CLXXI.—*Organic Derivatives of Silicon. Part XLIV. The Formation of Trichlorosilicane or of Silicon Dichloride from Phenylsilicon Trichloride.*

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When phenylsilicon trichloride is heated with sodium under the conditions previously prescribed (J., 1930, 1029; compare also J., 1929, 1180), it gives not only tri- and tetra-phenylsilicane but also hydrogen chloride and some volatile silicon halide, which is collected in benzene or toluene. The addition of water to this solution immediately precipitates an inorganic solid (X), which is rapidly and completely soluble in cold alkalis, with the evolution of hydrogen.

From the results of silica determinations and measurements of the hydrogen values of different preparations, it was concluded that the solid (X) had the composition $H_2Si_2O_3$, and had been produced either (*a*) by the hydrolysis of trichlorosilicane or (*b*) by the condensation of a dihydroxide, $[Si(OH)_2]_n$, formed from silicon dichloride; in either case it was mixed with some other silicon compound, probably silica, possibly silico-oxalic acid, and also contained free or combined water.

For various reasons determinations of the ratio, solid X to chlorine, in the products of the hydrolysis of the silicon halide did not decide between the alternatives (*a*) and (*b*); the results, however, pointed to the conclusion that the halide was not trichlorosilicane (p. 1296).

The product of the hydrolysis of crude trichlorosilicane, first described by Buff and Wöhler (*Annalen*, 1857, **104**, 94), was further investigated by Friedel and Ladenburg (*Annalen*, 1867, **143**, 118), who concluded that it had the composition $H_2Si_2O_3$ and named it silicoformic anhydride. Schwarz and Souard (*Ber.*, 1920, **53**, 14) prepared this compound (now called dioxodisiloxane) from trichlorosilicane, b. p. 33°, and found that after it had been dialysed in ice-cold water during 9 days and then dried over phosphoric oxide, it gave a hydrogen value corresponding with that required for 92% of $H_2Si_2O_3$. From this result they concluded that the compound must be relatively stable towards water, but there was no evidence that their original preparation was pure: their trichlorosilicane might have contained some other silicon halide which gave a product of hydrolysis having a hydrogen value lower than that of dioxodisiloxane; the authors themselves note that their crude trichloride contained fractions boiling from 21° to 33°.

Pure or practically pure dioxodisiloxane was prepared by Stock and Zeidler from trichlorosilicane, b. p. 31·5° (*Ber.*, 1923, **56**, 986); they describe it as "überraschend wasserbeständig." When left in water during 24 hours at the ordinary temperature, it underwent no appreciable change; "das fertige Dioxodisiloxan ist also wasserfest." These authors also found that when a cooled benzene solution of trichlorosilicane was shaken with water the filtered aqueous solution gave no hydrogen with alkalis and was free from silicon.

Now the solid (X) is appreciably decomposed by water at the ordinary temperature and apparently also to a slight extent even at 0°; further the filtered aqueous solution obtained in the preparation of (X) reduces silver nitrate, evolves a gas with alkalis, and contains some silicon compound; even when (X) has been left in water during some days, it still dissolves sufficiently to give a solution which reduces silver nitrate.

According to Buff and Wöhler (*loc. cit.*) the product of hydrolysis of trichlorosilicane is lighter than water and is not attacked even by concentrated nitric acid; the solid (X), on the other hand, is heavier than water and is readily acted on even by dilute nitric acid.

All these facts seem to prove that (X) cannot have been formed from trichlorosilicane, and further evidence to the same effect is obtained by comparing the properties of (X) with those of certain other silicon compounds. Oxomonosilane, $(SiH_2O)_n$, is not acted on by water even at 100°, and is not appreciably changed by fuming nitric acid (Stock, Somieski, and Wintgen, *Ber.*, 1917, **50**, 1754), whereas monox and the solid obtained by Cambi (*Atti R. Accad. Lincei*, 1911, **20**, i, 434) by the decomposition of silicon monosulphide are both decomposed by water. It seems probable, therefore, that

(X) differs fundamentally from oxomonosilane and from dioxodisiloxane, but is related to the two solids which may be regarded as derivatives of $Si(OH)_2$ or of $SiCl_2$.

