# LIV.—*Organic Derivatives of Silicon. Part XXXVIII. The Formation of Tri- and Tetra-phenylsilicane and Complex Synthetical Products from Octaphenyl*cyclo*silicotetrane.*

By Frederic Stanley Kipping and Arthur George Murray.

By the " distillation " of the glue-like substance (E) which is formed by the action of sodium on diphenylsilicon dichloride there was obtained a small proportion of a thick oil; this product, on oxidation, gave triphenylsilicol, and with acetone and alkali it gave hydrogen and triphenylsilicol; the weight of the triphenylsilicyl oxide obtained from the silicol was at least 80% of that of the crude oil (Kipping, J., 1927, 2726).

It was evident from these facts that this product contained $SiPh_3$– groups, but, as it had been formed in small quantities only from crude material, in which there might have been unsuspected impurities, its origin and its nature remained unknown.

Other results of the investigation of (E) having led to the conclusion that this amorphous substance is merely a physically different form of octaphenyl*cyclo*silicotetrane (B), it seemed to follow that crystalline (B) should also give a decomposition product from which triphenylsilicol could be obtained under the conditions already mentioned.

This deduction was proved to be a sound one : when pure octaphenyl*cyclo*silicotetrane is strongly heated in the absence of air, it yields a thick colourless oily distillate and a pale yellow resinous residue; towards the end of the operation a little frothing occurs, but there is no charring. The distillate soon deposits crystals of tetraphenylsilicane, mixed usually with some (B); when freed from these sparingly soluble compounds, the product is a colourless oil which seems to be almost quantitatively transformed into triphenylsilicol with evolution of hydrogen when it is treated with piperidine and alkali.

The results of combustions, silicon determinations and cryoscopic measurements in benzene solution seemed to show that the oil was triphenylsilicyl, $SiPh_3$, but, although it readily reduced potassium permanganate, it did not combine with iodine and when treated with a very small proportion of bromine in chloroform solution it immediately gave hydrogen bromide. Further, the hydrogen value (J., 1921, **119**, 848) of the oil did not agree with that required for triphenylsilicyl: $2SiPh_3 + 2H_2O = 2SiPh_3{\cdot}OH + H_2$ (hydrogen value = 42·9) but was in close accordance with that calculated for *triphenylsilicane:* $SiPh_3H + H_2O = SiPh_3{\cdot}OH + H_2$ (hydrogen value = 85·4).

Now a crystalline substance to which he gave the formula of triphenylsilicane was obtained by Ladenburg (*Ber.*, 1907, **40**, 2278) by heating triphenylsilicyl bromide with zinc ethyl and a little benzene in a sealed tube at 120°. This product was sparingly soluble in cold acetone or benzene and melted at 200—203°; the formula assigned to it was based on the results of one combustion and the percentage of silicon in it was not determined. Apart from the fact that the properties of this crystalline substance are hardly those which would be expected of a triphenylsilicane (compare footnote, p. 364), Ladenburg himself states that on repeating his experiments many times, although he endeavoured to keep the conditions the same as before, he obtained almost exclusively the normal product triphenylethylsilicane, which melted at 72—74° and was very readily soluble in acetone or benzene.

It is suggested, therefore, that Ladenburg's substance (m. p. 200—203°) cannot have been triphenylsilicane; the purity of his triphenylsilicyl bromide is not emphasised and his product may have been impure tetraphenylsilicane, as it was from this substance that the bromide had been prepared.*

Discounting the difficulty raised by Ladenburg's statements, it is concluded that the oil from octaphenyl*cyclo*silicotetrane is in fact triphenylsilicane, and the properties of the residue from the distillation may next be considered. This product contains about 20% of silicon, which corresponds approximately with that required for the ratio 2Si : 3Ph. With the aid of solvents it can be separated into fractions having graded properties, some of which have molecular weights probably exceeding 4000.

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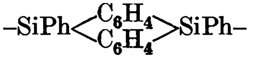
* In the same paper Ladenburg describes a barium salt of triphenylsilicolsulphonic acid, which, as previously shown (Kipping and Martin, J., 1909, **95**, 489), was in all probability a mixture of silica and barium salts of benzene-mono- and -di-sulphonic acids.

The largest fraction, a colourless granular powder, combines with only a very small proportion of iodine and seems therefore to contain a correspondingly small proportion of ter- (or bi-) valent silicon atoms. Its hydrogen value is considerably lower than that of $(SiPh_2)_4$, whereas the mere elimination of $SiPh_4$ or $SiPh_3-$ groups from that compound should give a product of enhanced hydrogen value.

When this largest fraction is treated with alkali and piperidine, only a small proportion is converted into compounds soluble in aqueous solutions of alkali, and diphenylsilicanediol could not be detected in these solutions; whether the portion insoluble in alkalis consists of unchanged substance or of condensation products of substituted silicols could not be definitely determined.

