VI.—*Organic Derivatives of Silicon. Part XX. Some Condensation Products of Dibenzylsilicanediol.*

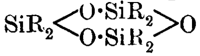
By ROBERT ROBISON and FREDERIC STANLEY KIPPING.

IN the last four papers on organic derivatives of silicon (T., 1912, **101**, 2108, 2125, 2142, 2156) it was shown that certain disubstituted silicanediols of the type $SiR_2(OH)_2$, in which at least one of the radicles is aromatic, are capable of existence at the ordinary temperature, and, therefore, are more stable than the corresponding derivatives of methane.

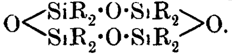
Such compounds, however, readily undergo change when they are heated alone, or when they are treated in solution with various reagents, such as alkali hydroxides, ammonia, or mineral acids. The result, as a rule, is the formation of a mixture of open- and closed-chain condensation products; from such mixtures representatives of the following types have already been isolated:

$HO\cdot SiR_2\cdot O\cdot SiR_2\cdot OH$

$HO\cdot SiR_2\cdot O\cdot SiR_2\cdot O\cdot SiR_2\cdot OH$



$SiR_2<\begin{matrix}O\cdot SiR_2\\ O\cdot SiR_2\end{matrix}>O$



$O<\begin{matrix}SiR_2\cdot O\cdot SiR_2\\ SiR_2\cdot O\cdot SiR_2\end{matrix}>O.$

Hitherto very little attention has been paid to the conditions under which each of these different types of condensation product is formed; the mixtures of these compounds were obtained more or less by chance during the preparation or purification of the diols.

Now the importance of gaining further information respecting these condensation products need hardly be emphasised; the study of the reactions by which they are formed cannot fail to throw some light on the processes, doubtless of an analogous character, which lead to the production of the complex mineral silicates.

For this reason we have continued our investigations along various lines, and have more particularly directed our attention to an examination of (*a*) the conditions under which the diols undergo condensation, (*b*) the conditions under which the open-chain are converted into closed-chain compounds, and (*c*) the comparative readiness with which the closed-chain compounds containing two, three, or four atoms of silicon respectively are formed. The results obtained from the study of dibenzylsilicanediol and its condensation products are described in this paper.

Dibenzylsilicanediol is very readily acted on by various reagents (p. 41), giving, as a rule, a mixture of anhydrobisdibenzylsilicanediol and trianhydrotrisdibenzylsilicanediol. The former compound does not seem to yield any further condensation product by the direct elimination of the elements of water; so far, we have not been able to prepare from it either dianhydrobisdibenzylsilicanediol, $Si(CH_2Ph){<}^{O}_{O}{>}Si(CH_2Ph)_2$, or the analogue of tetra-anhydrotetrakisdiphenylsilicanediol. In alcoholic solution, however, in presence of hydrogen chloride, anhydrobisdibenzylsilicanediol is transformed into trianhydrotrisdibenzylsilicanediol; this change is doubtless dependent on the hydrolysis of some of the anhydrobisdibenzylsilicanediol to dibenzylsilicanediol, but whether the trianhydro-compound is formed by the subsequent condensation of the dibenzylsilicanediol with the unchanged anhydrobisdibenzylsilicanediol, or by the direct condensation of three molecules of the simple diol, is not known.

Dianhydrotrisdibenzylsilicanediol,

$$HO\cdot Si(CH_2Ph)_2\cdot O\cdot Si(CH_2Ph)_2\cdot O\cdot Si(CH_2Ph)_2\cdot OH,$$

the analogue of dianhydrotrisdiphenylsilicanediol, may be obtained by carefully hydrolysing trianhydrotrisdibenzylsilicanediol with potassium hydroxide or hydrogen chloride in acetone solution; it is readily converted into trianhydrotrisdibenzylsilicanediol by traces of hydrogen chloride in alcoholic solution. These facts show that the hydrolysis and formation of these closed oxy-silicon chains are easily reversible reactions under the given conditions; it may also be concluded that the closed chain composed of three silicon and three oxygen atoms alternately linked together, is more easily formed than those containing either two or four atoms of both of these elements.

EXPERIMENTAL.

Dibenzylsilicanediol.

