LI.—Organic Derivatives of Silicon. Part XXI. The Condensation Products of Diphenylsilicanediol.*

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In the present paper we record the results of a further study of diphenylsilicanediol and of the open- and closed-chain condensation products derived from this diol (Kipping, T., 1912, 101, 2108, The compounds which have now been obtained are of the 2125).following types, of which No. IV has not hitherto been described:

- I. HO.SiPh. OH.
- II. HO·SiPh, O·SiPh, OH.
- III. HO·SiPh₂·O·SiPh₂·O·SiPh₂·OH.
- IV. $HO \cdot SiPh_2 \cdot O \cdot SiPh_2 \cdot O \cdot SiPh_2 \cdot O \cdot SiPh_2 \cdot OH$.
- V. $\operatorname{SiPh}_2 \stackrel{\circ}{\longleftrightarrow} \stackrel{\circ}{\operatorname{SiPh}_2} \stackrel{\circ}{\to} 0.$ VI. $\operatorname{O} \stackrel{\circ}{\leqslant} \stackrel{\circ}{\operatorname{SiPh}_2} \stackrel{\circ}{\to} 0. \stackrel{\circ}{\operatorname{SiPh}_2} \stackrel{\circ}{\to} 0.$

It will be seen that diphenylsilicone, SiPh₂O, and also the closedchain compound, $Ph_2Si <_O^O > SiPh_2$, which theoretically might be formed from anhydrobisdiphenylsilicanediol (II), have not yet

* In a previous paper (T., 1912, 101, foot note to p. 210) I mentioned the circumstances which led to the publication by Martin of a paper on some silicon compounds (Ber., 1912, 45, 403), and I pointed out that he had given a "very erroneous" account of diphenylsilicanediol; having spent a good deal of time in proving the inaccuracy of his results, I was able to suggest exactly how and why, in my opinion, he had fallen into error. In his reply (T., 1913, 103, 119), Martin tried to show that his results were practically identical with mine and that I had misrepresented him.

As to how far there is any resemblance between Martin's account of diphenylsilicanediol and my own, readers of the original papers (not Martin's tabular comparisons) may judge. Whether I used the word isomeride or modification in reference to Martin's two Modifikationen appears to me to be immaterial. as in my opinion his two modifications have no existence. I was not criticising his views, but his experimental results. His paper certainly suggested that he regarded his-Modifikationen as isomerides, but if, as he now implies, he considered them to be merely different crystallographic forms, then his methods for the conversion of the one into the other seem inexplicable.

In a later paper (Ber., 1912, 45, 2097), Martin published without my permission some further results of work carried out at my suggestion and under my supervision. I think it is only right to say that, after carefully considering all the experimental data at the time, I told him that I could not consent to the The whole of the evidence indicated that all the publication of the results. "compounds" subsequently described by him were complex mixtures and in my opinion the structural formulæ he assigns to these compounds are devoid of foundation. F. S. K.

been isolated. Although we have made several attempts to prepare these substances from diphenylsilicanediol and from anhydrobisdiphenylsilicanediol, we have not obtained any indication of their existence; these facts, together with the negative results of our efforts to produce the corresponding benzyl derivatives (Robison and Kipping, this vol., p. 40), seem to show that (a) the simple silicones, the analogues of the ketones, cannot be prepared from the diols, $SiR_2(OH)_2$, owing to the readiness with which the latter undergo condensation, and (b) a closed-chain consisting of two silicon and two oxygen atoms linked together alternately is very unstable compared with one containing three or four atoms of both of these elements.

The conditions under which diphenylsilicanediol and each of its open-chain condensation products undergoes change are, on the whole, very similar to those which are operative in the case of the corresponding benzyl derivatives. Small quantities of alkali hydroxide, or of piperidine, or of hydrochloric acid bring about condensation, with formation of one or both of the closed-chain compounds. The action, however, does not consist merely in the elimination of the elements of water; in all cases, apparently, hydrolysis and condensation occur simultaneously, and the nature of the final product is largely determined by that of the solvent employed and by the other conditions which prevail; thus, although anhydrobisdiphenylsilicanediol in ethereal solution seems to be mainly converted into tetra-anhydrotetrakisdiphenylsilicanediol in the presence of a small quantity of piperidine, an appreciable proportion of trianhydrotrisdiphenylsilicanediol is also produced. Under similar conditions, dianhydrotrisdiphenylsilicanediol does not give pure trianhydrotrisdiphenylsilicanediol, but a mixture of the latter with a very considerable proportion of tetra-anhydrotetrakisdiphenylsilicanediol.

That the formation of any closed-chain compound from the corresponding open-chain compound is a reversible reaction is also clearly proved by the preparation of dianhydrotrisdiphenylsilicanediol from the trianhydro-derivative by the action of sodium hydroxide in acetone-ethereal solution; similarly, it has been found that trianhydrotetrakisdiphenylsilicanediol may be obtained from the tetra-anhydro-compound by hydrolysing the latter with sodium ethoxide in alcoholic chloroform solution, and may be reconverted into tetra-anhydrotetrakisdiphenylsilicanediol with the aid of sodium hydroxide or hydrochloric acid in alcoholic solution.

