CCCLXII.—*Organic Derivatives of Silicon. Part XXXIII. An Amorphous Variety of Octaphenyl*cyclo*silicotetrane.*

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THE glue-like, readily soluble product (E) of the action of sodium on diphenylsilicon dichloride in toluene solution is so strikingly different in physical properties from the four very sparingly soluble silicohydrocarbons $[SiPh_2]_n$ (A, B, C, and D) by which it is accompanied (Kipping and Sands, J., 1921, **119**, 830) that it could hardly fail to arouse interest; its investigation, continued intermittently since 1921, has led to the conclusion that it consists mainly of an amorphous form of octaphenyl*cyclo*silicotetrane (B), the crystalline variety of which does not melt at 400° and is practically insoluble in cold acetone.

The acetone solution of (E) (*loc. cit.*, p. 836), kept in a closed vessel, continues to deposit crystals, but in gradually diminishing quantities, over periods of more than two years; these deposits consist of octaphenyl*cyclo*silicotetrane (B), but contain, as a rule, a very small proportion of the compound (C) (Kipping, J., 1924, **125**, 2291); octaphenylsilicotetrane (A), which is much more soluble than (C), but much less soluble than (B), in ordinary media, has never been detected. It seems, therefore, that (E) is partly and very slowly transformed into (B), since ordinary supersaturation could hardly continue so long. When the acetone solution is systematically fractionally precipitated with alcohol, a very small proportion of (B) and sometimes traces of (C) are found after each extended set of operations, and this separation or formation of insoluble matter seems to continue almost indefinitely; most of the original preparation, however, is merely resolved into a series of fractions, all miscible with acetone, the more sparingly soluble of which consist of an easily fusible resinous material of the composition $[SiPh_2]_n$, hereafter referred to as (E_1). The more soluble fractions are glue-like or oily, and contain combined oxygen, the origin of which was ultimately traced to the presence of phenoxy- and ethoxy-compounds in the diphenylsilicon dichloride (compare Kipping and Murray, this vol., p. 2734). This discovery and the difficulty of settling the nature of (E_1) made it advisable to hold back the results of its investigation until there was no doubt of its formation from the dichloride.

Even after prolonged fractionation from many different solvents, (E_1) yields no crystalline compound, other than a little (B) and traces of (C); it merely affords a series of graded fractions. Cryoscopic determinations in benzene solution give multiples of $SiPh_2$ ranging from about 7 to 9, and the high molecular complexity of the material is also proved by its non-volatility at high temperatures in a vacuum (p. 2725).

In chemical behaviour, (E_1) resembles octaphenyl*cyclo*silicotetrane (B) and is quite different from the reactive, open-chain isomeride (A); the fact that it does not combine with iodine seems to indicate, but does not prove [compare behaviour of (D), J., 1924, **125**, 2296], that it consists entirely of closed-chain molecules. It is oxidised by nitric acid, giving a small proportion of the rhomboidal oxide, $Si_4Ph_8O_2$ (J., 1921, **119**, 844), but practically the whole of it seems to be converted into diphenylsilicanediol and condensation products of the latter. It is decomposed by piperidine and aqueous alkali, giving hydrogen and diphenylsilicanediol (or condensation products). The observed hydrogen values (Kipping and Sands, *loc. cit.*, p. 848) are a little lower than that required for $SiPh_2 + 2H_2O = SiPh_2(OH)_2 + H_2$, probably owing to incomplete hydrolysis; the examination of the products (p. 2727) seems to prove, however, that the preparations do not contain any $SiPh_3$-groups, but consist entirely of molecules $[SiPh_2]_n$.

