XLVII.—*Organic Derivatives of Silicon. Triphenylsilicol and Alkyloxysilicon Chlorides.*

By F. Stanley Kipping, Ph.D., D.Sc., F.R.S., and Lorenzo L. Lloyd.

Although this research was commenced nearly three years ago (compare Proc., 1899, **15**, 174), its principal object, namely, the preparation of an optically active silicon compound, has not been attained; under these circumstances, it might perhaps have been better to postpone publication until more progress had been made, but as one of us has been obliged to abandon the investigation, we wish to place on record a brief account of the results obtained up to the present.

Our first attempts were directed towards the preparation of derivatives of silicon tetraphenyl, a compound which is obtained with comparative ease by the method described by Polis (*Ber.*, 1885, **18**, 1542). This substance, however, proved to be unsuitable for our purpose; although it can be nitrated without much difficulty (Polis, *loc. cit.*), the product did not crystallise, and appeared to be a mixture which was not easily resolvable into its components. Treatment of the silicon tetraphenyl with halogens under various conditions also failed to yield satisfactory results, and numerous attempts to prepare sulphonic derivatives were equally unsuccessful, the principal products of the action of ordinary sulphonating agents being silica and benzenesulphonic acid or diphenylsulphone; phosphorus pentachloride, hydrogen chloride, and other reagents were tried, but we found it impossible to isolate any suitable product even when reaction occurred. Attention was next directed to the bye-products which are formed in the preparation of silicon tetraphenyl, and from these we were able to isolate small quantities of triphenylsilicol, $(C_6H_5)_3Si{\cdot}OH$, a compound which is formed from the triphenylsilicium chloride contained in the mother liquors from the silicon tetraphenyl. Triphenylsilicol was first obtained by Polis (*loc. cit.*) by strongly heating silicon tetraphenyl with phosphorus pentachloride and treating the

product with dilute ammonia; as it crystallises well and already contains two different groups and is more readily soluble than the tetraphenyl derivative, we tried to obtain it in larger quantities by altering the proportions of silicon tetrachloride, chlorobenzene, and sodium used in the preparation of silicon tetraphenyl; the results, however, were not very satisfactory, and as we found that the silicol was of little use for our main object, we did not persevere with these experiments.

In attempting to nitrate triphenylsilicol we found that this alcohol is converted into an ether with extraordinary readiness; this change takes place when the alcohol is heated with a 10 per cent. solution of hydrogen chloride in acetic acid. The product, di-triphenylsilicyl ether, $[(C_6H_5)_3Si]_2O$, is a very stable compound although it is slowly hydrolysed by boiling alcoholic potash.

Various substances other than triphenylsilicol were isolated from the bye-products obtained in the preparation of silicon tetraphenyl, but they were of little interest, except perhaps one compound which seems to be diphenylsilicium ketone, $(C_6H_5)_2SiO$; this substance bears little, if any, resemblance to benzophenone, and is possibly a polymeride of high molecular weight.

Fatty alkyl derivatives of silicon have hitherto been obtained only by heating silicon tetrachloride with the zinc alkyl compounds, a method which is inconvenient and troublesome. We therefore studied the application of Fittig's reaction to the preparation of such compounds, and found that silicon tetraethyl could be prepared by this method with comparative facility, as a very fair yield is obtained when a mixture of silicon tetrachloride and ethyl bromide or iodide is digested with sodium in ethereal solution in presence of traces of ethyl acetate.

Little has been done with this alkyl compound up to the present, as other experiments which offered a possibility of more immediate success have been in progress.