In view of the facts just stated, it is clear that the relative solubilities of the two closed-chain compounds in a given solvent would have a preponderating influence on the relative proportions

кк2

in which the two substances would be obtained by evaporating a solution of any of the open-chain compounds in the given solvent with a particular reagent. Consequently, the results of experiments such as those referred to above give very little information as to the relative stabilities of the two closed chains, containing, respectively, three and four atoms of silicon and of oxygen.

It would seem, nevertheless, that a fairly strong inference may be drawn from a direct comparison of the behaviour of anhydrobis- and dianhydrotris-diphenylsilicanediol towards hydrochloric acid in methyl-alcoholic solution. Both these compounds are trianhydrotrisdiphenylsilicanediol, and converted intotetraanhydrotetrakisdiphenylsilicanediol is not formed in appreciable quantities in either case; but the rapidity with which the condensation occurs in the case of dianhydrotrisdiphenylsilicanediol is very much greater than in that of anhydrobisdiphenylsilicanediol. It seems, in fact, that the closed chain of three silicon and three oxygen atoms is easily and directly produced from dianhydrotrisdiphenylsilicanediol, but that tetra-anhydrotetrakisdiphenylsilicanediol, in spite of its slight solubility in methyl alcohol, is not formed anhydrobisdiphenylsilicanediol, owing \mathbf{to} \mathbf{the} relative from instability of the larger closed chain.

A similar conclusion, namely, that the closed chain of three silicon and three oxygen atoms is the more stable one, may be drawn from the results of other experiments in which the conditions do not favour, although they do not preclude, hydrolysis; thus by the action of heat on diphenylsilicanediol a much larger proportion of trianhydrotris- than of tetra-anhydrotetrakisdiphenylsilicanediol is formed; again, when dianhydrotrisdiphenylsilicanediol is heated it is almost quantitatively converted into trianhydrotrisdiphenylsilicanediol, whereas under similar conditions anhydrobisdiphenylsilicanediol gives a mixture of approximately equal quantities of trianhydrotris- and tetra-anhydrotetrakisdiphenylsilicanediol (Kipping, *loc. cit.*).

From these facts, and from the failure of our attempts to obtain a benzyl derivative corresponding with tetra-anhydrotetrakisdiphenylsilicanediol, we infer that the heterocyclic group of six is more stable than that of eight atoms.

The crystallographic examination of the compounds described in this paper was carried out by Mr. Vernon Stott under the supervision of Mr. A. Hutchinson, of the Mineralogical Laboratory, Cambridge; we are greatly indebted to these gentlemen for the reports which they have given us.

Calculated.

EXPERIMENTAL.

Diphenylsilicanediol.

The pure specimens of this compound, prepared more than a year ago (*loc. cit.*), have retained their properties; five meltingpoint tubes containing the crushed powder from one of the specimens were heated simultaneously, and in all cases the substance liquefied with effervescence at $128-132^{\circ}$. Diphenylsilicanediol, therefore, is stable at the ordinary temperature, and the great difficulties which attend its isolation (*loc. cit.*) are due to its sensibility towards alkalis, acids, and other reagents. The crystals deposited by the spontaneous evaporation of its solution in ethyl acetate were examined.

System: anorthic. Sub-class: holohedral.

a:b:c=0.5657:1:1.700.

$$\alpha = 90^{\circ}2'; \beta = 111^{\circ}20'; \gamma = 87^{\circ}27'.$$

Forms developed: b(010), m(110), $\mu(1\overline{1}0)$, c(001), t(013), $v(\overline{1}16)$.

No. Limits. Mean. 16 63°2′ -65°33′ 64°23′ 16 53°10′-55°52′ 55°40′ 15 59°34′-61°37′ 60°51′

Table of Angles.

$110:1\overline{10}$	16	53°10′–55°52′	55°40′	
110:010	15	59°34′61°37′	60°51′	60°57′
010:001	22	89°52′-90°30′	90°11′	
110:001	26	70°28′-71°16′	70°55′	70°56′
110:001	26	70°49′–71°57′	71°19′	
010:013	3	58°20'-61°40'	60°31′	
110:013	1	59°25′	59°25′	60°1′
110:013	1 I	8 8°38′	88° 38′	87°51′

The crystals are prismatic in habit. Of the prism faces b, m, and μ , b and μ are well developed, whilst m is but a small face. The angles of the prism zone, namely, $bm = 64^{\circ}23'$, $m\mu = 55^{\circ}40'$, $\mu b = 60^{\circ}57'$ all approximate to 60°, and give the crystals a pseudohexagonal character. The crystals are terminated by three planes at each end. These are c(001), t(013), and $v(\bar{1}16)$. The face c(001)is quite large, whilst t and v are tiny bevels on the edges cb and $c\mu'$ respectively. The faces t and v are very bad ones, particularly the latter, from which no trustworthy measurements could be obtained. The faces as a whole were very bad from a goniometrical point of view, as may be seen from the range of the angles in the preceding table.

Effect of Heat on Diphenylsilicanediol.

Some experiments on the action of heat on diphenylsilicanediol have already been described (*loc. cit.*, p. 2137). At 140-180° the

Angle.

010:110

diol loses approximately one molecule of water, and gives as the principal product trianhydrotrisdiphenylsilicanediol. Further experiments have shown that under these conditions a small proportion of the diol is converted into tetra-anhydrotetrakisdiphenylsilicanediol, but even when these two compounds have been removed as far as possible there remains some oil which is readily soluble in petroleum containing a little chloroform.

