XLIII.—*Organic Derivatives of Silicon. Part V. Benzylethylsilicone, Dibenzylsilicone, and other Benzyl and Benzylethyl Derivatives of Silicane.*

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The silicones, those derivatives of silicon analogous to the ketones in structure, have not yet been very carefully studied, and, in fact, only a few compounds of this type have hitherto been prepared.

The simplest known representative, diethylsilicone, Et_2SiO, was obtained long ago by Friedel (*Ann. chim. phys.*, 1866, [iv], **9**, 5); diphenylsilicone, Ph_2SiO, has been described by Dilthey (*Ber.*, 1905, **38**, 4132), and phenylethylsilicone, PhEtSiO, was prepared by one of us a short time ago (Trans., 1907, **91**, 218).

In the course of some recent experiments (Kipping, Trans., 1907, **91**, 720), it was found that benzylethylsilicon dichloride could be easily obtained in a pure state; as this compound is decomposed by water, giving benzylethylsilicone, BzEtSiO, we have studied the behaviour of this silicone in order to ascertain whether it shows any similarity to the corresponding ketone. We may say at once that it does not; benzyl ethyl ketone boils at 226° under atmospheric pressure; benzylethylsilicone at 305—315° under a pressure of 22 mm. This very high boiling point of the silicone doubtless indicates molecular complexity, and the results of ebullioscopic experiments bear out this indication, the values obtained in acetic acid and in acetone pointing to the termolecular formula $(BzEtSiO)_3$. In this respect, benzylethylsilicone resembles diphenylsilicone (Dilthey, *loc. cit.*); dibenzylsilicone, which is described in this paper (p. 452), is also represented by the molecular formula $(Bz_2SiO)_3$, and, judging from its high boiling point (above 360°), diethylsilicone has an analogous molecular complexity. It would seem, therefore, that silicones, as a class, differ from the ketones in readily forming comparatively stable molecular aggregates, but whether the latter are to be regarded as composed of loosely associated, or of chemically united, molecules we have as yet no satisfactory evidence before us.

This association, polymerisation, or union of the simple silicone molecules is probably one of the reasons, but not the only one, why in other respects also the silicones show no relationship with the ketones; thus we find that benyzlethylsilicone does not undergo change when it is treated with certain reagents which reduce ketones; we also find that the silicone does not react with hydroxylamine or with phenylhydrazine when treated with these reagents in the ordinary way. In both these cases, it is possible to account for the result on the assumption that the grouping Si:O of the simple silicone does not exist in the associated molecule, but, since we know from previous experiments (Kipping, *loc. cit.*) that the union between nitrogen and silicon is dissolved in presence of water, the non-formation of an oxime or hydrazone may not be in any way determined by the association of the silicone.

Having found that benzylethylsilicone did not react with the ordinary ketonic reagents, we attempted to prepare its sulphonic derivative. As a number of derivatives of silicane which contain a benzyl group undergo sulphonation very readily, whereas those containing phenyl or alkyl groups do not, it seemed extremely probable that in all the former the sulphonic group displaced hydrogen of the benzyl nucleus; this conclusion was confirmed by the fact that benzylethylsilicone could be sulphonated without difficulty, but, unfortunately, the salts of the acid, which is produced as the main product, did not crystallise well.

In the preparation of the benzylethylsilicon dichloride which was required for these and for other experiments, a considerable proportion of an oily by-product was invariably obtained (Kipping, *loc. cit.*, p. 721); having collected a large quantity of this oil from different preparations, it seemed worth while to try to isolate the dibenzylethyl silicyl chloride, of which we thought the product was mainly composed. After working at this by-product for some time, we realised that it was a far more complex mixture than we had supposed, and ultimately we found that it contained, in addition to dibenzyl and some stilbene, dibenzylethylsilicyl chloride, dibenzylsilicon dichloride, tribenzylsilicyl chloride, and other compounds which were not identified.

The occurrence in this mixture of dibenzylsilicon dichloride and of tribenzylsilicyl chloride is possibly due to the presence of silicon tetrachloride in the ethylsilicon trichloride used for the preparation of the benzylethyl derivative; as, however, ethylsilicon trichloride boils at 100°, and all the preparations which we used had been repeatedly fractionated, employing a rod and disk column, it hardly seems likely that they could have contained silicon tetrachloride (b. p. 58°), at any rate, in quantity sufficient to yield any appreciable proportion of its dibenzyl and tribenzyl derivatives. It seems more likely, therefore, that the observed formation of these compounds is due to the displacement of the ethyl by a benzyl group during the treatment of the ethylsilicon trichloride with magnesium benzyl chloride; such a reaction is not inherently improbable, and, for different reasons altogether, it has been already suggested that a change of this kind may occur (Kipping, *loc. cit.*, p. 730).