Now when the physical properties of (E_1) are compared with those of octaphenyl*cyclo*silicotetrane (B) and those of (C), which is possibly $[SiPh_2]_6$ or $[SiPh_2]_8$—leaving out of consideration those of the open-chain compounds (A) and (D)—the contrast is so striking that even if (E_1) were regarded as a mixture of several cyclic compounds $[SiPh_2]_n$, the latter could hardly be present as free molecules, capable of forming sparingly soluble crystalline structures of high melting point, like those of (B) and (C). It is therefore suggested that (E_1) consists of molecules of octaphenyl*cyclo*silicotetrane (B) which have got so entangled with one another during their formation that they are inseparable, or nearly so, by physical means at moderate temperatures. It is not assumed that the cyclic structures are joined together like the links of a chain, but that the molecules of (B) are held together by the interlocking of their phenyl groups, forming aggregates of irregular shape, which do not themselves pack into crystals and hinder the orderly arrangement of the whole; if some of these molecules were comparatively loosely attached, and the proportion of irregular aggregates was diminished, a slow deposition of ordinary crystals of (B) from solutions of (E_1) might be expected to take place to a certain extent, as actually occurs. It is possible that octaphenyl*cyclo*silicotetrane and its higher analogues might assume configurations in which the silicon atoms do not all lie in one plane, and that such configurations might be rendered stable by the steric effects of their phenyl groups. Such assumptions, however, would not account adequately for the properties of (E_1), which seems to be a complex mixture of molecules, incapable of crystallisation.

The view that (E_1) is merely a physically different form of (B) is borne out by the following: In one experiment, when (E) was heated under 5—0 mm., small quantities of oily "distillate," apparently decomposition products, were collected as the temperature of the liquid rose from about 300° to 400° and at the same time a very considerable proportion of crystalline matter separated from the residue, and did not all redissolve; this crystalline deposit consisted of octaphenyl*cyclo*silicotetrane (B) with a small proportion of octaphenylsilicotetrane (A). As it was hardly possible that so large a proportion of free (B) molecules could have been present in the crude (E), it must be concluded that these molecules had been set free by the action of heat.

Unfortunately, attempts to repeat this conversion of (E_1) into (B) have been unsuccessful, but the reverse operation is easily accomplished. When pure (B) is very rapidly heated above 400° until it is partly melted, and then immediately cooled, the glue-like melted portion is very readily soluble in cold acetone; the solution begins to deposit crystals of (B) after a variable interval and continues to do so during several days or weeks; it then gives with alcohol a flocculent precipitate, $[SiPh_2]_n$, melting indefinitely below 150°, and having a molecular weight of about 1500.

These results, the chemical similarity of (E_1) and (B), and all other facts seem to be best accounted for by the assumption that these two substances are physically different forms of octaphenyl*cyclo*silicotetrane.

The distillate referred to above, and a similar product from other samples of (E), consisted mainly of an oil which gave triphenylsilicol on oxidation, or, with evolution of hydrogen, on treatment with acetone and alkali; from these facts, it would appear that this oil contained triphenylsilicyl, pentaphenylsilicoethyl, or heptaphenylsilicopropyl. It is only formed from (E) very slowly and at high temperatures, but it is clear that the decomposition of the $[SiPh_2]_n$ molecules is accompanied by a transference of phenyl groups from one silicon atom to another.

EXPERIMENTAL.

The crystalline deposit which is formed when an acetone or ethereal solution of (E) is kept in a closed vessel does not redissolve when the supernatant solution is warmed; separated by filtration and treated with cold benzene, it often leaves a very small proportion of a residue which can be identified as (C) by crystallisation from benzene, etc. (compare J., 1924, **125**, 2294). The main portion of the deposit, soluble in cold benzene, was identified as octaphenyl*cyclo*silicotetrane (B) by direct comparison; it did not decolorise a very dilute benzene solution of iodine and was therefore free from octaphenylsilicotetrane (A).

As the formation of deposits in acetone solutions of (E) might conceivably be due to the action of alkali from the glass vessels, an acetone solution which had been kept some 3 months was filtered and acidified with a drop of hydrochloric acid; the solution (in a closed vessel, gave in the course of 6 months a deposit of (B), and the flask became coated with a very thin layer of some material insoluble in boiling benzene and other solvents, which could be detached in transparent, elastic films. Similar gelatinous films are often formed on the beakers used in fractionating (E) with acetone and alcohol; they char at a very high temperature but without melting and appear to be unchanged when boiled with acetone and potash. This material may be already contained in (E) and if so may be partly accountable for the low hydrogen values of (E_1), or it may be a very complex condensation product of diphenylsilicanediol (which will be described in a future paper), produced by the hydrolysis of (E_1). Crude (E) does not react appreciably with iodine, but it reduces silver nitrate in acetone solution very distinctly.