From the available evidence it must be presumed that in addition to the fission of Si–Si bindings and the migration of phenyl groups from one silicon atom to another, giving $SiPh_4$ and $SiPh_3-$, many other changes occur during the "distillation" of (B). It may therefore be suggested that $-SiPh_2-SiPh_2-$ complexes may be converted into  $-\mathrm{Si}\genfrac{<}{>}{0pt}{}{C_6H_4}{C_6H_4}\mathrm{Si}-$ with liberation of hydrogen, which combines with the $SiPh_3-$ groups to form triphenylsilicane; the low hydrogen value of the residue and its apparent freedom from $>SiPh_2$ groups may possibly be due to a somewhat similar transformation of $-SiPh_2-SiPh_2-$ into  $-\mathrm{SiPh}\genfrac{<}{>}{0pt}{}{C_6H_4}{C_6H_4}\mathrm{SiPh}-$ with fission of the Si–Si linkage. The complex character of the residue and the small quantities available, but more particularly the lack of known methods for attacking such problems, render it impossible to put these suggestions to the test of experiment; or to ascertain whether the production of the compounds of high molecular weight from the fragments of $Si_4Ph_8$ is due to combination between silicon and silicon, carbon and carbon, or carbon and silicon.

Octaphenylsilicotetrane (A), when strongly heated, also gives triphenyl- and tetraphenyl-silicane and it is of interest to note that this open-chain compound seems to yield none of its cyclic isomeride under these conditions; nor does the latter give any octaphenylsilicotetrane.

## EXPERIMENTAL.

*Destructive Distillation of Octaphenyl*cyclo*silicotetrane.*—The pure compound (1·5—2 g.) is placed in a very small distillation flask having a short (1—1½″) neck and the air in the flask and receiver is displaced by dry nitrogen: the flask is then heated in a metal bath in which it is immersed so far as possible, the delivery tube being pointed downwards almost vertically. When a 5″ flame of an ordinary Bunsen is used for heating the bath, the solid in the flask shows signs of sintering after the expiration of about 5 minutes and shortly afterwards most of it has melted; at the end of about 6 minutes oily drops appear above the molten layer and a colourless oil begins to collect in the receiver, but only very slowly. After 12—15 minutes time from the start of the operation the residue has turned faintly yellow and the apparent ebullition ceases, giving place to a slight frothing; at this stage the heating is stopped. No thermometer is used, but, as the octaphenyl compound only melts above 400°, it is probable that the temperature of the bath was above 450°; if the "distillation" is carried out under very low pressure, most of the octaphenyl*cyclo*silicotetrane sublimes and apparently there is little decomposition.

The distillate, which is approximately 40% of the material used, deposits colourless crystals either almost immediately or after the expiration of some hours; the quantity of this deposit seems to depend on the rapidity with which the operation has been conducted, a larger proportion of the cyclic compound passing over unchanged the more quickly it is heated. The distillate is mixed with 10—15 vols. of light petroleum and after it has been kept at 0° during some hours the solution is filtered. The crystalline residue fractionated from a mixture of chloroform and benzene gives well-defined pointed prisms, melting at 235—236°: this compound was identified as tetraphenylsilicane by direct comparison in various ways and by mixed melting point determinations. The mother-liquors from the tetraphenyl derivative give deposits which, fractionated from benzene and acetone, afford pure octaphenyl*cyclo*silicotetrane; this compound was identified by direct comparison and by heating it alone and mixed with a known sample on fusible metal, when both powders sintered and sublimed simultaneously.

During the separation of the tetraphenylsilicane from the cyclic compound microscopic examination revealed the presence, in some deposits, of a few large compact crystals; these proved to be an unusual form of tetraphenylsilicane, quite different from the slender pointed prisms ordinarily obtained. Both forms are often produced together by the slow evaporation of a benzene–chloroform solution, but from carbon tetrachloride at the ordinary temperature tetraphenylsilicane separates in rather ill-defined dome-shaped crystals and in rectangular, almost square, prisms the surfaces of which are deeply pitted.

*Formation of Hexaphenylsilicoethane from Silicon Tetrachloride.*—On comparing the crystals of the tetraphenylsilicane from octaphenyl*cyclo*silicotetrane with a sample of the tetraphenyl derivative which had been obtained by the interaction of silicon tetrachloride, chlorobenzene, and sodium (Kipping and Lloyd, J., 1901, **79**, 449) the deposits of the latter, from cold carbon tetrachloride, showed, under the microscope, the presence of some perfect transparent regular hexagons, some of which became black and opaque at 100°; these highly characteristic crystals were proved by direct comparison to be identical with those of hexaphenylsilicoethane, prepared by heating triphenylsilicyl chloride with sodium. The presence of this hexaphenyl derivative in the crude tetraphenylsilicane from the tetrachloride had been long suspected, as the percentage of silicon in the crude product was rather too high; after this lapse of time it is impossible to say definitely that the silicon tetrachloride (Kahlbaum's) was free from the hexachloride, but it seems very probable that this was so, and that the hexaphenyl derivative was formed from the former rather than from the latter.