On decomposing with water some of the impure dibenzylsilicon dichloride isolated from the product mentioned above, we obtained a crystalline substance melting at 101°, and the results of the examination of this compound led us to conclude that it was a hydrol of the formula $Bz_2Si(OH)_2$. The only reason for hesitation in coming to this conclusion was that Dilthey (*loc. cit.*) had recently described under the name dibenzylsilicol, a compound to which he assigned the formula $Bz_2Si(OH)_2$, and an approximate melting point of 76°. He obtained this compound by treating silicon tetrachloride with three molecular proportions of magnesium benzyl chloride, decomposing the product with water, and then crystallising from a mixture of benzene and light petroleum, rejecting the portions melting above 76° which contained tribenzylsilicol. As such a method could hardly yield a pure substance, as, in fact, seemed to be admitted by Dilthey himself, we thought it probable that his preparation, the melting point of which had been *lowered* to 76°, was a mixture of the hydrol and tribenzylsilicol. But as Dilthey's numerous analyses all gave results agreeing with those required for the hydrol alone, we thought it advisable to investigate the matter further.

Having prepared a considerable quantity of pure dibenzylsilicon dichloride, which crystallises in magnificent transparent prisms, some of this preparation was decomposed with water; the product after recrystallisation melted at 101°, and was identical with the supposed hydrol previously obtained. Further evidence of the nature of this product was afforded by its behaviour when heated; when kept at 110° for six hours, it was converted into dibenzylsilicone, a crystalline compound melting at 98°, and quite different from the hydrol in outward properties. At this stage, we were naturally very doubtful as to the purity of Dilthey's "dibenzylsilicol" melting at 76°, but, on attempting to prepare a further quantity of ketone by heating the hydrol (m. p. 101°) at 110°, we obtained instead a substance which was not dibenzylsilicone, and which, after repeated recrystallisation, melted at about 75°, but not sharply; this compound formed well-defined, transparent prisms, had the appearance of a pure substance, and on analysis gave results agreeing with those required by a hydrol of the formula $Bz_2Si(OH)_2$. Later, this hydrol melting at 75° was obtained directly in place of the hydrol melting at 101° by decomposing dibenzylsilicon dichloride with water, and crystallising the product from a mixture of ether and light petroleum. It seems very probable that the substance melting at 75° is identical with Dilthey's dibenzylsilicol (m. p. 76°); in any case, since our experiments show that both this and the compound melting at 101° have the molecular formula $Bz_2Si(OH)_2$, we are forced to the conclusion that the two hydrols are isomeric. Details of the experimental evidence leading to this conclusion are given, but it may be stated here that, in addition to the analyses and molecular weight determinations, it is shown that both the hydrols may be converted into dibenzylsilicone under suitable conditions.

In spite of their isomerism, the two hydrols, which we distinguish as α (m. p. 101°) and β (m. p. 75°), differ very greatly in outward characteristics, and also, in one noteworthy respect, in chemical properties; whereas the α-compound is practically unchanged in a dry vacuum, the β-hydrol becomes oily, owing to loss of the elements of water; further, although we have never succeeded in regenerating the α-hydrol after it has once lost the elements of water, the β-hydrol is readily formed again on exposing its oily decomposition product to moist air. This difference seemed to indicate a possible explanation of the observed isomerism; the α-hydrol might be regarded as a compound of the structure $Bz_2Si<\begin{smallmatrix}OH\\OH\end{smallmatrix}$, and the β-isomeride as unimolecular dibenzylsilicone crystallised with one molecule of water; the results of our cryoscopic experiments, however, do not lend any support to this view, which, after all, is barely susceptible of clear definition, and up to the present, unless we consider the possibility that the β-hydrol may have the constitution $Bz_2Si{:}O{:}O<\begin{smallmatrix}H\\H\end{smallmatrix}$, no other explanation has suggested itself. That examples of isomerism among derivatives of silicon containing oxygen, without parallel in the case of corresponding carbon derivatives, will be no uncommon occurrence, seems to be foreshadowed by these results, as well as by Dilthey's observations on the probable existence of isomeric termolecular diphenylsilicones (*loc. cit.*).

There are several points in connexion with these hydrols which have not yet been very satisfactorily settled, for example, the fact that neither compound gives pure ketone when it is heated at 100°; it is hoped that this and other matters of interest will be cleared up later, the publication of our results in their present state being necessitated by unavoidable circumstances.

EXPERIMENTAL.

Benzylethylsilicone, BzEtSiO.

The benzylethylsilicon dichloride employed in this investigation was prepared by the method recently described (Kipping, Trans., 1907, **91**, 720). As preliminary experiments showed that the silicone obtained from it would not be easily purified by distillation, the dichloride itself was very carefully fractionated, and the portion boiling constantly at 169° (100 mm.) collected separately. Analyses of these preparations were made by decomposing a weighed quantity with alcoholic silver nitrate solution in the manner previously described (*loc. cit.*, p. 217):

Preparation A : 0·6376 gave 0·8188 AgCl. Cl = 31·7.
Preparation B : 0·4736 „ 0·6134 AgCl. Cl = 32·0.
$C_9H_{12}Cl_2Si$ requires Cl = 32·3 per cent.

The fractions of benzylethylsilicon dichloride boiling just above 169° contained only a little dibenzyl as impurity; in later experiments, the silicone was prepared from some of these, and the dibenzyl separated by distillation in steam; the product thus obtained was scarcely less pure than that prepared from the fractions boiling at 169°.