Separation of Silicohydrocarbons (E_1).—Treated with alcohol, the acetone solution of (E) gives at first a white, plastic precipitate which can be pulled out into long, silk-like threads; the latter change into a very brittle solid when the solvents evaporate. By systematic fractional precipitation in this way, or with water, continued until each of the original fractions (say 8) has been redissolved and reprecipitated several times, the most sparingly soluble portion, now precipitated in a flocculent form, if again treated with cold acetone, usually gives a very small separation of (B) with traces of (C). Another systematic series of operations with the whole set of fractions, starting from the most soluble portion, yields a similar result, and it seems that this very sparingly soluble matter is being continually produced.

Many different preparations of the less soluble fractions (but miscible with acetone) have been analysed; most of them retained solvent very tenaciously and lost in weight during more than 30 days in a vacuum * (Found : Si, 15·3, 15·7, 15·5, 15·6, 15·4, 15·6; C, 77·6, 78·2, 77·9, 78·3; H, 5·9, 5·8, 5·9, 5·8; *M*, cryoscopic in benzene, 1558, 1395, 1456, 1225, 1410; hydrogen values, 110, 108, 113, 116. $SiPh_2$ requires Si, 15·5; C, 79·0; H, 5·5%; *M*, 182; hydrogen value, 122) (compare J., 1921, **119**, 848).

The somewhat low combustion results are partly due to the difficulty of burning the last traces of carbon in the silica residue;

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* The best way of obtaining a sample ready for analysis is to dissolve it (2—3 g.) in a very little dry ether in a 300 c.c. beaker, evaporate the solvent on the water-bath to a " glue," and then, while the " glue " is still warm, evaporate the rest of the solvent quickly under reduced pressure; the residue froths and fills the beaker with a white foam, which after 10—15 minutes becomes very brittle and can be easily broken up. Even such preparations do not become constant in weight in less than 3 to 5 days in a vacuum; to the unaided eye they appear to be beautifully crystalline.

the silicon determinations are trustworthy, since the residue obtained on ignition with sulphuric acid containing a little nitric acid is colourless.* The low hydrogen values have not been accounted for satisfactorily; they are partly due to the presence of some non-hydrolysable matter, possibly an amorphous form of (C).

When (E) has been prepared from diphenylsilicon dichloride of about 95—97% purity (compare Kipping and Murray, *loc. cit.*),† the product after two precipitations contains about 15·1% of silicon, consists mainly of (E_1), and does not give phenol on hydrolysis; the isolation of (E_1) then presents no very great difficulty. The earlier crude preparations of (E), however, contained only 12·5—14% of silicon, and the isolation of (E_1) required a prolonged series of fractional precipitations whereby a large proportion of rather more soluble glue-like matter was gradually separated; this material gave phenol and ethyl alcohol on hydrolysis.

The Silicohydrocarbon (E_1).—Many preparations of the composition $[SiPh_2]_n$ were fractionally extracted with boiling alcohol or boiling light petroleum, precipitated from hot phenol with alcohol, etc., but their properties underwent but little change, and no crystalline product, except perhaps traces of (B), could be isolated. The fractional diffusion of an acetone solution through unglazed earthenware also failed to afford crystals.

The preparations have no definite melting point but gradually liquefy over a range of 20° or 30° or so, beginning to sinter from about 110° to 130°; they are miscible with cold ether, benzene, chloroform and many other solvents, from all of which they separate as "glues," which very gradually become brittle, but they are only sparingly soluble in boiling light petroleum and very sparingly in boiling alcohol or glacial acetic acid. Preparations kept in the solid state during 4—5 years are still miscible with cold acetone.

(E_1) does not react appreciably with iodine in cold benzene

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* The silica is very hygroscopic and may absorb as much as 28·4% of water on exposure to the air.

