CLVII.—*Organic Derivatives of Silicon. Part XL. Attempts to prepare Unsaturated Compounds from Phenylsilicon Trichloride.*

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AT the present time there is no evidence of the existence of a compound containing the group $>Si=C<$ (Kipping, J., 1927, 104), and when dichlorides R_2SiCl_2 are heated with sodium the products do not contain the complex $>Si=Si<$ but are either open- or closed-chain structures consisting entirely of $-SiR_2-SiR_2-$ groups (Kipping and Sands, J., 1921, **119**, 830, 848; Kipping, J., 1923, **123**, 2590; 1924, **125**, 2291; 1927, 2719); the only known case of unsaturation in silicohydrocarbons, as judged by the property of combining with iodine, is that of octaphenylsilicotetrane, which contains 2 atoms of tervalent silicon.

Several attempts have been made during the last ten years to produce unsaturated silicon compounds by the action of sodium on phenylsilicon trichloride under different conditions. The results seem to have shown that $SiPh\equiv SiPh$ cannot be obtained in this way; in its place there results a mixture of very complex products, most of which apparently are saturated compounds.

At about 180°, in the absence of a solvent, the trichloride is very slowly but almost entirely transformed into a greyish insoluble powder which contains 25·1—26·8% Si (SiPh requires 26·8%), does not combine with iodine or even with bromine and is not attacked by a mixture of piperidine and aqueous alkalis.

In boiling benzene or toluene solution, the action of sodium on the trichloride is inappreciable; experiments were therefore made with naphthalene as a solvent. At the boiling point of the solution, the reaction with sodium is definitely exothermic and is completed very much more rapidly than when no solvent is used, although the temperature is about the same in the two cases. Only a very small proportion of the product is insoluble in organic solvents; this contains a much larger percentage of silicon than the insoluble powder referred to above and, unlike the latter, gives hydrogen readily with caustic alkalis. The main product, fractionated from various solvents, gives preparations all of which contain oxygen; while some appear to contain $>SiPh_2$ groups, and possibly naphthyl radicals.

In benzene solution at about 150°, in a sealed tube, or in boiling xylene, the trichloride is attacked by sodium fairly readily at first, but prolonged heating is required to complete the interaction;

potassium was therefore added towards the end of the operation in most of the experiments with xylene. With either solvent there is only a small proportion of insoluble product, which seems to be similar to that obtained in naphthalene solution.

The soluble matter from the xylene solutions, prepared in an atmosphere of nitrogen, has been studied more closely than that obtained with other solvents. It is a pale yellow resin which, judging from its iodine absorption, contains only a small proportion of unsaturated, probably tervalent, silicon atoms. It is easily separated into two main fractions with cold acetone, and further fractionation gives a graded series of colourless powders together with preparations of a more gelatinous character.

All the fractions seem to be complex mixtures which either char without melting or liquefy over a wide range of temperature. The more soluble ones contain $>SiPh_2$ groups, a fact which shows that phenyl groups have been transferred from one silicon atom to another, just as are benzyl radicals during the interaction of sodium and dibenzylsilicon dichloride (Steele and Kipping, J., 1928, 1431); as in the latter case and also in that of diphenylsilicon dichloride, the trichloride gives with sodium metallic derivatives which impart a deep red colour to the xylene solution : if sodium phenyl is thus produced, it would no doubt react with $>SiPhCl$ to form $>SiPh_2$ groups.

