TABLE II.

32. *Organic Derivatives of Silicon. Part LI (and last). Bis-dihydroxytetraphenylethane Orthosilicate.*

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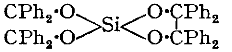
When ethyl bromide is added to an ethereal solution of silicon tetrachloride in the presence of magnesium, the precipitated magnesium salt is mixed with insoluble products which give hydrogen with alkalis and therefore contain linked silicon atoms (Martin and Kipping, J., 1909, **95**, 302).

(I.)

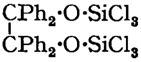


In the course of attempts to ascertain how such compounds are formed, the interaction of silicon tetrachloride, magnesium, and ether in the presence of benzophenone has been studied. One of the products is a *spiro*-orthosilicic *ester* of *s*-dihydroxytetraphenylethane (I). From the results as a whole it is inferred that the linkage of silicon atoms, under the conditions stated above, is brought about by magnesium monohalide.

COMPOUNDS containing linked silicon atoms are slowly produced from silicon tetrachloride, magnesium, and ether in the absence of a preformed Grignard reagent, but silicon tetrachloride alone, or its solution in diphenyl or dibenzyl ether, has no action on magnesium. Since ether reacts with silicon tetrachloride to a very slight extent (Kipping and Murray, J., 1927, 2736), the ethyl chloride which is probably formed may give, in the presence of magnesium, a Grignard reagent; but even so the production of linked silicon atoms would not be explained, since Grignard reagents and silicon tetrachloride, in the absence of magnesium, do not give any such result.

It seemed possible, therefore, that in the presence of ether, silicon tetrachloride might give with magnesium a compound, $SiCl_3{\cdot}MgCl$, which would react with the tetrachloride to form the hexachloride, and by further reactions of a similar kind, compounds containing long chains of silicon atoms might be produced.

In the hope that such a magnesium silicon halide, if formed, would combine with benzophenone and give a recognisable compound, $SiCl_3{\cdot}CPh_2{\cdot}OMgCl$, silicon tetrachloride, magnesium, ether and benzophenone were warmed together. Reactions set in very slowly, although much more quickly than in the absence of benzophenone, as shown by the separation of a colourless powder, and after the lapse of some days or weeks, the sparingly soluble crystalline siliconic *ester* (I) could be isolated from the solution. Most of the tetrachloride, however, was converted into substances, very soluble in ether, which were readily hydrolysed on the addition of water, giving variable mixtures of α- and β-benzpinacolins, dihydroxytetraphenylethane and silica, together in some cases with small proportions of tetraphenylethylene.

The main, readily soluble product, therefore, is probably  $\begin{matrix}CPh_2{\cdot}O{\cdot}SiCl_3\\ |\\ CPh_2{\cdot}O{\cdot}SiCl_3\end{matrix}$ (II), from which, under the stated conditions, all the above-named compounds, and others described later (p. 84) are formed.

The ether-insoluble product consisted mainly of some compound of benzophenone and magnesium chloride which did not deliquesce in moist air; sometimes it contained a small proportion of the chloromagnesium derivative of dihydroxytetraphenylethane. In no case was there any indication of the production of a compound $SiCl_3{\cdot}CPh_2{\cdot}OMgCl$.

A clue to the explanation of these results seems to be afforded by the fact that, in ethereal solution, benzophenone, with iodine and magnesium, is quantitatively converted into $OMgI{\cdot}CPh_2{\cdot}CPh_2{\cdot}OMgI$ in consequence of the change $MgI_2 + Mg \rightleftharpoons 2MgI$ (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 236). Since in the benzophenone reaction mixture, traces of magnesium dichloride may be formed as the result of known changes, magnesium monochloride and then the compounds $-CPh_2{\cdot}OMgCl$ and $OMgCl{\cdot}CPh_2{\cdot}CPh_2{\cdot}OMgCl$ may be successively produced. The interaction of either of these products with silicon tetrachloride might then give the crystalline siliconic ester or the very soluble hexachloro-derivative (II), and further quantities of magnesium dichloride would become available for a continuance of the earlier stages.

