CCXXIII.—*Organic Derivatives of Silicon. Part XVI. The Preparation and Properties of Diphenylsilicanediol.*

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THE primary object of this research was to ascertain the relation between the two dibenzyl compounds of the composition $C_{14}H_{16}SiO_2$, which had been obtained by Robison and Kipping (Trans., 1908, **93**, 439) by the hydrolysis of dichlorodibenzylsilicane (dibenzylsilicon dichloride). For this purpose a comparative study of the products of hydrolysis of dichlorodiphenylsilicane seemed to be desirable.

At that time, one such product, namely, diphenylsilicanediol ("diphenylsilicol"), had already been described by Dilthey and Eduardoff (*Ber.*, 1904, **37**, 1139), who obtained it by decomposing highly impure dichlorodiphenylsilicane with water; they described it as crystallising from benzene in needles, which melted at 138—139°. Quite recently the results of an investigation of "dibenzylsilicol" and "diphenylsilicol" have been published by Martin (*Ber.*, 1912, **45**, 403).*

In the experiments described in this paper, dichlorodiphenylsilicane was prepared by the interaction of silicon tetrachloride and magnesium phenyl bromide, and the pure compound was decomposed with water, ammonium hydroxide solution, or a dilute solution of potassium hydroxide. At first consideration it might not seem to be a very difficult task to hydrolyse the dichloro-

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* The examination of the dibenzyl compounds, referred to above, having been left unfinished, owing to the departure from Nottingham of Dr. Robison, I continued the work in conjunction with Dr. Martin, with whom I also resumed the study of diphenylsilicanediol. After many months of strenuous application, Dr. Martin came to the conclusion that he had obtained two isomeric "diphenylsilicols," and had also devised methods for their conversion one into the other, but before the research was really finished he was obliged to abandon it, in order to take up an appointment elsewhere. On his departure, Dr. Martin handed to me a record of his work, which, a short time afterwards, I began to consider, with a view to the publication of a joint paper. As some of the statements in this record seemed to me to require verification, I repeated some of Dr. Martin's more important experiments; having failed to confirm them, I informed him of the results of my observations and that I thought it necessary to revise the whole of the work before sending the paper to be published. After some discussion, it was finally left to him to decide whether or not he should communicate his own results under his own name; his decision led to the publication of the paper referred to above, in which, unfortunately, as will be shown later, he gave a very erroneous account of diphenylsilicanediol.

derivative by these processes, and to isolate the compound which had been formed, and yet the task proved to be an exceptionally troublesome one.

Although it was easy enough to obtain a crystalline product, different preparations varied greatly in their behaviour, and under certain conditions were so readily changed that the results were most perplexing; some preparations, for example, when warmed with solvents, were converted into viscid, glue-like products; some of these glues were readily soluble in alcohol, others almost insoluble. A further difficulty was due to the fact that the preparations did not melt, but decomposed with effervescence, when they were heated, and although they liquefied in this process, the temperature at which decomposition occurred varied very greatly with different preparations, even after they had been recrystallised.

As illustrations of the behaviour here outlined, the following summary of the results of hydrolysing the dichloride under different conditions may be given, accompanied by the statement that pure diphenylsilicanediol usually decomposes at about 128—132°, and is readily and completely soluble in a 5 per cent. aqueous solution of potassium hydroxide.

The decomposition of dichlorodiphenylsilicane with cold water results in the formation of a crystalline solid, which contains a large proportion of the dihydroxy-compound; after having been washed with cold chloroform, which extracts an oily mixture of at least three substances, this product begins to liquefy and decompose at about 145—150°; but liquefaction is not complete until the temperature has risen to about 165°. When the washed preparation is heated with solvents in order to crystallise it, it may be completely converted into an oil, which is readily soluble in alcohol, or it may give crystalline deposits, which vary considerably in decomposition point; all such deposits are impure, as they do not dissolve completely in a 5 per cent. aqueous solution of potassium hydroxide, and the impurity is not eliminated by recrystallisation from various anhydrous solvents.

The decomposition of dichlorodiphenylsilicane with excess of a concentrated solution of ammonium hydroxide results in the formation of a viscid oil, which is practically free from diphenylsilicanediol, and is a mixture of at least three compounds.

The hydrolysis of the dichloride with excess of a 5 per cent. aqueous solution of potassium hydroxide results in the production of a clear solution of the potassium derivative, $SiPh_2(OK)_2$ or $SiPh(OH)\cdot OK$; from this solution, diphenylsilicanediol is precipitated on the addition of acids or certain salts, but the properties of the precipitate vary very considerably with the nature and the quantity of the precipitant.

