzyl derivatives is doubtless due to the formation of sodium or potassium compounds at some stage of the interaction and it may therefore be suggested that the $>Si(CH_2Ph)_2$ groups of some of the intermediate products give $>Si(CH_2Ph)Na$ and CH_2PhNa; the latter reacting with unchanged dichloride would then yield the tetra- and tri-benzyl derivatives, and the products containing the $>Si(CH_2Ph)Na$ complexes, on treatment with water, would give the material insoluble in toluene and rich in silicon. The great difference between the products from diphenyl- and those from dibenzyl-silicon dichloride would thus be due to the relative instability of the $>Si(CH_2Ph)_2$ complex towards alkali metals.

The resinous product, separated from the tetrabenzylsilicane (and tribenzylsilicyl oxide) by systematic fractionation, is somewhat similar in outward properties to the non-crystalline substance obtained from diphenylsilicon dichloride (J., 1927, 2719). When alcohol is added to its acetone solution, it is precipitated as an oil which gradually hardens to a resin, but it may be obtained as a highly lustrous flaky solid by frothing its ethereal solution.

A prolonged investigation of this product has given results which seem to prove that it is an octabenzylsilicotetrane oxide, $[Si(CH_2Ph)_2]_4O$, mixed possibly with analogous oxides; since successive fractions are practically identical in composition, it may be concluded with some confidence that they are homogeneous or if not that they consist entirely of very nearly related substances.

The proportion of oxygen in a compound $[Si(CH_2Ph)_2]_4O$ is so small (1·8%) that its estimation by difference might give very untrustworthy results; it seems certain, however, that the fractions do not consist of silicohydrocarbons, because when decomposed with alkalis they all give a hydrogen value (J., 1921, *loc. cit.*) of about 80, corresponding closely with that (79) required for $[Si(CH_2Ph)_2]_4O + 7H_2O = 4Si(CH_2Ph)_2(OH)_2 + 3H_2$ and widely different from that (107) required for $[Si(CH_2Ph)_2]_4$. This result is certainly not due to the presence of tetrabenzylsilicane or tribenzylsilicyl oxide, and it seems most improbable that all the fractions could consist of a mixture of silicohydrocarbons with about 20% of dibenzylsilicanediol or its condensation products, quite apart from the difficulty of accounting for the formation of the diol; the amorphous product must therefore be regarded as the oxide $[Si(CH_2Ph)_2]_4O$.

The source of the combined oxygen in this resinous substance and in the tribenzylsilicyl oxide has not been traced. Dibenzylsilicon dichloride, unlike the diphenyl analogue, is easily obtained free from ethoxy-compounds, and only pure material was used; further, after some preliminary experiments had shown the formation of tribenzylsilicol, the interaction with sodium was carried out in an atmosphere of nitrogen, oxygen and moisture being carefully excluded. Nevertheless, when the original toluene solution, filtered as far as possible in an atmosphere of nitrogen, is rapidly evaporated under reduced pressure and the residue mixed with dry ether, the solution usually gives a precipitate of tribenzylsilicyl oxide. Now the 0·02 g. of oxygen in the oxide thus obtained might originate in traces of moisture in the materials and apparatus and from traces of dibenzylsilicon hydroxychloride,

$$Si(CH_2Ph)_2(OH)Cl,$$

in the dichloride; but the 0·3 g. of oxygen contained in the fractionated product from 50 g. of the dichloride must have some other source. Analytical results seem to prove that the oxygen is taken up before exposure to the air or to any solvents containing water; moreover, the freshly prepared product (containing tetrabenzylsilicane) seems to be inert towards atmospheric oxygen, even at 100°, and does not combine with iodine to an appreciable extent; presumably, therefore, the oxygen in the fractionated product is not due to the action of the air or of aqueous solvents on some unstable compound containing tervalent silicon analogous to octaphenylsilicotetrane (A).