Benzylethylsilicon dichloride is rapidly decomposed by water, and a considerable rise in temperature occurs. The oily product was extracted with pure ether, the solution washed with water, dried, and evaporated. The residue was a colourless, viscous oil; it was left for some time in a vacuum over sulphuric acid, and then analysed with the following results:

0·3294 gave 0·1218 SiO_2. Si = 17·3.
0·1959 „ 0·4668 CO_2 and 0·1291 H_2O. C = 65·0; H = 7·3.
$C_9H_{12}OSi$ requires Si = 17·3; C = 65·7; H = 7·4 per cent.

Benzylethylsilicone is insoluble in water, but miscible with ether, light petroleum, and other organic solvents.

When the silicone is distilled under reduced pressure (22 mm.), 70—80 per cent. of the whole passes over between 305° and 315°, but there then remains a dark-coloured residue which does not distil at 360°; on redistilling the portion collected from 305—315°, 70 to 80 per cent. again passes over between the same temperatures as before, and again there remains a dark-coloured residue of much higher boiling point. Water seems to be formed in small quantity, and on opening the flask there is generally a very strong odour of benzaldehyde. The distillate is nearly colourless, and on analysis proves to be the unchanged silicone, whereas the residue, which is very viscous, gives a higher percentage of silicon.

The following results were obtained with the distilled benzylethylsilicone:

0·3508 gave 0·1292 SiO_2. Si = 17·2.
0·1582 „ 0·3815 CO_2 and 0·1060 H_2O. C = 65·8; H = 7·4.
$C_9H_{12}OSi$ requires Si = 17·3; C = 65·7; H = 7·4 per cent.

Since the boiling point of benzylethylsilicone is so much higher than that of the corresponding carbon compound, benzyl ethyl ketone (b. p. 226°/760 mm.), it seemed very probable that the molecule of the former was highly associated and not represented by the simple formula BzEtSiO. This view was confirmed by molecular weight determinations made by the ebullioscopic method. Both the undistilled and the distilled silicone were used, but the two preparations gave similar results :

Undistilled Benzylethylsilicone.

Solvent.	Weight of substance in grams.	Weight of solvent in grams.	Percentage con-centration.	Δ.	Mol. wt.
Acetic acid	0·374	15·4	2·3	0·150°	429
	0·761	15·4	4·7	0·290	441
	1·104	15·4	6·7	0·368	493
Acetone	0·248	10·0	2·4	0·093	445
	0·526	10·0	5·0	0·193	455
	0·896	10 0	8·2	0·323	463

Distilled Benzylethylsilicone.

Solvent.	Weight of substance in grams.	Weight of solvent in grams.	Percentage con-centration.	Δ.	Mol. wt.
Acetic acid	0·311	10·5	2·9	0·180°	416
	0·673	10·5	6·0	0·356	454
	1·016	10·5	8·8	0·510	480
	1·356	10·5	11·4	0·666	490

As the formula BzEtSiO requires a molecular weight of 164·5, it seems clear that the liquid silicone is a compound of complex molecules $(BzEtSiO)_3$.

Diphenylsilicone, according to the observations of Dilthey (*Ber.*, 1905, **38**, 4134), exists in two modifications, namely, in a gelatinous form, melting at 105—110°, and in a crystalline form, melting at 188°; the molecular weights of these two substances were determined by him in benzene solution, and, whereas in the case of the latter the results indicated a termolecular association $(Ph_2SiO)_3$, in the former they were apparently not conclusive, although pointing to a similar complexity. We have not observed the formation of any solid form of benzylethylsilicone; the substance has been kept for several months in a desiccator over sulphuric acid, it has been kept for a long time at 0°, and also treated with a drop of acetic anhydride, a reagent which converts gelatinous diphenylsilicone into the crystalline form, but without any obvious result.

The very viscid, brown residue which remains on distilling benzylethylsilicone under reduced pressure does not seem to be simply another form of the silicone, but a condensation product; as it could not be purified, we merely determined the silicon in the crude substance and carried out some molecular weight determinations with the following results :

0·3049 gave 0·1200 SiO_2. Si = 18·4.

Solvent.	Weight of substance in grams.	Weight of solvent in grams.	Percentage con-centration.	Δ.	Mol. wt.
Acetic acid	0·397	10·4	3·7	0·155°	622
	0·770	10·4	6·9	0·245	764
	1·037	10·4	9·1	0·355	711
Acetone	0·423	10·0	4·1	0·103	686

Behaviour of Benzylethylsilicone towards Ketonic Reagents.

Phenylhydrazine seems to have no action on benzylethylsilicone; equal quantities of the base and the silicone were warmed together at 100° for two hours, and the two substances were also heated together at 100° for two hours in glacial acetic acid solution. In each case, after shaking the ethereal solution of the silicon compound with very dilute hydrochloric acid and evaporating, the resulting oil was free from nitrogen.

Hydroxylamine also seems to have no action on the silicone in alcoholic potash solution.

Attempts were made to prepare derivatives of the silicone by treating benzylethylsilicon dichloride with bases such as phenylhydrazine and *p*-toluidine, but a definite compound was not isolated in either case; even if the expected interaction occurred, the product was decomposed by the acid or water employed in removing the excess of the base, and was free from nitrogen.

Benzylethylsilicone is not reduced by sodium and alcohol. A sample which had been thus treated with a large excess of the theoretical quantity of sodium was as viscous as before, and gave no effervescence with sodium. It was next dissolved in ether, the solution poured on to a concentrated solution of potassium hydroxide, and, finally, sodium added in small quantities at a time, using a large excess. The product showed no signs of having been reduced, and on analysis gave results which showed it to be the unchanged silicone.