Analyses of the freshly prepared, unfractionated, soluble material indicate the presence of at least 4% of oxygen; a further quantity of oxygen is absorbed at 120°, the material becoming much less soluble, but its glue-like character at that temperature prevents very accurate determinations; it does not seem to oxidise in the air at the ordinary temperature, although perhaps it may do so slowly in solution. The source of the oxygen present in the unexposed products has not been ascertained. When the reddish xylene solution is filtered, the filtrate sometimes effervesces distinctly; it rapidly becomes pale yellow on exposure to the air and gives an alkaline solution with water. If, therefore, some of the sodium in the solution is combined with silicon, a portion of the combined oxygen in those products which have been in contact with water may be due to the action of alkali on $>SiPhH$ groups. In order to make sure that the presence of oxygen was not the result of the hydrolysis of $>SiPhCl$ groups, the solution of the trichloride was always boiled with excess of metal until a portion of the filtered liquid gave with water an alkaline extract, and the product in the xylene solution, ignited with sodium, gave a negative halogen reaction. As some of the oxygen might be derived from sodium or potassium oxide, an experiment was made with sodium, which had been melted in nitrogen and filtered through glass wool; the xylene filtrate seemed to be rather richer than usual in sodium derivatives but otherwise the product differed little, if at all, from previous preparations and contained about 4% of oxygen.

The results of many analyses seem to show that the more sparingly soluble fractions are composed principally of compounds containing oxidised $\geq$SiPh groups, whereas the components of the more soluble fractions contain in addition a considerable proportion of $>SiPh_2$ groups.

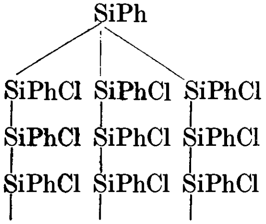
Cryoscopic determinations in benzene and in camphor show that the average molecular weight of the components of the most sparingly soluble fraction is about 5,000, that of the substances in the most soluble material being about 900. The crude product, therefore, seems to be a mixture of compounds containing from about 6 to at least 50 silicon atoms in their molecules.

All the fractions are attacked by aqueous piperidine, and by aqueous alkalis in the presence of an organic solvent, with evolution of hydrogen and fission of Si–Si linkages. It was expected, therefore, that the principal product of fission would be orthophenylsiliconic acid, $SiPh(OH)_3$; that $>SiPh_2$ groups, if present, would give diphenylsilicanediol, $SiPh_2(OH)_2$; and that any silicon atoms not combined with carbon would yield orthosilicic acid. Further, if the preparations contained any compounds which were not attacked, or which gave crystalline fragments immune from further change, the investigation of such material might yield important information. Unfortunately, however, the identification of the products of fission is surrounded by difficulties; the organic hydroxides just formulated undergo a reversible condensation in the presence of alkalis and some of their numerous condensation products are not only insoluble in organic solvents (Kipping and Murray, this vol., p. 360) but are also very difficult to hydrolyse. Consequently it is not easy to ascertain in any given case whether or not all the Si–Si links have undergone fission; the material which does not become soluble in aqueous alkalis may be either an unchanged substance, a fragment, some stable condensation product, or a mixture of all these, and its ill-defined properties render its identification almost impossible.

When the more sparingly soluble preparations were heated with piperidine and alkali hydroxide until hydrogen ceased to be evolved, only a small proportion became soluble in aqueous alkalis; the solution gave with acids a gelatinous precipitate, which appeared to be a mixed condensation product of orthophenylsiliconic acid and orthosilicic acid. The material insoluble in aqueous alkali seemed to be a mixture of condensation products of orthophenylsiliconic acid and diphenylsilicanediol. The presence of the last-named compound in the products of hydrolysis of the most readily soluble preparations was definitely established. The hydrogen values of some samples of the original product and of many of the fractions were determined, but as the proportion of unchanged material, if any, could not be ascertained, and the presence of oxygen created other complications, the quantitative results afforded little information.

It will be evident from the above account that, under all the different experimental conditions, the trichloride is converted into a complex mixture of products, the components of which contain not only $\geq$SiPh and $>$SiPh$_2$ groups but also silicon atoms uncombined with carbon; some of the silicon atoms seem to be unsaturated, probably tervalent, but most of them have become saturated by combination with oxygen.