When the original toluene solution contained in a flask filled with nitrogen is poured on to a dry filter, a vigorous effervescence is often observed not only on the filter but also in the filtrate (collected in nitrogen). This gas evolution, which soon ceases, is apparently due to the admission of moisture, whereby the metallic derivatives in solution or in suspension are decomposed with the formation of alkali hydroxide; the latter then reacts with some unstable silicon compounds, possibly containing $Si(CH_2Ph)_2H$ groups, with liberation of hydrogen and formation of oxides:

$$\begin{matrix}-Si(CH_2Ph)_2H\\-Si(CH_2Ph)_2H\end{matrix} + H_2O = \begin{matrix}-Si(CH_2Ph)_2\\-Si(CH_2Ph)_2\end{matrix}\!>O + 2H_2.$$

The effervescence thus brought about is very transitory, and in most experiments any further action of alkali was inhibited by the addition to the filtrate of a few drops of acetic acid; it is therefore almost impossible to believe that the whole of the oxygen in the product originates in this way, and the only reasonable suggestion seems to be that it is obtained from oxides present in the alkali metals. So large a proportion of these metals is used that even about 3% of oxygen would be sufficient to account for the results. From the whole of the evidence it is inferred that during the earlier stages of the interaction, the dibenzylsilicon dichloride is converted into $Si(CH_2Ph)_2Cl{\cdot}Si(CH_2Ph)_2Cl$ and then into

$$Si(CH_2Ph)_2Cl{\cdot}Si(CH_2Ph)_2{\cdot}Si(CH_2Ph)_2{\cdot}Si(CH_2Ph)_2Cl;$$

the latter, instead of giving the open- and closed-chain compounds corresponding with octaphenylsilicotetrane (A) and octaphenyl*cyclo*silicotetrane (B), is partly decomposed by the alkali metals, giving sodium benzyl and products rich in silicon, the rest reacting with alkali oxides to form octaphenylsilicotetrane oxide: the sodium benzyl with unchanged dichloride gives tetrabenzylsilicane and tribenzylsilicyl chloride, the latter being then transformed into the oxide: $2Si(CH_2Ph)_3Cl + Na_2O = [Si(CH_2Ph)_3]_2O + 2NaCl$.

Some of the evidence on which these views are based is derived from the results of parallel researches now in progress; an account of these will be published later and it is hoped that light may then be thrown on the unsolved problems of this investigation. One interesting question is, Why is the oxide $[Si(CH_2Ph)_2]_4O$ amorphous?

The corresponding phenyl derivative, $(SiPh_2)_4O$, is crystalline and melts above 200°; possibly, therefore, the benzyl compound exists in two forms, analogous respectively to the crystalline and the amorphous variety of octaphenyl*cyclo*silicotetrane.

The many difficulties met with in this work have been enhanced by the unsuspected fact that some benzyl derivatives of silicon are easily attacked by alkalis, with fission of the carbon–silicon binding; dibenzylsilicol, for example, is decomposed into toluene and silica or benzylsiliconic acid at temperatures below 100°.

EXPERIMENTAL.

All the dibenzylsilicon dichloride used in these experiments was very carefully purified, first by distillation,* and then by recrystallisation from light petroleum; it melted at 47—48° † and was completely soluble in a cold aqueous solution of potassium hydroxide, showing its freedom from tri- and tetra-benzyl derivatives. All samples gave 25·0—25·1% of chlorine [$Si(CH_2Ph)_2Cl_2$ requires Cl, 25·2%].

Sodium ($2\frac{1}{4}$ atoms), freshly freed under toluene from superficial oxide, is quickly added to a solution of the dichloride (1 mol.; 50 g.) in dry toluene (500 c.c.) contained in a flask through which dry nitrogen ‡ is immediately passed, and after all the air is expelled, heat is applied. A reaction starts when the toluene nears its boiling point, a dark brown, almost black crust being formed on the globules of sodium; later on, the flask is vigorously shaken from time to time in order to expose fresh surfaces of the metal. After some 20 hours of gentle ebullition a test portion of the filtered yellow solution usually shows the presence of silicon halides, and gives with water an acid reaction and a precipitate with silver nitrate solution. As such halides or the hydroxy-compounds to which they would give rise would have contaminated the product, and as their complete removal with sodium takes a very long time —during which there is a constant danger of a fracture of the flask —potassium (1—2 g.) is now added and the boiling continued during about 5 hours until the decomposition is complete. The toluene solution is then pale yellow, or it may have acquired a mahogany colour; in the former case, it gives a neutral, in the latter a strongly

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* The fractions of low boiling point gave ethyl alcohol on hydrolysis and doubtless contained ethoxy-derivatives (compare Kipping and Murray, J., 1927, 2734).