Starting from silicon tetrachloride, we tried to prepare asymmetric derivatives directly by the successive displacement of the chlorine atoms by three different groups; these attempts were successful, and products, such as phenoxymethoxyethoxysilicon chloride, were obtained by the following series of interactions:

$$\begin{aligned} SiCl_4 + PhOH &= SiCl_3\cdot OPh + HCl \\ SiCl_3(OPh) + MeOH &= SiCl_2(OMe)\cdot OPh + HCl \\ SiCl_2(OPh)(OMe) + EtOH &= SiCl(OPh)(OMe)\cdot OEt \end{aligned}$$

Although the final product of these reactions contains the desired asymmetric silicon atom, we were unable to resolve it into enantiomorphously related components, owing to its sensitiveness towards moisture; when treated with the dry silver salt of an optically active

acid in dry ethereal solution, interaction took place, apparently in the normal manner, but the product decomposed even when kept over sulphuric acid. Other experiments in which aniline and toluidine were employed in the place of phenol or the alcohols in the above reaction gave products which were equally unstable. We next tried treating the phenoxymethoxyethoxysilicon chloride with menthol, in the hope that by displacement of the chlorine by the menthyl radicle we might obtain a crystalline product which would be directly resolvable into the menthyl derivatives of two enantiomorphously related silicon compounds by fractional crystallisation; unfortunately, this product did not solidify even when cooled to $-40°$, and it was also readily decomposed by water.

For the estimation of the silicon in some of the compounds which were examined, we employed a new and very simple method, namely, treatment with concentrated sulphuric acid followed by ignition; this method gives very satisfactory results except in the case of volatile, stable compounds such as silicon tetraethyl.

Experimental.

Preparation of Silicon Tetraphenyl.—The preparation of silicon tetrachloride by Gattermann's method, and the conversion of this substance into silicon tetraphenyl under the conditions laid down by Polis (*loc. cit.*), need not be described. We may state, however, that when ether is used as solvent in the latter preparation the reaction takes place spontaneously, and usually so vigorously that the contents of the flask require cooling in ice water, so that the addition of ethyl acetate is unnecessary; the interaction proceeds gently during about 8 hours and is completed by heating on the water-bath for about 1 hour. The product is then separated by filtration, washed with alcohol and water consecutively, and dried. The yield is almost theoretical.

The nitration of silicon tetraphenyl has been carried out by Polis (*loc. cit.*), and he describes the product as being amorphous; following his directions, we also obtained a substance from which nothing crystalline, except traces of unchanged silicon tetraphenyl, could be isolated. On fractional precipitation from acetic acid by addition of water, we obtained it in colourless, flocculent, apparently amorphous particles, but successive fractions had not the same melting point, and on analysis gave nitrogen varying from about 12 to 15 per cent. Silicon tetranitrotetraphenyl requires 10·9 per cent. The crude preparation did not seem to afford a base when treated with any of the ordinary agents which reduce nitro-compounds, and when boiled with

caustic alkalis it seemed to be completely decomposed into silica and nitrobenzene.

Nitric acid alone seems to have no action on silicon tetraphenyl at the ordinary temperature, and in presence of varying quantities of sulphuric acid either nitration is very incomplete or a product similar to that just described is obtained.

A solution of hydrogen chloride in acetic acid slowly decomposes silicon tetraphenyl at 130—140°, giving benzene and traces of triphenylsilicol; at higher temperatures, silica and benzene seem to be the only products.

When silicon tetraphenyl is cautiously added to 30 per cent. anhydrosulphuric acid, it slowly dissolves, giving a brownish, very viscous solution, which, when poured on to powdered ice, does not deposit silica; after neutralising with barium carbonate, a solution is obtained which on evaporation deposits barium benzenesulphonate.

Silicon tetraphenyl dissolves readily in well-cooled chlorosulphonic acid with evolution of hydrogen chloride; the product consists principally of a mixture of benzenesulphonic chloride and diphenylsulphone.

When silicon tetraphenyl is dissolved in acetic anhydride and treated with anhydrosulphuric acid, it gives benzenesulphonic acid and soluble silicic acid; in order to prevent such a decomposition, we tried to sulphonate with sulphur trioxide, the silicon tetraphenyl being mixed with dry sand in order to moderate the action. Under these conditions, we recovered a considerable quantity of silicon tetraphenyl, but the portion soluble in water again gave an acid which appeared to consist entirely of benzenesulphonic acid.