It may be suggested that in the first stages of the reaction silicon atoms are linked to give structures such as



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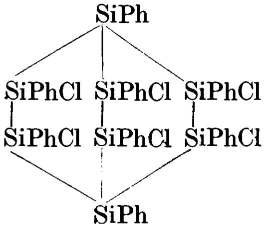

which increase in complexity so long as there is any unchanged trichloride present, until molecules containing fifty or more silicon atoms have been formed. As the supply of trichloride becomes exhausted, the further elimination of halogen probably leads to the production of bridged rings of different types. When this stage has been passed and, owing to steric influences, ring formation is brought to an end, the removal of the rest of the chlorine probably gives rise to tervalent silicon atoms; some of the halogen may also be displaced by sodium, and some by oxygen probably derived from sodium oxide. In addition some of the phenyl radicals are displaced by sodium with the probable formation of sodium phenyl, which then reacts with $>$SiPhCl groups; it is possible that some chlorine atoms are displaced by hydrogen present in the sodium.

In the course of the above work it was found that various silicon compounds such as "phenylsiliconic anhydride" and diphenylsilicanediol are completely converted into volatile products by evaporation with an aqueous solution of hydrogen fluoride.

EXPERIMENTAL.

Phenylsilicon Trichloride.—Phenylsilicon trichloride prepared in the ordinary way (J., 1912, **101**, 2113; 1914, **105**, 681) is not easily obtained in the pure state; fractions collected from about 148—153°/200 mm., after repeated distillation, contain some ethoxy-compound, probably $SiPhCl_2(OEt)$ (compare Kipping and Murray, J., 1927, 2734), and give alcohol on hydrolysis. When prepared by the modified method (*loc. cit.*) with the proportion $2SiCl_4 : 1\frac{1}{2}MgPhBr$, the pure trichloride (b. p. 152—153°/200 mm.) is easily isolated. The yield is about 100 g. from 170 g. of the tetrachloride (Found: Cl, 50·2, 50·5. $C_6H_5Cl_3Si$ requires Cl, 50·3%). The pure trichloride was used in all the xylene experiments; in the earlier ones the liquid which had been fractionated carefully and boiled at 198—200°/760 mm. was assumed to be pure.

Action of Sodium on the Trichloride.—(1) *No solvent.* The trichloride (10 g.) and sodium (4 g.) are heated in a flask with a 30″ air-condenser and a calcium chloride tube and when the metal has melted the flask is vigorously shaken; the temperature is then slowly raised to about 190°. The globules of sodium gradually become covered with a very dark brown crust, and after the lapse of some 8 hours, during which the flask is again shaken from time to time, decomposition seems to be complete. The dark granular mass is cooled, extracted with boiling benzene, and cautiously added to a mixture of alcohol and excess of glacial acetic acid; the solution is diluted with water, warmed, and filtered and the residue, a light brown powder, is thoroughly washed with water, alcohol, and benzene successively, and dried at 110°. The yield is about 4·6 g. (theoretical for SiPh, 5·4 g.).

Five different preparations gave Si = 26·5, 25·7, 26·8, 25·1, 26·3. Although these figures point to the formula SiPh (which requires Si, 26·8%), the later results seem to show that this product is a mixture and contains a considerable proportion of oxygen.*

(2) *Naphthalene as solvent.* The trichloride (10 g.), sodium (4 g.), and naphthalene (20 g.) are heated together in a flask fitted up as described and when the solids have melted the flask is vigorously shaken and again heated. Directly the mixture begins to boil, an exothermic reaction sets in and ebullition continues for some

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* These experiments and also those with naphthalene were carried out by Mr. Maltby; later, the trichloride was heated with sodium in an atmosphere of nitrogen, but even after prolonged heating (20 hours) with a large excess of the metal, silicon halides were still present, a part of the product was soluble in benzene, and the insoluble portion gave hydrogen with alkali. These different results are no doubt due to the presence of atmospheric oxygen in the one case and not in the other.—F. S. K.

time without external heat; the metal becomes coated with a very dark brown spongy solid and the liquid turns yellow. When ebullition slackens, the contents of the flask are again boiled and vigorously shaken; at the end of about 15 minutes the solution is free from silicon halides.