0·1981 gave 0·4693 CO_2 and 0·1370 H_2O. C = 64·7; H = 7·7.

$C_9H_{12}OSi$ requires C = 65·7; H = 7·4 per cent.

$C_9H_{14}OSi$ „ C = 64·8; H = 8·5 „ „

Although the above experiments show that benzylethylsilicone is relatively a very inert substance, a vigorous reaction takes place when it is mixed with an ethereal solution of magnesium ethyl bromide; unfortunately, we have not yet been able to investigate the product.

Sulphobenzylethylsilicone, $EtSiO{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$.

When the silicone is heated with ordinary sulphuric acid (2 vols.) at 100° for about two hours, it passes into solution and no precipitate is produced on subsequently diluting with water. The aqueous solution, having been neutralised with barium carbonate, filtered, and evaporated, gives the *barium* salt of a sulphonic derivative of silicon as a colourless, but not visibly crystalline, solid residue. This substance is sparingly soluble in cold, but readily so in hot, water, except that there is always a slight residue which does not dissolve; it is insoluble in alcohol. The crude product was separated into two parts by fractional crystallisation from water, and each portion was analysed by heating a weighed quantity with distilled sulphuric acid.

Less Soluble Portion:

0·2570 gave 0·1432 residue $(SiO_2 + BaSO_4) = 55·7$.

More Soluble Portion:

0·2894 gave 0·1580 residue $(SiO_2 + BaSO_4) = 54·6$.
$(EtSiO{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3)_2Ba$ requires $(SiO_2 + BaSO_4) = 56·7$ per cent.

A little of the salt was decomposed with the exact amount of sulphuric acid, the solution filtered, and the filtrate evaporated. The sulphonic acid so obtained was a colourless, viscous liquid, and gave a residue of silica on ignition.

These experiments having indicated that the sulphonation product was a monosulphonic derivative of benzylethylsilicone, a portion of the barium salt was treated with excess of ammonium carbonate solution; after filtering, evaporating, and heating until all the ammonium carbonate was expelled, there remained a colourless, very hygroscopic *ammonium* salt, which was also freely soluble in methyl and ethyl alcohols. A solution of this salt was treated with solutions of silver nitrate, lead acetate, calcium chloride, and a number of other metallic salts, but no precipitate was obtained; solutions of *p*-toluidine, quinine, cinchonine, and cinchonidine hydrochlorides gave colourless solid precipitates, but all attempts to obtain these compounds in a well-crystallised state were unsuccessful.

The *quinine* salt, after drying at 100°, melted at 180—200°; although it did not seem to be at all hygroscopic, mere contact with a little methyl alcohol, ethyl alcohol, acetone, ethyl acetate, or mixtures of these solvents converted it into an oil. Having failed to obtain a crystallised derivative, we returned to the barium salt; the original preparation was fractionally precipitated from its aqueous solution by the addition of alcohol; in this way, we finally obtained from it a relatively very small quantity of a salt almost insoluble in warm water, but soluble in presence of the other portion of the original preparation. This sparingly soluble salt was boiled with excess of ammonium carbonate solution, and the filtrate was heated until all ammonium carbonate was expelled. The residue was then dissolved in dilute alcohol, and the solution allowed to evaporate spontaneously; flat, colourless prisms were then deposited, but only a small quantity of these well-defined crystals was obtained. As this salt was not analysed, its composition cannot be stated with certainty, but, as it contained silicon and gave ammonia when heated with potash, it is very probable that it was a pure ammonium salt of benzylethylsiliconesulphonic acid.

The readily soluble portion of the barium salt was dried at 100° until constant and then analysed:

0·3074 gave 0·1726 residue $(SiO_2 + BaSO_4) = 56·1$.

$C_{18}H_{22}O_8S_2BaSi_2$ requires $(SiO_2 + BaSO_4) = 56·7$ per cent.

This salt was also converted into the ammonium salt, which, however, did not crystallise well; it was a colourless, hygroscopic substance, only moderately soluble in alcohol.

From the above experiments, we conclude that in the sulphonation of the silicone two isomeric acids (probably the ortho- and para-compounds) are formed.

By-products from the Preparation of Benzylethylsilicon Dichloride.

The product of the interaction of ethylsilicon trichloride and magnesium benzyl chloride is a complex mixture; after separating the benzylethylsilicon dichloride, which is contained in the fraction collected below 200° under a pressure of 100 mm., there remains a considerable quantity of a rather viscid, brown, fuming liquid. Having accumulated a considerable quantity of this by-product from a number of different experiments, we submitted the whole to systematic fractional distillation under reduced pressure (100 mm.) in a long-necked flask provided with a rod and disk column. The fractions of lowest boiling point thus obtained solidified on cooling, and consisted principally of dibenzyl, which accumulated in the portions distilling from about 190° to 244°; those portions distilling between 220° and 244° also contained a little stilbene.

