# CLXXXVII.—*Organic Derivatives of Silicon. Part XXXVI. Highly Complex Condensation Products of Diphenyl- and Di*-p-*tolyl-silicanediol. Fission of the* Si–Ph *Link.*

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THREE open-chain and two closed-chain condensation products of diphenylsilicanediol have been described (Kipping, J., 1912, **101**, 2108; Kipping and Robison, J., 1914, **105**, 484); all these compounds crystallise well and their molecular weights have been determined cryoscopically.

By the action of hot alkalis on diphenylsilicanediol two much more complex substances have been obtained : the one, $(SiPh_2O)_A$, is practically insoluble in all ordinary solvents, whereas the other, $(SiPh_2O)_B$, is appreciably but only sparingly soluble in boiling benzene, and both seem to be amorphous. The compound $(SiPh_2O)_B$ gives in camphor $M = 3900$, corresponding with $B = 19$ or $20$; judging from its insolubility, the other product is even more complex.

The known condensation products of di-*p*-tolylsilicanediol are the open- and the closed-chain compounds formed from three molecules of the diol, and a substance (m. p. 186—187°) which is probably $[Si(C_7H_7)_2O]_4$ (Pink and Kipping, J., 1923, **123**, 2833). Two new substances, which seem to correspond respectively with the two diphenyl analogues described above, have been obtained. The product insoluble in benzene, $[Si(C_7H_7)_2O]_A$, gives in camphor $M = 3450$, but the results are not trustworthy owing to the slight solubility of the substance; the more soluble compound gives $M = 4150$, a value which is probably approximately correct.

If the actual molecular weights are of the indicated order of magnitude, as seems very probable, the open-chain compound $HO{\cdot}SiR_2(O{\cdot}SiR_2)_n{\cdot}O{\cdot}SiR_2{\cdot}OH$ would have practically the same composition as the closed-chain compound; so that although the results of silicon determinations agree very closely in all cases with those required for $SiR_2O$, one or more of the products may have the open-chain structure; it is also possible that one or more of the products may be a mixture.

In any case the compounds are not without theoretical interest : if they consist of closed chains of some 20 $-SiR_2O-$ groups, their existence would emphasise the conclusions which may be drawn from the results of Ruzicka's work on the cyclic ketones; if, on the other hand, they are open-chain compounds, it would seem that the silicanediols, like methylene glycol, may give rise to a very extended series of condensation products.

In the course of the above experiments and in many previous investigations in which diphenylsilicanediol, its condensation products, and other compounds containing the $-SiPh_2-$ group were heated with alkalis, the formation of benzene was never observed. Recently, however, it has been found that certain dibenzylsilicon derivatives are decomposed by sodium hydroxide solution with fission of the carbon–silicon binding and it seemed possible that diphenyl analogues might behave in a similar manner.

Experiments then showed that diphenylsilicanediol is slowly decomposed by 20% potassium hydroxide solution at 95—100°, with evolution of benzene, and it is therefore almost certain that a portion of the diol is decomposed in this way during the formation of the above-described condensation products. The results of the silicon determinations seem, however, to prove conclusively that the compounds in question contain two aryl groups for every silicon atom; if even one phenyl group were displaced by hydroxyl in a compound $(SiPh_2O)_{20}$, the percentage of silicon would be raised to 14·5.

## EXPERIMENTAL.

The two diphenylsilicanediol derivatives are precipitated, together with smaller quantities of the more soluble condensation products, when diphenylsilicon dichloride (10 g.), dissolved in a little acetone, is gradually added to a 10% aqueous solution of potassium hydroxide (200 c.c.) and the clear liquid is then evaporated on the water-bath to about 75 c.c.; the solution is then practically free from diol. The insoluble products are not formed if the original solution is merely heated at 100° on a reflux apparatus, as, apparently, a certain concentration of alkali must be reached. For instance, with a 2½% solution of alkali under the conditions stated, an oily product, probably dianhydrotrisdiphenylsilicanediol, is obtained, whereas with a 5% solution, crystalline products (trianhydrotris- and tetra-anhydrotetrakis-diphenylsilicanediol) are formed and these are only very slowly converted into the more complex substances by further evaporation at 100°. The insoluble products are also formed when a 5% solution of potassium hydroxide is added rapidly to diphenylsilicon dichloride.