† The melting point (50—52°) given by Martin and Kipping (J., 1909, **95**, 307) seems to be rather too high.

‡ Earlier unpublished experiments carried out by Dr. Robison and one of us having shown that tribenzylsilicol could be isolated from the reaction product, it seemed advisable to exclude oxygen.

alkaline, aqueous extract when a filtered portion is shaken with water, but in either the extract is free from chlorides. When cold, the contents of the flask are quickly transferred to a filter, so enclosed between two desiccator covers that the whole operation can be conducted in a stream of nitrogen. The toluene filtrate, immediately evaporated under reduced pressure, gives a thick yellow or mahogany-coloured oil, described later (p. 1436). In the case of the mahogany-coloured solutions the momentary exposure to the air during their transference to the filter sets up the brisk effervescence referred to on p. 1433.

The Insoluble Product.—The bulky dark brown mass on the filter is well washed with toluene * and is then cautiously added to cooled alcohol containing a permanent excess of acetic acid in order to avoid the decomposition of silicon compounds by alkali. The metals having been transformed into their acetates, water is added to dissolve the dark brown mass of halides; there results a colourless solution containing in suspension a flocculent or granular material, which is separated by filtration, well washed with water, and then extracted with hot acetone to free it from a small proportion of glue-like matter.

This product is a slightly greyish powder, insoluble in all common solvents, including boiling phenol, aniline, etc., and it does not give hydrogen when it is heated with an acetone or alcoholic solution of potassium hydroxide. Different preparations contained 28—34% of silicon [$Si{\cdot}CH_2Ph$ requires Si, 23·5%. $(CH_2Ph{\cdot}SiO)_2O$ requires Si, 19·8%], and when evaporated two or three times with hydrofluoric acid they left from 12 to 17% of a dark carbonaceous residue free from silicon; it was therefore impossible to prove the presence of silica. It is clear, however, that this product bears no relation to the insoluble substance (D) obtained from diphenylsilicon dichloride (*loc. cit.*); possibly it is a mixture of silica and condensation products of benzylsiliconic acid from the action of water on sodium silicide and sodium benzylsilicide, respectively.

The yield of this material is about 1 g. from 50 g. of the dichloride; its total silicon content corresponds roughly with that calculated from the estimated weight of the tetrabenzylsilicane which is produced in the reaction.

Isolation of Tribenzylsilicyl Oxide.—In the first experiments carried out in nitrogen the *yellow* toluene filtrate of the crude product kept in a closed flask deposited crystals of tribenzylsilicyl oxide in the course of some days; as this might have been the result of atmospheric oxidation, in later experiments the solution was

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* As air is admitted during this operation, the washings are not added to the original filtrate.

immediately evaporated and the oily residue mixed with dry ether (6—8 vols.), the air in the flask being displaced by nitrogen. The crystalline product (about 1 g.) then precipitated was, after recrystallisation, fully identified as tribenzylsilicyl oxide by its melting point (205—206°), analysis {Found : Si, 9·1. Calc. for $[Si(CH_2Ph)_3]_2O$: Si, 9·1%}, direct comparison, and a mixed melting point determination.