A considerable quantity of a fuming liquid, boiling almost constantly at 244—248° (100 mm.), was the next fraction collected; this product is described below. Above 248°, the thermometer rose continuously and fairly rapidly to about 300°, and this portion of the distillate yielded no definite product. From 300° to 360°, there passed over a rather thick, yellow liquid containing tribenzylsilicyl chloride, the isolation of which is also described later (p. 450).

a-Dibenzylsilicol, $Bz_2Si(OH)_2$.

The fraction boiling at 244—248° (100 mm.) seemed to be a fairly pure compound, and, from its boiling point, was thought to consist of dibenzylethylsilicyl chloride, $Bz_2EtSiCl$. A sample was analysed by decomposing it with aqueous ammonia, evaporating until neutral, and then titrating with silver nitrate solution (1 c.c. = 0·00178 Cl):

0·1940 required 19·5 c.c. Cl = 17·9.
0·2005 „ 20·1 c.c. Cl = 17·8.

$C_{16}H_{19}ClSi$ requires Cl = 13·0; $C_{14}H_{14}Cl_2Si$ requires Cl = 25·2 per cent.

These results showed that the liquid contained a large proportion of some substance far richer in chlorine than dibenzylethylsilicyl chloride, and the only compound which fulfilled this condition and the presence of which seemed possible was dibenzylsilicon dichloride; as this substance would probably have a boiling point approximately the same as that of dibenzylethylsilicyl chloride, and, if present, could hardly be separated by further fractional distillation, the whole of the chloride, was decomposed with water and the resulting oil extracted with ether. On evaporation, there was obtained a colourless solid substance, which, however, contained some oil; this latter was removed by washing with light petroleum, but attempts to purify the solid substance further by recrystallisation from benzene, a mixture of light petroleum and ether, or light petroleum and benzene, were only partly successful; each time the substance was dissolved, decomposition seemed to take place, and the quantity of solid rapidly diminished. At last, however, by the spontaneous evaporation of an alcoholic solution, a small quantity of substance was obtained in long, asbestos-like prisms, melting at 101°. This compound was readily soluble in ether, benzene, or alcohol, but almost insoluble in light petroleum and insoluble in water. When kept at a temperature slightly below its melting point for a short time, it liquefied; on cooling a little, crystals reappeared, but the substance did not solidify entirely until the temperature fell to 50°. Its behaviour resembled that of a solid crystallising from its saturated solution, but with this modification, that as long as the temperature was maintained above 50° the solid changed into the liquid phase at an appreciable rate. After having been heated at about 160°, the substance remained entirely liquid at 0°.

An analysis of the crystals, melting at 101°, which had been dried over sulphuric acid gave the following results:

0·1974 gave 0·4978 CO_2 and 0·1200 H_2O. C = 68·8; H = 6·7.

$C_{14}H_{16}O_2Si$ requires C = 68·7; H = 6·5 per cent.

From its behaviour during the combustion, the boiling point of this substance, or rather that of the liquid into which it changes, must be very high, probably above 400°.

The method of formation of this compound, its behaviour on solution and when heated, and the analytical results, led us to conclude that it was dibenzylsilicol, $Bz_2Si(OH)_2$; such a compound when heated would doubtless lose water, giving the silicone, and the latter would then probably pass into a substance of very high boiling point, represented by the molecular formula $(Bz_2SiO)_3$, analogous to the polymeric modification of benzylethylsilicone (p. 444). The further investigation of this compound is described later (p. 452).

Dibenzylethylsilicol, $Bz_2EtSi\cdot OH$.

The oily portion of the product obtained by treating the chloride with water and separated from the dibenzylsilicol by filtration (together with the oil obtained from the decomposition of the hydrol during recrystallisation) was fractionally distilled under a pressure of 25 mm. The thermometer rose immediately to about 205°, and between this temperature and 215° about 40 per cent. of the whole liquid distilled; the thermometer then rose again very rapidly to about 360°, at which temperature heating was discontinued; the undistilled residue formed about 50 per cent. of the whole; it was not further examined, but it seems very probable that it consisted principally of the polymerised dibenzylsilicone, $(Bz_2SiO)_3$, formed by the decomposition of the hydrol already described. The fraction collected between 205° and 215° was redistilled under the same pressure (25 mm.) as before, and the portion boiling at 207—212° collected separately. When kept for some time in a freezing mixture, this liquid deposited a small quantity of a crystalline substance which was ultimately found to be a mixture of stilbene and a compound containing silicon and melting at 54°. The stilbene was identified by its melting point, 120—121°, and by converting it into its well-crystallised dibromide (*a*), which melted at 233°; its presence cannot be accounted for. The crystalline silicon compound (m. p. 54°) is described later. After separating the crystalline deposit, the oil was analysed:

0·7610 gave 0·1627 SiO_2. Si = 10·0.
0·3624 „ 0·0775 SiO_2. Si = 10·1.
0·2517 „ 0·6967 CO_2 and 0·1800 H_2O. C = 75·5; H = 7·9.
$C_{16}H_{20}OSi$ requires Si = 10·9; C = 75·0; H = 7·8 per cent.

The results of the combustion agree satisfactorily with those required for dibenzylethylsilicol, and in spite of the discordance between the theoretical and experimental values for the percentage of silicon we are of the opinion that this preparation was a moderately pure sample of the silicol; this conclusion is rendered extremely probable by the facts described below.

Dibenzylethylsilicyl Oxide, $(Bz_2EtSi)_2O$.