† It is no easy matter to ascertain whether—or when—the reaction with sodium is at an end. The toluene solutions of the product, which give no sign of a green flame with copper, afford an aqueous extract containing halogen. This seems to be partly present as sodium chloride, which is slightly soluble in toluene solutions of (E). The heating was usually stopped when an aqueous extract gave a neutral reaction to litmus, but even this test seems to be untrustworthy, and (E) may still contain halogen. If the heating with sodium is continued beyond a certain point, the filtered toluene solution gives an alkaline reaction, and the crude (E), obtained by evaporation, effervesces when treated with (undried) acetone; if this occurs, the fractional precipitation of the acetone solution with alcohol (after removing B) yields a large proportion of trianhydrotrisdiphenylsilicanediol, and the isolation of (E_1) is difficult or impossible.

solution; in carbon tetrachloride solution, a little bromine is absorbed, but many hours elapse before the proportion reaches $Br_2 : [SiPh_2]_2$. In some cases traces of a crystalline bromo-compound were obtained, but the principal solid product was a very little rhomboidal oxide, probably formed by the hydrolysis of a dibromide, $SiPh_2Br{\cdot}SiPh_2Br$, and subsequent condensation of the diol; the reaction seemed also to involve the partial separation of phenyl groups as bromobenzene without precipitation of silica.

When (E_1), partly dissolved and partly suspended in glacial acetic acid, is cautiously oxidised with nitric acid, it yields the rhomboidal oxide, but is almost entirely converted into crystalline and oily condensation products of diphenylsilicanediol.

Formation of (*B*) *and* (*A*) *from* (*E*).—A solution of (E) (30—35 g.) in undried commercial ether, which had been kept about 3 weeks in a closed vessel and then filtered from the deposit of (B), was evaporated and the residue heated in a very short-necked (2″) flask under 6 mm. pressure. At first a little (0·2 g.) diphenyl came over; the temperature then rose rapidly to about 300° (thermometer in liquid) and a very slow "distillation" commenced, fractions, each of about 1½ c.c., being collected at 300—330°, 330—350° and 350—360°. The temperature then rose slowly to 400° (5 mm.), but no further distillation occurred and crystals which had been splashed on to the sides of the flask had not liquefied when the heating was stopped.

When cold, the glue-like mass was treated with acetone and left over-night; most of it dissolved, leaving some crystalline matter (about 2 g.), which was washed with acetone. This product was almost completely soluble in cold chloroform, and was reprecipitated by acetone in short, rectangular prisms which were identified as those of octaphenyl*cyclo*silicotetrane (B) by a direct comparison. The portion insoluble in cold chloroform (about 0·1 g.) crystallised from benzene in short, flat prisms and was proved to be octaphenylsilicotetrane (A) by its behaviour towards iodine and in other ways.

In order to prove that the cyclic silicohydrocarbon (B) had not been held in solution by the liquid "distillate" of (E), some of it was dissolved in a portion of this distillate; the solution, diluted with ether or with acetone, gave an immediate precipitate and apparently the whole of the dissolved (B) was deposited.

Of the three fractions referred to above, the two more volatile ones fumed very slightly in the air and contained halogen.* All three fractions deposited traces of trianhydrotrisdiphenylsilicanediol, reduced an aqueous solution of silver nitrate in a marked manner, and gave hydrogen very readily with acetone and aqueous

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* The heating with sodium had been continued during at least 6 hours.

alkali. The whole of this thick, oily " distillate " was poured into glacial acetic acid (about 4 vols.)—in which it was only very sparingly soluble—and then a few drops of concentrated nitric acid were added; oxidation set in very readily and after the non-homogeneous mixture had been warmed on the water-bath during some 2 hours and then cooled, a considerable quantity of crystalline matter separated very slowly from the oily layer. This crystalline product, purified by recrystallisation from alcoholic chloroform, was conclusively proved to be triphenylsilicol by analysis, mixed melting-point determinations, etc., and by converting it into triphenylsilicyl oxide (m. p. 222—223°).

The fact that this oil gave a large proportion (at least 25%) of triphenylsilicol on oxidation, whereas undistilled (E) gives no such product, seemed to prove that a migration of phenyl groups had occurred without separation of silicon or silica. The acetone solution of the residue from the distillation, fractionally treated with alcohol, gave precipitates of much the same character as (E_1); they were, however, less readily soluble in acetone, and contained 16—17% of silicon ($SiPh_2$ requires 15·4%), the percentage increasing with the duration of the " distillation."