Dibenzylsilicanediol is converted into anhydrobisdibenzylsilicanediol when it is heated at about 110° (*loc. cit.*, p. 2148), treated with hydrogen chloride in alcoholic solution (*loc. cit.*, p. 2150), or treated with acetyl chloride; in the last two cases trianhydrotrisdibenzylsilicanediol is also formed and may even be the principal product, but no other crystalline substance has been isolated from the oily matter, which is usually produced from the diol in these and other experiments.

Dibenzylsilicanediol is also condensed by alkalis; when a solution of the diol in a 6 per cent. solution of sodium hydroxide is kept at the ordinary temperature exposed to the air, in the course of a day or two it deposits an oil, sometimes a solid, which is insoluble in a dilute aqueous solution of sodium hydroxide, but completely soluble in cold ethyl alcohol; this product is therefore probably a mixture of anhydrobisdibenzylsilicanediol and dianhydrotrisdibenzylsilicanediol (p. 43). If, however, the alkaline solution is heated at about 100° during some hours, the precipitate is only partly soluble in cold alcohol, and contains a considerable proportion of trianhydrotrisdibenzylsilicanediol.

The separation of these condensation products from a cold alkaline solution of the diol certainly takes place more quickly in the presence than in the absence of air; it is improbable, however, that the atmospheric carbon dioxide has any direct action except that of diminishing the concentration of the sodium hydroxide. Apparently the solution contains the sodium derivative, or derivatives, of the diol in equilibrium with a very small quantity of one or more of the condensation products of the diol:

$$Si(CH_2Ph)_2(ONa)_2 + H_2O \longleftrightarrow Si(CH_2Ph)_2(ONa)\cdot OH + NaOH$$

$$H_2O + 2Si(CH_2Ph)_2(ONa)\cdot OH \longleftrightarrow HO\cdot Si(CH_2Ph)_2\cdot O\cdot Si(CH_2Ph)_2\cdot OH + 2NaOH,$$

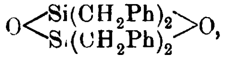
and the conversion of the alkali into carbonate merely disturbs the equilibrium.

The behaviour of all the other diols towards dilute solutions of alkali hydroxides appears to be similar to that of the dibenzyl compound, but except in the case of diphenylsilicanediol, the condensation products have not been isolated; it would also seem that dibenzylstannanediol undergoes condensation under similar conditions (Smith and Kipping, T., 1913, **103**, 2034).

Dibenzylsilicanediol also undergoes condensation when its alcoholic solution is treated with a drop or two of piperidine; trianhydrotrisdibenzylsilicanediol is formed, together with an oil, the components of which have not been isolated.

Anhydrobisdibenzylsilicanediol.

Several further attempts have been made to convert this compound into dianhydrobisdibenzylsilicanediol,



$O{<}\begin{smallmatrix}Si(CH_2Ph)_2\\Si(CH_2Ph)_2\end{smallmatrix}{>}O$,

or tetra-anhydrotetrakisdibenzylsilicanediol, but without success. Acetyl chloride, as already stated (*loc. cit.*, p. 2154), seems to have little or no action on the compound; in a recent experiment a solution of anhydrobisdibenzylsilicanediol in excess of the acid chloride was kept during some months and then evaporated, but the oily residue was readily and completely soluble in ethyl alcohol, and appeared to be free from higher condensation products. The alcoholic solution subsequently deposited crystals of trianhydrotrisdibenzylsilicanediol, but this compound had probably been formed by the action of traces of hydrogen chloride on anhydrobisdibenzylsilicanediol (see below).

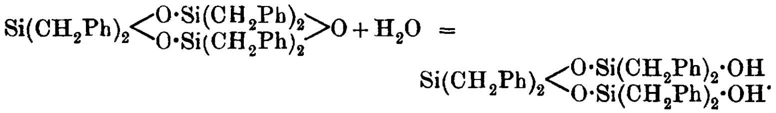
The behaviour of anhydrobisdibenzylsilicanediol towards alkalis was also examined in alcoholic solution, but crystalline compounds could not be isolated from the oily product which was formed in the course of some days. The action of piperidine in alcoholic solution was similar to that of potassium hydroxide, and led to the formation of an oily condensation product.

