

CCXXIV.—*Organic Derivatives of Silicon. Part XVII.*  
*Some Condensation Products of Diphenylsilicane-*  
*diol.*

By FREDERIC STANLEY KIPPING.

ONE of the main factors that has retarded the development of the chemistry of silicon compounds is, undoubtedly, the insolubility in neutral solvents of all those inorganic derivatives which contain

combined oxygen. This insolubility, of course, may be attributed, at any rate in part, to the great molecular complexity of all such compounds, which apparently is the result of a process of condensation brought about by the elimination of the elements of water from two or more molecules, such as those of silicic acid, containing the group  $\text{>Si}\cdot\text{OH}$ .

Now when the silicon atom in such a group is directly combined with hydrocarbon radicles, the resulting compounds have properties very different from those of the inorganic silicates; although the tendency to undergo condensation is still very marked, even in substances such as the alkyl and aryl derivatives of the type  $\text{R}_3\text{Si}\cdot\text{OH}$  (Kipping, *Trans.*, 1907, **91**, 718), the condensation products of such organic derivatives are still soluble in many neutral solvents, and, consequently, lend themselves to the ordinary methods of investigation.

It would seem, therefore, that our knowledge of the chemistry of silicon is more likely to be extended by a study of the organic derivatives of this element than by that of its mineral compounds.

Now during the investigation of the products of hydrolysis of dichlorodiphenylsilicane (this vol., p. 2108) it was found that diphenylsilicanediol was very easily decomposed by acids and by alkalis, and, even when particular precautions were taken in working with this compound, it was difficult to avoid the formation of oily or glue-like substances.

In view of the probability that these various by-products were mixtures of compounds formed by the condensation of diphenylsilicanediol, and of the possibility that their study might throw some light on the nature of the complex mineral silicates, it seemed worth while to attempt the otherwise uninviting task of isolating the different components of the oils or glues in question; the results of this work are described in the present paper.

So far, four compounds, which are directly related to one another and to diphenylsilicanediol, have been obtained in a pure state from these mixtures, but from observations made during this investigation and from the results of some experiments carried out by Martin (compare *Ber.*, 1912, **45**, 1139, and footnote, this vol., p. 2108), it would appear that several other condensation products, more complex than those described below, may be obtained without difficulty.

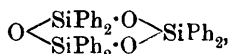
As was anticipated, all these four compounds are derived from diphenylsilicanediol by the loss of the elements of water; subsequent experiments with pure diphenylsilicanediol have shown that their formation is due to the action of traces of alkali or of small quantities of acids on this diol.

The simplest of these condensation products is a compound of the constitution  $\text{HO}\cdot\text{SiPh}_2\cdot\text{O}\cdot\text{SiPh}_2\cdot\text{OH}$ , which is formed from two molecules of diphenylsilicanediol by the loss of one molecule of water, and which is called *anhydrobisdiphenylsilicanediol*, in accordance with the scheme of nomenclature already suggested (this vol., p. 2107).

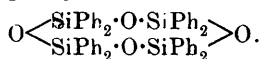
The second condensation product of diphenylsilicanediol, which has been isolated, is produced from three molecules of diphenylsilicanediol by the loss of two molecules of water; this compound has the constitution  $\text{HO}\cdot\text{SiPh}_2\cdot\text{O}\cdot\text{SiPh}_2\cdot\text{O}\cdot\text{SiPh}_2\cdot\text{OH}$ , and, therefore, is named *dianhydrotrisdiphenylsilicanediol*.

Anhydrobisdiphenylsilicanediol and dianhydrotrisdiphenylsilicanediol are both beautifully crystalline compounds, which are freely soluble in most of the ordinary solvents; the former is rapidly converted into a soluble potassium derivative when it is treated with a cold dilute solution of potassium hydroxide, but the latter is not appreciably changed by this reagent.

The other two condensation products of the diol which have been obtained are "multimolecular diphenylsilicones"; the one melts at 188—189°, and is doubtless a *trianhydrotrisdiphenylsilicanediol* of the constitution



whilst the other melts at 200—201°, and must be regarded as a *tetra-anhydrotetraakisdiphenylsilicanediol* of the constitution



Trianhydrotrisdiphenylsilicanediol is easily obtained by heating diphenylsilicanediol, or by treating it with acetic chloride; tetra-anhydrotetraakisdiphenylsilicanediol is formed, together with the trianhydro-compound, when anhydrobisdiphenylsilicanediol is treated with acetyl chloride, and also when dichlorodiphenylsilane is hydrolysed with less than the theoretical quantity of an aqueous solution of an alkali hydroxide.

From the observations so far made it would seem that all the above compounds are produced from diphenylsilicanediol by a process of condensation, and that the "multimolecular silicones" are not directly formed by the polymerisation of diphenylsilicone. It is, in fact, rather doubtful whether diphenylsilicone is produced or not by the elimination of water from the diol; oily products, which possibly contain this silicone, are very easily formed from diphenylsilicanediol under various conditions, but as such oils are complex mixtures, it has not yet been found possible to identify all their components. The evidence pointing to the presence in them

of diphenylsilicone is, that when the oils have been freed so far as possible from diphenylsilicanediol, anhydrobisdiphenylsilicanediol, and dianhydrotrisdiphenylsilicanediol, they yield trianhydrotrisdiphenylsilicanediol and tetra-anhydrotetraakisdiphenylsilicanediol on treatment with hydrochloric acid in alcoholic solution; this evidence, however, is inconclusive.