When the alkaline solution is just neutralised with acetic acid, the air-dried precipitate almost invariably decomposes, and liquefies completely at about 105—110°, and when heated with solvents, such as ether or ethyl acetate, it may be completely converted into a glue-like substance, which is practically insoluble in alcohol. It may be recrystallised from various solvents in the cold, and thus obtained in colourless anhydrous needles, decomposing at about 115°, but the decomposition point of such preparations often rises to about 140° when the specimens are merely kept for a short time at the ordinary temperature. When ammonium chloride, or a considerable excess of hydrochloric acid, is used to precipitate the diphenylsilicanediol from its alkaline solution, the air-dried precipitate liquefies with effervescence at about 145—155°; such precipitates may be recrystallised from hot solvents without their undergoing much observable decomposition, but even then they are invariably heterogeneous, and leave an insoluble residue when they are treated with a 5 per cent. aqueous solution of potassium hydroxide.

Observations such as those summarised above, the undoubted existence of the two dibenzyl compounds of the composition $C_{14}H_{16}SiO_2$ described by Robison and Kipping (*loc. cit.*), and the statement in Martin's record that he had isolated two isomeric forms of diphenylsilicanediol, decomposing at 140° and 160° respectively, all seemed to point in the one direction, and many attempts were made to isolate the two or more compounds, which were presumably contained in the above preparations.

In the course of these attempts it was found that the diphenylsilicanediol, precipitated from its alkaline solution with acetic acid, could be obtained in an apparently pure condition in colourless prisms, which were completely soluble in a 5 per cent. potassium hydroxide solution, and decomposed with effervescence at 115—118°; on the other hand, the compound, precipitated with excess of hydrochloric acid, was also obtained in needles, which, in spite of the fact that they were not quite pure, and were not completely soluble in potassium hydroxide solution, did not decompose and liquefy until about 140—145°.

As various specimens of the preparations, decomposing at 115—118°, gave on analysis results agreeing well with those required for a diphenylsilicanediol, it had to be assumed provisionally that they represented an isomeride or a polymeride of the compound, $SiPh_2(OH)_2$, described by Dilthey and Eduardoff as melting at 138—139°, and also of that described by Martin as decomposing at about 160°. It was further observed that the preparations decomposing at 115—118° were transformed into those having the higher decomposition point when they were recrystallised from cold solvents in the presence of a mere trace of hydrochloric acid; this fact, of course, was compatible with the view that the acid had brought about some isomeric or polymeric change.

There was, however, apart from all theoretical considerations, one experimental difficulty which, obviously, had to be overcome before a definite conclusion could be reached, namely, the removal from the preparations decomposing at temperatures above 140° of the small proportion of impurity, which was insoluble in potassium hydroxide solution. It certainly did not seem very probable that these recognisably impure preparations could be an impure form of the apparently pure substance decomposing at 115—118°, but it was a possibility which had to be considered, and which could only be decided by eliminating the impurity. For this purpose the preparations in question were systematically fractionally crystallised from various anhydrous solvents and various mixtures of such solvents, but the results were most unsatisfactory; although the deposits were well crystallised, and, as a rule, appeared homogeneous, they invariably retained impurity, as shown by their behaviour towards potassium hydroxide solution; moreover, the decomposition points of the various fractions were most irregular, and ranged from about 140° to 165°.

It was ultimately discovered that by the use of aqueous acetone and chloroform alternately, in the manner described later (p. 2121), the impurities in all such fractions could be removed, and that the pure diphenylsilicanediol which was thus obtained (usually) liquefied completely at 128—132°.

By the same method of purification, diphenylsilicanediol was also isolated from those apparently pure preparations which liquefied completely at about 118°.

The impurity which was thus removed from any preparation was relatively small in quantity, and consisted as a rule of an oily mixture of several compounds; as this mixture was readily soluble in ether, ethyl acetate, and other anhydrous solvents, and yet was not removed when the impure diphenylsilicanediol was recrystallised repeatedly from these solvents, it would seem that the impurities of which the mixture was composed had been adsorbed by the crystals of the diol.

Whatever may be the cause of the great difficulty of separating diphenylsilicanediol from relatively small quantities of certain soluble impurities, innumerable observations have shown that all those specimens of the diol which contain an appreciable proportion of the substances insoluble in a 5 per cent. aqueous solution of potassium hydroxide, invariably decompose at a much higher temperature than 128—132°, sometimes not until about 165°; pure specimens of diphenylsilicanediol, on the other hand, as stated above, usually decompose and liquefy completely below 132°, although very occasionally the decomposition does not occur until the temperature has been raised to about 160°.