The cooled product is mixed with benzene (250 c.c.), the solution filtered (with difficulty), and the residue well washed with boiling benzene, after which it is treated exactly as previously described. The insoluble product is a buff-coloured, amorphous powder (only about 0·25 g.). Five different samples gave Si = 33·9—34·7 (SiPh requires Si, 26·8%). It yields hydrogen very readily with caustic soda: three different samples gave, respectively, 1·0, 1·2, and 1·0 atoms of hydrogen per atom of silicon (SiPh should give 3 atoms), but about 25% was undissolved in each case; even if the undissolved matter yields no hydrogen, the results indicate that the rest of the material contains a very considerable proportion of oxygen. About 80% of the powder volatilised on evaporation with hydrofluoric acid; the residue contained only 15% of silicon. From these data it may be inferred that the insoluble product is a mixture of very complex compounds containing $\geqq SiPh$ and $>SiPh_2$ groups as well as silicon atoms which are not combined with carbon; the residue after treatment with hydrofluoric acid seems to consist of derivatives of $>SiPh_2$ ($SiPh_2O$ requires Si, 14·2%).

The yellow benzene filtrate, which shows a green fluorescence, is submitted to steam distillation and the glue-like residue is dissolved in benzene and reprecipitated with alcohol; when dried, it is an amorphous yellow powder (about 5 g.). When this product is treated with cold acetone a portion dissolves readily, but the rest is only very sparingly soluble. The former is readily soluble in ether and carbon tetrachloride but practically insoluble in alcohol and glacial acetic acid; six different samples dried at 100° gave Si = 20—20·7% and when treated with sodium hydroxide evolved 0·95—1·06 atoms of hydrogen per atom of silicon (M, cryoscopic in benzene, 2100, 2200). The less soluble fraction is also practically insoluble in ether and alcohol but readily soluble in benzene and carbon tetrachloride; dried at 100°, it gave on the average Si = 24·5% and approximately one atom of hydrogen per silicon atom (M, cryoscopic in benzene, 4000). The proportions of these two fractions varied in different experiments from 3 : 2 to 2 : 3; with caustic alkalis, all the samples gave a considerable proportion of insoluble matter and the alkali solutions afforded gelatinous precipitates when acidified.

A large quantity of the crude benzene-soluble product was fractionally precipitated systematically from carbon tetrachloride with ether and then from benzene with alcohol; the product was thus separated into eight fractions all consisting of yellow amorphous powders, which were dried at 100° and analysed with the following percentage results :—

Fraction.	C, %.	H, %.	Si, %.	O, %.	H (c.c.) per g.	Atoms of H per atom of Si.	
1	61·6	4·4	22·9	11·1	147	1·6	Practically insoluble in acetone.
2	62·4	4·0	21·9	11·7	132	1·5	
3	64·2	4·1	21·8	9·9	146	1·7	
4	—	—	—	—	—	—	Intermediate fractions.
5	66·8	4·0	—	—	—	—	
6	66·5	4·3	21·8	7·4	146	1·7	Readily soluble in acetone.
7	65·0	4·9	20·1	10·0	—	—	
8	—	—	—	—	—	—	Not examined.

These data show that the fractions 5, 6, and 7 contain a larger proportion of carbon than that required for Si : 6C. The proportion of hydrogen to carbon is much lower than that required for 5H : 6C, an indication that the material contains naphthyl radicals as well as $>\mathrm{SiPh}_2$ groups. The large proportion of oxygen in these products is noteworthy, but as no particular precautions were taken to exclude air, its presence may be attributed, principally at any rate, to atmospheric oxidation.

(3) *Benzene as solvent.* The trichloride (10 g.) was heated with benzene and excess of sodium in sealed tubes at about 130° and while just below that temperature the tubes were shaken vigorously from time to time, After about 8 hours the temperature was raised to 150—160°; if then, at the end of 1—2 hours more, the globules of metal remained bright the heating was discontinued, and when cold, the deep reddish-yellow solution was quickly filtered. The residue, after being well washed with benzene and then treated as described above, afforded a grey powder (about 0·3 g.) insoluble in all organic solvents; different samples contained Si = 30—31·5% and gave about 1·35 atoms of hydrogen per atom of silicon with sodium hydroxide solution. When evaporated with hydrofluoric acid, about 45% of the powder volatilised, and the residue contained 13·5% of silicon. This material therefore seems to be very similar to the insoluble product from the experiments with naphthalene.