The existence of a dianhydrobisdiphenylsilicanediol of the constitution  $\text{O} \begin{smallmatrix} \text{SiPh}_2 \\ \text{SiPh}_2 \end{smallmatrix} \text{O}$ , derived from one molecule of anhydrobisdiphenylsilicanediol by the loss of one molecule of water, is also doubtful; the facts that anhydrobisdiphenylsilicanediol is relatively very stable towards heat, and that, when treated with acetyl chloride, it gives tetra-anhydrotetraakisdiphenylsilicanediol (mixed with trianhydrotrisdiphenylsilicanediol), seem to show that the closed chain of two silicon and two oxygen atoms is not easily formed.

A "termolecular diphenylsilicone," melting at  $188^\circ$ , to which he gave the constitution assigned above to trianhydrotrisdiphenylsilicanediol, has been previously described by Dilthey (*Ber.*, 1905, **38**, 4132), and was also obtained by Martin (*loc. cit.*); judging by its melting point, the author's trianhydrotrisdiphenylsilicanediol is identical with Dilthey's crystalline "termolecular silicone," but there are certain statements in Dilthey's paper which are rather in conflict with this view.

By heating diphenylsilicanediol, Dilthey obtained a gelatinous mass, to which, from the results of analyses and molecular-weight determinations, he assigned the formula  $[\text{SiPh}_2\text{O}]_3$ ; this gelatin, according to his statements, was converted into the crystalline "termolecular silicone" when it was brought into contact with a drop of alcohol or acetic anhydride, a change which Dilthey regarded as a process of polymerisation.

The molecular weight of this crystalline silicone was found to be 605 in benzene solution, and apparently, from the statement, "rasches Erhitzen ist erforderlich," its melting point varied with the rate of heating; it was partly converted into the gelatin when it was recrystallised from benzene.

Now the author's trianhydrotrisdiphenylsilicanediol gave a molecular weight of 490 in benzene solution, its melting point did not vary with the rate of heating, and it was not changed in any way by benzene or other neutral solvents. In view of these facts the identity of trianhydrotrisdiphenylsilicanediol and Dilthey's "termolecular silicone" might be questioned, but in the author's opinion there is no sufficient reason to do so; the variability of the melting point of Dilthey's preparation, if, in fact, such varia-

bility was observed, and the supposed partial transformation of this crystalline compound into a gelatinous substance, would be accounted for if the samples had not been completely separated from the other products which are formed by the action of heat on diphenylsilicanediol.

With regard to the gelatinous mass, which Dilthey considered to be convertible into the crystalline silicone, the author's experiments seem to show conclusively that it was merely a mixture of trianhydrotris(diphenylsilicanediol) and other dehydration or condensation products of diphenylsilicanediol (compare p. 2137).

Martin (*loc. cit.*) states that his observations confirmed those of Dilthey as regards the existence of two forms of a "termolecular diphenylsilicone," but he does not give any particulars in support of this statement, except that various viscid masses, obtained by treating the diol with hydrochloric acid, gave the crystalline "termolecular silicone" when they were warmed with acetic anhydride; here, again, as in the case of Dilthey's gelatin, the crystalline compound was probably already present in the viscid mass, or was produced from some unchanged diphenylsilicanediol by the action of the acetic anhydride, and the experiments do not afford the slightest evidence of the existence of a gelatinous "termolecular diphenylsilicone."

In Martin's paper there is also some account of a substance melting at 100—111°, of which, however, no analysis is given, and a reference to two other crystalline compounds, melting at 125° and 186° respectively, which were obtained in very small quantities. The first of these substances (m. p. 100—111°) was probably an impure preparation of anhydrobis(diphenylsilicanediol), which melts at 113—114°; whereas the third was possibly a mixture of trianhydrotris(diphenylsilicanediol) and tetra-anhydrotetrakis(diphenylsilicanediol) (compare p. 2140); no compound melting at 125° has been obtained during the present investigation.

#### EXPERIMENTAL.

When dichlorodiphenylsilane is hydrolysed with cold water, a considerable proportion of the product consists of a pale yellow oil, which is readily soluble in cold chloroform (this vol., p. 2114), and also in cold alcohol; an oil having these properties is also obtained as the only product when the dichloride is decomposed with a cold concentrated solution of ammonium hydroxide (this vol., p. 2115).

Similar oils are, or may be, obtained, owing doubtless to the action of acids, during the recrystallisation of the crude diphenylsilicanediol, prepared by some of the methods already described (pp. 2115, 2119). If, however, the crude diphenylsilicanediol contains

traces of potassium hydroxide, as probably do those samples obtained by neutralising solutions of its potassium derivative with acetic acid (p. 2116), the original by-products, or those formed during recrystallisation, are of a different character; they are more glue-like in consistency, and although readily soluble in chloroform are only partly soluble in cold ethyl alcohol.