The fact that attempts to synthesise the crystalline siliconic ester by treating the iodomagnesium derivative of dihydroxytetraphenylethane with silicon tetrachloride were unsuccessful (p. 84) is a possible objection to this view, but it may be the product $-CPh_2{\cdot}OMgCl$, and not the derivative of the glycol, which reacts with the tetrachloride, giving $Si(O{\cdot}CPh_2-)_4$, from which the saturated ester is subsequently formed. Moreover, ethylmagnesium iodide cannot be successfully used instead of the bromide for the preparation of ethylsilicon trichloride.

Since the production of compounds containing linked silicon atoms from silicon tetrachloride, magnesium and ether occurs in the absence but not to any appreciable extent in the presence of benzophenone, it seems probable that this is because the ketone immediately combines with magnesium monochloride, and that the linking which occurs in the absence of benzophenone is due to reactions of the type $2SiCl_4 + 2MgCl = Si_2Cl_6 + 2MgCl_2$; $2Si_2Cl_6 + 2MgCl = Si_4Cl_{10} + 2MgCl_2$; etc. Although experiments showed that, in the absence of ether, magnesium chloride, silicon tetrachloride, and magnesium do not undergo any appreciable change, the explanation just suggested may still be upheld; magnesium and iodine, or even bromine, do not react in the presence of benzene, but do so when ether is added, and this may also be the case with magnesium chloride and magnesium.

In the presence of ether, especially when an alkyl or aryl halide is also added, the final products of the interaction of silicon tetrachloride and magnesium would be mixtures of hydrocarbon substitution products of complex silicon halides, the variable extent of substitution depending on the experimental conditions; such a view accounts for the little that is known of the compounds in question.

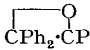
EXPERIMENTAL.

Magnesium, kept under silicon tetrachloride during several years, remained perfectly bright; even at 200° during 8 hours there was no sign of any change. Similarly, when silicon tetrachloride, magnesium, and diphenyl ether or dibenzyl ether were heated together at 200° during 8 hours, no appreciable reaction occurred. Ethylsilicon trichloride, phenylsilicon trichloride, or silicon tetrachloride to which a small proportion of ethyl alcohol had been added to form some ethoxysilicon trichloride, was also without action on the metal. Furthermore the mixed anhydrous magnesium salts, obtained by treating ethylmagnesium bromide with silicon tetrachloride and then evaporating at 200°, did not bring about any reaction between magnesium and the tetrachloride.

An ethereal solution of silicon tetrachloride attacked magnesium very slowly at the ordinary temperature; when the mixture was boiled during 8—10 hours, the metal became coated with a greyish film and compounds containing linked silicon atoms were formed. A very small proportion of these compounds was obtained in the ethereal solution, but the filtered liquid contained only traces of magnesium. Owing to the very small yield, even after prolonged boiling, the nature of the soluble material could not be established. Samples, which, no doubt, had undergone partial hydrolysis by atmospheric moisture, contained 30—33% of silicon and 20—22% of chlorine, and had a hydrogen value (Kipping and Sands, J., 1921, **119**, 848) of about 47—51. The matter which was insoluble in ether did not dissolve in benzene or acetone; it contained magnesium chloride and gave hydrogen readily with alkali, but its investigation was fruitless.

Magnesium, in the thimble of a Soxhlet apparatus, was submitted to the action of a boiling ethereal solution of silicon tetrachloride during 15 hours in the hope that the compounds containing linked silicon atoms might be sufficiently soluble to be obtained free from magnesium chloride. The solution was then distilled; the insignificant volatile product, which passed over above 100°, gave no appreciable hydrogen evolution with alkali, but the residue, non-volatile at 350°, which was mostly insoluble in ether and almost free from magnesium, gave hydrogen quite readily. Most of the active material, however, remained in the thimble, mixed with magnesium chloride.