Phosphorus pentachloride has no action on melted silicon tetraphenyl at 250°, and very little action when the two substances are heated together in a sealed tube at 250—260° for 12 hours, only small quantities of triphenylsilicyl chloride being formed; as most of the tubes burst at this temperature, the experiments were discontinued.

Triphenylsilicol and its Derivatives.

The ethereal filtrate from the mixture of silicon tetraphenyl, sodium chloride, and unchanged sodium, obtained in the preparation of the first-named compound, usually contains small quantities of chlorobenzene, diphenyl, and various other substances which are formed as bye-products; on evaporating the ether, there remains an oily liquid from which the chlorobenzene can be separated by distillation under atmospheric pressure. The thick, oily residue, when distilled under 10 mm. pressure, gives first a fraction passing over

between 120° and 160° which consists largely of diphenyl, and then very little distils until the temperature rises to about 210°; between this temperature and about 260°, a thick, almost colourless liquid passes over, and a non-volatile, pasty mass containing a large quantity of combined silicon remains in the distilling flask.

The fraction collected between 210° and 260° seems to consist of a mixture of triphenylsilicyl chloride, triphenylsilicol, and silicon tetraphenyl, and when, owing to absorption of moisture during manipulation of the bye-products, most of the first-named compound has been converted into the second, the latter separates in crystals often in such quantities that the distillate becomes nearly solid. This crystalline product may be separated by filtration, washed with a mixture of light petroleum and ether, and then repeatedly crystallised, to free it from silicon tetraphenyl. As an alternative method, the whole of the fraction collected between 210° and 260° may be boiled for a short time with a little alcoholic soda to decompose the chloride, in which case the silicon tetraphenyl is separated by careful precipitation with water, and the crude triphenylsilicol, deposited slowly from the alcoholic filtrate, is purified by crystallisation from a mixture of ether and light petroleum. The compound obtained in this way melts at 148° and has been briefly described by Polis (*loc. cit.*), who prepared it by heating silicon tetraphenyl with phosphorus pentachloride and treating the resulting chloride with dilute ammonia; as the melting point of triphenylsilicol according to him is 139—141°, the nature of our preparation seemed doubtful until established by the following analyses:

0·1618 gave 0·4665 CO_2 and 0·0859 H_2O. C = 78·6; H = 5·9.
0·21 ,, 0·0451 SiO_2. Si = 10·02.
$C_{18}H_{16}OSi$ requires C = 78·2; H = 5·9; Si = 10·14 per cent.

Triphenylsilicol crystallises from a mixture of ether and light petroleum in well-defined, massive, transparent prisms and is readily soluble in acetic acid, benzene, chloroform, carbon disulphide, ether, or alcohol.

As only very small quantities of triphenylsilicol were obtained from the bye-products resulting from the preparation of silicon tetraphenyl in the manner described by Polis, many experiments were made in order to ascertain whether the yield of this alcohol could be increased by altering the proportions of silicon tetrachloride, chlorobenzene, and sodium; it was found, however, that the reaction expressed by the equation,

$$SiCl_4 + 3C_6H_5Cl + 6Na = Si(C_6H_5)_3Cl + 6NaCl,$$

cannot be brought about except to a very limited extent; working with these relative quantities, 15 grams of silicon tetrachloride give

only about 2 grams of the crude product boiling at 210—260° under 10 mm. pressure, and even when smaller proportions of chlorobenzene and sodium are used, silicon tetraphenyl is always the principal product, a correspondingly larger amount of silicon tetrachloride remaining unchanged.

Triphenylsilicol is insoluble in 30 per cent. anhydrosulphuric acid, but dissolves in ice-cold chlorosulphonic acid with evolution of hydrogen chloride. The only products which were isolated from this solution were diphenylsulphone and benzenesulphonic acid, the latter in the form of its sodium salt. When triphenylsilicol is dissolved in chloroform and then treated with chlorosulphonic acid, the results are similar, diphenylsulphone and benzenesulphonic chloride being obtained together with some unaltered triphenylsilicol.