Anhydrobisdibenzylsilicanediol was also heated with phosphoric oxide; the oily product was completely soluble in ethyl alcohol, and apparently did not contain trianhydrotrisdibenzylsilicanediol in appreciable quantity. When, however, an alcoholic solution of anhydrobisdibenzylsilicanediol, to which a few drops of concentrated hydrochloric acid had been added, was kept at the ordinary temperature, crystals of trianhydrotrisdibenzylsilicanediol were deposited in the course of twenty-four hours. It must therefore be concluded that the anhydro-derivative is hydrolysed by the hydrochloric acid, giving dibenzylsilicanediol, which then undergoes condensation under the influence of the same reagent.

Dianhydrotrisdibenzylsilicanediol,

$\mathrm{HO\cdot Si(CH_2Ph)_2\cdot O\cdot Si(CH_2Ph)_2\cdot O\cdot Si(CH_2Ph)_2\cdot OH}$.

Although this compound is very probably present in the oils which are formed by the action of dilute alkali hydroxides on dibenzylsilicanediol and on anhydrobisdibenzylsilicanediol, it has not yet been isolated from these products. Attempts were therefore made to prepare it by the hydrolysis of trianhydrotrisdibenzylsilicanediol in accordance with the equation:



$$\mathrm{Si(CH_2Ph)_2} < \begin{matrix} \mathrm{O\cdot Si(CH_2Ph)_2} \\ \mathrm{O\cdot Si(CH_2Ph)_2} \end{matrix} > \mathrm{O + H_2O} = \mathrm{Si(CH_2Ph)_2} < \begin{matrix} \mathrm{O\cdot Si(CH_2Ph)_2\cdot OH} \\ \mathrm{O\cdot Si(CH_2Ph)_2\cdot OH} \end{matrix}$$

The trianhydro-derivative, although practically insoluble in alcohol, slowly dissolves in an alcoholic solution of potassium hydroxide at the ordinary temperature, owing to the occurrence of hydrolysis; from freshly prepared solutions water precipitates a solid, and the filtered solution gives with acetic acid a precipitate of dibenzylsilicanediol. An examination of the solid obtained in this way from the alkaline solution showed that it consisted of anhydrobisdibenzylsilicanediol, or of a compound melting at 82°, or of a mixture of these two substances, and that its nature varied with the conditions of the experiment, owing to the occurrence of progressive hydrolysis. In order to find a suitable method for the preparation of the compound melting at 82°, which was the desired dianhydro-derivative, various experiments were made under different conditions; the results showed that with the aid of acetone, in which trianhydrotrisdibenzylsilicanediol is readily soluble, the primary product of hydrolysis is readily obtainable as follows:

A solution of trianhydrotrisdibenzylsilicanediol in cold acetone is treated with a 3 per cent. solution of potassium hydroxide (2 mols.), and thirty seconds afterwards a slight excess of dilute acetic acid is added. The solution is then further diluted with water, and the oily precipitate is separated by filtration or extracted with ether. The ethereal solution of the oil is mixed with light petroleum and left to evaporate; the crystals which separate are then recrystallised several times from a mixture of the two solvents just mentioned.

Dianhydrotrisdibenzylsilicanediol is thus obtained in large, transparent crystals, melting at 82°; the samples for analysis were dried over sulphuric acid:

0·1899 gave 0·5019 CO_2 and 0·1088 H_2O. C = 72·2; H = 6·4.
0·1733 „ 0·4600 CO_2 „ 0·0993 H_2O. C = 72·4; H = 6·4.
$C_{42}H_{44}O_4Si_3$ requires C = 72·3; H = 6·3 per cent.

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

0·253, in 13·55 grams of benzene, gave Δt −0·12°. M.W. = 761.
0·446, „ 13·55 „ „ „ Δt −0·21°. M.W. = 771.

These results agree only moderately with the calculated molecular weight ($C_{42}H_{44}O_4Si_3$ requires M.W. 696), and indicate a considerable degree of association in benzene solution; in this respect they correspond closely with the values obtained under similar conditions in the case of other condensation products of this character, such as anhydrobisdiphenylsilicanediol and dianhydrotrisdiphenylsilicanediol (Kipping, *loc. cit.*, p. 2132, 2134); they may therefore be regarded as satisfactory.