Very small quantities of phenylmagnesium bromide were added to an ethereal solution of silicon tetrachloride in the presence of magnesium, but without attaining the desired object of obtaining soluble compounds containing linked silicon atoms. Furthermore, when the products formed by heating an ethereal solution of the tetrachloride with magnesium during 30 hours were heated with a large proportion of phenylmagnesium bromide, in the hope of converting the insoluble into soluble hydrogen-giving compounds, the products containing linked silicon atoms were decomposed.

Reactions with Benzophenone.—Magnesium (2 atoms), silicon tetrachloride (1 mol.; 14 g.), and benzophenone (2 mols.) did not react in the absence of ether, but a solution of the two compounds in ether (60—70 c.c.) acted on the metal, which became visibly coated with a white solid in the course of about 2 hours, the solution becoming yellowish-green and faintly turbid; these effects appeared much more quickly than any changes which occur in the absence of benzophenone. When the heating had been continued during 40—60 hours, or when from the outset the mixture was kept during some weeks at the ordinary temperature, a loose light powder was deposited on the coated metal, which latter, unless stirred from time to time, formed a hard greyish cake. The filtered greenish fuming solution, concentrated by the distillation of most of the ether, and then cooled, gave a crystalline deposit, which consisted of practically pure *bisdihydroxytetraphenylethane orthosilicate* (I) or of a mixture of this compound with variable proportions of β-benzpinacolin, $CPh_3{\cdot}COPh$, and possibly some α-benzpinacolin,  $\overset{\text{———O}}{CPh_2{\cdot}CPh_2}$. The result depends apparently on the extent to which moisture has had access to the solution during the whole prolonged experiment. If great care has been taken to exclude it, the ethereal solution seems to be free from pinacolins; in such cases, after the separation of the crystalline ester, further concentration, followed by the addition of a small proportion of light petroleum, does not produce any precipitation, but the solution, if then evaporated sufficiently, may give a deposit of benzophenone. From the filtrate more ketone, silica, and large yields of β-benzpinacolin, mixed usually with the α-compound, and possibly with dihydroxytetraphenylethane and tetraphenylethylene, may, however, be isolated after hydrolysis with water; the proportion of some of these products depends, no doubt, on the conditions during and after hydrolysis.

With the proportions of the reagents as given above the silicon tetrachloride alone was completely used up, apparently, after a sufficiently long period; some magnesium, protected by its dense coating, remained unchanged, and a considerable proportion of the benzophenone was removed from solution in the form of an insoluble compound with magnesium chloride (p. 84). The given proportions were at first chosen rather at random; they were modified in later experiments, but the results were not noticeably different.

s-Dihydroxytetraphenylethane was identified by its m. p. (decomp.), its conversion into diphenylcarbinol (m. p. 68°) and benzophenone by alcoholic potash, and into α- and β-benzpinacolins by alcoholic hydrochloric acid. It is very readily recognised by a mere inspection of the characteristic flat, rectangular, efflorescent prisms deposited from its acetone solution; it also crystallises from carbon tetrachloride in characteristic, very slender, efflorescent needles.

α-Benzpinacolin was identified by its m. p., analysis (Found: C, 89·8; H, 6·0%), stability towards alcoholic potash, and its conversion into β-benzpinacolin by acetyl chloride.

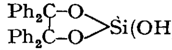
β-Benzpinacolin was identified by its m. p., analysis (Found: C, 89·7; H, 5·9. Calc.: C, 89·3; H, 5·95%) and by its conversion into triphenylmethane (m. p. 92°) and benzoic acid by boiling alcoholic potash.

Tetraphenylethylene was identified by its m. p., analysis (Found: C, 93·5; H, 6·1. Calc.: C, 94·0; H, 6·0%), and its oxidation to benzophenone by chromium trioxide.

The very misleading statement in Beilstein, for which Wertheimer (*Monatsh.*, 1905, **26**, 1533) seems to be responsible, that α- and β-benzpinacolins become dark yellow or light brown when they are melted and colourless when they are cooled again, is certainly incorrect; no change in colour occurs, and, as may be inferred from Wertheimer's reference to a greenish-yellow by-product, his observations were doubtless due to the presence of some impurity in his preparations.