The Main Components.—The yellow oil, obtained from the ethereal filtrate, slowly changes to a transparent resinous mass as the last portions of solvent volatilise. This material is miscible with all the common solvents with the exception of alcohols, acetic acid, and light petroleum, in which it is only sparingly soluble. In benzene solution it does not combine with iodine to an appreciable extent and seems, therefore, to be free from compounds containing tervalent silicon. It does not seem to undergo atmospheric oxidation even at 100°, but its glue-like character and the tenacity with which it retains solvent preclude accurate gravimetric or volumetric determinations, and it is possible that some slight oxidation may occur. Its acetone solution reduces silver nitrate in a marked manner, but no definite oxidation product could be isolated. Various preparations, freed from solvent by exposure to reduced pressure during many days, gave 11·9 to 12·2% of silicon, and hydrogen values of 58—60 [$Si(CH_2Ph)_2$ requires Si, 13·4%; H.V., 107]; these results are considered later (p. 1438).

Isolation of tetrabenzylsilicane. The crude product is fractionally precipitated with alcohol from its solution in cold acetone and is thus directly separated into 8—12 portions, each of which is systematically treated in a similar manner many times, but without increasing the number of fractions. The precipitate is an oil in all cases, but, as the oil is mixed with a considerable proportion of solvent, each precipitation gives a very partial separation. After these operations the solutions of the two or three more soluble portions deposit a crystalline compound which, after recrystallisation from chloroform and light petroleum, melts at 128—129° and is further identified as tetrabenzylsilicane by analysis [Found : Si, 7·15. Calc. for $Si(CH_2Ph)_4$: Si, 7·2%].

The quantity of tetrabenzylsilicane which can be isolated is about 4—5 g. from 50 g. of the dichloride, but a little no doubt remains in the neighbouring fractions of the glue-like matter; so far as can be ascertained, the crude soluble product, after removal of the tribenzylsilicyl oxide, contains about 15% of the tetrabenzyl compound.

The principal product. The 8—10 less soluble fractions, from which no further crystalline deposits are obtained by continued operations, consist of thick oils which gradually harden to transparent or translucent, brittle masses. The least soluble (I) and the next two (II, III) are frothed up (Kipping, J., 1927, 2719), and the resulting scaly products—which look beautifully crystalline to the unaided eye—freed from solvent in a vacuum—an operation lasting many days. Such preparations melt indefinitely over a range of 10° between 40° and 60°, show no sign of crystalline structure under the microscope, and give the following analytical results :

Fraction.	Si %.	C %.	H %.	*M.*	H.V.
I.	13·2	78·3	6·8	857	82
II.	13·3	78·1	6·8	785	79·8
III.	13·3	—	—	734	78·5
$[Si(CH_2Ph)_2]_4$ requires	13·4	80·0	6·6	840	107
$[Si(CH_2Ph)_2]_4O$ requires	13·2	78·5	6·5	856	78
$[Si(CH_2Ph)_2]_3O$ requires	13·1	78·0	6·5	646	69
$Si(CH_2Ph)_2O$ requires	12·5	74·0	6·0	226	—

These data seem to show that the three fractions are practically identical in composition and even the more soluble ones (IV, V) give only slightly lower hydrogen values and contain a slightly larger proportion of oxygen; the fractions I—III, therefore, are in all probability homogeneous, or else composed of mixtures of closely related compounds. Analytical data practically identical with the above were given by fractions from other preparations in which the ethereal solution of the crude *yellow* product was precipitated with alcohol; some of these fractions were systematically extracted with boiling light petroleum or boiling alcohol, but in no case was it possible to obtain the principal component in a crystalline form.

From the above results, especially the hydrogen values, it must be concluded either that the main products are oxides or that, if they consist principally of silicohydrocarbons $[Si(CH_2Ph)_2]_n$, the latter must be mixed with about 20% of some impurity which does not give hydrogen with alkali. But it can be shown that the preparations do not contain any substance $[Si(CH_2Ph)_2]_n$ analogous to (C) which resists fission, because they can be completely converted into compounds soluble in aqueous alkali (p. 1438); unless, therefore, the impurity in question is dibenzylsilicol or one of its condensation products, the presence of which is not excluded by this fact, the preparations cannot consist of $[Si(CH_2Ph)_2]_n$.