*Triphenylsilicane.*—The light petroleum solution of the product of distillation (see above), when evaporated, gave a colourless oil which was freed from solvent under reduced pressure and then at 100°; it did not solidify at 0°.* Various samples thus prepared were analysed without further purification; it is very unlikely that they contained more than traces of tetraphenylsilicane or octaphenyl*cyclo*silicotetrane, both of which are practically insoluble in light petroleum; but from the results the presence of a very small proportion of diphenylsilicane is not excluded (Found: C, 81·6; H, 6·1; † Si, 11·3, 11·1; *M*, cryoscopic in benzene, 265; hydrogen value, 84·2, 85·0. $SiPh_3H$ requires C, 83·0; H, 6·1; Si, 10·8%; *M*, 260; hydrogen value, 85·4).

*Triphenylsilicane* has no appreciable smell, but when heated at 100° it has a slight odour recalling that of diphenyl. It is miscible with all the common solvents except the lower alcohols and acetic acid, in which it is only very sparingly soluble in the cold. When heated in a test-tube over a free flame, it puffs and a pale blue flame passes down the tube, a slight deposition of carbon taking place. It does not decolorise a dilute chloroform solution of iodine at the ordinary temperature, but when the solvent is evaporated and the

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* From the following it would seem that the melting point of triphenylsilicane is lower than that of triphenylmethane :

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|---|---|---|---|
| Tetraphenylsilicane ......... | 235° | Triphenylsilicyl chloride ... | 90—91° |
| Tetraphenylmethane ......... | 285 | Triphenylmethyl chloride | 108—111 |
| Triphenylsilicol ............... | 148 | Triphenylsilicane ............ | oil |
| Triphenylcarbinol ............ | 165 | Triphenylmethane ......... | 92° |
| Triphenylsilicyl bromide ... | 118 | | |
| Triphenylmethyl bromide | 152 | | |

† In the first combustion the oil in the boat was mixed with copper oxide, as the substance seemed to be rather explosive; a very sudden decomposition occurred and the results (C, 80·9; H, 6·0%) were low; in the second combustion copper oxide was not added and the oil, heated very cautiously, decomposed quietly.

residue is heated on a water-bath with excess of the halogen, hydrogen iodide is freely evolved and an oil, probably iodobenzene, volatilises. Treated with a dilute solution of bromine in chloroform, the compound gives an immediate evolution of hydrogen bromide; after the addition of slightly less than one mol. of the halogen and evaporation of the solvent, there remains an oil which, mixed with light petroleum, gives colourless prisms, m. p. 114—118°. This product is doubtless triphenylsilicyl bromide (m. p. 118°); decomposed with aqueous acetone, it yields hydrogen bromide and triphenylsilicol; the latter was identified by means of a mixed melting point determination, etc. Triphenylsilicane is readily oxidised by nitric acid in acetic acid solution, giving triphenylsilicol; it reduces a dilute solution of permanganate in acetic acid at the ordinary temperature.

The most conclusive evidence that the oil is triphenylsilicane is obtained by studying quantitatively its behaviour towards alkalis. It is decomposed by a 5% solution of potassium hydroxide in aqueous acetone at the ordinary temperature with evolution of hydrogen and after some time, if the proportion of acetone is small, triphenylsilicol separates in crystals. When the whole of the acetone has been expelled and the filtered alkaline solution is acidified, there is no precipitation of diphenylsilicanediol; this fact shows that the compound is practically free from $>SiPh_2$ groups. The crystalline residue of triphenylsilicol, when evaporated with alcohol containing a small proportion of potassium hydroxide, and then heated at 100° for some time, becomes only partly soluble in cold alcohol and by repeated treatment a large proportion of the original product of hydrolysis is transformed into triphenylsilicyl oxide. This compound separates from benzene in very lustrous, well-defined, transparent, rhomboidal crystals which become opaque slowly on exposure to the air, rapidly when heated at 100°.* The hydrogen values given above were obtained by treating the oil with piperidine and an aqueous solution of potassium hydroxide and heating gently to complete the decomposition.