As it seemed possible that this oil might contain diphenylsilicone or dianhydrobisdiphenylsilicanediol or both these compounds, a weighed quantity of the pure substance was heated in a xylene bath at about 125-128°. In the course of some hours it changed into a transparent glue, and at the end of about fifteen hours the total loss in weight amounted to 7.5 per cent., but the weight had not become quite constant; the theoretical loss for 1 mol. of water is 8.3 per cent. The gelatinous or vitreous mass obtained in this way showed no signs of crystallising even when kept during some months, and it did not crystallise when it was treated with a little ethyl acetate; this last fact showed that, unlike the vitreous product formed at 140-180°, it did not contain a large proportion of trianhydrotrisdiphenylsilicanediol. The product was fractionally extracted with warm light petroleum, in which it was moderately easily soluble, and finally the whole passed into solution. The various extracts were then fractionally crystallised from mixtures of chloroform and light petroleum, and in this way a small quantity of dianhydrotrisdiphenylsilicanediol was isolated; the rest of the crystalline material seemed to consist of a mixture of anhydrobis- and dianhydrotris-diphenylsilicanediol, but a considerable proportion of the original product remained as an oil.

Another sample of the pure diol was heated in a xylene bath at about 125—128°; the loss in weight was about 6.8 per cent. at the end of six hours, and 7.8 per cent. at the end of about twenty-six hours. From the product, anhydrobis- and dianhydrotris-diphenylsilicanediol were isolated, but again there remained a considerable proportion of an oil, from which crystals could not be obtained, and neither of the closed-chain compounds seemed to have been produced.

As the loss in weight in these two experiments was not very different from that (8.5 per cent.) required for the elimination of one molecule of water from one molecule of the diol, and was therefore much greater than that corresponding with the production of dianhydrotrisdiphenylsilicanediol, or of a mixture of this compound and anhydrobisdiphenylsilicanediol, the results pointed to the formation of diphenylsilicone. The further examination of the oily products just referred to did not, however, bear out this view; when these oils were heated at about 200° a vigorous effervescence occurred, owing to the liberation of steam, and the products, treated with ethyl acetate, immediately crystallised. The solids thus obtained gave a small proportion of a very sparingly soluble powder, and crystals of trianhydrotrisdiphenylsilicanediol, together with what seemed to be tetra-anhydrotetrakisdiphenylsilicanediol. The behaviour of these oily products was, in fact, just that of a mixture of anhydrobis- and dianhydrotris-diphenylsilicanediol. When these oily products were submitted to distillation in steam the distillate was free from any visible suspended matter; since diphenylsilicone would probably be volatile in steam, this fact might be taken as evidence of the absence of this compound.

If diphenylsilicone and dianhydrobisdiphenylsilicanediol are not formed when diphenylsilicanediol is heated, it would seem that a part of the loss which occurs must be due to the volatilisation of the diol or of its condensation products, or to its oxidation, followed by the volatilisation of some of the products of oxidation. A weighed quantity (0.478 gram) of the diol was therefore heated in a bromobenzene bath at a temperature which varied from 130-140° in order to ascertain whether a loss greater than the theoretical would take place. At the end of six hours the loss was 7.1 per cent., at the end of nine hours 7.8 per cent., at the end of fourteen hours 8.6 per cent., at the end of sixteen and a-half hours 9 per cent., and at the end of twenty-two hours it was 9.5 per cent. During the first period of heating the sides of the weighing bottle containing the substance became coated with oily drops, which extended right up to the neck of the bottle, but no increase in this deposit seemed to occur during the remaining periods.

The vitreous product when rapidly heated to and kept at 200° during about five minutes evolved vapours which could be clearly seen; the total loss in weight had then reached 10 per cent. It is evident, therefore, that since the loss in weight is not entirely due to the escape of water vapour, the quantitative results cannot be taken as pointing to the formation of diphenylsilicone. The oily matter, in which the presence of this compound was suspected, is, no doubt, merely a mixture of anhydrobis- and dianhydrotrisdiphenylsilicanediol, the separation of which, as already shown, is a task of very considerable difficulty, particularly when only small quantities of material are available.

Action of Heat on Diphenylsilicanediol in Xylene Solution.

As these experiments failed to give the desired products, the pure diol was heated in boiling toluene and boiling xylene solution. It

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is moderately soluble in both these liquids at their boiling points, and the hot saturated solutions give when cooled a considerable deposit of the unchanged substance; if, however, the solutions are heated for a short time, decomposition sets in, with liberation of In experiments with each of the solvents, in which the steam. solutions were boiled for a short time only, dianhydrotrisdiphenylsilicanediol was isolated from the product. A xylene solution which had been boiled during one hour gave on evaporation a product which was readily and completely soluble in cold chloroform, and did not, therefore, contain any considerable proportion of the unchanged diol; from this product a large proportion of trianhydrotrisdiphenylsilicanediol was isolated, and smaller proportions of anhydrobis- and dianhydrotris-diphenylsilicanediol. There then remained a relatively very small quantity of a viscid oil, from which crystals could not be obtained. All these results seem to show that diphenylsilicone and dianhydrobisdiphenylsilicanediol are not formed in appreciable quantities by heating the diol alone or in solution; the diol first undergoes condensation, giving anhydrobis- and dianhydrotris-diphenylsilicanediol, and if the temperature is sufficiently high these compounds are almost completely transformed into trianhydrotris- and tetra-anhydrotetrakisdiphenylsilicanediol, the former of which is always produced in much the larger proportion.