This irregular and unusual behaviour, in the author's opinion, is not due to the existence of an isomeride of the compound $(C_6H_5)_2Si(OH)_2$, to which, indeed, it would be difficult to assign a structural formula, but is to be explained as follows: The crystalline form of diphenylsilicanediol, which separates from solvents at temperatures within the limits of those employed (about 10—60°), decomposes and liquefies completely at about 128—132°; but when near its decomposition point, this form, *A*, is in a metastable condition, and may change into another crystalline modification, *B*, which only decomposes at much higher temperatures, namely, at about 160°. The pure compound, as a rule, decomposes before the change in crystalline form occurs; in presence, however, of a sufficiently large proportion of those substances which are insoluble in a 5 per cent. aqueous solution of potassium hydroxide, its partial or complete transformation into the crystalline form of higher decomposition point invariably takes place, probably because one or more of these imporities is isomorphous with this form, *B*.

Whether this suggested explanation of the observations is true in all particulars or not, there does not seem to be any evidence of the existence of the isomeric diphenylsilicanediols described by Martin, and judging from the methods of preparation and decomposing points of his supposed isomerides, both must be regarded as impure specimens of the diol. In justice to Martin, however, it should, perhaps, be pointed out, that not only was he misled by a presumed analogy between dibenzylsilicanediol and diphenylsilicanediol, which, in fact, did not exist, but that the difficulties presented by the investigation of the last-named compound were altogether exceptional, and might have led into error a much more experienced chemist.

The results of further experiments on diphenylsilicanediol, which are described later, elucidate many of the observations which are recorded in this paper. For the sake of clearness it may be briefly stated here that diphenylsilicanediol is very readily decomposed by traces of alkalis, and also, but not so readily, by traces of acids, giving compounds which in their turn are further changed by these same reagents; consequently, the product obtained from the dichloride by the various methods indicated above may contain variable quantities of impurities, the nature of which depends on its method of preparation and subsequent treatment; further, unless the product is completely freed from alkali or acid before it is heated with solvents, it may be completely decomposed and converted into oily or glue-like mixtures.

EXPERIMENTAL.

Preparation of Dichlorodiphenylsilicane, $SiPh_2Cl_2$.

The action of different quantities of magnesium phenyl bromide on silicon tetrachloride was studied by Dilthey and Eduardoff (*loc. cit.*), who found that the product always consisted of a mixture, even when molecular proportions of the materials were employed; they described their methods for the preparation of chlorotriphenylsilicane and dichlorodiphenylsilicane, but they did not isolate these compounds; they hydrolysed their crude reaction mixtures with ice-cold water, and then purified the products of hydrolysis.

The author's observations confirm those of Dilthey and Eduardoff that the above interaction gives a mixture, no matter what proportions of magnesium phenyl bromide are used; nevertheless, with a suitable quantity of the Grignard reagent, a fairly satisfactory yield of diphenyldichlorosilicane can be obtained.

The following method was employed: Silicon tetrachloride (170 grams) is cooled to 0° in a flask, provided with a stirrer, and a carefully prepared ethereal solution of magnesium phenyl bromide (2¼ mols.) is slowly added in the course of about one and a-half hours. The contents of the flask are then left at the ordinary temperature during about twelve hours; it is advisable to shake the flask vigorously at intervals during this time, otherwise the magnesium salt, as it separates, may form a solid cake, which cannot afterwards be removed. The flask is next heated during about three hours on a reflux apparatus; this is a very necessary operation, as the interaction is not complete at the ordinary temperature, and, moreover, the magnesium salt is still in a gelatinous condition, and, at this stage, cannot be easily separated by filtration. The ethereal solution of the silicon compounds is then filtered from the crystalline magnesium salt in absence of moisture (compare Kipping, Trans., 1907, **91**, 216), the residue is washed with pure ether, and the combined filtrate and washings are evaporated on the water-bath; towards the end of this operation a further quantity of magnesium salt is almost invariably deposited, and the separation gradually increases when the oily mixture is heated on the water-bath during about half an hour. It would seem, therefore, either that the magnesium salt at first remains dissolved in the ethereal solution, or that the reaction is not complete, even after the ethereal solution has been boiled during about three hours. In consequence of this separation of magnesium salt, the oily product must again be filtered and the residue washed with ether.

The clear, brownish-yellow oil is distilled from an ordinary distillation flask, under a pressure of 50 mm. After traces of ether and bromobenzene have passed over, the thermometer rises and remains for some time in the neighbourhood of 110—120°, and the fraction collected between these temperatures consists principally of trichlorophenylsilicane; the thermometer then rises rapidly to about 190°, and a very large fraction, consisting principally of dichlorodiphenylsilicane, is collected between this temperature and about 225°. Another rapid rise then occurs, and the fractions collected from about 260—300° deposit crystals of chlorotriphenylsilicane in the course of some hours Above 300° little distils, but there remains in the flask a considerable quantity of a very viscid, black oil. The various fractions are systematically redistilled, those containing the diphenyl compound preferably under diminished pressure; in this way, from 170 grams of silicon tetrachloride there are ultimately obtained about 30 grams of trichlorophenylsilicane, boiling at 197—202° (atmospheric pressure), about 110 grams of dichlorodiphenylsilicane, boiling at 200—210°/45 mm., and about 15 grams of crystalline chlorotriphenylsilicane, together with smaller quantities of mixtures of these compounds, and possibly a little diphenyl.