Triphenylsilicyl acetate, $(C_6H_5)_3SiO\cdot CO\cdot CH_3$.—Acetic anhydride, even in the presence of zinc chloride, has no action on triphenylsilicol, but the acetyl derivative can be obtained by boiling the alcohol with acetyl chloride until it has passed into solution. One gram of silicol requires boiling about 2 hours with 10 c.c. of acetyl chloride before the change is complete. The liquid is then evaporated, and the residue crystallised from light petroleum (b. p. 60—80°), in which it is readily soluble on boiling, and from which it is deposited in long, thick prisms melting at 91·5°.

0·1623 gave 0·450 CO_2 and 0·0832 H_2O. C = 75·62; H = 5·75.
0·3210 „ 0·0607 SiO_2. Si = 8·82.
$C_{20}H_{18}O_2Si$ requires C = 75·78; H = 5·66; Si = 8·8 per cent.

Triphenylsilicyl acetate is readily soluble in benzene, chloroform, carbon disulphide, alcohol, or acetic acid, but only sparingly so in cold light petroleum; it decomposes slowly on exposure to air and is rapidly hydrolysed by boiling dilute alcohol.

Triphenylsilicyl chloride, $Si(C_6H_5)_3Cl$.—This compound is sometimes obtained directly from the mixture of bye-products already referred to (p. 452) after distilling off the chlorobenzene under atmospheric and then fractionating the residue under 10 mm. pressure; the fraction collected between 220° and 240° sometimes solidified to a mass of colourless crystals, which were readily soluble in light petroleum, and on evaporating this solution, triphenylsilicyl chloride was deposited in an almost pure condition. It may also be obtained, but with great difficulty, by heating silicon tetraphenyl with phosphorus pentachloride as described by Polis.

0·3006 gave 0·1447 AgCl. Cl = 11·93.
$C_{18}H_{15}ClSi$ requires Cl = 12·06 per cent.

Triphenylsilicyl chloride crystallises from light petroleum in trans-

parent prisms, melts at 88—89°, and dissolves freely in most ordinary solvents; it does not fume in the air, but is readily hydrolysed by dilute alcoholic potash.

Di-triphenylsilicyl Ether, $[Si(C_6H_5)_3]_2O$.

Triphenylsilicol dissolves in concentrated nitric acid, but only very slowly, giving a solution from which a nitro-compound is not precipitated on the addition of water. It dissolves more readily in a mixture of nitric acid (1 part) and sulphuric acid (3 parts), and on pouring the solution into water an oil which contains nitrogen and is soluble in potash is precipitated; when, however, it is heated with nitric acid in acetic acid solution, it is converted into triphenylsilicyl ether. This compound is easily prepared by dissolving triphenylsilicol in acetic acid, heating to boiling, and then adding concentrated nitric acid drop by drop until the mixture becomes turbid; the solution, which gradually acquires a deep red colour, soon deposits crystals which are filtered off and recrystallised from acetic acid.

0·2 gave 0·5947 CO_2 and 0·1002 H_2O. C = 81·1; H = 5·56.
0·2 „ 0·5920 CO_2 „ 0·0978 H_2O. C = 80·78; H = 5·43.
0·2 „ 0·450 SiO_2. Si = 10·5.
$C_{36}H_{30}OSi_2$ requires C = 80·9; H = 5·6; Si = 10·48 per cent.

Di-triphenylsilicyl ether crystallises in small, shining plates melting at 222°. It is practically insoluble in methyl alcohol and cold acetic acid, and only very sparingly soluble in ethyl alcohol, but it dissolves more readily in acetic anhydride and is very soluble in ether or benzene. It gradually goes into solution in boiling alcoholic potash, passing into triphenylsilicol.

Triphenylsilicyl ether can also be obtained by boiling a solution of triphenylsilicol in a mixture of acetic acid and 10 per cent. hydrochloric acid for about 8 hours, and then crystallising the deposit from acetic acid; also by boiling for a considerable time a solution of triphenylsilicol in methyl alcohol and concentrated hydrochloric acid.

Diphenyl Silicone, $SiPh_2O$.