The preparation of dibenzylethylsilicol just described was left over sulphuric acid in a vacuum previous to making another analysis; it was then observed that the oil had deposited crystals, which melted at 54°, like those previously separated. An analysis of the remaining oil also showed that the percentage of carbon was now much higher than before, an indication that some decomposition, probably the elimination of water, had occurred:

0·1842 gave 0·5204 CO_2 and 0·1336 H_2O. C = 77·0; H = 8·0.

After some time, practically the whole of the oil became changed into these crystals, which were purified by recrystallisation from alcohol. They then melted sharply at 55°, and on analysis gave results agreeing with those required for the oxide of dibenzylethylsilicol, $(Bz_2EtSi)_2O$, thus confirming the constitution of the oil from which they were derived:

0·1976 gave 0·5617 CO_2 and 0·1399 H_2O. C = 77·5; H = 7·9.
0·1717 ,, 0·4870 CO_2 ,, 0·1192 H_2O. C = 77·4; H = 7·7.
$C_{32}H_{38}OSi_2$ requires C = 77·6; H = 7·7 per cent.

A molecular weight determination was also made by the ebullioscopic method in acetone solution with the following result:

0·387 in 10·2 acetone gave Δt – 0·135. Mol. wt. = 452.

As the calculated molecular weight for the silicol is 257 and for the oxide 495, there does not seem to be much doubt as to the nature of the compound. *Dibenzylethylsilicyl oxide* crystallises in glistening plates, is moderately soluble in warm alcohol, and readily so in ether. A little of the substance was boiled with potassium hydroxide for a short time to try to reconvert it into the silicol, but its melting point was found to be unchanged by this treatment.

Tribenzylsilicyl Chloride, Bz_3SiCl.

The fraction of the original by-product (p. 447) collected from 300° to 360° (100 mm.) slowly deposited long needles. These were quickly separated by filtration, and spread on porous earthenware in a desiccator. After recrystallising twice from light petroleum, they were obtained in slender, colourless prisms, moderately soluble in hot light petroleum, readily so in ether, but very sparingly so in cold light petroleum. The compound melted at 141°, and, although it did not fume perceptibly in the air, it was readily decomposed by water;

a chlorine estimation was made by the volumetric method (1 c.c. $AgNO_3 = 0{\cdot}00178$ Cl):

0·2735 required 16·2 c.c. $AgNO_3$; Cl = 10·5.
$C_{21}H_{21}ClSi$ requires Cl = 10·5 per cent.

Tribenzylsilicol, $SiBz_3{\cdot}OH$.

The chloride just described was warmed with moist alcohol, and the product recrystallised from light petroleum; it separated in colourless needles, melting sharply at 104°, and was readily soluble in ether, but only moderately so in light petroleum:

0·1024 gave 0·2974 CO_2 and 0·0665 H_2O. C = 79·2; H = 7·2.
$C_{21}H_{22}OSi$ requires C = 79·1; H = 7·0 per cent.

Tribenzylsilicol has recently been described by Dilthey (*loc. cit.*), who gives its melting point as 106°.

Dibenzylsilicon Dichloride, Bz_2SiCl_2.

In order to confirm some of the results of the experiments described above, a quantity of dibenzylsilicon dichloride was prepared from silicon tetrachloride. To 1 molecule of the latter, $2\frac{2}{5}$ molecules of magnesium benzyl chloride were slowly added with vigorous cooling and stirring. The whole was allowed to stand overnight, the ether then evaporated, and the residue heated at 100° for three hours. It was then extracted with ether in the apparatus already described (Kipping, Trans., 1907, **91**, 216). After distilling off the ether, the residual oil was fractionally distilled under a pressure of 100 mm., using a long-necked flask with rod and disk column. A small quantity passed over below 200°, and then a large fraction between 200° and 240° which became solid on cooling, and consisted of dibenzyl; from about 240°, the thermometer rose very slowly, and a large proportion of the whole distilled below 250°; above 250°, the thermometer rose more rapidly to 360°, but there still remained a considerable residue of viscid, brown oil which did not distil at 360°. The fraction 241—250° was distilled twice more, and, finally, the portion boiling between 241—245° was collected separately; after having been kept in a closed vessel for some time, the colourless oil solidified completely. It was then recrystallised from light petroleum, from which it was obtained in magnificent, colourless prisms; these were moderately soluble in light petroleum, and melted at 50—52°; they fumed somewhat in the air, and, when previously reduced to a powder, were readily decomposed by water; otherwise a thin film of the insoluble decomposition product was formed at the surface and prevented further action of the water. An analysis of these crystals was carried out volumetrically (1 c.c. $AgNO_3$ = 0·00178 Cl):

0·1385 required 19·9 c.c. $AgNO_3$; Cl = 25·5.
0·2407 „ 34·4 c.c. $AgNO_3$; Cl = 25·4.
$C_{14}H_{14}Cl_2Si$ requires Cl = 25·2 per cent.