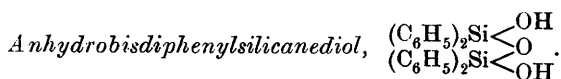
All those oily by-products which are soluble in ethyl alcohol seem to be mixtures of anhydrobisdiphenylsilicanediol (m. p. 113—114°) and dianhydrotrisdiphenylsilicanediol (m. p. 111—112°), containing also a small proportion of trianhydrotrisdiphenylsilicanediol (ter-molecular diphenylsilicone) and a variable but very considerable proportion of other components; the three crystalline compounds just named may be isolated in the following manner: The oil is dissolved in a considerable quantity of chloroform, and the solution is diluted with light petroleum until it begins to turn turbid. If, when the solution is allowed to evaporate at the ordinary temperature, it gives a crystalline deposit, it is left undisturbed until an oil begins to separate with the crystals; the mother liquor is then decanted. If, however, the solution merely deposits an oil, a considerable quantity of light petroleum is added in order to precipitate a suitable proportion of the dissolved substance, and the clear solution is then decanted. The crystalline deposit or the precipitated oil is again dissolved in chloroform, and the solution, having been mixed with light petroleum, is left to evaporate at the ordinary temperature; the original mother liquors are either left to evaporate spontaneously, or a further proportion of the dissolved matter is immediately precipitated with the aid of light petroleum.

As the result of such operations, carried out systematically, the original oil is separated into various fractions, some of which give crystalline deposits when their solutions in a mixture of chloroform and light petroleum are evaporated at the ordinary temperature.

These crystalline fractions sometimes contain a very small quantity of diphenylsilicanediol, which is now easily and almost completely removed by treatment with cold chloroform, in which the diol is only sparingly soluble. The chloroform solution is then evaporated, the residue is dissolved in a very little ether (or ethyl acetate), and the solution is diluted with light petroleum until a turbidity is produced. The crystalline material which first separates from such solutions at the ordinary temperature generally contains, or consists principally of, trianhydrotrisdiphenylsilicanediol; as this compound is rather sparingly soluble in ether (or ethyl acetate) and practically insoluble in light petroleum, its separation from the other two components of the mixture is accomplished by further systematic treatment with these solvents.

The trianhydrotris(diphenylsilicanediol) having been removed as completely as possible, the ethereal-petroleum solution is evaporated, the residue is again dissolved in a mixture of chloroform and light petroleum, and the solution is left to evaporate at the ordinary temperature. The first crystalline deposit which is then obtained may consist almost entirely of anhydrobis(diphenylsilicanediol); the subsequent fractions, however, are equilibrium mixtures of this substance and dianhydrotris(diphenylsilicanediol). The separation of the two compounds just named from one another is a matter of great difficulty; as fractional crystallisation gives very unsatisfactory results, the most convenient method to adopt is a mechanical one. The chloroform-petroleum solution is evaporated slowly at the ordinary temperature in order to obtain large crystals; the dianhydrotris(diphenylsilicanediol) is then deposited in massive, transparent, rhomboidal crystals, which are distinguishable by inspection from the prisms of anhydrobis(diphenylsilicanediol). The crystals of the former having been picked out, the residue is crystallised again under the same conditions as before, and any crystals of the dianhydrotris(diphenylsilicanediol) are removed from the deposit; these operations are continued until the separation is as complete as possible, and the two products are then further purified by recrystallisation from chloroform containing a little light petroleum.

When the original oily by-product has been repeatedly and systematically fractionated with the aid of chloroform and light petroleum in the manner described, and the various crystalline mixtures of anhydrobis(diphenylsilicanediol), dianhydrotris(diphenylsilicanediol), and trianhydrotris(diphenylsilicanediol) have been removed, there remains a considerable proportion of the original material as a viscid oil, from which no further crystalline deposit can be obtained. This oil is no longer completely soluble in cold alcohol; a large proportion of it dissolves freely, leaving a viscid, glue-like mass. These products are referred to later (p. 2141).



The mechanical separation of this compound from dianhydrotris(diphenylsilicanediol) having been carried out as far as possible, the crude substance is recrystallised from a mixture of chloroform and light petroleum at the ordinary temperature; it is thus obtained in beautiful, transparent crystals, melting sharply at 113—114°.

Anhydrobis(diphenylsilicanediol) was thus isolated from the

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by-products previously mentioned, and its occurrence in these oils shows that it is produced from diphenylsilicanediol by the action of hydrochloric acid, and also by the action of a concentrated solution of ammonium hydroxide on dichlorodiphenylsilicane.

Two different preparations were analysed:

0.1726 gave 0.4396  $\text{CO}_2$  and 0.0850  $\text{H}_2\text{O}$ .  $\text{C} = 69.5$ ;  $\text{H} = 5.5$ .

0.1376 „ 0.3504  $\text{CO}_2$  „ 0.0700  $\text{H}_2\text{O}$ .  $\text{C} = 69.5$ ;  $\text{H} = 5.6$ .

$\text{C}_{24}\text{H}_{22}\text{O}_3\text{Si}_2$  requires  $\text{C} = 69.7$ ;  $\text{H} = 5.3$  per cent.

Molecular-weight determinations were made by the cryoscopic method in benzene solution:

0.53 in 11.2 benzene gave  $\Delta t = -0.4$ .  $\text{M.W.} = 579$ .

0.234 „ 11.3 „ „  $\Delta t = -0.16$ .  $\text{M.W.} = 539$ .