In the hope of confirming these results, another preparation of (E), which had been kept in dry ethereal solution during 19 days, was separated from the usual deposit, and the crude (E) (12 g.) obtained on evaporation of the solvent was heated under 1—1·5 mm. (thermometer in the liquid) in a very short-necked flask. From about 283° to 310°, about 1½ c.c. of a thick oil very slowly collected in the receiver, but there was no separation of crystals from the distillate or from the residue, even when the latter was treated with acetone.

The distillate contained only traces of halogen, reduced an aqueous acetone solution of silver nitrate, and gave triphenylsilicol on oxidation with a glacial acetic acid solution of nitric acid; when treated with alkali in acetone solution, it gave hydrogen readily at the ordinary temperature, and, after some of the solvent had been expelled, crystals of triphenylsilicol were deposited; these, left on porous earthenware, without having been freed from alkali, passed into crystals of the silicyl oxide. The mother-liquor from the silicol, warmed again with alcohol and alkali, gave further deposits of triphenylsilicyl oxide, and finally at least 80% of a portion of the original distillate was transformed into this compound.

All attempts to isolate triphenylsilicol or the oxide from other portions of this distillate without using nitric acid or alkali were unsuccessful; the oil certainly did not contain the oxide, nor did it give any crystals of the latter after it had been heated for a long time with alcohol and hydrochloric acid. The residue from this "distillation" solidified to a very brittle resin, which behaved on hydrolysis quite differently from ordinary samples of (E), inasmuch as it gave, in addition to diphenylsilicanediol, a considerable proportion of triphenylsilicyl oxide. A direct comparison of two samples of the same preparation of (E), one of which had been heated at about 350° for some time, proved that only the latter gave triphenylsilicyl oxide on hydrolysis; from 3·7 g. of the unheated material, only about 0·25 g. was not ultimately convertible into diphenylsilicanediol or other products soluble in aqueous alkali.

It must be concluded from these results that at high temperatures some of the molecules composed entirely of $SiPh_2$ groups are decomposed, giving triphenylsilicyl, $SiPh_3$·, or some other compound containing a $SiPh_3$-group.

*Conversion of Octaphenyl*cyclo*silicotetrane into an Amorphous Form.*—When pure (B) is very rapidly heated in a test-tube over a free flame in an inert atmosphere, it can be partly melted, and when the cooled product is treated with cold acetone, the melted portion dissolves, leaving the crystalline matter; by repeating these operations, the whole of any sample of (B) can be obtained in solution in about 1—2% of the volume of solvent which would have been required to dissolve the crystals, but not more than 0·1 g. of (B) should be heated at a time. The acetone solution begins to deposit crystals of pure (B) either within a few minutes or only after some hours, and this deposition may continue during many days: the filtered solution gives with alcohol an apparently amorphous, flocculent precipitate, which, when separated and freed from solvent, melts very indefinitely from 110° to 150° and contains 15·4% of silicon ($SiPh_2$ requires Si, 15·5%); the molecular weight in camphor was found to be 1500, whereas under the same conditions crystalline (B) gives the normal results for $[SiPh_2]_4$ (J., 1924, **125**, 2291). The alcoholic acetone filtrate from the amorphous precipitate gives on evaporation a little more of an apparently identical product.

As there is no charring, or evolution of vapour, or separation of insoluble matter when (B) is thus heated, and as the whole of the product seems to be silicohydrocarbon $[SiPh_2]_n$, it is concluded that the soluble amorphous product is merely a form of octaphenyl*cyclo*silicotetrane in which the molecules have become entangled with one another. It is not suggested that this form, produced by melting (B), is identical with (E_1); it seems to differ from (E_1) in being more readily and more completely transformed into the crystalline variety, and may be regarded rather as a mixture of (B) molecules analogous to that which is contained in the original toluene solution of (E) and from which a considerable proportion of (B) is rapidly precipitated on the addition of acetone.

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