The dichlorodiphenylsilicane boiling at about 200—210°/45 mm. generally contains a very small proportion of diphenyl, but for most purposes this is of no consequence. When further purified, the dichloride is obtained as a colourless liquid, boiling at 202—204°/45 mm., which fumes slightly in moist air; a sample of such a preparation was analysed, with the following result:

0·7414 gave 0·8443 AgCl. Cl = 28·14.

$C_{12}H_{10}Cl_2Si$ requires Cl = 27·9 per cent.

Decomposition of Dichlorodiphenylsilicane with Water.

Dichlorodiphenylsilicane is readily decomposed by cold water, with development of heat. In preparing the dihydroxy-compound by this method, the oily dichloride was slowly dropped into a large volume of water, which was vigorously stirred and cooled during the whole operation. The somewhat pasty solid was washed with water and dried in the air. It was first extracted with warm light petroleum to remove any diphenyl which might be present, and then with cold chloroform, which dissolved a considerable quantity of a pale yellow oil. The perfectly colourless, crystalline residue thus obtained usually began to sinter at about 150°, but did not liquefy completely until about 165°. When treated with various solvents, such as ether, ethyl acetate, acetone, etc., it sometimes gave orange-yellow solutions, which, however, gave colourless deposits when they were completely evaporated at the ordinary temperature. These colourless deposits again gave the coloured solutions, and so on.

Some preparations were completely or partly converted into oily products when attempts were made to recrystallise them from hot solvents, such as ether or ethyl acetate. This behaviour was doubtless due to the presence of traces of hydrochloric acid, which had been retained when the pasty solid was washed with water. Other preparations separated from hot ethyl acetate, etc., in colourless needles, and were fractionally crystallised; although the various fractions appeared to be homogeneous and identical, they decomposed at different temperatures, the most sparingly soluble at about 158—165°, the most readily soluble at about 140—150°. All the fractions were impure, and left a residue when they were treated with a 5 per cent. aqueous solution of potassium hydroxide, the most sparingly soluble portion giving the largest quantity of insoluble matter. From these impure, although repeatedly recrystallised specimens, pure diphenylsilicanediol was finally isolated by the method described later (p. 2121).

Decomposition of Dichlorodiphenylsilicane with Ammonium Hydroxide Solution.

As it seemed to be probable that the impurities contained in the diphenylsilicanediol, prepared by the foregoing method, were produced by the action of the hydrochloric acid on the original product of hydrolysis, experiments were made on the decomposition of the dichloride with a cold concentrated solution of ammonium hydroxide. The results, however, were most unsatisfactory.

When the dichloride was slowly dropped into a well-stirred solution of ammonium hydroxide, it was completely converted into a pale yellow oil, which after having been extracted with cold light petroleum and thus freed from traces of diphenyl, remained liquid during many weeks. This oil was soluble in alcohol; it did not contain any appreciable proportion of diphenylsilicanediol, because, when treated with a 5 per cent. aqueous solution of potassium hydroxide, it gave an extract from which acids precipitated only small quantities of the dihydroxy-compound.

The further investigation of this oil will be described in the following paper.

Decomposition of Dichlorodiphenylsilicane with a Solution of Potassium Hydroxide.

At an early stage of this investigation it was observed that the crude diphenylsilicanediol, precipitated from a solution of its potassium derivative with dilute acetic acid, had a much lower decomposition point than specimens obtained by precipitation with hydrochloric acid, and generally contained a relatively small quantity of matter which was insoluble in potassium hydroxide solution; as this observation seemed to confirm the conclusion that the dihydroxy-compound was changed by hydrochloric acid, the following method of preparation was tried. Dichlorodiphenylsilicane (1 mol.) was slowly dropped into a 5 per cent. aqueous solution of potassium hydroxide (more than 4 mols.); as a slight development of heat occurred, the solution was cooled with water and well stirred during the operation.

The pure dichloride gave a clear, colourless solution of the potassium derivative, but unless the dichloro-compound had been very carefully fractionated, it contained traces of diphenyl, which remained suspended in the alkaline solution and necessitated filtration. During this operation the solution and the filtrate nearly always became turbid, owing to the absorption of atmospheric carbon dioxide, and it was very necessary to carry out the operation as quickly as possible, because the turbidity was difficult to remove by further filtration.