The precipitate is repeatedly washed with water and then extracted in a Soxhlet apparatus with acetone during 6—8 hours to remove the lower condensation products. The extraction is then continued with boiling benzene during 2—3 days and the residue (A) is finally extracted with boiling water. The benzene extracts when cooled deposit a gelatinous product (B), which is separated by filtration: the mother-liquors contain traces of the crystalline condensation products.

The insoluble residue (A) is colourless and does not melt at 360°, but decomposes at much higher temperatures; it seems to be amorphous (Found: Si, 14·2, 14·2, 14·1. $SiPh_2O$ requires Si, 14·3%). It is practically insoluble in all the ordinary solvents and is only very sparingly soluble in melted camphor, but it dissolves freely in boiling aniline; from this solvent it separates again when the solution is cooled as an amorphous powder even after the solution has been boiled during 2 hours, but in presence of a little water it undergoes hydrolysis and in the course of 4 hours is completely decomposed, giving trianhydrotrisdiphenylsilicanediol and other soluble condensation products, together apparently with a little of the substance (B). Its behaviour towards phenol is much the same as towards aniline. It is not appreciably changed when it is boiled with a 5% solution of potassium hydroxide in aqueous acetone during several hours, but when heated with very concentrated alkali at 150° it is slowly decomposed, giving benzene and a silicate.

The product (B), which forms only a very small proportion of the original mixture, separates from benzene or chloroform in a gelatinous form, but soon becomes brittle as the solvent evaporates, giving a colourless, apparently amorphous powder (Found: Si, 14·2, 14·2. $SiPh_2O$ requires Si, 14·3%. $M$ in camphor 3900, 3710). It is practically insoluble in acetone, alcohol, ether, etc., and is only sparingly soluble in benzene and chloroform. It begins to sinter at about 300° and gradually liquefies at a considerably higher temperature. It is very slowly hydrolysed by an acetone solution of potassium hydroxide, giving a salt of diphenylsilicanediol.

Di-*p*-tolylsilicon dichloride, dissolved in a 10% aqueous solution of potassium hydroxide (25 parts), gives first an oily and finally a solid product when the solution is evaporated on the water-bath, and practically the whole of the diol undergoes condensation. The solid is washed with water and then extracted with boiling acetone, which dissolves a little of the compound, m. p. 186—187° (*loc. cit.*), and some oily matter. When the residue is extracted with boiling benzene, about one half of it, $[Si(C_7H_7)_2O]_B$, dissolves, leaving the product $[Si(C_7H_7)_2O]_A$, which is again extracted with water.

The insoluble substance, $[Si(C_7H_7)_2O]_A$, is a colourless, amorphous powder, not appreciably soluble in the common solvents [Found: Si, 12·5. $Si(C_7H_7)_2O$ requires Si, 12·5%. $M = 3450$]. It shows signs of sintering at 270°, but it is not completely melted at 360°. When it is boiled with a 5% aqueous solution of potassium hydroxide it is not appreciably changed.

The benzene extract (see above), when evaporated or mixed with petroleum, gives a gelatinous solid similar to the corresponding diphenyl compound [Found: Si, 12·4. $Si(C_7H_7)_2O$ requires Si, 12·5%. $M = 4150$]. It sinters at about 260°, but does not melt completely at 360°; it is readily soluble in camphor, benzene, and chloroform, but is practically insoluble in acetone; it is only very slowly hydrolysed by a 5% solution of potassium hydroxide in aqueous acetone.

The fission of the Si–Ph binding was proved by heating diphenylsilicanediol with a 20% aqueous solution of potassium hydroxide on the water-bath under reduced pressure, and collecting the benzene in wash-bottles containing nitric and sulphuric acids. After 3 hours' heating, the quantity of benzene produced, estimated as the dinitro-derivative, was about 1% of the diol used, and the alkaline solution gave at once a heavy precipitate with acids. On prolonged heating, however, the filtered alkaline solution gave no immediate precipitate when acidified, and the flocculent deposit which gradually formed was insoluble in organic solvents and seemed to consist principally of silica.

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