Action of Piperidine on Diphenylsilicanediol.

Diphenylsilicanediol undergoes condensation in acetone solution in the presence of a trace of piperidine. When such a solution was allowed to evaporate spontaneously, it gave a solid, somewhat sticky residue, which was readily and completely soluble in cold chloroform, and therefore did not contain any appreciable proportion of the original diol. This residue was gently warmed on a water-bath in order to expel the piperidine, and then dissolved in ethyl acetate; the solution ultimately deposited crystals of tetra-anhydrotetrakisdiphenylsilicanediol (m. p. 200°), together with a small proportion of a colourless powder, which was only sparingly soluble in ethyl acetate, and probably represented a condensation product more complex than tetra-anhydrotetrakisdiphenylsilicanediol. The mother liquors from the tetra-anhydrocompound gave crystals melting indefinitely from about 160° to 170°, which were probably a mixture of trianhydrotris- and tetraanhydrotetrakis-diphenylsilicanediol, but the presence of the former was not conclusively established.

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Action of Ammonium Hydroxide on Diphenylsilicanediol.

In the presence of a little ammonium hydroxide, diphenylsilicanediol undergoes condensation in acetone solution at the ordinary temperature, and the solution deposits an oil. From this product, with the aid of chloroform and light petroleum, crystals melting at 113°, which dissolved in a 5 per cent. solution of potassium hydroxide, were obtained; this substance was anhydrobisdiphenylsilicanediol. In another experiment, carried out in a similar manner, the oily condensation product gave crystals melting at 112°, which were insoluble in a 5 per cent. solution of potassium hydroxide; this product was dianhydrotrisdiphenylsilicanediol. The closed-chain condensation products were not obtained in these experiments.

Anhydrobisdiphenylsilicanediol.

The crystals deposited from a mixture of chloroform and light petroleum were examined goniometrically.

System: anorthic. Sub-class: holohedral.

a:b:c=0.6536:1:1.868.

$$\alpha = 92^{\circ}28'; \beta = 115^{\circ}40'; \gamma = 86^{\circ}24'.$$

Forms developed: b(010), m(110), $\mu(1\overline{1}0)$, c(001), q(011), $s(\overline{11}4)$.

Table of Angles.

Angle.	No.	Limits.	Mean.	Calculated.
010:110	10	61°5′ –62°1′	61°36′	
110 : 110	10	60°10′-61°33′	60°58′	
110:010	10	56°40′-57°56′	57°26′	57°26′
010:011	20	29°52′-30°42′	30°22′	
110:011	24	52°18′-53°14′	52°49′	52°53′
110:011	24	105°44′106°39′	106°8′	106°14′
010:001	18	88°38′–89°29′	89°4′	89°0′
110:001	20	66°41′67°25′	67°3′	
110:001	20	68°26′-68°44′	68°37′	69°8′
011:001	11	58°8′ –59°9′	58°38′	
$110:\bar{1}\bar{1}2$	24	142°43′143°19′	143°1′	143°21'
010:112	24	119°5′119°55′	119°31′	119°22′
110:112	24	105°22′106°38′	106°1′	106°11'

The forms b, m, and μ constitute a prism zone; the forms b and m are large and μ small. The angles of the prism zone are: $bm = 61^{\circ}36'$, $m\mu = 60^{\circ}58'$, $\mu b' = 57^{\circ}26'$. They all approach the value 60°, and so the crystals are pseudo-hexagonal. Of the three terminal forms, c(001) is much the largest, q and s being small faces on the edges bc and m'c respectively.

Action of Piperidine on Anhydrobisdiphenylsilicanediol.

When anhydrobisdiphenylsilicanediol is heated, it gives tetraanhydrotetrakis- and some trianhydrotris-diphenylsilicanediol, together with a small proportion of a colourless powder, which is probably a highly complex condensation product (*loc. cit.* p. 2133); when treated with acetyl chloride it is converted principally into tetra-anhydrotetrakisdiphenylsilicanediol.

In ethereal solution, in the presence of a small quantity of piperidine, it undergoes change, giving a mixture of products, which remains as an oil when the solution evaporates spontaneously; from this oil the transparent, rectangular crystals melting at about $184-186^{\circ}$ (*loc. cit.*, p. 2140) were obtained; this observation shows that both trianhydrotris- and tetra-anhydrotetrakis-diphenylsilicanediol had been produced, the former, however, in relatively small quantities. The action of the piperidine, therefore, is two-fold; it not only brings about the condensation of the anhydrobisdiphenylsilicanediol, but also hydrolyses some of this compound to diphenylsilicanediol, which then undergoes condensation, giving a little trianhydrotrisdiphenylsilicanediol.

Action of Hydrochloric Acid on Anhydrobisdiphenylsilicanediol.