Dianhydrotrisdibenzylsilicanediol is readily soluble in ether or alcohol, and in all the other common organic solvents with the exception of cold light petroleum, in which it is only sparingly soluble; it is practically insoluble in water, and also in a cold dilute solution of potassium hydroxide.

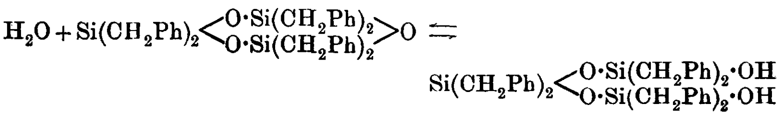
It is obvious from the above-described method of preparation of dianhydrotrisdibenzylsilicanediol that the rupture of the closed chain contained in the trianhydro-derivative takes place very rapidly under the influence of the potassium hydroxide, whereas the further hydrolysis, which results in the formation of anhydrobisdibenzylsilicanediol and dibenzylsilicanediol takes place more slowly. Although the above-mentioned quantity of the alkali was generally used, the proportion of this substance seemed to be of much less importance than the time during which hydrolysis was allowed to proceed. If, for example, more than a few minutes elapse between the addition of the alkali and that of the acetic acid, the product always contains a considerable quantity of dibenzylsilicanediol, even when only two molecular proportions of potassium hydroxide are present.

Hydrolysis of Trianhydrotrisdibenzylsilicanediol with Hydrogen Chloride.

It has already been shown that dibenzylsilicanediol is slowly converted into trianhydrotrisdibenzylsilicanediol when it is treated with concentrated hydrochloric acid in alcoholic solution (*loc. cit.*, p. 2150), and that under similar conditions anhydrobisdibenzylsilicanediol is also transformed into the same condensation product. In the latter case it is clear that hydrolysis of the anhydro-derivative must precede condensation; the reaction brought about by the hydrochloric acid is therefore a reversible one, and the production of trianhydrotrisdibenzylsilicanediol in almost theoretical quantities is determined merely by the insolubility of the latter in alcohol. Experiments were therefore made to ascertain whether under suitable conditions trianhydrotrisdibenzylsilicanediol could be hydrolysed with hydrochloric acid; it was thus found that the trianhydro-derivative could be converted into dianhydrotrisdibenzylsilicanediol in the following manner.

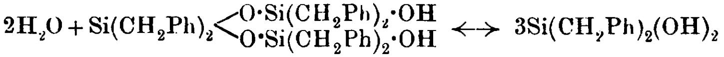
Trianhydrotrisdibenzylsilicanediol is dissolved in acetone and one drop of concentrated hydrochloric acid is added; after about half an hour's time the solution is diluted with water and stirred vigorously. The precipitated solid is separated by filtration, and extracted with cold alcohol, which leaves a residue of unchanged trianhydrotrisdibenzylsilicanediol; the alcoholic solution is then diluted with water and the oily precipitate extracted with ether. The ethereal solution contains dianhydrotrisdibenzylsilicanediol, which is purified by recrystallisation from a mixture of ether and light petroleum. In this way only about 15 per cent. of the trianhydro-derivative is transformed into the dianhydro-compound, but by submitting the unchanged substance to the same treatment again, further quantities of the dianhydro-compound may be obtained.

It might be concluded therefore that in acetone solution the hydrolysis of trianhydrotrisdibenzylsilicanediol by hydrogen chloride is a reversible reaction:



$$\mathrm{H_2O + Si(CH_2Ph)_2}{<}\begin{matrix}\mathrm{O\cdot Si(CH_2Ph)_2}\\ \mathrm{O\cdot Si(CH_2Ph)_2}\end{matrix}{>}\mathrm{O} \rightleftharpoons \mathrm{Si(CH_2Ph)_2}{<}\begin{matrix}\mathrm{O\cdot Si(CH_2Ph)_2\cdot OH}\\ \mathrm{O\cdot Si(CH_2Ph)_2\cdot OH}\end{matrix}$$