The residue left after distilling off the triphenylsilicol (p. 453) from the crude bye-product, does not volatilise at 280° under 10 mm. pressure, and solidifies on cooling to a pale yellow, vitreous mass; when boiled with alcoholic potash, traces of triphenylsilicol and some silicon compound which is precipitated again on the addition of hydrochloric acid are dissolved, and there remains a considerable quantity of a neutral substance. The latter, after having been dried, is extracted with carbon disulphide, and light petroleum (b. p. 40—60°)

added to the extract; this precipitates a sticky mass, which is purified by dissolving it in ether and precipitating with alcohol.

The substance thus obtained melts, not sharply, at about 109° and from the following analysis it would seem to be diphenyl silicone, but we were unable to obtain it in a crystalline condition, so that its nature is not definitely established.

0·2082 gave 0·5526 CO_2 and 0·0982 H_2O. C = 72·38; H = 5·24.
0·2 „ 0·0616 SiO_2. Si = 14·38 per cent.
$C_{12}H_{10}OSi$ requires Si = 14·64; C = 72·72; H = 5·05 per cent.

This compound is practically insoluble in acetic acid, alcohol, or light petroleum, but readily soluble in ether, chloroform, benzene, or carbon disulphide.

Preparation of Silicon Tetraethyl, $Si(C_2H_5)_4$.

The preparation of silicon tetraethyl by the interaction of zinc ethyl and silicon tetrachloride being a very troublesome and expensive process, we made experiments to find out whether this compound could be obtained by the application of Fittig's reaction. For this purpose, silicon tetrachloride (10 grams) and ethyl bromide (26 grams) were dissolved together and added to sodium wire (12 grams) in dry ether; as no reaction occurred after heating on the water-bath for some time, a little ethyl acetate was added, whereupon change set in and proceeded very gently, sodium bromide separating; after digesting for two days, the solution was filtered, the ethereal filtrate and washings evaporated, and the residual liquid fractionated. It began to boil at about 100°, and the thermometer rose fairly quickly to 140°, but between 140° and 160° a considerable quantity passed over; only a small portion distilled between 160° and 170°. The fraction collected between 140° and 160° (about 5 grams) was dissolved in a little ether, washed with dilute sodium carbonate to remove acid, dried, and redistilled, the portion boiling at 154—155° being collected separately. This fraction (about 3 grams) consisted of silicon tetraethyl practically free from impurity, as shown by the following analysis:

0·2005 gave 0·4878 CO_2 and 0·2527 H_2O. C = 66·31; H = 14·00.
$C_8H_{20}Si$ requires C = 66·66; H = 13·88 per cent.

The silicon could not be easily estimated by heating with sulphuric acid, as in the case of the other silicon compounds, which were analysed in this way; different determinations were made, but the results were not concordant, being 18·01 and 17·45 per cent. of silicon respectively, the calculated amount being 19·44 per cent.

The lack of agreement between these two results, and the low per-

centage of silicon actually found, may be ascribed to volatilisation of the silicon tetraethyl.

The effect of substituting ethyl iodide for bromide in the method of preparation just described is not advantageous; quantities corresponding with the above were mixed with dry ether and then heated on the water-bath, but action took place very slowly, and the solution turned dark brown; after heating for 3 days, the product was isolated as before, but from 20 grams of silicon tetrachloride we only obtained about 5 grams of silicon tetraethyl boiling at 154—155°; the purity of this preparation is shown by the following analysis:

0·2136 gave 0·5208 CO_2 and 0·2684 H_2O. C = 66·48; H = 13·98.
$C_8H_{20}Si$ requires C = 66·66; H = 13·88 per cent.

Phenoxymethoxysilicon Dichloride, $SiCl_2(OMe)\cdot OPh$.—This compound was obtained by adding a solution of phenol (1 mol.) in ether drop by drop to an ethereal solution of silicon tetrachloride (1 mol.), and then slowly running in an ethereal solution of methyl alcohol (1 mol.); after evaporating the ether, the product was fractionated under atmospheric pressure, and the portion passing over between 210° and 220° collected separately; this formed the principal portion of the crude product, and after further fractionation it gave a colourless, mobile liquid boiling at 216° under 752 mm. pressure. On analysis, the following result was obtained:

0·2201 gave 0·2864 AgCl. Cl = 32·18.
$C_7H_8O_2Cl_2Si$ requires Cl = 31·8 per cent.