The possible existence of silicon dichloride in the products of the interaction of silicon and hydrogen chloride seems to be indicated by certain results of Gattermann (*Ber.*, 1889, **22**, 192), who thus obtained a very volatile silicon halide, which apparently was not trichlorosilicane but on hydrolysis gave a solid similar to dioxodisiloxane in composition. A repetition of some of Gattermann's work during this investigation showed that a solid obtained as he described, like (X), was appreciably decomposed by water and therefore contained presumably some component which had not been formed from trichlorosilicane.

The chloride from which (X) is obtained does not seem to combine with iodine; as, however, a silicon dichloride would probably polymerise, giving mainly a saturated closed-chain compound, and since, moreover, iodo-derivatives of organic silicon compounds may be very unstable (J., 1921, **119**, 830), this evidence is of little value.

When benzene, toluene or xylene solutions of the halide are distilled to a small volume, sometimes the whole, sometimes a considerable proportion of the halide, remains in the residue (p. 1297); this seems to show that the halide, which when freshly prepared is very volatile, has in fact undergone polymerisation, which it could not do if it were trichlorosilicane.

In spite of a prolonged investigation with the hope of establishing the existence of silicon dichloride and of proving the origin of (X), it has been impossible to decide between the alternatives already given; this is partly due to the very small yields of the silicon halide, but more particularly to the inherent difficulties of the problem. From the whole of the evidence, however, it may be provisionally concluded that (X) is a mixture of condensation products of $[Si(OH)_2]_n$.

The formation of the volatile compounds known or suspected to be produced during the interaction of sodium and phenylsilicon trichloride may be expressed as follows :

$PhSiCl_3 + 2Na = NaPh + NaSiCl_3 : NaSiCl_3 + 3NaPh = NaSiPh_3 + 3NaCl : PhSiCl_3 + 3NaPh = SiPh_4 + 3NaCl : NaSiPh_3 + HCl = HSiPh_3 + NaCl : PhSiCl_3 + 2Na = NaPh + NaCl + SiCl_2 : NaSiCl_3 + HCl = HSiCl_3 + NaCl.$

It is suggested that the hydrogen chloride which is known to be produced is formed by a change such as

$$\geqq \mathrm{SiPh} + \mathrm{SiCl} \leqq \; = \; \geqq \mathrm{Si{\cdot}C_6H_4{\cdot}Si} \leqq + \mathrm{HCl}.$$

EXPERIMENTAL.

Many attempts have been made to ascertain the best conditions for the formation of the volatile silicon halide. The experiments were carried out substantially as already described (*loc. cit.*), but an additional drying tower containing phosphoric oxide was used and a by-pass was provided from the reaction flask so that the escaping nitrogen could be tested from time to time. The temperature, the rate of heating, and the state of division of the sodium were varied so far as possible and the best yields were obtained by heating to about 200° in the course of 2—3 hours and then keeping the mixture at about 200—220°, the flask being shaken *very gently* from time to time from about 130°; if the temperature were raised to 220° too quickly, or if the flask were shaken too vigorously, the yields were diminished and might be negligible. Even after they have been kept at 200° during some 10—15 hours, a vigorous agitation of the contents of the flask may bring about a very violent reaction accompanied by flashes of light. The best yields were only about 0·2 g. from 15 g. of the trichloride.

In the later experiments, in which the ratio, solid : chlorine, was determined (p. 1296), the phenylsilicon trichloride was heated alone at about 160° in the nitrogen stream during some hours in order to expel hydrogen chloride or silicon tetrachloride if present; no tetrachloride was found in any case, but, after the addition of sodium and heating, hydrogen chloride was always obtained, and the weight of this gas was always much greater than that of the product (X) subsequently isolated. With a gas stream at the rate of about one litre per hour, at least four benzene or toluene wash-bottles, each containing about 15 c.c., must be used, otherwise a portion of the product is not absorbed. Each experiment occupied some 20 hours.