When a very small quantity of hydrochloric acid is added to a solution of anhydrobisdiphenylsilicanediol in methyl alcohol, no visible change occurs immediately, but after some time a small quantity of an oil is deposited. The solution, left to evaporate at the ordinary temperature, gives a residue which is partly crystalline, partly oily. If the whole is treated again with methyl alcohol containing a little hydrochloric acid, and the solution is left to evaporate, the residue then contains a larger proportion of the crystalline product than before. This substance when freed from oil with the aid of alcohol, separates from ethyl acetate in colourless prisms, melting at 188°. It consists of pure trianhydrotrisdiphenylsilicanediol. The presence of the tetra-anhydro-derivative in the crude, crystalline product could not be detected.

Hydrochloric acid, therefore, under the conditions stated, does not bring about the condensation of anhydrobisdiphenylsilicanediol, but hydrolyses it to the simple diol, which then undergoes condensation.

Dianhydrotrisdiphenyl silican ediol.

The crystals deposited from a mixture of chloroform and light petroleum were examined.

System: anorthic. Sub-class: holohedral.

$$a:b:c=0.5068:1:1.491.$$

$$\alpha = 90^{\circ}42'; \ \beta = 106^{\circ}56'; \ \gamma = 86^{\circ}30'$$

Forms developed: b(010), m(110), $\mu(\overline{110})$, c(001), r(012), $u(\overline{114})$.

Table of Angles.

Angle.	No.	Limits.	Mean.	Calculated.
010:110	6	66°42′-67°21′	66°58′	
$110:1\bar{1}0$	7	51°4 ′-52°4′	51°39′	
$1\bar{1}0:0\bar{1}0$	10	60°4′61°53′	61°32′	61°23
010:001	16	89°7 ′ –90°51′	90°19′	
110:001	8	74°9′–74°55′	74°35′	74°34′
lī0:001	15	74°16′–75°28′	75°1′	
010:012	1	54°42′	54°42′	
110:012	1	63°11′	63°11′	63°33′
$1\bar{1}0:012$	1	94°50′	94°50′	93°54 ′
$010:\bar{1}14$	3	67°34′69°11′	68°36′	69°25′
110:114	3	120°28′124°2′	$122^{\circ}47'$	120°57'
110:114	3	103°44′ –105°14′	104°27′	103°0′

The dominant forms are: b(010), $\mu(\bar{1}10)$, and c(001). Many crystals are simply four-sided prisms, terminated by c planes. The prism face m is often missing, and when present it is only small. The face r(012) was present on one crystal only. The form $u(\bar{1}14)$ was only developed on two crystals, and even then the faces were very poor ones. This accounts for the divergence between the calculated and measured angles. The crystals may be described as short, stumpy prisms. The prism angles show some approach to hexagonal development: $bm = 66^{\circ}58'$; $m\mu = 51^{\circ}39'$; $\mu b' = 61^{\circ}32'$.

If in the crystals of diphenylsilicanediol t is given the indices (011) instead of (013), then v will become (112) instead of (116). The remaining indices would be unchanged. The axial ratios would now be 0.5657:1:0.5666 instead of 0.5657:1:1.700.

Similarly, if in the crystals of dianhydrotrisdiphenylsilicanediol r is made (011) instead of (012), then u would be (112) instead of (114), and the remaining indices would be unaltered. The axial ratios would be:

$$0.5068:1:0.7455,$$

 $0.5068:1:1.491.$

To bring the axial ratios of the crystals of anhydrobisdiphenylsilicanediol into line, q would have to be made (031) instead of (011), and the ratios would then be 0.6536:1:0.6227 instead of 0.6536:1:1.868. The indices of $s(\overline{112})$ would then become ($3\overline{32}$).

Action of Piperidine on Dianhydrotrisdiphenylsilicanediol.

When an ethereal solution of dianhydrotrisdiphenylsilicanediol, to which a drop of piperidine had been added, was left to evaporate slowly at the ordinary temperature, it gave a somewhat brown and

instead of

oily residue, from which, with the aid of ethyl acetate, there was separated a small proportion of a colourless, very sparingly soluble powder. The ethyl acetate solution gave a crystalline deposit, from which pure tetra-anhydrotetrakisdiphenylsilicanediol was isolated. The mother liquors from this compound seemed to contain trianhydrotrisdiphenylsilicanediol, but the latter was not identified with certainty. It is obvious from these results that dianhydrotrislike anhydrobis-diphenylsilicanediol, is hydrolysed by piperidine, the products of hydrolysis then undergoing condensation to the closed-chain compounds.

In these circumstances the nature of the product or products doubtless varies with the conditions of the experiment, but a comparison of the results obtained by the action of piperidine on diphenylsilicanediol, anhydrobisdiphenylsilicanediol, and dianhydrotrisdiphenylsilicanediol seems to show that the principal product is in all cases tetra-anhydrotetrakisdiphenylsilicanediol.

The Action of Hydrochloric Acid on Dianhydrotrisdiphenylsilicanediol.

The action of hydrochloric acid on dianhydrotrisdiphenylsilicanediol in methyl-alcoholic solution is very different from that of the same acid on anhydrobisdiphenylsilicanediol. After a few moments the solution becomes quite milky, owing to the separation of an oil, the quantity of which rapidly increases, and when the solution is evaporated at the ordinary temperature it gives a crystalline residue, which is free from any appreciable quantity of oil. The crystalline product seemed to be practically pure; when recrystallised from ethyl acetate it gave colourless prisms of pure trianhydrotrisdiphenylsilicanediol, melting sharply at 188°.