When the clear alkaline solution was cautiously neutralised, or rendered very slightly acid, with acetic acid, it gave a somewhat gelatinous precipitate, which was so bulky that the mixture became a thick, white paste; the precipitate, which under the microscope appeared to consist of amorphous particles, was readily separated by filtration and washed with water by the aid of the pump, but even when it had been well pressed and left on porous earthenware during some hours, it retained an extraordinarily large proportion of water. The freshly precipitated substance was readily and completely dissolved by a 5 per cent. solution of potassium hydroxide, but, as a rule, it changed so quickly that by the time it had been washed, it was no longer completely soluble.

A great many different samples of air-dried preparations obtained in the above manner were examined; when heated slowly from the ordinary temperature, they all began to decompose at about 105°, and at about 107—110° they had completely liquefied, effervescence taking place owing to the escape of steam. Some air-dried preparations, which were heated at 100°, decomposed and liquefied completely in the course of ten to twenty minutes.

When attempts were made to purify the precipitated diphenylsilicanediol by recrystallisation, it behaved in a very curious manner. On being warmed with solvents such as ether, ethyl acetate, etc., it seemed as a rule to be completely decomposed, and on subsequent evaporation at the ordinary temperature, the solutions gave a viscid, oily residue, which was very sparingly soluble in alcohol. When dissolved in these solvents at the ordinary temperature it was sometimes deposited, by the spontaneous evaporation of the solutions, as a lustrous powder, which liquefied at about 140—155°; at other times the solutions gave crusts of ill-defined prisms, whilst a considerable proportion of oily matter (readily soluble in chloroform) remained in the mother liquor. These crusts usually decomposed with effervescence, and liquefied completely at about 113—115°, but even when well washed with chloroform they still retained some impurity which was insoluble in a 5 per cent. potassium hydroxide solution. If such partly purified preparations were recrystallised from cold ether or ethyl acetate, colourless needles, decomposing at about 113—115°, might be obtained; on the other hand, the decomposition point of the needles might suddenly rise to about 135—140°.

This change in properties was apparently not due to the removal of some impurity in the mother liquor, because a given sample, repeatedly dissolved in cold ether, nearly always changed, sometimes after the first, sometimes after the second or third operation, even when the solvent was completely evaporated each time. It was also observed that those preparations, which decomposed at 113—115°, sometimes changed spontaneously in the course of a few hours at the ordinary temperature; they became white and opaque, and in such cases the decomposition point was found to have risen to about 138—145°.

In spite of the fact that some preparations changed, apparently spontaneously, at the ordinary temperature, it was sometimes possible to recrystallise small quantities of material from hot ethyl acetate or chloroform without any rise in decomposition point taking place; the first time, in fact, that a preparation of this low decomposition point was obtained, no sign of instability was observed and no special precautions were taken in its purification, and yet it was obtained in fairly large prisms liquefying at about 116°.

As the addition of a trace of hydrochloric acid to a solution of these preparations invariably brought about a rise in decomposition point to about 145°, it seemed possible that the behaviour just referred to might be due to the presence of traces of acids in the solvents employed. Some specimens were therefore recrystallised from ether at the ordinary temperature, the ethereal solution resting on water which contained a trace of potassium hydroxide; in these circumstances the diphenylsilicanediol was deposited in beautiful, lustrous prisms, which were completely soluble in potassium hydroxide solution, and decomposed with effervescence at 115—118°. Similar results were obtained when the preparations were recrystallised from ether in presence of a trace of piperidine, but neither method gave very satisfactory results, as, unless the operation was conducted quickly, the diphenylsilicanediol was decomposed.

A very simple modification in the method of obtaining diphenylsilicanediol from its alkaline solution seemed to give a pure preparation, or, at any rate, one which was completely soluble in potassium hydroxide solution; this was the addition of a little ether to the solution of the potassium salt before precipitating with acetic acid. In presence of the ether, the precipitate lost entirely its gelatinous character; it was far less bulky, quite distinctly crystalline, and was readily freed from water when it was pressed on porous earthenware. As such preparations appeared to be homogeneous under the microscope, were completely soluble in potassium hydroxide, and had the same decomposition point as the prisms obtained from ether, they seemed to be pure diphenylsilicanediol.

The following analyses of three different air-dried specimens agreed with this view:

I. 0·1454 gave 0·3554 CO_2 and 0·0750 H_2O. C=66·7; H=5·7.
II. 0·1610 „ 0·3932 CO_2 „ 0·0838 H_2O. C=66·6; H=5·8.
0·1956 „ 0·0547 SiO_2. Si=13·2.
III. 0·1743 „ 0·4254 CO_2 and 0·0885 H_2O. C=66·6; H=5·6.
0·1489 „ 0·0419 SiO_2. Si=13·2.
$C_{12}H_{12}O_2Si$ requires C=66·6; H=5·6; Si=13·1 per cent.

Notwithstanding this evidence, there is little doubt that these samples contained a small proportion of impurity, which lowered the decomposing point of the diol, but which could be removed by the method given later.