Now it is difficult to believe that a mixture of silicohydrocarbons and dibenzylsilicol (or condensation products thereof) would remain constant in composition after exhaustive fractionation; and to assume that such impurities are present would necessitate the conclusion that a large proportion of the original product $[Si(CH_2Ph)_2]_n$ undergoes fission during its treatment with acetone and alcohol. Further, the original product gives a hydrogen value (58—60) much lower than that of a mixture of $[Si(CH_2Ph)_2]_n$ with the estimated proportion of tetrabenzylsilicane; if free from oxygen, therefore, it must contain about 50% of $Si(CH_2Ph)_4$, in which case it would give only 10·3% of silicon instead of 11·9—12·2 as actually found (p. 1436).

For these reasons it is concluded that the main product consists of the oxide $[Si(CH_2Ph)_2]_4O$, formed in the manner already suggested.

Products from Mahogany-coloured Solutions.—The rapid darkening of the toluene solutions observed in some cases occurs only towards the end of the experiment; it seems very probable, however, that the soluble sodium compounds, to which the colour is due, may be formed at much earlier stages, but are decomposed again so long as any halogen remains combined with silicon. The residue, obtained by filtering and evaporating the solution in absence of air, mixed with ether, gives a dark, flocculent substance (about 1 g. from 50 g. of the dichloride), the solution losing its colour.

This product was soluble in chloroform, from which it separated as a blood-red resin; treated with acetic acid, it gave a colourless, glue-like mass, from which nothing crystalline was obtained. The ethereal filtrate from the dark precipitate did not give any appreciable quantity of tribenzylsilicyl oxide, but the yellow oil obtained from it, systematically fractionated in the manner described above (p. 1436), gave the usual proportion of tetrabenzylsilicane. Analyses of the less soluble fractions showed that they had hydrogen values considerably lower than the corresponding preparations from the yellow toluene solutions; the data indicated mixtures of $[Si(CH_2Ph)_2]_4O$ and $[Si(CH_2Ph)_2]_4O_2$. It seems, therefore, that when the heating is continued beyond a certain stage some of the oxide $[Si(CH_2Ph)_2]_4O$ is converted into sodium or potassium derivatives from which other oxides are subsequently formed.

Fission of the $\geqslant$Si-CH$_2$Ph *Linkage.*

During the early stages of this work it seemed that the main product from the dichloride must be a silicohydrocarbon $[Si(CH_2Ph)_2]_n$ and that the low hydrogen values might be due to the presence of some 20% of a compound $[Si(CH_2Ph)_2]_n$ which, like the substance (C) from diphenylsilicon dichloride, was not attacked by alkalis.

Various samples of the fractionated substance were therefore heated with aqueous acetone and alkali until effervescence ceased; the acetone was then evaporated and the aqueous solution of the sodium derivative of the diol filtered from insoluble matter. By one such treatment, only a portion of the material was obtained in a soluble form, because of the formation of condensation products of the diol; after repeated operations, however, practically the whole was obtained in aqueous alkali solution, the residue (less than 1%, if any) consisting of tribenzylsilicyl oxide. Some of the aqueous alkaline solutions obtained in this way gave with acids a bulky precipitate of dibenzylsilicol; but others did not: the latter, after variable periods, deposited gelatinous matter which was insoluble in organic solvents, but soluble in caustic alkalis: various samples of this product gave 26—36% of silicon [$Si(CH_2Ph)_2O$ requires Si, 12·4%], results which indicate mixtures of silica with condensation products of $CH_2Ph{\cdot}Si(OH)_3$.

Further experiments showed that toluene was formed when the fractionated resin was heated on a water-bath during about ½ hour with piperidine and a 5% aqueous solution of sodium hydroxide; and that the percentages of silicon in the gelatinous matter just referred to depended on the duration of the treatment with acetone and alkali.

This unsuspected instability of the $Si–CH_2Ph$ binding towards alkali * is also shown by the fact that when dibenzylsilicol is heated on a water-bath with a 5—10% solution of sodium hydroxide in aqueous acetone during about 30 minutes it is almost completely decomposed with formation of toluene; the gelatinous precipitate obtained by acidifying the solution gave Si, 42·7%, whereas SiO_2 requires Si, 46·9%.

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