Trianhydrotrisdiphenyl silicanediol.

This closed-chain compound is hydrolysed by alcoholic potassium hydroxide, and finally gives a solution of the potassium derivative of diphenylsilicanediol; when the alcohol is evaporated and the residue is treated with a slight excess of dilute acetic acid, the diol is precipitated in the usual form (Kipping, *loc. cit.*, p. 2116).

If, however, hydrolysis is carried out very cautiously and the process is interrupted at a very early stage, the following reaction may be realised:

 $O \stackrel{\text{SiPh}_2 \cdot O}{\underset{\text{SiPh}_2 \cdot O}{\text{SiPh}_2 + H_2O}} = HO \cdot \text{SiPh}_2 \cdot O \cdot \text{SiPh}_2 \cdot O \cdot \text{SiPh}_2 \cdot OH.$

For this purpose the trianhydro-derivative (0.25 gram) was dissolved in a mixture of acetone and a little ether, and a 3 per cent. aqueous solution of sodium hydroxide (0.05 gram) was added; a few seconds later the solution was acidified with dilute acetic acid, and the acetone and ether were rapidly evaporated at the ordinary temperature in a stream of air. The product was extracted with ether, the ether was evaporated, and the oily residue was treated with a little alcohol; the small proportion of insoluble matter, which doubtless consisted of unchanged trianhydrotrisdiphenylsilicanediol, was then separated by filtration. The alcoholic solution, when rapidly evaporated at the ordinary temperature, gave an oil, which separated from a mixture of chloroform and light petroleum in colourless crystals; this product was pure dianhydrotrisdiphenylsilicanediol.

Trianhydrotrisdiphenylsilicanediol, like the corresponding benzyl derivative, may also be converted into the open-chain compound by hydrolysing it with hydrogen chloride. The trianhydro-compound was dissolved in a mixture of chloroform and acetone, and a few drops of concentrated hydrochloric acid were added; after six hours the solution was neutralised with ammonium hydroxide, and the solvents were rapidly evaporated at the ordinary temperature. The somewhat pasty residue was extracted with alcohol, and the solution was filtered from unchanged trianhydrotrisdiphenylsilicanediol and evaporated; the oily residue consisted essentially of dianhydrotrisdiphenylsilicanediol, which was obtained in a state of purity by recrystallisation from a mixture of chloroform and light petroleum.

Since hydrogen chloride condenses dianhydrotrisdiphenylsilicanediol, the above hydrolysis is a readily reversible reaction, just as in the case of the corresponding benzyl derivative (Robison and Kipping, this vol., p. 40). The action of piperidine on trianhydrotrisdiphenylsilicanediol was also examined in acetone solution. The product was a mixture, from which a small proportion of a powder, practically insoluble in acetone, was isolated; the remainder seemed to consist of a mixture of trianhydrotris- and tetraanhydrotetrakis-diphenylsilicanediol.

The crystals of trianhydrotrisdiphenylsilicanediol, deposited from ethyl acetate solution, were measured.

System: orthorhombic. Sub-class: bisphenoidal.

a:b:c=0.7750:1:0.4993.

Forms developed: a(100), b(010), m(110), p(111).

Table of Angles.

Angle.	No.	Limits.	Mean.	Calculated.
100:010	19	89°50′90°7′	90°0′	90°0′
100:110	19	37°21′38°12′	37°48′	37°48′
010:110	19	51°55′–52°29′	52°12′	
100:111	17	59°54′60°17′	60°7′	60°3′
010:111	18	66°58′-67°27′	67°14′	
110:111	16	50°34′51°13′	50°48‡′	50°50′
111:11	8	78°8′ –78°29′	78°15'	78°23′
110:111	12	80°30′-81°27′	81°3′	80°57′

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The crystals occur in two well-marked habits. One of these is prismatic, a and b being large faces, whilst the m faces are small. In other cases the crystals are markedly tetrahedral.

Trianhydrotetrakisdiphenylsilicanediol, HO·SiPh₂·O·SiPh₂·O·SiPh₂·O·SiPh₂·O·SiPh₂·OH.

This condensation product of diphenylsilicanediol, the most complex open-chain silicon compound so far obtained, may be prepared by cautiously hydrolysing tetra-anhydrotetrakisdiphenylsilicanediol,

$0 < \underbrace{\operatorname{SiPh}_2 \cdot \operatorname{O} \cdot \operatorname{SiPh}_2}_{\operatorname{SiPh}_2 \cdot \operatorname{O} \cdot \operatorname{SiPh}_2} > \operatorname{O} + \operatorname{H}_2 \operatorname{O} = \operatorname{HO} \cdot \operatorname{SiPh}_2 \cdot \operatorname{O} \cdot \operatorname{SiPh}_2 \cdot \operatorname{SiPh}_2$

When the closed-chain compound is warmed with excess of alcoholic potassium hydroxide, it seems to be completely hydrolysed, giving the potassium derivative of diphenylsilicanediol, but owing to the fact that tetra-anhydrotetrakisdiphenylsilicanediol is almost insoluble in alcohol, the reaction takes place rather slowly. In acetone solution hydrolysis takes place more rapidly, as the tetra-anhydro-derivative is more soluble in this liquid, but it is difficult to interrupt the process at the desired stage. Hydrogen chloride seems to have little effect on tetra-anhydrotetrakisdiphenylsilicanediol; when solutions of the substance in acetone or ether, or acetone and chloroform, are treated with a little concentrated hydrochloric acid, and kept during periods varying from thirty minutes to one day, most of the original compound is recovered unchanged, and only traces of a product soluble in cold alcohol are obtained.