It would seem from subsequent observations that the behaviour of the diphenylsilicanediol, precipitated with acetic acid as described above, is due to the presence of traces of potassium hydroxide which are adsorbed from the alkaline solution by the somewhat gelatinous precipitate, and are not removed when the solution appears to be neutralised, or when the precipitate is subsequently washed with water; as a result of the action of the alkali, small quantities of products, some of which are insoluble in potassium hydroxide, are formed, and, by the continued action of the alkali before or after recrystallisation, these products may be further changed, and even the whole of the diphenylsilicanediol may be decomposed. When precipitation occurs in presence of ether, the precipitate is not colloidal, and does not adsorb alkali, or does so to a limited extent only, in consequence of which it is far more stable; such precipitates, however, contain a small proportion of impurity, which is soluble in solutions of alkali hydroxides.

Precipitation of Diphenylsilicanediol with Hydrochloric Acid.

When a solution of diphenylsilicanediol in potassium hydroxide was treated with hydrochloric acid, it gave a bulky precipitate, which seemed to have much the same gelatinous character as that obtained with acetic acid, but which, when air-dried, had a much higher decomposition point than the latter; the decomposition point, moreover, seemed to vary with the quantity and concentration of the acid which was used, and with the time which elapsed before the precipitate was separated and washed. If, for example, the solution was only just neutralised, and the precipitate was immediately separated, the decomposition point of the air-dried sample might be 130—135°; if, however, the solution was strongly acidified and the precipitate was not separated until the next day, the sample might only sinter slightly at about 140°, and not liquefy until about 160—165°. Such preparations, especially those which had remained for some time in contact with hydrochloric acid, contained a variable quantity of matter which was readily soluble in cold chloroform; when this had been extracted and the residue was fractionally crystallised from ether, ethyl acetate, acetone, etc., deposits, which decomposed from 160° to 170°, or from 135° to 145°, or at intermediate temperatures, were obtained. All these fractions appeared homogeneous, but left a variable quantity of an insoluble residue when treated with a 5 per cent. potassium hydroxide solution.

Repeated attempts were made to obtain from them a pure sample of the diol, but fractional crystallisation from the different media already mentioned did not give the desired result. During these experiments it was noticed that when solutions in ether or ethyl acetate were evaporated on the water-bath, crystallisation did not take place, even when the solutions had become highly supersaturated, but when such solutions were then cooled, they gave either a transparent gelatinous mass or a cotton-wool-like solid, which then gradually changed to a crystalline powder.

Preparations apparently very similar in character to those just described, but nearly free from matter soluble in cold chloroform, were obtained when alkaline solutions of the diol were treated with excess of ammonium chloride, which precipitated the whole of the diphenyl compound; the fractional crystallisation of these preparations failed to give a product which was completely soluble in potassium hydroxide solution, and the decomposition points of the well crystallised fractions varied from about 135 to 160°.

Isolation of Diphenylsilicanediol.

In the course of the experiments recorded above there had accumulated a considerable quantity of recrystallised, impure diol, which had been produced by the decomposition of the dichloride with water, or from the potassium derivative of the diol, by precipitation with hydrochloric acid or ammonium chloride. Different samples or fractions of this material showed very considerable differences in decomposition point, some liquefying at about 130—140°, others at 140—150°, or even up to 160°. Preparations of an apparently similar character had also been obtained from those decomposing at about 115°; when the latter were dissolved in ethyl acetate with the addition of a trace of hydrochloric acid, the solutions gave on spontaneous evaporation colourless needles or prisms, decomposing from about 145° up to 160°.

Many of these samples had been repeatedly fractionally crystallised from ethyl acetate, ether, acetone, benzene, etc., and from mixtures of chloroform and ether, and chloroform and acetone, but in no case had a pure preparation been obtained; although the crystals which separated from warm solvents consisted of beautiful, lustrous needles or prisms, and appeared homogeneous, they invariably left an insoluble residue when treated with potassium hydroxide solution. The deposits obtained by the spontaneous evaporation of the solutions occasionally appeared to be heterogeneous, and consisted of lustrous needles, together with white, cauliflower-like masses, which crept up and over the side of the beaker; these apparently different deposits had, however, practically the same decomposition points, and their mechanical separation led to no result. In nearly all cases the more sparingly soluble portions had the higher decomposition points (up to 170°), and seemed to be the more impure.

It was also observed that specimens decomposing at about 140°, when left exposed to the air at the ordinary temperature, sometimes underwent some change, and then did not decompose until 160—165°; this behaviour was not due to loss of solvent, and is referred to later.

Up to this time the use of aqueous solvents for the purification of the diol had been avoided because it had been observed that hot aqueous alcohol and acetic acid decomposed the compound; as a last resource, however, aqueous acetone was tried, with the following results.