0.617 „ 13.3 „ „  $\Delta t = -0.375$ .  $\text{M.W.} = 601$ .

$\text{C}_{24}\text{H}_{22}\text{O}_3\text{Si}_2$  requires  $\text{M.W.} = 414$ .

These results do not agree well with the theoretical values, probably because the hydroxy-compound is associated in benzene solution; other determinations in acetic acid or alcoholic solution were not made, as the compound is changed by these solvents. There is, however, a certain amount of independent evidence in favour of the molecular formula given above, as will be explained later.

Anhydrobisdiphenylsilicanediol crystallises well from benzene or from a mixture of benzene and light petroleum in transparent prisms, but from ether, ethyl acetate, and acetone it is often deposited as an oil; it also separates from aqueous acetone as an oil, which does not crystallise readily. It is very soluble in all the anhydrous solvents named above, except cold light petroleum, in which it is practically insoluble.

Anhydrobisdiphenylsilicanediol is converted into a soluble potassium derivative when it is treated with a cold solution of potassium hydroxide; small crystals, when placed on the surface of such a solution, often rotate, or move about rapidly, as they dissolve. With acetic acid the solution gives a crystalline precipitate, which is sparingly soluble in cold chloroform, and which is doubtless diphenylsilicanediol.

Anhydrobisdiphenylsilicanediol is very readily soluble in cold methyl or ethyl alcohol; when such solutions are evaporated at the ordinary temperature, it separates to a very great extent unchanged. It is, however, partly decomposed by these solvents, and when the solutions are kept for a long time, or heated, they deposit a white powder, which seems to be a mixture of condensation products. This transformation takes place so slowly that it



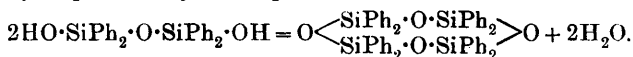
is very incomplete, even after the solutions have been boiled during about an hour.

Anhydrobisdiphenylsilicanediol is stable at 100°, and even at 200° it seems to be only slowly decomposed, bubbles of aqueous vapour escaping from the liquid mass; when heated more strongly in a test-tube over a flame, a rapid effervescence takes place, a very pronounced odour of burnt petroleum is observed, and after a short time decomposition is practically complete. The residue, which solidifies on being cooled, is not completely soluble in warm ethyl acetate; the insoluble matter is a white powder, which is probably a highly complex condensation product. The soluble portion separates from the filtered solution in well-defined crystals; when these are heated at 110° about one-half of them become opaque, whilst the rest remain transparent; the former melt at about 184°, and consist principally of tetra-anhydrotetrakisdiphenylsilicanediol (m. p. 200—201°), whilst the latter melt at about 188° and consist of practically pure trianhydrotrisdiphenylsilicanediol (compare p. 2140).

Since it would seem that under the above conditions a dianhydrobisdiphenylsilicanediol of the constitution  $O \begin{smallmatrix} \text{SiPh}_2 \\ \text{SiPh}_2 \end{smallmatrix} O$  is not produced, it may be inferred that a closed chain of two silicon and two oxygen atoms is not formed so readily as one containing three silicon and three oxygen atoms, or four silicon and four oxygen atoms. The production of trianhydrotrisdiphenylsilicanediol is not easily accounted for, except on the assumption that at the high temperature employed some of the anhydrobisdiphenylsilicanediol is hydrolysed by the water which is formed during the operation. Whether this is so or not, the formation of the trianhydro-compound seems to show that the closed chain of six atoms is more stable than that of eight. It is also of interest to note that the behaviour of anhydrobisdiphenylsilicanediol at high temperatures differs from that of anhydrobisdibenzylsilicanediol (p. 2151), inasmuch as the latter, apparently, does not give a product corresponding with tetra-anhydrotetrakisdiphenylsilicanediol.

Anhydrobisdiphenylsilicanediol dissolves freely in acetyl chloride at the ordinary temperature, and when the solution is evaporated in a desiccator over soda-lime it gives a crystalline deposit, which consists essentially, if not entirely, of tetra-anhydrotetrakisdiphenylsilicanediol. The presence of trianhydrotrisdiphenylsilicanediol was not detected in this product, and although a relatively small quantity of a powder sparingly soluble in ethyl acetate was formed, and the purification of the tetra-anhydrotetrakisdiphenylsilicanediol

was thereby rendered somewhat troublesome, the main reaction was obviously expressed by the equation:



*Dianhydrotris(diphenylsilicanediol),*  
 $\text{HO}\cdot\text{SiPh}_2\cdot\text{O}\cdot\text{SiPh}_2\cdot\text{O}\cdot\text{SiPh}_2\cdot\text{OH}.$

The large crystals of this compound, which have been separated from the anhydrobis(diphenylsilicanediol) mechanically (p. 2131), are practically free from impurity, and are merely recrystallised from a mixture of chloroform and light petroleum; the pure substance is then deposited in beautiful, rhomboidal prisms, melting sharply at 111–112°.

It was thus obtained from the same by-products as those which gave anhydrobis(diphenylsilicanediol); it is therefore formed by the action of acids on diphenylsilicanediol, and by the action of a concentrated solution of ammonium hydroxide on dichlorodiphenylsilicane.