Under the following conditions, however, the partial hydrolysis of tetra-anhydrotetrakisdiphenylsilicanediol may be accomplished. The closed-chain compound is dissolved in chloroform, and a considerable excess (5-6 mols.) of an alcoholic solution of sodium ethoxide is added, care being taken to use sufficient chloroform to prevent the precipitation of the anhydro-derivative. After an interval of not more than one minute, a slight excess of very dilute acetic acid is added, the liquids are well shaken together, the chloroform solution is separated, and the aqueous solution is extracted with a little chloroform. The combined chloroform extracts are rapidly evaporated at the ordinary temperature, and the solid residue is extracted two or three times with cold ethyl alcohol, which leaves undissolved a considerable proportion of the original tetra-anhydrotetrakisdiphenylsilicanediol. The filtered alcoholic extract is diluted with water and vigorously stirred; the precipitated trianhydrotetrakisdiphenylsilicanediol is then separated by

filtration, dried in the air, and crystallised several times from a mixture of chloroform and light petroleum.

The yield by this method is rather poor, but the crude substance is not contaminated to any great extent with other products of hydrolysis; moreover, the unchanged tetra-anhydrotetrakisdiphenylsilicanediol, which is recovered, may be treated again, and the operations may be repeated until practically the whole of the original substance has been transformed into trianhydrotetrakisdiphenylsilicanediol. When attempts are made to increase the yield by allowing a longer time to elapse between the addition of the sodium ethoxide and the neutralisation with acetic acid, although a larger proportion of the tetra-anhydro-compound is hydrolysed, the product is a mixture, from which it is difficult to isolate the components; this is so even when the theoretical quantity of sodium ethoxide is used.

Trianhydrotetrakisdiphenylsilicanediol separates from a mixture of ether and light petroleum in short, colourless prisms; when heated moderately quickly it melts sharply at 128^{.5°}, but when heated very slowly it sinters at about 127°, probably owing to incipient decomposition.

The samples for analysis were dried over sulphuric acid:

0.1572 gave 0.4091 CO₂ and 0.0736 H₂O. C = 71.0; H = 5.2.

0.1965 , 0.5124 CO₂ , 0.0932 H₂O. C=71.1; H=5.3.

 $C_{48}H_{44}O_5Si_4$ requires C=71.0; H=5.2 per cent.

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

0.262 in 12.1 benzene gave $\Delta t - 0.12^{\circ}$. M.W.=884. 0.494 ,, 12.1 ,, ,, $\Delta t - 0.23^{\circ}$. M.W.=870. $C_{48}H_{44}O_5Si_4$ requires M.W.=811.

These results, like those obtained under similar conditions in the case of the other open-chain condensation products of diphenylsilicanediol, are higher than the theoretical values, but the extent of association, as indicated by the experimental results, rapidly falls as the molecular weight of the condensation product rises; this is shown by the following data:

	MW.	M . W .	Difference,
	(Found).	(Calculated).	per cent.
Anhydrobisdiphenylsilicanediol	573	414	38
Dianhydrotrisdiphenylsilicanediol	755	613	23
Trianhydrotetrakisdiphenylsilicanediol	877	811	8

Trianhydrotetrakisdiphenylsilicanediol resembles the other two open-chain condensation products of diphenylsilicanediol. It separates from a mixture of ether and light petroleum in massive, transparent prisms, and is readily soluble in chloroform, acetone, and most of the ordinary solvents, but only sparingly so in cold

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ethyl alcohol, and practically insoluble in cold light petroleum. It does not dissolve appreciably in a 5 per cent. solution of potassium hydroxide.

Conversion of Trianhydro- into Tetra-anhydro-tetrakisdiphenylsilicanediol.

The conversion of trianhydro- into tetra-anhydro-tetrakisdiphenylsilicanediol is easily accomplished. When an alcoholic solution of the former is warmed with a trace of sodium hydroxide, a crystalline precipitate is soon formed, and in a short time most of the dissolved trianhydro-derivative has undergone the desired transformation; the air-dried precipitate melts at 200°, and when recrystallised once from ethyl acetate it melts sharply at 201°, and consists of pure tetra-anhydrotetrakisdiphenylsilicanediol.

When an alcoholic solution of trianhydrotetrakisdiphenylsilicanediol is warmed with a few drops of concentrated hydrochloric acid, a precipitate forms much more slowly than when sodium hydroxide is used, and the tetra-anhydrotetrakisdiphenylsilicanediol which is deposited is impure; the air-dried precipitate melts from about 187° to about 200°, but when recrystallised from ethyl acetate it gives a deposit of pure tetra-anhydrotetrakisdiphenylsilicanediol. The results of the action of sodium hydroxide and of hydrogen chloride vary, however, with the conditions of the experiment; if, for example, an alcoholic solution of trianhydrotetrakisdiphenylsilicanediol is treated with a drop of concentrated hydrochloric acid and left at the ordinary temperature for a day or two, it deposits crystals melting at about 185°, which probably consist of a mixture of trianhydrotris- and tetra-anhydrotetrakis-diphenylsilicanediol (Kipping, loc. cit., p. 2140). This is due, no doubt, to the fact that the acid causes both hydrolysis and condensation to occur, just as it was shown to do in the case of dianhydrotrisdibenzylsilicanediol (Robison and Kipping, loc. cit.).