The benzene solution on evaporation afforded a pale yellow resin which contained C = 65·5, H = 4·7, Si = 22·6% (two concordant analyses) and gave about two atoms of hydrogen per silicon atom when heated with piperidine and sodium hydroxide solution. The carbon to silicon ratio is again greater than 6C : Si and although the product had been kept out of contact with air so far as possible during its isolation the analyses indicated the presence of about 7% of oxygen. The soluble product was systematically precipitated with alcohol from several different solvents; it gave a graded series of preparations some of which were powders, sparingly soluble in acetone; others were glue-like in character and very readily soluble. The results of the further investigation of this material were very similar to those obtained with the product of the xylene experiments (see below) so that their description may be omitted.

(4) *Xylene as solvent.* The pure trichloride (50 g.) in pure xylene (500 c.c.) is heated with excess of sodium (approximately 25 g.) in an atmosphere of pure nitrogen. The reaction starts as soon as the solution begins to boil, the sodium becoming coated with a very dark brown or black deposit, which is detached by shaking the vessel vigorously from time to time. At the end of 10—12 hours the solution, as a rule, still contains silicon halide, to decompose which potassium (1 to 2 g.) was added in most of the experiments and the heating continued; after 5—7 hours longer, the solution acquires a deep brownish-red colour and a portion, if treated with water, gives an alkaline extract. The liquid is then filtered and the residue washed with hot xylene, both operations being conducted in an atmosphere of pure nitrogen; the washings are kept separate from the original filtrate.

The saline mass (which may immediately inflame on exposure to the air if much potassium has been used) is treated in the usual manner and the insoluble matter is washed with water, alcohol, and boiling benzene successively. The residue (about 2·5 g.) is a grey powder insoluble in all organic solvents; different samples contain Si = 30·8—32·3% and give hydrogen with sodium hydroxide solution; when evaporated with hydrofluoric acid six times, 80% volatilised and the glue-like residue contained only about 13% of silicon ($SiPh_2O$ requires Si, 14·2%), a fact which indicates the presence of $>SiPh_2$ groups in the powders; it seems, therefore, that this insoluble material is very similar to that obtained in the experiments with naphthalene and benzene.

Xylene filtrate. Three entirely different preparations, P_1, P_2, P_3, were examined; in the case of P_3 potassium was not used in the reaction (p. 1191). Aqueous extracts of portions of the solutions gave an alkaline reaction but only an inappreciable precipitate with silver nitrate; the products in the xylene solutions gave only traces of sodium chloride when they were ignited with sodium. The red filtrates became yellow if exposed to the air or if neutralised with glacial acetic acid or phthalic acid.

Absorption of oxygen and of iodine. A portion of the red xylene solution P_1 was treated with phthalic acid, the pale yellow liquid evaporated under reduced pressure, and the residue heated at 120° in an atmosphere of carbon dioxide during some hours. The sample

(1·18 g.) thus obtained was then exposed to oxygen in a flask connected with a manometer; no absorption occurred at the ordinary temperature after the expiration of several hours. At 100°, 27 c.c. were absorbed in 1 hour and an additional 10·6 c.c. in 2 hours more; the calculated increase in weight for 37·6 c.c. is 0·0536 g. and the observed increase was 0·0542 g., so that apparently there was no loss during oxidation and about 5% of oxygen was taken up. Further oxidation occurred at 160° and the product was then practically insoluble in benzene and chloroform.

A different preparation (about 1 g.) obtained by the direct evaporation of the red xylene solution P_2 absorbed only 18·3 c.c. of oxygen at 100—120° in the course of 10 hours and did not become insoluble in chloroform; this smaller absorption was possibly due to the more viscous character of the sample, as further oxidation occurred when fresh surfaces were exposed by treatment with solvents.