Two different samples were analysed:

0.1941 gave 0.5010  $\text{CO}_2$  and 0.0937  $\text{H}_2\text{O}$ . C = 70.4; H = 5.3.

0.1826 „ 0.4726  $\text{CO}_2$  „ 0.0893  $\text{H}_2\text{O}$ . C = 70.6; H = 5.4.

$\text{C}_{36}\text{H}_{32}\text{O}_4\text{Si}_3$  requires C = 70.4; H = 5.2 per cent.

Its molecular weight was determined by the cryoscopic method in benzene solution:

0.283 in 13.3 benzene gave  $\Delta t = -0.14$ . M.W. = 745.

0.617 „ 13.3 „ „  $\Delta t = -0.32$ . M.W. = 766.

One determination, possibly not a very trustworthy one, was made in chloroform by the ebullioscopic method:

0.48 in 18.5 chloroform gave  $E = 0.13$ . M.W. = 730.

As the calculated molecular weight for a compound of the composition  $\text{C}_{36}\text{H}_{32}\text{O}_4\text{Si}_3$  is 613, the above experimental values, like those obtained in the case of anhydrobis(diphenylsilicanediol), are very much too high, and indicate the presence of associated molecules in the given solvents. If, however, the average results obtained with the two compounds in benzene solution are compared, it will be seen that the difference in molecular weight is found by experiment to be about 182, which corresponds closely with the calculated difference. Further evidence in support of the formula assigned to dianhydrotris(diphenylsilicanediol) is afforded by the fact that this compound may be readily and quantitatively converted into the “termolecular silicone” (trianhydrotris(diphenylsilicanediol)) as shown later.

Dianhydrotris(diphenylsilicanediol) resembles anhydrobis(diphenyl-

silicanediol in its general behaviour towards solvents; it is very readily soluble in chloroform, ether, acetone, or ethyl acetate, but practically insoluble in cold light petroleum. It also dissolves freely in cold benzene, from which it separates in massive, transparent, rhomboidal crystals; these contain benzene, which they slowly lose on exposure to the air:

1.0942 lost 0.1244 at 100°.  $C_6H_6 = 11.4$ .

$C_{36}H_{32}O_4Si_3$ ,  $C_6H_6$  requires  $C_6H_6 = 11.3$  per cent.

From aqueous acetone dianhydrotris(diphenyl)silicanediol separates as an oil which does not crystallise readily; it dissolves freely in cold methyl alcohol, but, like anhydrobis(diphenyl)silicanediol, it is slowly acted on by this solvent, and the solution deposits a colourless powder, a part of which is insoluble in ethyl acetate and doubtless consists of some condensation product of very high molecular weight.

Dianhydrotris(diphenyl)silicanediol is not appreciably acted on by a 5 per cent. aqueous solution of potassium hydroxide; small crystals left in contact with such a solution show no visible diminution in size, even after many hours. This marked difference in behaviour between anhydrobis- and dianhydrotris(diphenyl)silicanediol is very useful for distinguishing the two compounds and for testing the purity of the former. Alcoholic potassium hydroxide hydrolyses dianhydrotris(diphenyl)silicanediol at the ordinary temperature, giving a solution from which acetic acid precipitates a colourless compound; this precipitate is only very sparingly soluble in cold chloroform, and doubtless consists of diphenylsilicanediol.

Dianhydrotris(diphenyl)silicanediol seems to be decomposed by heat rather more readily than is anhydrobis(diphenyl)silicanediol, and at about 170° it begins to lose water with appreciable rapidity. When it is heated over a free flame the escaping steam causes an effervescence, and a strong odour of burnt petroleum is noticed; the residue solidifies readily, and when crystallised from ethyl acetate gives pure trianhydrotris(diphenyl)silicanediol, which, apparently, is the principal, if not the only, product of the reaction.

Dianhydrotris(diphenyl)silicanediol is readily soluble in acetyl chloride; when the solution is slowly evaporated in a desiccator over soda-lime, trianhydrotris(diphenyl)silicanediol is deposited in well-defined crystals, and the yield seems to be quantitative. The readiness with which the dianhydro- is converted into the trianhydro-compound may be taken as confirmatory evidence of the supposed relation between the two compounds; also as indicative of the stability of the closed chain containing three silicon and three oxygen atoms.



This compound is present in relatively small quantities in the oil which is formed when dichlorodiphenylsilicane is decomposed with a concentrated solution of ammonium hydroxide, and also in the oil which is formed when diphenylsilicanediol is heated with solvents in presence of traces of acids; it is also present, usually in larger quantities, in those glue-like products which are formed by the action of traces of alkalis on the diol. One method for the isolation of this compound from such mixtures has already been described (p. 2130), but a much simpler process may sometimes be used at the sacrifice of any anhydrobis(diphenylsilicanediol) and dianhydrotris(diphenylsilicanediol) which are contained in the mixture; the oily product is extracted with an aqueous solution of potassium hydroxide, the washed residue is treated with cold methyl alcohol, and the undissolved crystalline matter is recrystallised from ethyl acetate. In this way pure trianhydrotris(diphenylsilicanediol) is sometimes obtained very easily; in many cases, however, the crystals which are deposited from the ethyl acetate solution are a mixture of trianhydrotris(diphenylsilicanediol) and tetra-anhydrotetra-kis(diphenylsilicanediol), the separation of which is rather troublesome (p. 2142).