Trianhydrotetrakisdiphenylsilicanediol may also be converted into the tetra-anhydro-derivative with the aid of heat. The openchain compound seems to begin to decompose at about 135° , but the action does not become rapid until the temperature has risen to about $180-190^{\circ}$; at this stage the escape of bubbles of steam may be clearly observed, but when the liquid mass has been heated at $190-200^{\circ}$ during about fifteen minutes, decomposition seems to cease. The cooled product is a vitreous solid, which crystallises on the addition of a little ether, and from which cold alcohol extracts only a small proportion of soluble matter; the residue melts indefinitely at about 185° , but when repeatedly recrystallised from hot acetone it gives pure tetra-anhydrotetrakisdiphenylsilicanediol (m. p. 200°).

Although it was thus proved that the open-chain is converted into the closed-chain compound by the action of heat, the reaction does not take place quantitatively; the crude tetra-anhydro-derivative is mixed with a certain proportion of some substance which lowers its melting point, and which is only removed with difficulty. This other product is in all probability trianhydrotrisdiphenylsilicanediol, because the mother liquors from the pure tetraanhydro-derivative yield a residue which separates from cold ethyl acetate in large, transparent rhombs, and these crystals have the properties of the crystalline mixture of trianhydrotris- and tetraanhydrotetrakis-diphenylsilicanediol previously described (loc. cit., 2140). The formation of trianhydrotrisdiphenylsilicanediol **р**. could be easily accounted for on the assumption that some of the trianhydrotetrakisdiphenylsilicanediol is partly hydrolysed to dianhydrotrisdiphenylsilicanediol and diphenylsilicanediol by the steam which is liberated during the formation of the tetra-anhydrocompound.

Tetra-anhydrotetrak is diphenyl silicaned iol.

The well-defined, almost rectangular plates in which this compound is sometimes deposited from ethyl acetate solution at the ordinary temperature were measured.

System: anorthic. Sub-class: holohedral.

$$a: b: c = 0.5614: 1: 0.5770.$$

$$\alpha = 83^{\circ}56'$$
; $\beta = 103^{\circ}52'$; $\gamma = 96^{\circ}44'$.

Forms observed: $a\{100\}, b\{010\}, c\{001\}, m\{110\}, q\{011\}, y\{1\overline{2}0\}.$

Table of Angles.

Angle.	No.	Limits.	Mean.	Calculated
010:110	3	56°23′–57°16′	56°56'	57°61′
110:100	4	27°13′-27°48′	27°30′	27°25́′
100:120	10	50°32′50°46′	50°38′	
$1\bar{2}0:0\bar{1}0$	6	44°46′-44°59′	44°501′	
010:001	8	94°26′-94°53′	94°37'	
110:001	6	80°39′–81°57′	81°8′	80°58'
100:001	11	76°31′76°47′	76°41′	
$1\bar{2}0:001$	12	76°29′-77°18′	76°54‡′	76°57‡
010:011				64°8′ [°]
110:011	1	65°27′	65°27'	
100:011	1	74°38′	74°38′	75°9′
$1\overline{2}0:011$	1	98°31′	98°31′	99°3′

The crystals are flat, almost square plates, the pinacoid $a\{100\}$ being predominant, and the forms $b\{010\}$ and $c\{001\}$ being developed along the edges of the plates.

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As diphenylsilicone could not be obtained by heating diphenylsilicanediol, the action of heat on tetra-anhydrotetrakisdiphenylsilicanediol was studied; it seemed possible that at a high temperature the last named compound might decompose, yielding diphenylsilicone, just as paraformaldehyde, for example, gives formaldehyde.

In order to avoid atmospheric oxidation, a small quantity of the pure substance was heated in a bent tube in an atmosphere of coal gas; it distilled at a very high temperature, giving a colourless distillate, and no appreciable charring took place. The distillate solidified immediately to a hard mass, which was free from any appreciable quantity of oily matter, and melted from about 180-185°. On crystallisation from ethyl acetate the product was deposited in the well-defined, rectangular plates described above, but these melted indefinitely from about 185-190°, and it was only after three or four further recrystallisations that pure tetraanhydrotetrakisdiphenylsilicanediol (m. p. 200-201°) was ob-In spite of this fact, the original product of distillation tained. seemed to consist almost entirely of the one substance. The small proportion of impurity which was certainly contained in it, and which was so difficult to remove, was not definitely identified, but in all probability it consisted of trianhydrotrisdiphenylsilicanediol. The most soluble deposit obtained from the last ethyl acetate mother liquors melted at about 180-185°, and contained a very small proportion of crystals, which did not become opaque when heated, but melted at 186-188°; this substance was doubtless trianhydrotrisdiphenylsilicanediol. It is obvious from these results that diphenylsilicone is not formed in appreciable quantities under the above conditions.

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