The solid (X), which separates immediately when crushed ice is added to the benzene solution, is at first gelatinous and cannot be separated easily by filtration; bubbles of gas can be seen adhering to it, and sometimes rising to the surface. In the course of an hour or so the solid becomes granular, but unless it is left with water during some hours longer it may still retain halogen; it is finally separated by filtration, washed with ice-cold acetone and then with benzene. Although acetone decomposes it to a visible extent, the washing with this solvent is essential; if omitted, the preparations may contain some organic matter soluble in acetone, possibly a condensation product of $PhSi(OH)_3$ and $[Si(OH)_2]_n$.

Properties of (*X*).—When the air-dried solid (X) is placed in water at the ordinary temperature, it is not wetted and floats; with the aid of a lens, bubbles of gas, possibly air, may be seen adhering to the particles. When, however, the powder is damped with acetone, alcohol, or very dilute acetic acid and then placed in water it immediately sinks: particles then begin to rise, carried upwards by adhering bubbles, and this gas evolution may continue during some hours, the particles rising and falling as the gas forms and then escapes. Ammonia and cold aqueous alkalis attack (X) vigorously at the ordinary temperature, hydrogen being evolved. It is readily acted on by warm dilute nitric acid, but even after it has been heated with this (or acetic) acid at about 100° during 3—4 hours, the washed solid still gives hydrogen with alkalis.

The solid which has been in contact with water during 10—15 days, if placed in fresh distilled water, gives a solution which reduces silver nitrate. It reduces permanganate both in acid and in neutral solution and is quickly turned brown by an aqueous solution of silver nitrate. When heated alone in a test-tube over the free flame, it puffs suddenly, and when a mixture of the substance with manganese dioxide or red lead is similarly heated a definite explosion takes place. The solid leaves no residue when it is evaporated with hydrofluoric acid.

The aqueous filtrate from the preparation of (X), as already stated, has reducing properties and gives hydrogen with alkalis; on evaporation the solution gives a very small gelatinous residue which still gives hydrogen.

The following are some of the analytical data obtained with six different preparations; about the same number of other samples, H.V. = 300—330, were obtained but were not further examined quantitatively.

$H_2Si_2O_3$ requires H.V. 420; SiO_2, 113·1%. $Si(OH)_2$ requires H.V., 360; SiO_2, 96·8%.

	Found.		Calculated (A).			Calculated (B).		
	H.V.	SiO_2.	$H_2Si_2O_3$.	SiO_2.	H_2O.	$H_2Si_2O_3$.	$H_2Si_2O_4$.	H_2O.
I	364	99·2	86·7	1·2	12·1	78·2	12·8	9·0
II	352	101·1	83·8	6·4	9·8	85·6	2·4	12·0
III	364	105·2	86·7	7·2	6·2	80·3	14·6	5·1
IV	364	101·9	86·7	3·9	9·4	83·2	7·9	8·9
V	334	104·3	79·5	14·5	6·0	66·7	29·4	3·9
VI	360	104·4	85·7	7·4	6·8	79·1	15·2	5·7

I, pressed on porous earthenware and left during 2 hours over sulphuric acid. II, III, and IV, air-dried until constant. V, dried over sulphuric acid and then at 160°. VI, prepared from a distilled toluene solution; dried at 200°.

Assuming that the only hydrogen-giving component of (X) is $[H_2Si_2O_3]_n$, which may be either dioxodisiloxane or a condensation product of $[Si(OH)_2]_n$, the compositions of these samples, calculated from the H.V. and silica determinations, would be as shown above (A); the compositions given under (B) are calculated on the assumption that (X) is a mixture of $H_2Si_2O_3$ and silico-oxalic acid (H.V. = 184; $SiO_2 = 98{\cdot}4\%$), which does not seem to be probable and in any case does not help to settle the origin of (X). The presence of silica would be expected if (X) is formed from $[Si(OH)_2]_n$, because it is proved that the product is partly decomposed by water; if (X) is dioxodisiloxane, it must be concluded that the silica has been formed from silicon tetrachloride. The presence of water (by difference) in samples V and VI cannot be accounted for if (X) is dioxodisiloxane, because this compound is anhydrous when it has been dried over sulphuric acid; if, on the other hand, (X) is a condensation product of $[Si(OH)_2]_n$, it may still retain combined water in the form of $>Si(OH)_2$ groups.* In either case, the percentage of water is calculated by difference, and as it is impossible to assert that the samples V and VI were quite free from organic matter, such as a condensation product of $PhSi(OH)_3$ with $[Si(OH)_2]_n$, the actual figures are only approximations.