When any of the preparations of impure diphenylsilicanediol, which decomposes above about 135°, was dissolved in acetone, and the solution diluted with a small proportion of water, the liquid became milky, and when left to evaporate at the ordinary temperature the milky fluid deposited colourless prisms. After a few days' time practically the whole of the diol had crystallised out, and was easily separated from the milky mother liquors, which passed unchanged through an ordinary filter; as a rule, in fact, the crystals were so large that the mother liquor might be merely decanted from them.

The milkiness of the original solutions appeared to be a rough measure of the impurity in the diol; according to this criterion, the preparations obtained by precipitating the alkaline solution with ammonium chloride were the least impure, whilst those obtained by decomposing the dichloride with water were less impure than those produced by precipitating the diol with hydrochloric acid. The crystals which separated from the milky fluid were covered with an oily film, which was easily removed by washing them with cold chloroform. When the washed crystals were again dissolved in acetone, and the solution was diluted with a little water, a milky fluid was again produced, but for any given sample the milkiness was far less pronounced than it was at the first treatment. The crystals which were subsequently deposited, when again washed with chloroform and then dissolved in acetone, usually gave solutions which did not become milky on the addition of water, but which immediately deposited a crystalline precipitate if sufficiently diluted. In those cases in which a milkiness was produced, the purification was still incomplete, but after a repetition of the operations a pure compound was obtained.

The crystalline substance, isolated in this way and then finally recrystallised from hot ethyl acetate or acetone, was pure diphenylsilicanediol; the milky mother liquors, which often remained unchanged in appearance during many months, and the chloroform washings of the crystals, contained the relatively small quantity of impurity, which apparently could not be removed by recrystallisation from anhydrous solvents, and seemed so greatly to affect the decomposition point of the pure diol. This impurity, so far as has been ascertained, is usually a mixture of three or four compounds.

By the use of aqueous acetone and chloroform alternately, it was also possible to isolate diphenylsilicanediol from the recrystallised preparations decomposing at about 115°, which had been originally obtained by precipitation with acetic acid. Such preparations gave with aqueous acetone, solutions which, as a rule, were not very milky, but from which on spontaneous evaporation, there gradually separated both crystals and oil; the latter was easily removed with the aid of cold chloroform, and the crystalline residue was redissolved in aqueous acetone. The solutions then gave a deposit containing far less oil, and by a repetition of these processes the pure diol was finally obtained. When two or three air-dried preparations, which had been obtained from the potassium derivative by precipitation with acetic acid and then kept during some weeks, were examined in this way, they were found to be highly impure, and apparently the longer a sample had been kept the greater the proportion of impurity.

Diphenylsilicanediol, $SiPh_2(OH)_2$.

The various samples of diphenylsilicanediol, isolated from the different preparations by the method described, were carefully compared; they all had the characteristics of a pure compound, and were identical with one another:

0·1480 gave 0·3605 CO_2 and 0·0743 H_2O. C = 66·4; H = 5·6.
0·1480 „ 0·0412 SiO_2. Si = 13·1.
$C_{12}H_{12}O_2Si$ requires C = 66·6; H = 5·6; Si = 13·1 per cent.

Diphenylsilicanediol crystallises from ether, ethyl acetate, acetone, etc., in long, colourless needles or prisms, which often exceed 20 mm. in length; when its solutions in ethyl acetate evaporate spontaneously, it is sometimes obtained in large, well-defined crystals, suitable for goniometrical measurement.

It is practically insoluble in water or light petroleum, only sparingly soluble in cold chloroform, and very moderately so in boiling benzene, but it dissolves more readily in warm ether, and freely in boiling ethyl acetate or acetone.

All the freshly prepared, air-dried specimens of diphenylsilicanediol, purified in the manner described above, and finally recrystallised from ethyl acetate, showed at first the same behaviour when they were heated and directly compared; they began to sinter slightly at about 125°, and if then the temperature was slowly raised, they liquefied completely at about 128—132°, and a vigorous effervescence was observed owing to the escape of steam. In the case of any given sample, however, the temperature at which decomposition set in and complete liquefaction took place, varied slightly with the conditions of the experiment, principally with the rate of heating, but also with the state of division of the substance.

The temperatures just given, and most of the decomposition points recorded in this paper, were observed when the rate of heating (about 100°) was a rise of about 10° per minute.

Although up to a certain time many freshly prepared samples of the pure diol had been heated, none had shown a decomposition point above 132°, and it seemed that the behaviour of the pure compound was invariable. When, however, four such preparations were examined again some two months after they had been obtained, one of them seemed to have undergone some change, and further observations were made.