As stated above, trianhydrotris(diphenylsilicanediol) is easily obtained from dianhydrotris(diphenylsilicanediol), and is also formed together with tetra-anhydrotetra-kis(diphenylsilicanediol) by the action of heat on anhydrobis(diphenylsilicanediol); it is most conveniently prepared by heating pure diphenylsilicanediol first at about  $150^\circ$  and finally at about  $180^\circ$  until approximately the theoretical loss in weight has taken place.

As soon as the temperature of the bath rises to about  $140^\circ$ , the diol rapidly liquefies, and a vigorous effervescence is observed; after about ten minutes at this temperature, the effervescence practically ceases, but the decomposition is still incomplete, and the loss in weight is only about 6 per cent. (starting with about 0.5 gram of the diol). The temperature is then slowly raised to about  $180^\circ$  in the course of about twenty-five minutes, at the end of which time the loss in weight is about 8.0 per cent., which corresponds approximately with the theoretical quantity (8.3 per cent.). The cooled residue may crystallise, or it may remain for a long time as a transparent glass; if, however, the latter is again heated at about  $120$ – $130^\circ$  for a moment, or rubbed with a glass rod, or treated with small quantities of various solvents, it gives a crystalline mass of trianhydrotris(diphenylsilicanediol), which is purified by recrystallisation from ethyl acetate.

Although the pure diol may have been heated until approximately the theoretical loss in weight has occurred, the product does not consist of pure trianhydrotris(diphenylsilicanediol), and the ethyl acetate mother liquors contain an appreciable proportion of an oily substance, which is readily soluble in light petroleum containing a little ethyl acetate; the nature of this oil has not been determined, but it seems possible that it may contain diphenylsilicone and anhydrobis(diphenylsilicanediol).

In view of the above results it seems improbable that the gelatin obtained by Dilthey by heating diphenylsilicanediol at  $140^{\circ}$  consisted of or contained any silicone isomeric with trianhydrotris(diphenylsilicanediol (m. p.  $188^{\circ}$ ); his product was probably a supercooled impure form of the last-named compound.

Some quantitative experiments on the effect of heat on diphenylsilicanediol were made by Martin (*loc. cit.*), who found that at  $140^{\circ}$  there was a loss in weight of 13.3 per cent. at the end of five hours. In the above experiments the diol was heated in a test-tube, and the weight became practically constant in the time stated; as, however, the conditions were so different in the two sets of observations, the results are hardly comparable. A possible explanation of the high loss observed by Martin is, that atmospheric oxidation occurred, with subsequent loss of the oxidation product; this would account for the high percentage of silicon which Martin found in the residue.

Trianhydrotris(diphenylsilicanediol may also be obtained by dissolving diphenylsilicanediol in excess of acetyl chloride, and evaporating the solution in a desiccator over soda-lime; although the residue consists mainly of trianhydrotris(diphenylsilicanediol, it also contains a small proportion of tetra-anhydrotetraakis(diphenylsilicanediol, and, for the isolation of the former, repeated recrystallisation from ethyl acetate or acetone is necessary.

Trianhydrotris(diphenylsilicanediol crystallises very well from cold ethyl acetate, and is very readily soluble in chloroform or benzene, sparingly so in cold ether, and practically insoluble in light petroleum and the two common alcohols. Its partial conversion into a gelatin, as described by Dilthey, by recrystallisation from chloroform, ether, or benzene, has never been observed; imperfectly purified samples give, it is true, deposits which are contaminated with a very viscid substance, but the pure compound gives only clean, lustrous crystals, and Dilthey's observations to the contrary are certainly incorrect, if his crystalline "termolecular silicone" is identical with trianhydrotris(diphenylsilicanediol.

The pure compound melts very sharply at  $188-189^{\circ}$ , and its melting point does not vary with the rate of heating; Dilthey's

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statement that "rasches Erhitzen ist erforderlich" seems an indication that his specimen was not pure.

In view of these discrepancies between Diltthey's and the author's observations and of Martin's statement that his experiments confirmed those of Diltthey an analysis of the compound melting at 188—189° was made:

0.1560 gave 0.4154 CO<sub>2</sub> and 0.7600 H<sub>2</sub>O. C=72.6; H=5.4.

C<sub>36</sub>H<sub>30</sub>O<sub>3</sub>Si<sub>3</sub> requires C=72.6; H=5.0 per cent.

Its molecular weight was also determined by the cryoscopic method in benzene solution:

0.165 in 13.3 benzene gave  $\Delta t = -0.114$ . M.W.=490.

0.302 „ 13.3 „ „  $\Delta t = -0.214$ . M.W.=490.

0.383 „ 13.3 „ „  $\Delta t = -0.29$ . M.W.=490.

0.427 „ 16.4 „ „  $\Delta t = -0.272$ . M.W.=477.

C<sub>36</sub>H<sub>30</sub>O<sub>3</sub>Si<sub>3</sub> requires M.W.=594.