Another portion of P_1 was treated with iodine in benzene solution; only about one-ninth of its weight of iodine was absorbed, so that many more silicon atoms combined with oxygen than with the halogen. P_2 absorbed about one-quarter of its weight of iodine (after deducting the quantity which had combined with the sodium present), and P_3 (p. 1191) absorbed about one-tenth of its weight.

As there seemed to be no atmospheric oxidation at the ordinary temperature, the main bulk of P_1 was treated with a little warm acetone, containing sufficient acetic acid to decompose the sodium derivatives, and with warm benzene, in which it dissolved completely except for a little sodium acetate; the solution was then fractionally precipitated with acetone, these operations being repeated systematically until every fraction except the most soluble had been precipitated seven times. The fractions I (2 g.), II (3 g.), III (2 g.), and IV (3 g.) (I was the least soluble) were colourless powders, which charred without melting and dissolved freely in benzene and chloroform but were practically insoluble in acetone and ether; the most soluble fraction (VII, 3·5 g.) was rather gluelike in consistency, melted gradually from about 110° to 130°, and dissolved freely in warm acetone; fractions V (0·5 g.) and VI (1 g.) had intermediate properties and were not further examined.

Fraction I, ignited with sodium, yielded only traces of sodium chloride; when freed from solvent in a vacuum, it gave Si = 23·1% and 1·7 atoms of hydrogen per silicon atom. It was very difficult to burn; when mixed with copper oxide it gave C = 64·8, H = 4·8% as the average of three fairly concordant results. It was too sparingly soluble in camphor to give a measurable depression of the melting point, but a cryoscopic determination in benzene gave $M = 5780$.

Fractions III and IV (1·7 atoms of hydrogen per silicon atom), which seemed to be very similar to I in outward properties, were mixed together and precipitated with acetone from their solution in chloroform. After several operations, in which a small proportion of the most soluble material was discarded, the remainder, freed from solvent in a vacuum, was divided into two parts, one of which (A) was kept under reduced pressure and the other (B) was heated at 120° in air; the former lost in weight to a slight extent, but the latter gained about 4% in 3—4 days and was then practically insoluble in chloroform [Found for A: Si, 23·1; C, 64·1; H, 4·9; O (by diff.), 7·9%; 1·8 atoms of hydrogen per silicon atom. Found for B: Si, 22·1; C, 60·0; H, 4·4; O (by diff.), 13·5%; 1·1 atoms of hydrogen per silicon atom].

These results show that the fractions I—IV, which formed about two-thirds of the total product, are practically identical in composition and that the components of this material absorb nearly as much oxygen at about 120° as is already present.

The most soluble fraction (VII), precipitated from its acetone solution with alcohol and freed from solvent under reduced pressure, gave Si = 21·1, C = 69·3, H = 5·3, O = 4·3% and 2·1 atoms of hydrogen per atom of silicon; *M*, in camphor, 1132; *M*, cryoscopic in benzene, 934. It did not increase in weight appreciably when heated at 120° in the air during 3—4 days and was still completely soluble in warm acetone, but its hydrogen value decreased nearly 50%.

Fission products. Some of the more sparingly soluble material (II) was heated with a mixture of piperidine and a 20% aqueous solution of potassium hydroxide, in which it dissolved completely, until the evolution of hydrogen had ceased, and the aqueous layer was then separated so far as possible from the piperidine. The former, with excess of concentrated hydrochloric acid, gave a flocculent precipitate soluble in potassium hydroxide solution but insoluble in organic solvents; dried at 120°, it contained 24·1% of silicon. This result indicated a mixed condensation product of phenylsiliconic acid and silicic acid, since $(PhSiO)_2O$ contains Si = 21·9%. As, however, it might be a mere mixture of silica and phenylsiliconic acid, attempts were made to eliminate the former by evaporation with hydrofluoric acid, but only about 0·1% of residue was obtained. Experiments with phenylsiliconic anhydride, prepared directly from the trichloride (Meads and Kipping, J., 1914, **105**, 679), then showed that this compound is decomposed by hydrofluoric acid, about 90% of it volatilising during one treatment.