and that under the conditions described above, equilibrium is attained when the proportion of dianhydrotris- to trianhydrotris-dibenzylsilicanediol is about 1 : 5 or 1 : 6. Probably the above equation expresses only one of several reversible reactions which occur, others being the following:



$$2\mathrm{H_2O} + \mathrm{Si(CH_2Ph)_2}\begin{array}{l}\diagup \mathrm{O\cdot Si(CH_2Ph)_2\cdot OH}\\ \diagdown \mathrm{O\cdot Si(CH_2Ph)_2\cdot OH}\end{array} \longleftrightarrow 3\mathrm{Si(CH_2Ph)_2(OH)_2}$$

$$2\mathrm{Si(CH_2Ph)_2(OH)_2} \longleftrightarrow \mathrm{HO\cdot Si(CH_2Ph)_2\cdot O\cdot Si(CH_2Ph)_2\cdot OH} + \mathrm{H_2O}.$$

Conversion of Di- into Tri-anhydrotrisdibenzylsilicanediol.

If the formation of dianhydrotrisdibenzylsilicanediol from the trianhydro-derivative in the manner just described is really a reversible reaction, then in alcoholic solution the change expressed by the above equation should proceed almost completely from right to left, owing to the insolubility of the trianhydro-compound in alcohol. This conclusion was fully confirmed by experiment.

When an alcoholic solution of dianhydrotrisdibenzylsilicanediol, to which a drop of concentrated hydrochloric acid has been added, is kept at the ordinary temperature, it soon deposits a crystalline precipitate, melting at 98°, which consists of pure trianhydrotris-dibenzylsilicanediol.

A quantitative experiment, made in the following manner, showed that the change is practically complete. A known quantity of dianhydrotrisdibenzylsilicanediol, contained in a weighing bottle, was dissolved in alcohol, to which one drop of concentrated hydrochloric acid had been added; after the solution had been kept for about twelve hours, during which time it deposited crystals of trianhydrotrisdibenzylsilicanediol, it was evaporated in a desiccator over sulphuric acid and potassium hydroxide, and the residue was dried at about 90° until constant in weight. The loss amounted to 2·48 per cent., against a theoretical loss of 2·58 per cent.

Dianhydrotrisdibenzylsilicanediol also undergoes condensation in alcoholic solution in presence of a trace of sodium hydroxide, even more readily than in presence of hydrogen chloride; within an hour, crystals of trianhydrotrisdibenzylsilicanediol are deposited from the solution.

Acetic anhydride seems to have little action on dianhydrotris-dibenzylsilicanediol; a small quantity of the compound was heated with this reagent for a short time, but was afterwards recovered unchanged.

The action of acetyl chloride was also studied. In one experiment the residue obtained by evaporating an acetyl chloride solution of the dianhydro-compound at the ordinary temperature was treated with alcohol; it yielded crystals of trianhydrotrisdibenzylsilicanediol. In another experiment, a weighed quantity of the substance was gently warmed with a small amount of acetyl chloride until the latter had evaporated, and was then heated to 110°; no loss in weight, however, could be detected. The same sample was again treated with acetyl chloride, and after the latter had been evaporated, the residue was heated to about 125° in the course of forty-five minutes. The total loss in weight was 2·9 per cent., the theoretical loss for one molecule of water being 2·6 per cent. When the residue was warmed with alcohol, it gave a sparingly soluble powder, which separated from a mixture of ether and light petroleum in crystals melting at 98°. These results prove that dianhydro- may be converted into trianhydro-trisdibenzylsilicanediol by the treatment described, but they do not show whether it is the acetyl chloride itself which brings about condensation, or the traces of hydrogen chloride which are doubtless formed in the course of the experiment.

Effect of Heat on Dianhydrotrisdibenzylsilicanediol.