Samples of (X) kept at the ordinary temperature or heated did not give, as a rule, increased hydrogen values corresponding with the loss in weight. Sample I, for example, H.V. = 364, lost 7·5% in weight over sulphuric acid and then gave H.V. = 370 instead of 393. Sample III, H.V. = 364, lost 1·64% over sulphuric acid and an additional 1·6% at 130° and then gave H.V. = 342 instead of 375 (compare also p. 1297). These results seem to show that oxidation had occurred, or decomposition into silica and hydrogen by a reaction such as $H_2Si_2O_3 + H_2O = 2SiO_2 + 2H_2$; in either case the observed change in weight would give little indication of the actual loss of water, free or combined. The results seem to be incompatible with the known behaviour of dioxodisiloxane.

Ratio, Solid (X) : Chlorine.—Assuming that the products of hydrolysis of trichlorosilicane are $H_2Si_2O_3$ and 6HCl and those of $SiCl_2$ are $Si(OH)_2$ and 2HCl, the ratios of solid to chlorine would be 1 : 2 and 1 : 1·15 respectively; the pure chlorides might thus be distinguished. In the case under consideration the exact weight of the hydrogen-giving component of (X) is not known and the benzene solutions from which (X) is obtained contain $SiPh_4$, $PhSiH_3$,

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* This seems to be an improbable, but not an impossible assumption. It is known that hydroxy-silicon compounds may differ widely in stability. The trihydroxide, $HSi(OH)_3$, for example, seems to be converted into $H_2Si_2O_3$ at the ordinary temperature, whereas the air-dried product of hydrolysis of silicon hexachloride has the composition $Si(OH)_3{\cdot}Si(OH)_3$ and is only converted into $H_2Si_2O_4$ (and not into Si_2O_3) over sulphuric acid or at 150°; the aryl dihydroxides $R_2Si(OH)_2$ are also relatively stable.

$SiPhCl_3$, HCl and possibly $SiCl_4$, Si_2Cl_6 and diphenyl (impurity in original material) and other compounds; determinations of the ratio, solid (X) : chlorine, after hydrolysis of the silicon halide, could not therefore give the exact composition of that compound. The presence of hydrogen chloride and also that of phenylsilicon trichloride (which gives products of hydrolysis soluble in acetone) would largely increase the proportion of chlorine, and silicon tetrachloride if present would give a larger proportion of chlorine than that calculated for $SiO_2 : 2Cl_2$, because some of the silica would remain in solution as silicic acid. In spite of these considerations many determinations of the ratio (X) : chlorine were made in the hope that the results might decide between the alternatives.

In order to eliminate so far as possible the error due to the presence of hydrogen chloride, the series of benzene wash-bottles was disconnected from the reaction flask when heating had ceased and the stream of dry nitrogen was passed through the solution until the escaping gas began to give a deposit of (X) beyond the mercury seal. The solutions in the first two wash-bottles were then treated separately in the ordinary way and the weights of solid (X) and of chlorine in the aqueous solution and washings were determined : Found : (first wash-bottle) 1—1·9, (second wash-bottle) 1—1·8.

In two following experiments the wash-bottles were not disconnected to avoid the possibility of moisture getting into the solution, but the stream of nitrogen was continued after heating had ceased until deposits of (X) formed beyond the mercury seal; the combined solutions from the first two wash-bottles gave a ratio of 1 : 1·9 in one experiment and 1 : 1·34 in the other; a third experiment of an exactly similar kind gave 1 : 1·5, but the solid was subsequently found to have a H.V. of only about 315.