Bisdihydroxytetraphenylethane Orthosilicate (I).—This substance crystallises from ethyl acetate in transparent rectangular plates, some of which are almost square, others six- or eight-sided; these crystals effloresce on exposure to air [Found: C, 82·3; H, 5·4; Si, 3·7, 3·7; *M*, in camphor, 700 (approx). $C_{52}H_{40}O_4Si$ requires C, 82·5; H, 5·3; Si, 3·7%; *M*, 756]. The *ester* is very readily soluble in hot chloroform and in cold benzene; the crystals from the former contain solvent and resemble those from ethyl acetate. It is also readily soluble in boiling acetone, separating from the cold solution in ill-defined pointed prisms, which become opaque in the air; the compound is fairly soluble in boiling carbon tetrachloride, but practically insoluble in boiling alcohol or light petroleum. When it is quickly heated, it melts at about 240—245° without visible charring, solidifying again when cooled to a product of much lower and indefinite melting point. It is, in fact, decomposed at the m. p., and when it is kept at about 240°, it gives a distillate of pure benzophenone and a residue which becomes more and more siliceous and less and less fusible as the heating is continued; in the course of 15—20 minutes decomposition seems to be complete, but the residue still contains some organic matter. As the residue gives no appreciable gas evolution with alkali, it would seem that oxidation occurs.

Hydrolysis of the Crystalline Ester.—When the ester was boiled with alcoholic hydrochloric acid, it was very slowly dissolved and hydrolysed with the separation of siliceous matter; the solution then contained a mixture, the nature of which depends no doubt on the conditions of the hydrolysis. In one experiment, after prolonged boiling, the main product which was isolated was identified as α-benzpinacolin; in addition a very small proportion of benzophenone was obtained (in the form of its phenylhydrazone). According to the literature, hydrochloric acid converts dihydroxytetraphenylethane into β-benzpinacolin; the authors found that alcoholic hydrochloric acid gave a mixture of the α- and the β-compound, in which the former predominated.

In order to obtain dihydroxytetraphenylethane, and thus establish conclusively the structure of the orthosilicic ester, attempts were made to hydrolyse the compound in the absence of acid or alkali. When it was boiled with 95—98% alcohol alone, it was very slowly hydrolysed and passed into solution; 0·2 g. dissolved in *ca.* 5 hours (15 c.c. of alcohol) but 1 g. (in 40—50 c.c.) required 35 hours for complete solution, the time no doubt depending on the state of division of the crystals. Even after such prolonged boiling there was no appreciable separation of silica, and the result seemed to be the formation of a complex mixture which might contain $HO{\cdot}CPh_2{\cdot}CPh_2{\cdot}O{\cdot}Si(OH)_3$ and  $\begin{matrix}Ph_2C{-}O\\ |\\ Ph_2C{-}O\end{matrix}\!\!>\!Si(OH)_2$, and their numerous condensation products, in addition to the glycol. The solution, concentrated to a very small volume, gradually deposited ill-defined crusts, which dissolved again, slowly but completely, in a few c.c. of alcohol. In some cases a solution of this mixed product in acetone gave the highly characteristic crystals of dihydroxytetraphenylethane, which were firmly embedded in a layer of glue-like matter. The presence of benzophenone was also proved, but its mode of formation was not determined. When the mixtures thus obtained were dissolved in acetone, and the solution warmed with a little concentrated aqueous ammonia on the water-bath, there was a precipitation of gelatinous silica; the filtered solution, on evaporation at the ordinary temperature, gave a homogeneous deposit of the highly characteristic, efflorescent crystals of the above-named glycol. When the ester was warmed directly with acetone and ammonia, it gradually dissolved, with the separation of silica, and the filtered solution, on evaporation to dryness in the air, gave a deposit of pure dihydroxytetraphenylethane. There is no doubt, therefore, about the structure of the ester.