Although dianhydrotrisdibenzylsilicanediol is so readily converted into the closed-chain compound by acids or alkalis, this change cannot be satisfactorily accomplished by merely heating the dianhydro-compound (in the air). Quantitative experiments showed that at 130° only a very slow loss in weight took place; at higher temperatures, the loss was more rapid, but the residue had a strong odour of benzaldehyde, probably owing to atmospheric oxidation. In one case, during one hour at 175°, 0·3125 gram of substance lost 5·4 per cent., but there was no indication of a constant weight having been attained; as the theoretical loss for one molecule of water is only 2·58 per cent., more than one-half of the observed loss was doubtless due to the volatilisation of the benzaldehyde formed by atmospheric oxidation. The residue yielded less than 0·1 gram of trianhydrotrisdibenzylsilicanediol, together with an oil from which crystals of dianhydrotrisdibenzylsilicanediol (m. p. 82°) were isolated.

Trianhydrotrisdibenzylsilicanediol.

Crystals of this compound deposited from a mixture of chloroform and light petroleum have been examined for us by Mr. Vernon Stott under the direction of Mr. A. Hutchinson, M.A., of the mineralogical laboratory, Cambridge; we are indebted to these gentlemen for the following report:

System: **oblique.** **Sub-class:** holohedral.

$a : b : c = 2{\cdot}797 : 1 : 1{\cdot}643$; $\beta = 94°38'$.

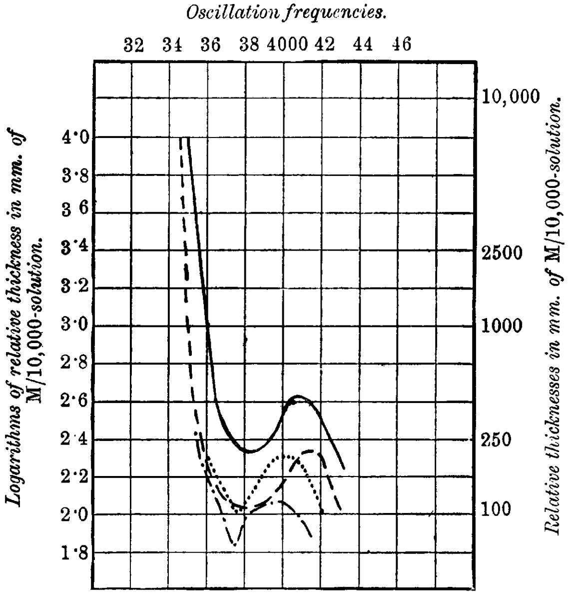
Forms developed: $a\{100\}$, $c\{001\}$, $m\{110\}$, $s\{101\}$, $r\{\bar{1}01\}$.

Table of angles:

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
100 : 101	9	59°20′—60°11′	59°43′	59°29′
101 : 001	9	25 14 —26 13	25 38	25 53
100 : $\bar{0}$01	9	85 2 —85 40	85 22	—
001 : $\bar{1}$01	11	27 2 —28 4	27 38	27 47
$\bar{1}$01 : $\bar{1}$00	9	66 31 —67 4	66 51	—
100 : 110	23	70 0 —70 36	70 14	70 16
101 : 110	33	80 0 —80 33	80 15	80 3
110 : $\bar{1}$10	16	39 11 —39 43	39 28	—
001 : 110	42	88 13 —88 54	88 30	88 27
$\bar{1}$01 : 110	47	96 59 —97 58	97 33	97 38

The crystals are prismatic in habit, being elongated in a direction perpendicular to the diad axis. The *m* faces are in general much larger than the *a* faces.

At our request, Dr. I. M. Heilbron has very kindly photographed



Full curve: *Dibenzylsilicanediol in alcohol, with or without alkali.*
Dot curve: *Anhydrobisdibenzylsilicanediol in alcohol.*
Dash curve: *Dianhydrotrisdibenzylsilicanediol in alcohol.*
Dash-dot curve: *Trianhydrotrisdibenzylsilicanediol in chloroform.*

the absorption spectra of dibenzylsilicanediol and of the various condensation products of this diol, which, so far, have been prepared. From the curves, which are given in the accompanying diagram, it will be seen that the spectra of all the four compounds are very similar, and show one fairly broad band, which covers the region of the first four or five bands shown by benzene (Baly and Collie, T., 1905, **87**, 1332). In the case of those compounds which contain four or six benzyl groups, this band is found at lower molecular concentrations than in the case of dibenzylsilicanediol itself. It will also be seen that the addition of alkali to the alcoholic solution of the last-named compound brings about no alteration in the absorption spectrum.

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