In two further experiments carried out in this way the dissolved matter in the benzene–acetone–aqueous filtrates from (X) was also determined; it was impossible to ascertain the composition of this matter, but as the nitrogen stream had been passed through a U-tube surrounded by a freezing mixture in order to condense tri- and tetra-phenylsilicane it seems probable that the dissolved organic matter consisted almost entirely of phenylsiliconic acid. On that assumption the uncorrected values 1 : 1·5 and 1 : 1·5 actually found in these two experiments, corrected for the chlorine derived from phenylsilicon trichloride, became 1 : 1·1 and 1 : 1·4 respectively, but the validity of the corrections may be questionable and the experimental errors are considerable. On the whole, however, the results seem to point distinctly to the conclusion that the halide is the dichloride, since the highest uncorrected ratio was found to be

1 : 1·9 and all but one of the sources of error would greatly increase the proportion of halogen.

With the object of eliminating the phenylsilicon trichloride before hydrolysis some of the benzene or toluene solutions of the silicon halide were distilled to a small volume directly from the wash-bottles (small distillation flasks), every precaution being taken to exclude moisture. In one experiment the distillate gave no appreciable quantity of (X) on the addition of water, but the clear residual liquid gave 0·12 g.; in another, the proportion of (X) from the distillate and the residue respectively was roughly 2 : 1; in another, 4 : 1. Similar results with xylene solutions had been obtained at an early stage of the investigation and had been attributed to a partial hydrolysis of the halide during the transference of the solution from the wash-bottle to the distillation flask. The later experiments seemed to exclude this possibility and to be most reasonably explained by assuming that the volatile halide is $SiCl_2$ and that it undergoes polymerisation. This view would also account for the fact that the stream of nitrogen, containing the halide, passed through four wash-bottles of ice-cold toluene may give a deposit of (X) when it is led into water, although the third and fourth wash-bottles are practically free from the halide, most of which is absorbed in the first one. Whatever may be the explanation of these observations, the distillation experiments were not continued because it was found that phenylsilicon trichloride volatilises when its benzene solution is distilled, and also because the sub-division of the already very small quantity of product was undesirable.

The Action of Water on (X).—An air-dried sample of (X), heated at 80° with 5 c.c. of water containing one drop of acetic acid during 1 hour, gave a H.V. = 78; a solution of sodium hydroxide was then added to the residue, which gave H.V. = 242, the total for the air-dried sample being H.V. = 320. A portion of the same sample dried at 200° lost 7% in weight and then gave a H.V. of only 31 when heated with acidified water during 1 hour at 80°; the residue with sodium hydroxide gave an additional H.V. of 294, making a total H.V. = 325. By calculation the dried sample should have given H.V. 344 if no decomposition had occurred (p. 1295).

A different air-dried preparation, treated in the same way at 80°, gave a H.V. = 67 at the end of 2 hours and a total of 102 at the end of 6 hours; the rate of decomposition then rapidly diminished and only reached 122 at the end of about 20 hours at 80—85°, plus some 50 hours at the ordinary temperature; even at the end of some 50 hours' heating, the total H.V. only reached 235 and the residue still gave hydrogen with alkalis.

These results may be taken to show that (X) is a mixture of two or more hydrogen-giving compounds, condensation products of open- and closed-chain hydroxides $[Si(OH)_2]_n$; or that its most reactive component is converted into a more stable compound, such as silico-oxalic acid, which still gives hydrogen; neither view would be tenable if (X) is formed from trichlorosilicane. There is, however, the possibility that the rapid fall in the rate of decomposition is merely due to the formation of a layer of silica on the unchanged substance.

Although, as stated, some of Gattermann's work was repeated, the task of preparing pure dioxodisiloxane for purposes of direct comparison with (X) was too great to be undertaken; it has been impossible, therefore, to confirm the recorded statements as to the properties of dioxodisiloxane, but as these rest on the authority of skilled investigators there is every reason to accept them, and by doing so to conclude that the silicon halide from phenylsilicon trichloride is silicon dichloride.

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