Phenoxymethoxysilicon dichloride boils under the ordinary pressure without appreciable decomposition; it is very readily decomposed by water, giving silica, hydrochloric acid, phenol, and methyl alcohol.

Phenoxymethoxyethoxysilicon chloride, $SiCl(OMe)(OEt)\cdot OPh$.—This compound is easily prepared by slowly adding an ethereal solution of ethyl alcohol to an ethereal solution of the preceding compound; after evaporating the ether and repeatedly fractionating the product under atmospheric pressure, it is obtained as a colourless, oily liquid boiling at 241°.

0·3201 gave 0·1896 AgCl. Cl = 15·34.
$C_9H_{13}O_3ClSi$ requires Cl = 15·29 per cent.

This substance is decomposed by water with separation of silica, but not with very great rapidity; although it seemed relatively stable in presence of moisture, attempts to displace the chlorine atom by an acid radicle were unsuccessful. When digested with dry silver bromocamphorsulphonate in ethereal solution, silver chloride separated, and the

ethereal solution, on evaporation in a desiccator, gave an oil which, however, seemed to be almost immediately resolved into bromocamphorsulphonic acid, phenol, and other products.

Methoxyethoxysilicon Dichloride, $SiCl_2(OMe)\cdot OEt$.—As it seemed possible that a more stable substance could be obtained by substituting a fatty alkyl group for phenol in the preceding substance, we treated silicon tetrachloride first with methyl alcohol (1 mol.), and then with ethyl alcohol (1 mol.), in ethereal solution; the product, after repeated fractional distillation, afforded a colourless liquid boiling at 128° under the ordinary pressure. On analysis, the following result was obtained:

0·1625 gave 0·2679 AgCl. Cl = 40·78.

$C_3H_8O_2Cl_2Si$ requires Cl = 40·57 per cent.

Methoxyethoxyisobutyloxysilicon chloride, $SiCl(OMe)(OEt)\cdot OBu^{\beta}$.—On treating the preceding compound with *iso*butyl alcohol under the conditions previously described, interaction took place readily, and the principal product, isolated by fractional distillation, boiled at 159—160° under atmospheric pressure.

0·3724 gave 0·2475 AgCl. Cl = 16·42.

$C_7H_{17}O_3ClSi$ requires Cl = 16·7 per cent.

Methoxyethoxy*iso*butyloxysilicon chloride is a colourless, fairly mobile oil, but it seems to be just as readily decomposed by water as the phenoxy-derivative; it interacts with amino-compounds in ethereal solution, but the products are also unstable towards water.

Phenoxyethoxymethoxyanilinosilicon, $Si(OMe)(OEt)(OPh)\cdot NHPh$.—In order to ascertain whether a stable anilino-derivative could be obtained from the phenoxyethoxymethoxysilicon chloride, a considerable quantity of the latter was gradually treated with aniline (2 mols.) in ethereal solution; the aniline hydrochloride which was free from silica was then separated by filtration, and the ethereal solution evaporated. The residue, a thick oil, crystallised in colourless needles when cooled with a mixture of carbon dioxide and ether, but as it melted again at a very low temperature, and was readily decomposed by water with separation of silica, it was not examined further.

Phenoxyethoxymethoxymenthoxysilicon, $Si(OMe)(OEt)(OPh)\cdot OC_{10}H_{19}$, was prepared by treating the phenoxymethoxyethoxysilicon chloride described above with menthol (1 mol.) in ethereal solution, and was obtained as a thick, colourless oil which did not solidify when cooled with ether and carbon dioxide; it was readily decomposed by water, giving silica, menthol, phenol, and the alcohols.

We beg to express our thanks to the Government Grant Committee of the Royal Society for a grant by which part of the cost of this work has been met.

UNIVERSITY COLLEGE,
NOTTINGHAM.