These results, which agree exceptionally well among themselves, are very different from those (609 and 601) obtained by Diltthey; they are, moreover, very considerably lower than the calculated value. As the readings were very constant and the author has no reason to doubt their accuracy, the fact that the observed are about 20 per cent. lower than the theoretical value cannot be accounted for; it will be seen, however, that corresponding results are obtained in the case of the similar but more complex compound described below.

*Tetra-anhydrotetrakis(diphenylsilicanediol),*  $\text{O} \begin{array}{c} \text{SiPh}_2 \cdot \text{O} \cdot \text{SiPh}_2 \\ \text{SiPh}_2 \cdot \text{O} \cdot \text{SiPh}_2 \end{array} \text{O}.$

This compound may be prepared, as stated above, by treating anhydrobis(diphenylsilicanediol) with acetyl chloride; it is also formed, together with trianhydrotris(diphenylsilicanediol), when anhydrobis(diphenylsilicanediol) is heated alone, and, further, when those oily by-products which contain anhydrobis(diphenylsilicanediol) (and other substances) are heated with an alcoholic solution of hydrochloric acid.

It may be obtained in one operation by gradually adding dichlorodiphenylsilicane to an aqueous solution of potassium hydroxide, but the most suitable conditions for its formation in this way have not been determined. When excess of potassium hydroxide is used, a clear solution of the potassium derivative of diphenylsilicanediol is formed (this vol., p. 2116); when, however, such a quantity of potassium hydroxide is present that the solution becomes acid to litmus after about two-thirds of the dichloro-compound have been added, the addition of the remainder results

in the separation of a pasty solid. This product, having been washed with water and dried in the air, crystallises from ethyl acetate, but the solution deposits two kinds of crystals, which may be separated from one another mechanically. The larger proportion of the deposit consists of long, slender, not very well defined prisms, which melt at about  $197^{\circ}$ ; the remainder consists of short, compact, well-defined crystals, which melt at about  $184^{\circ}$ , and which are referred to below.

The product, melting at about  $197^{\circ}$ , is slightly impure tetra-anhydrotetrakis(diphenylsilicanediol); when recrystallised several times from ethyl acetate its melting point becomes constant at  $200-201^{\circ}$ :

0.1362 gave 0.3636  $\text{CO}_2$  and 0.0606  $\text{H}_2\text{O}$ .  $\text{C}=72.8$ ;  $\text{H}=4.94$ .

0.1524 „ 0.0472  $\text{SiO}_2$ .  $\text{Si}=14.6$ .

$\text{C}_{48}\text{H}_{40}\text{O}_4\text{Si}_4$  requires  $\text{C}=72.6$ ;  $\text{H}=5.0$ ;  $\text{Si}=14.4$  per cent.

Its molecular weight was determined by the cryoscopic method in benzene solution:

0.271 in 13.2 benzene gave  $\Delta t = -0.15$ . M.W. = 685.

0.29 „ 13.3 „ „  $\Delta t = -0.16$ . M.W. = 674.

0.546 „ 13.3 „ „  $\Delta t = -0.30$ . M.W. = 669.

$\text{C}_{48}\text{H}_{40}\text{O}_4\text{Si}_4$  requires M.W. = 792.

These results, like those obtained in the case of trianhydrotris(diphenylsilicanediol), are about 20 per cent. lower than the calculated value, but as the readings were very sharp and constant, there is no reason to doubt their accuracy. In so far as the relation between tetra-anhydrotetrakis(diphenylsilicanediol) and trianhydrotris(diphenylsilicanediol) is concerned, the determinations show a difference of about 189 as against a theoretical difference of 198; on the whole, therefore, the results support the molecular formulæ respectively assigned to these two compounds.

Tetra-anhydrotetrakis(diphenylsilicanediol) is readily soluble in cold chloroform or benzene, only very moderately so in cold acetone or ethyl acetate, and very sparingly so in the common alcohols or light petroleum. It nearly always separates from warm ethyl acetate or acetone in long, slender, very imperfect prisms, but when crystallisation occurs at the ordinary temperature the compound is generally deposited in well-defined, almost rectangular plates, or in long, well-defined prisms. The crystals obtained from cold ethyl acetate solution become opaque at temperatures below  $100^{\circ}$ , but do not contain solvent.

The crystalline product melting at about  $184^{\circ}$  which was obtained together with tetra-anhydrotetrakis(diphenylsilicanediol) in the manner described above, and separated from it mechanically,



seemed to be a pure compound; when recrystallised from ethyl acetate at the ordinary temperature it gave massive, transparent, well-defined, rhomboidal crystals, melting fairly sharply at  $184\text{--}186^\circ$ , and sometimes of such a size that individual crystals weighed more than 0.5 gram. It also crystallised well from hot ethyl acetate and from cold acetone, giving transparent, almost rectangular plates, indistinguishable by inspection from those of tetra-anhydrotetrakis(diphenylsilicanediol), but which melted at  $184\text{--}186^\circ$ , instead of at  $200\text{--}201^\circ$ , which is the melting point of the last-named compound.

It was ultimately discovered that this apparently pure and beautifully crystalline compound, melting at  $184\text{--}186^\circ$ , was, in fact, a mixture of tetra-anhydrotetrakis(diphenylsilicanediol) and trianhydrotris(diphenylsilicanediol); by repeated fractional crystallisation, first from warm acetone, and then from ethyl acetate, it was gradually resolved into the pure compound, melting at  $200\text{--}201^\circ$ , and a small quantity of trianhydrotris(diphenylsilicanediol).