Attempts to prepare the crystalline orthosilicic ester by the interaction of silicon tetrachloride (1 mol.) and the glycol (2 mols.) were unsuccessful; the containing vessel became coated with a thin film of what seemed to be silica, and the soluble product consisted of approximately equal quantities of α-benzpinacolin and unchanged glycol, together with a small proportion of β-benzpinacolin. The product of the interaction of an ethereal benzene solution of benzophenone (4 mols.) with iodine (2 mols.) and magnesium (4 atoms) was treated with silicon tetrachloride (1 mol.); there was no sign of the formation of the crystalline ester, and a considerable proportion of dihydroxytetraphenylethane was finally isolated from the mixture.

The iodomagnesium derivative of the glycol (2 mols.), prepared exactly as described by Gomberg and Bachmann (*loc. cit.*), was also treated with silicon tetrachloride (1 mol.), but again a large proportion of the glycol was obtained from the product, which seemed to be free from the crystalline ester. Some of the glycol was transformed into tetraphenylethylene. Glue-like, very soluble products containing silicon were obtained, as well as some siliceous matter which effervesced freely with acetone and alkali; the formation of the latter was probably due to the presence of magnesium monoiodide.

Other Derivatives of Silicic Acid.—When the fuming ethereal mother-liquors from the crystalline ester were distilled on a water-bath, there remained a thick greenish oil having a garlic-like odour. The gradual addition of light petroleum to this oil produced precipitates of greenish, fuming, sticky solids, and from the final mother-liquor very small deposits of tetraphenylethylene were sometimes obtained. This very well-defined compound has also been isolated in larger quantities in other ways (above and p. 83 and below); although practically insoluble in light petroleum, it is found here because it dissolves in the presence of benzophenone.

The fuming solids, on exposure to the air, gave friable products which were then only partially soluble in the common solvents; these contained β-benzpinacolin and insoluble substances, rich in silicon, which were slowly hydrolysed by boiling alcoholic hydrochloric acid, giving more β-benzpinacolin and silica.

When the fuming ethereal solution, after concentration, was treated with an excess of dilute aqueous ammonia, a yellowish solid was precipitated; this product, extracted with acetone, gave a residue of silica, and a solution, usually rich in benzophenone, from which dihydroxytetraphenylethane could be readily isolated.

In order to hydrolyse the $-CPh_2{\cdot}O{\cdot}SiCl_3$ groups suspected to be present without causing the fission of the –O–Si links, the fuming ethereal solution was treated with a warm light petroleum solution of *p*-toluidine. The yellowish precipitate which was immediately produced was separated, treated with water to dissolve the *p*-toluidine hydrochloride and to decompose the toluidine derivatives of the silicic esters, and then with alcohol to free it from *p*-toluidine. The residue was, at first, completely soluble in cold ether, and by the fractional precipitation of the solution with alcohol, there was obtained a colourless powder; a part of this product became insoluble in ether when it was kept for some time or heated at 100°, and the soluble portion gave more insoluble matter when the treatment was repeated. Two apparently amorphous, colourless powders were thus obtained; (1) soluble in ether and acetone, and (2) practically insoluble in ether and only partly soluble in acetone. After having been heated at about 100°, (1) gave 39·3% of silica on ignition with sulphuric acid, and (2) gave 39·7%. Further quantities of similar products were precipitated by alcohol from the original filtrate from the *p*-toluidine hydrochloride; much benzophenone, a small proportion of β-benzpinacolin, and rather less tetraphenylethylene were also isolated from one or other portions of this toluidine reaction product, the investigation of which was very much hampered by the continuous production of dark coloured matter.

Compounds, even richer in silicon, but similar to those just described, were obtained by distilling the original decanted fuming solution until the ether and any silicon tetrachloride had been removed, then adding ether containing a small proportion of aqueous alcohol, and repeatedly washing the solution with water to remove all hydrochloric acid. Little if any insoluble matter was formed, and, on evaporation, there resulted a pasty mass, which was extracted with cold alcohol to remove benzophenone. The residue, still miscible with a small proportion of ether, gave a flocculent precipitate when larger volumes of that solvent were added; the precipitate was practically insoluble in ether, but was very soluble in acetone, from which, on evaporation, it was obtained as a pale yellow, brittle resin; when kept for a long time, it became insoluble in acetone or benzene. It gave 45% of silica on ignition with sulphuric acid.