This pure dichloride was decomposed by dissolving it in ether and shaking the solution with water until free from hydrochloric acid. The substance obtained melted at 101°, softening slightly at 98°, and was identical with the α-dibenzylsilicol previously described (p. 448), as proved by the following analyses:

0·4200 gave 0·1058 SiO_2. Si = 11·8.
0·1960 „ 0·4953 CO_2 and 0·1206 H_2O. C = 68·9; H = 6·8.
0·1172 „ 0·2963 CO_2 „ 0·0711 H_2O. C = 68·9; H = 6·8.
$C_{14}H_{16}O_2Si$ requires Si = 11·6; C = 68·7; H = 6·5 per cent.

Molecular weight determinations were carried out by the cryoscopic method with the following results:

0·184 in 18·3 acetic acid gave Δt – 0·155°. Mol. wt. = 251.
0·347 „ 18·3 „ „ „ „ 0·295°. „ „ = 249.
0·625 „ 18·0 „ „ „ „ 0·570°. „ „ = 236.
0·838 „ 19·2 „ „ „ „ 0·730°. „ „ = 232.
$C_{14}H_{16}O_2Si$ requires Mol. wt. = 244·6.

Dibenzylsilicone, Bz_2SiO.

The substance just referred to as α-dibenzylsilicol, and prepared by decomposing pure dibenzylsilicon dichloride with water, was certainly not identical with the substance (m. p. 76°) obtained by Dilthey (*loc. cit.*), and to which he assigned the formula $Bz_2Si(OH)_2$.

In order to obtain some further confirmation of the nature of our compound, we heated a small quantity of it at 110° for six hours with the object of converting it into the corresponding ketone. The oily product was then dissolved in a mixture of alcohol and ether, from which it separated in colourless prisms, and after recrystallisation from light petroleum these melted at 98°. The compound was readily soluble in ether, and moderately so in alcohol or light petroleum. A preparation was analysed with the following results:

0·1707 gave 0·4653 CO_2 and 0·1002 H_2O. C = 74·3; H = 6·5.
0·1549 „ 0·4220 CO_2 „ 0·0892 H_2O. C = 74·3; H = 6·4.
$C_{14}H_{14}OSi$ requires C = 74·2; H = 6·2 per cent.

It seemed clear from these observations that the supposed hydrol had been converted in a normal manner into the corresponding ketone (the termolecular form, p. 439), and that the melting point given by

Dilthey was incorrect; further experiments, however, led to the discovery of another hydrol, probably identical with the compound obtained by Dilthey.

β-Dibenzylsilicol, $Bz_2Si(OH)_2$.

On attempting to prepare a further quantity of ketone in the same manner as before, namely, by heating the *α*-hydrol (m. p. 101°) at 110° for several hours, an altogether different result was obtained; a solution of the oily residue in light petroleum deposited, not the ketone, but a crystalline substance, melting at 65—70°. This product was repeatedly recrystallised, the best results being obtained by dissolving it in a very little ether and adding a considerable quantity of light petroleum; it was then deposited, in the course of about half an hour, in beautiful, transparent prisms, which melted at 75°, softening at 70°. Repeated recrystallisation failed to render the melting point more precise, although to all appearance the preparation was quite pure. Unless the recrystallisation was carried out rapidly, and at a low temperature, some slight decomposition occurred, and the mother liquor deposited a small quantity of an oil. Analyses of samples dried in the air gave results which agreed with those required for the hydrol, $Bz_2Si(OH)_2$, although the percentage of carbon was always a trifle too high:

I. 0·1760 gave 0·4457 CO_2 and 0·1076 H_2O. C = 69·1; H = 6·8.
II. 0·1554 „ 0·3946 CO_2 „ 0·0934 H_2O. C = 69·2; H = 6·7.
III. 0·1711 „ 0·4334 CO_2 „ 0·1026 H_2O. C = 69·1; H = 6·7.
$C_{14}H_{16}O_2Si$ requires C = 68·7; H = 6·5 per cent.

Sample III was prepared by crystallising sample II three times from ether and light petroleum.

Molecular weight determinations made by the cryoscopic method gave the following results:

0·514 in 16·5 benzene gave Δ*t* – 0·290°. Mol. wt. = 540.
0·703 „ 17·4 „ „ „ 0·360°. „ „ = 560.
0·287 „ 22·4 acetic acid „ „ 0·190°. „ „ = 260.
0·844 „ 17·8 „ „ „ „ 0·700°. „ „ = 263.
$C_{14}H_{16}O_2Si$ requires Mol. wt. = 244.

Most of the substance was recovered apparently unchanged when the benzene and acetic acid solutions were allowed to evaporate, but a trace of the oily decomposition product (see above) had doubtless been formed.

As this compound melting at 75° was thus found to be isomeric with the *α*-hydrol melting at 101°, it was natural to suppose that the two substances were merely different crystalline forms of one and the same substance. This view, however, had to be abandoned; samples of the two different preparations were crystallised under exactly the same conditions from a mixture of ether and light petroleum, but each retained its own distinctive properties. It was also found later that the two compounds could be deposited side by side from one and the same solution.

In one experiment, a fresh sample of dibenzylsilicon dichloride, boiling at 241—245° (100 mm.), prepared as before (which, although apparently pure, could not be crystallised), was decomposed with water and the product extracted with ether. When the solution was left to evaporate spontaneously, instead of becoming almost solid from the separation of pure α-hydrol, it deposited the β-hydrol in fine, large crystals, which, after recrystallisation from ether and light petroleum, melted at 75°, softening at about 70°. On the addition of light petroleum to the oily mother liquor, the whole became a thick paste of what seemed to be a mixture of the two forms of the hydrol. Attempts to separate these by recrystallisation were not very successful, as their solubilities were practically the same in all solvents, but at last a small quantity of the α-hydrol was isolated in a moderately pure condition.