The separated piperidine solution, treated with excess of hydrochloric acid, gave a glue-like material readily soluble in warm acetone but insoluble in a 20% aqueous solution of potassium hydroxide, by which it was only very slowly and incompletely hydrolysed. When dried, it contained 17·6% of silicon, and was apparently a mixed condensation product of phenylsiliconic acid and diphenylsilicanediol ($SiPh_2O$ requires Si, 14·2%). Subsidiary experiments showed that it would be useless to try to obtain the diol from this product by evaporation with hydrofluoric acid, since, like phenylsiliconic anhydride, the diol is completely decomposed if so treated.

In an attempt to isolate the diol a portion of fraction VII, which, judging from the analyses, contained a considerable proportion of $>SiPh_2$ groups, was boiled with alcoholic potash until hydrogen ceased to be evolved and the whole of the material had dissolved; the alcohol was then evaporated, and the filtered aqueous solution poured into a considerable excess of dilute acetic acid. In the course of about one minute crystals separated and, after filtration, the solution very slowly deposited glue-like matter. The crystalline product was identified as diphenylsilicanediol.

So far the experimental results explained why the ratio of carbon to silicon in part of the product is greater than 6C : Si, but the source of the oxygen in the fractionated material was still unknown. The red xylene solution P_2 was transferred to a flask filled with nitrogen, and the solution evaporated under reduced pressure; a little chloroform was then added without any air being admitted and by rapid evaporation the resin was frothed up into a bulky porous mass, which was heated at 100° in the same vessel during some hours under low pressure to free it from solvents. This product gave Si = 18·0% (after correction for the sodium salts present) and 1·5 atoms of hydrogen per silicon atom. Since $\geqq$SiPh gives 3 and $>SiPh_2$ gives 2 atoms of hydrogen for each atom of silicon, it is obvious that this product already contains oxygen or else a considerable proportion of it is not decomposed by alkali. The rest of the xylene solution P_2 was treated with a few drops of glacial acetic acid without admission of air; a crystalline precipitate of alkali acetates was produced and the pale yellow solution was then evaporated and the residue extracted with pure ether; the filtered extract, concentrated and then frothed up, gave a brittle resin. The portion not dissolved by ether was treated with chloroform, and the solution filtered from the residue of alkali acetates (about 0·3 g.); the filtrate was evaporated and frothed up. In all these operations air was excluded so far as possible.

When freed from solvent under reduced pressure in an inert atmosphere, the product (3·5 g.) from the ethereal solution gave Si, 18·3; C, 70·8; H, 5·7%; 1·6 atoms of hydrogen per silicon atom, and the product (0·5 g.) from the chloroform solution gave Si, 20·1%; 1·5 atoms of hydrogen per silicon atom.

It will be seen from these results that, in spite of the precautions taken, the product in P_2 had combined with oxygen in the course of its preparation or subsequent treatment.

The red xylene solution P_3 had been prepared without using any potassium, because the ordinary balls of this metal might well contain appreciable quantities of oxide. The sodium which was used was melted and then filtered through glass wool in an atmosphere of nitrogen into the nitrogen-filled reaction flask containing the xylene solution of the trichloride (13 g.). The heating was continued during about 15 hours; the solution then gave as usual an alkaline reaction with water, and a portion of the resin obtained by evaporating the xylene gave only a faint indication of halogen when it was ignited with sodium. The whole of the red solution (filtered in nitrogen) was treated with a few drops of glacial acetic acid, filtered from a bulky precipitate of sodium acetate, and evaporated under reduced pressure, air being excluded in these operations so far as possible. The residue contained (two concordant analyses) Si = 20·3, C = 69·4, H = 5·5, O (by diff.), 4·8%, and it gave 2·1 atoms of hydrogen per atom of silicon. Heated in the air at 120° during many hours, it became only partly soluble in benzene and then gave only 0·9 atom of hydrogen per atom of silicon.

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