*Other Decomposition Products.*—The residue from the destructive distillation of octaphenyl*cyclo*silicotetrane, when cold, is a brittle resin having the colour of pale honey. Treated with cold chloroform, a small proportion separates in the form of yellow flakes, which have probably been produced from the most strongly heated portions of the material and form only about 4% of the original silicohydrocarbon. This gelatinous product is insoluble in all the

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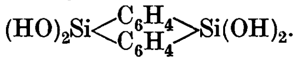
* The statement by Kipping and Lloyd (J., 1901, **79**, 455) that this oxide is " very soluble in ether and benzene " is misleading and should have been " much more soluble in ether and benzene "; its solubility in cold benzene is less than 1 part in 40.

common solvents, even in boiling aniline; it chars, without melting, at a high temperature and contains 20·2% of silicon, a quantity which corresponds roughly with that required for 2Si : 3Ph. It does not combine with iodine. With an aqueous acetone solution of potassium hydroxide it gives hydrogen very readily, but only a small proportion dissolves even on prolonged heating; the alkaline solution, freed from acetone and filtered, gives with acids an immediate precipitate which is gelatinous and seems to be free from diphenylsilicanediol.

The yellowish chloroform filtrate from the yellow flakes, mixed with acetone, gives a colourless precipitate. The product thus obtained from the combined chloroform solutions from several preparations was again dissolved and precipitated, these operations being repeated systematically many times; four fractions of graded solubility were thus obtained.

*Fraction I.* The most sparingly soluble portion, which formed about 50% of the total material, was a colourless, apparently amorphous powder which charred at a very high temperature without melting; it contained 20·1% of silicon (2Si : 3Ph requires Si, 19·6%). In chloroform solution it combined with about one-tenth of its weight of iodine, a fact which indicates the presence of some tervalent silicon atoms. It was readily soluble in chloroform and benzene, but practically insoluble in alcohol and acetone. It dissolved completely in a mixture of piperidine and an aqueous solution of potassium hydroxide and gave a hydrogen value of 108, but on the addition of water after the hydrogen evolution had ceased a very considerable precipitate was obtained and the filtered solution gave only a slight gelatinous deposit on the addition of excess of acid. It also gave hydrogen when it was heated with a solution of potassium hydroxide in aqueous acetone, but only a small portion dissolved in the course of some hours; after evaporating the organic solvent and acidifying the filtered solution, there was obtained a gelatinous precipitate which seemed to be free from diphenylsilicanediol; the matter insoluble in aqueous alkali was treated again several times in the same way, but although a little more of it became soluble after each operation, it was not completely hydrolysed at the end of some 30 hours.

From these observations it was possible that the low hydrogen value of this product was due to the presence of some compounds which are not attacked, or only very slowly attacked, by alkali, and attempts to isolate this stable material were therefore made. The powder was dissolved in piperidine and the solution heated with concentrated alkali until the hydrogen evolution ceased; excess of water was then added and the precipitate separated, washed and dried. It contained 14·4% of silicon and therefore probably consisted of some diphenylsilicane or diphenylenesilicane derivative ($SiPh_2O$ requires Si, 14·1%), but as it seemed to be a mixture and separated from solvents in a glue-like form, its nature could not be determined. So far as could be ascertained, this "glue" was not a component of the original material but had been formed by hydrolysis; if so, it may possibly contain condensation products of



$$(HO)_2Si{<}\substack{C_6H_4\\C_6H_4}{>}Si(OH)_2.$$

*Fraction II* was more gelatinous than I; it charred without melting and its molecular weight in camphor was found to be 4800, but the result was probably rather too high, as a clear solution was not obtained.

*Fraction III* was still more gelatinous; it melted at a high temperature (heated on a spatula) before it charred and its molecular weight in camphor was found to be 1800, a value which is probably trustworthy.

*Fraction IV* was of a glue-like character; it melted indefinitely below 250° and was slightly soluble in hot acetone.

*Decomposition of Octaphenylsilicotetrane.*—When this open-chain compound (A) is heated under as nearly as possible the same conditions as those used in the case of its cyclic isomeride, it gives approximately the same proportion of an oily distillate which is a mixture of unchanged (A), tetraphenylsilicane, and a substance miscible with cold light petroleum. The two crystalline compounds are very easily separated with the aid of cold benzene and the tetraphenylsilicane which is obtained from the benzene solution appears to be quite free from octaphenyl*cyclo*silicotetrane; the tetraphenyl compound was fully identified.

The oil from the light petroleum solution, examined qualitatively, seemed to be identical with the product from (B); that it is in fact triphenylsilicane is proved by its hydrogen value (Found: 85·5. Calc. for $SiPh_3H$: 85·4) and a silicon determination (Found: 11·2. Calc.: 10·8%). The residue from the distillation seemed to be similar to that from (B) and was not investigated further.

Since triphenylsilicyl chloride is not immediately decomposed by cold water, various attempts were made to reduce it to triphenylsilicane with some of the ordinary aqueous reducing agents, but none was successful.

The cost of some of the material used in this investigation was defrayed from a grant received from the Government Grant Committee of the Royal Society; this assistance is gratefully acknowledged.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, January 9th, 1929.*]