One of these specimens, *A*, had been kept in a loosely-covered beaker, exposed to the laboratory air, and one of them, *B*, in a closed weighing-bottle; the other two, *C* and *D*, had been kept on clock glasses in a desiccator which contained a little damp soda-lime. The specimens *A* and *B* had not changed in appearance, and consisted of transparent needles. The specimen *C* seemed to have changed very slightly in appearance as the needles seemed somewhat opaque in parts. The specimen *D*, which consisted of rather small crystals, had obviously undergone some change, the previously transparent needles having become white and opaque; although this specimen sometimes decomposed completely below about 132°, it usually showed no signs of change until about 150°, and decomposed with effervescence at about 155—160°; further, it was no longer readily and completely soluble in a 5 per cent. aqueous solution of potassium hydroxide, but gave a very small proportion of a flocculent substance, which did not dissolve in the course of about ten minutes.

The other three specimens, *A*, *B*, and *C*, usually decomposed completely at 128—132°, but occasionally one of them did not sinter until about 150°, and decomposed with effervescence at about 155—159°; they were all completely soluble in a 5 per cent. aqueous solution of potassium hydroxide.

The results of a great many more experiments with the samples *A*, *B*, and *C*, and with various freshly prepared pure specimens, proved that diphenylsilicanediol might show one of two very different decomposition points; when six to eight melting-point tubes, all containing the same finely powdered sample, were heated simultaneously, the contents of one, or possibly two, of the tubes might not decompose until about 145° or even 158°, those of all the others having completely liquefied below 132°.

Now as it is most improbable that the observed difference in behaviour between identical samples under as nearly as possible identical conditions could be due merely to a difference in the rate of decomposition, it seems necessary to conclude that diphenylsilicanediol is dimorphous; that the crystalline form which is deposited from solvents and which decomposes below 132° may pass into a more stable one, which does not decompose until about 160°.

This conclusion, which appears to be fully established, affords an explanation of many of the apparently anomalous facts recorded in this paper. In the first place, it is obvious from the behaviour of the pure compound, that the change in crystalline form which sometimes occurs is due to some inappreciable and fortuitous difference in the experimental conditions; consequently, it is not only possible, but highly probable, that the presence of impurity of a particular kind might condition the change in crystalline form, especially if the impurity were isomorphous with the form which is stable at the higher temperature. The fact that all specimens of diphenylsilicanediol containing a certain proportion of those substances which are insoluble in potassium hydroxide solution have always, and those containing traces of such impurities have generally, the high decomposition point, would thus be explained; as these impurities are probably trianhydrotrisdiphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol (compare following paper), neither of which would be melted at 132°, the presence of even a trace of either substance might cause the crystalline transformation of the diol to take place.

The fact that those impure specimens of the diol which contain small quantities of substances soluble in potassium hydroxide solution, and which decompose at about 118°, have a much higher decomposition point after they have been crystallised in presence of an acid, may also be accounted for; the impurity which lowers the decomposition point of the diol is some compound or mixture of low melting point which is changed by the acid into one of the above-named substances of high melting point; experimental evidence which strongly supports this assumption is given later (p. 2141).

The spontaneous rise in decomposition point which was often observed in the case of impure samples of the diol might, of course, have been apparent only, that is to say, the sample might not have changed until its decomposition point was being taken; in any case, unless the specimen were free from alkali and acid, a change in the decomposition point might well occur as the result of chemical changes in the impurity present, or in the diol itself; such changes might lead to the formation of the substance or substances which favour the crystalline transformation of the diol.

So far the only instance in which a highly purified sample appears to have changed is that of the specimen *D*, referred to above; whatever may be its cause or its nature, this change was only very superficial, and the opaque crystals immediately became transparent when they were moistened with acetone.

One further point remains to be considered, namely, how Martin was led to believe that the preparations which he regarded as isomeric diphenylsilicols could be transformed one into the other by the methods which he describes (*loc. cit.*). According to his statements, when the "isomeride" decomposing at about 160° was dissolved in an aqueous solution of potassium hydroxide, and the solution then treated with acids, the "isomeride" decomposing at about 144° was obtained, but if alcoholic potassium hydroxide was used, the original "isomeride" decomposing at about 160° was precipitated. These statements are doubtless incorrect in so far as any question of isomerism is concerned, but it is possible that the actual observations are to be accounted for as follows: The crude preparation decomposing at about 160° contained a considerable proportion of impurity which was insoluble in an aqueous solution of potassium hydroxide; when aqueous alkali was used and this impurity became visible, it was separated by filtration before the solution was acidified, so that the precipitated diol was less impure than the original sample, and decomposed at a rather lower temperature. When, however, the original sample was dissolved in alcoholic potassium hydroxide, the impurity was not precipitated, or was only partly precipitated, and consequently the diol finally obtained on the addition of an acid was just as impure as before, and decomposed at approximately the same temperature as the original sample.

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