It is obvious, therefore, that when tetra-anhydrotetrakis(diphenylsilicanediol) separates from an ethyl acetate solution which contains a sufficient quantity of trianhydrotris(diphenylsilicanediol), the two substances crystallise together, apparently in fixed proportions, giving a product of almost constant melting point. Moreover, massive, well-defined crystals of this product are far more easily obtained than are large crystals of pure tetra-anhydrotetrakis(diphenylsilicanediol); whereas the latter generally separates from warm ethyl acetate and acetone in slender prisms, quite unsuitable for goniometrical examination, the mixture melting at about  $184\text{--}186^\circ$ , is usually deposited in the well-defined, rectangular plates from the warm solvents, and in the massive, rhomboidal prisms from cold ethyl acetate.

Mixtures of trianhydrotris(diphenylsilicanediol) and tetra-anhydrotetrakis(diphenylsilicanediol), as already stated, are obtained from diphenylsilicanediol in various ways, and such mixtures sometimes have a very indefinite melting point of about  $160\text{--}170^\circ$ ; if they are recrystallised from ethyl acetate at the ordinary temperature, they give a crystalline deposit, which, from a cursory ocular inspection, seems to be homogeneous; when, however, such deposits are heated on the water-bath, some of the crystals become white and opaque, others remain perfectly transparent. The latter are the crystals of trianhydrotris(diphenylsilicanediol), whilst the former are a mixture of this compound with tetra-anhydrotetrakis(diphenylsilicanediol), similar to that described above. The two kinds of crystals may be separated mechanically, and the opaque ones, when



fractionally crystallised from hot acetone, ultimately give the compound melting at 200—201°, and small quantities of the compound melting at 188—189°.

*Formation of Trianhydrotris(diphenylsilicanediol) and Tetra-anhydrotetrakis(diphenylsilicanediol) from Oily Mixtures.*

The very viscid oil, which is obtained by the evaporation of the petroleum-chloroform mother liquors, from which anhydrobis(diphenylsilicanediol), dianhydrotris(diphenylsilicanediol), and trianhydrotris(diphenylsilicanediol) have been separated as far as possible (p. 2131), seems to be practically free from these compounds; when fractionally precipitated from chloroform, with the aid of light petroleum, it gives oily products, some of which are readily, others only sparingly, soluble in cold methyl alcohol, but although a partial separation of the components of the mixture may thus be accomplished, none of the fractions gives a crystalline deposit. So far the nature of these final fractions has not been determined, but it is possible to obtain from them a considerable proportion of crystalline products by suitable methods.

When the crude, non-crystallisable oil is treated with methyl alcohol, most of it passes into solution quite freely, whilst a small quantity of a sparingly soluble oil separates, and remains undissolved even after the addition of a large volume of the alcohol; if, now, a few drops of hydrochloric acid are added to the solution, most of the dissolved oil is rapidly precipitated, and after some time the separation of crystals commences. The methyl-alcoholic solution is then poured off and left to evaporate spontaneously; the residual, very viscid oil is warmed for a short time with methyl alcohol containing a few drops of hydrochloric acid, and the following day the solution is decanted. If these operations are repeated daily, the sparingly soluble oil becomes more and more viscous and diminishes in quantity, whilst the methyl-alcoholic extracts slowly deposit crystals.

This crystalline product can hardly be present in the original mixture, and is doubtless formed by the action of the methyl-alcoholic hydrochloric acid on some substance or substances contained in the oil. It is possible, although it does not seem very probable, that these substances are anhydrobis(diphenylsilicanediol) and dianhydrotris(diphenylsilicanediol); if this possibility be excluded, the origin of the crystalline product may be the yet unknown diphenylsilicone,  $\text{SiPh}_2\text{O}$ .

The crystalline product just referred to is a mixture of trianhydrotris(diphenylsilicanediol) and tetra-anhydrotetrakis(diphenylsilicanediol); when repeatedly crystallised from ethyl acetate or acetone, it

may yield a small proportion of one of these compounds in a pure state, but the subsequent deposits consist of mixtures of these two substances, the separation of which is a very troublesome matter. Perhaps the simplest method is that already described. The mixture is slowly crystallised from ethyl acetate at the ordinary temperature, and as soon as a deposit of large crystals has been produced the mother liquor is decanted and the beaker containing the deposit is heated on the water-bath for a few minutes; the transparent crystals, which consist of trianhydrotris(diphenylsilicanediol), are then separated mechanically from those which have become opaque, and the latter, which consist of tetra-anhydrotetrakis(diphenylsilicanediol), or of the mixture melting at about  $184^{\circ}$ , are redissolved. These operations are repeated until the trianhydrotris(diphenylsilicanediol) has been separated so far as possible, and the impure tetra-anhydrotetrakis(diphenylsilicanediol) which remains is then repeatedly recrystallised from hot acetone until its melting point rises to  $200-201^{\circ}$ .

The facts recorded in this series of papers (Part XVI. to XIX.) have an important bearing on the views which may be held regarding the structures of many of the inorganic derivatives of silicon; this matter will be discussed in a future communication.

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