Conversion of the β-Hydrol into Dibenzylsilicone.

The conversion of the β-dibenzylsilicol into the corresponding silicone seemed at first an extremely simple operation. A small quantity of the pure compound was gently heated in a test tube over a bunsen flame until the escape of water vapour ceased, and the resulting oil was dissolved in light petroleum; on cooling, the solution deposited crystals of pure dibenzylsilicone (m. p. 97—98°). On repeating the experiment with the same sample of β-hydrol under as nearly as possible the same conditions, instead of the silicone, the original β-hydrol was finally deposited from the light petroleum solution; several further similar experiments also gave this result, in spite of the fact that the water produced during the heating of the hydrol was clearly visible on the sides of the test tube. Many other attempts were made to transform the β-hydrol into the silicone; for example, the compound was heated at 150° for five minutes in an open dish, but, on crystallising the residue from light petroleum, practically the whole of the hydrol was ultimately recovered, although mixed with some oily product. Only in a few cases did we obtain any crystalline silicone.

Formation of the β-Hydrol from Dibenzylsilicone.

These perplexing results were explained to some extent by the discovery of the extraordinary fact that the oily product formed by the dehydration of the β-hydrol combines readily with water, the β-hydrol being regenerated. When the pure β-hydrol is kept in a vacuum over sulphuric acid at the ordinary temperature, it is converted in the course of about twenty-four hours into a very viscous, colourless oil; when this oil is exposed again to moist air, it is slowly reconverted into the β-hydrol, and if rubbed with a little water the change takes place in a few minutes.

Further Experiments on the Conversion of the Hydrols into the Silicone.

Quantitative experiments on the transformation of the β-hydrol into silicone at the ordinary temperature were not attempted, as the oily silicone formed at the surface prevents the decomposition of the crystals underneath; such experiments, however, carried out at 100° showed that after about seventy hours' heating the weight became practically constant, the loss being 6·6 instead of 7·4 per cent. as required by theory. Although the transformation of the hydrol into the silicone is a very simple change theoretically, and the last experiment seemed to show that it occurred almost quantitatively, some of our observations are not easily explained; thus the oil obtained by heating the β-hydrol at 100° did not give either crystalline silicone or β-hydrol when it was dissolved in ether and light petroleum or rubbed with water, differing in this respect from the oily silicone obtained in a vacuum at the ordinary temperature. Further, we have not been able to elucidate the nature of the oil which is produced in small quantities when the pure hydrol is recrystallised from various solvents, except that in some cases we have obtained from it the crystalline silicone by heating at 100°. It seems tolerably certain that, whereas the dehydration of the β-hydrol at the ordinary temperature leads simply to the formation of a unimolecular oily silicone which readily recombines with water, the effects of heating are more complex and lead to the formation of the termolecular crystalline silicone as well as that of other compounds.

The α-hydrol differs notably from the β-isomeride in stability; when kept over sulphuric acid in a vacuum, it does not change appreciably in appearance, although it becomes somewhat sticky in the course of a few days. A quantitative experiment on the decomposition of the α-hydrol (m. p. 101°) gave unsatisfactory results. The pure compound was heated at 110° in an open vessel; the weight decreased slowly and fairly regularly until after about twenty-five hours the theoretical loss (7·4 per cent.) for the formation of silicone had taken place; after about twenty-five hours' further heating, the loss amounted to about 11 per cent., but even then the weight of the oily product showed no sign of becoming constant. In no case have we been able to regenerate the α-hydrol from the product of its dehydration.

Action of Acetyl Chloride and Acetic Anhydride on the Hydrols.

Having failed to ascertain the precise conditions necessary for the conversion of the hydrols into the crystalline silicone by the action of heat alone, we studied their behaviour towards acetyl chloride and acetic anhydride.

Both compounds dissolved readily in acetyl chloride, but, on allowing their solutions to evaporate, they were finally both recovered unchanged; in the case of the β-hydrol, it is quite possible that the oily unimolecular silicone had really been formed, but that it absorbed water again on exposure to the air. When, however, the hydrols were separately heated in test tubes over a free flame until the ebullition caused by the escape of water ceased, and the residue then warmed with a little acetic anhydride, they were converted, apparently almost quantitatively, into crystalline dibenzylsilicone. These experiments with acetic anhydride were repeated several times with fairly constant results.

The molecular weight of the crystalline dibenzylsilicone, obtained in this way from the β-hydrol, was determined, and the results showed that the compound had the termolecular formula $(Bz_2SiO)_3$; the ebullioscopic method was used, with benzene as solvent:

0·585 in 14·0 benzene gave Δt − 0·18°. Mol. wt. = 620.
0·92 ,, 14·0 ,, ,, ,, 0·30°. ,, = 587.
0·96 ,, 13·0 ,, ,, ,, 0·29°. ,, = 674.
0·845 ,, 14.3 ,, ,, ,, 0·21°. ,, = 737.

$(Bz_2SiO)_3$ requires Mol. wt. = 678.

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