On the addition of alcohol to the concentrated ethereal filtrate from this product, a colourless powder was precipitated; the solution then contained β-benzpinacolin and dihydroxytetraphenylethane. The powder, purified by reprecipitation, gave 38·5% of silica on ignition with sulphuric acid; * it became partly insoluble in ether after it had been heated for a short time at 110—120°, and the insoluble portion gave 48·5% of silica; a part of this, which was practically insoluble in acetone, gave 49·6% of silica.

These different preparations, rich in silica, including those obtained in the experiments with toluidine, do not melt; when they are treated with acetone and ammonia, they all give silica and dihydroxytetraphenylethane, and on prolonged boiling with alcoholic hydrochloric acid they afford silica and β-benzpinacolin. They all show the general behaviour of "siliconic acids," that is to say, of the products of hydrolysis of compounds containing the $-SiCl_3$ group (Meads and Kipping, J., 1914, **105**, 689; 1915, **107**, 459); their silicon content, however, is much higher than that of a compound of the empirical formula $HO_2SiO{\cdot}CPh_2{\cdot}CPh_2{\cdot}O{\cdot}SiO_2H$, which would give only 24·6% of silica; and since they do not contain linked silicon atoms, they probably consist mainly of condensation products of the glycol orthosilicate with orthosilicic acid, formed during the hydrolysis of the chloro-esters. Compounds of the empirical formula $-CPh_2{\cdot}O{\cdot}SiO{\cdot}O{\cdot}SiO_2H$ and $-CPh_2{\cdot}O{\cdot}SiO{\cdot}O{\cdot}SiO{\cdot}O{\cdot}SiO_2H$, for example, would give about 49 and 50% of silica respectively.

The light colourless powder from the original reaction vessel could be decanted with the ethereal solution, from the dense caked mass below it, separated by filtration and washed with ether. It did not deliquesce on exposure to the air and had a strongly alkaline reaction to moist litmus paper; when treated with a little water, it gave a faintly acid solution and a pasty mass containing benzophenone, magnesium compounds and traces of siliceous matter. Most of it dissolved in cold (undried) ethyl acetate and the filtered solution gave at once a strongly alkaline deposit of magnesium salt; the decanted liquid gave practically pure benzophenone. A sample of the solid from the complete evaporation at the ordinary temperature of the ethyl acetate solution gave, when exhaustively extracted with light petroleum, 0·45 g. of insoluble matter and 0·6 g. of benzophenone; another experiment gave 1·0 and 1·4 g. respectively. After exposure to the air for some time, the powder was no longer soluble in ethyl acetate, which then extracted from it benzophenone only. The powder did not contain any chloromagnesium derivative of dihydroxytetraphenylethane and did not give any appreciable gas evolution with acetone and alkali; it seemed, therefore, to consist of a compound of magnesium halide and benzophenone, possibly $MgCl{\cdot}CPh_2{\cdot}OMgCl$ (compare Gomberg and Bachmann, *loc. cit.*).

The dense caked mass from which the powder had been decanted did not deliquesce on exposure to the air; it contained a variable proportion of magnesium, gave with water a strongly alkaline, pasty mass containing benzophenone, and in some cases dihydroxytetraphenylethane could be isolated from it, but so far as could be ascertained it did not contain any $Ph_2C(OMgCl){\cdot}SiCl_3$, and it did not give any appreciable gas evolution with acetone and alkali.

Envoi.—As this is my last paper, may I express here my sincere thanks to the Chemical Society for having published so much of my work over so very long a period.—F. S. K.

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* The silica was very hygroscopic, and absorbed 22% of its weight of moisture on exposure to the air.