

CXXVII.—*Organic Derivatives of Silicon. Part XLII.*  
*cycloHexyl Derivatives of Silicane and Silicoethane.*

By KEITH WILLIAM PALMER and FREDERIC STANLEY KIPPING.

As the only known compounds containing tervalent silicon atoms are octaphenylsilicotetrane (J., 1923, **123**, 2590) and octa-*p*-tolylsilicotetrane (Steele and Kipping, J., 1929, 2545), prepared from the dichlorides  $R_2SiCl_2$ , it seemed of interest to try to obtain aliphatic analogues of these substances, especially as, at the same time, several outstanding problems relating to certain very sparingly soluble products (J., 1924, **125**, 2291) might be elucidated. As, however, the simple dialkyl derivatives of silicon tetrachloride are not very easily isolated, it was thought that *dicyclohexylsilicon dichloride* would be a more suitable starting point for the attainment of the objects in view.

Silicon tetrachloride was therefore treated with an ethereal solution of magnesium *cyclohexyl* bromide (about  $2\frac{1}{2}$  mols.), and the crude product, isolated in the usual way, was submitted to distillation (35 mm.). Except for *dicyclohexyl* and an unexpectedly small yield of impure *cyclohexylsilicon trichloride*, hardly any volatile product was obtained; at a certain temperature the oil began to froth and quickly changed into a bulky yellow solid, which was neither Grignard compound nor magnesium salt, and during this transformation, *cyclohexene*, *dicyclohexyl*, and hydrogen chloride were formed.

The attempted distillation of the crude oil under 1—2 mm. gave practically the same results as under the higher pressure; some

trichloride and a very little impure *dicyclohexylsilicon* dichloride were found in the distillate, but most of the product remained as a brittle solid. It was evident that the results of the interaction of silicon tetrachloride and magnesium *cyclohexyl* bromide, or of the distillation of the *cyclohexyl* derivatives of silicon tetrachloride, must be entirely different from those observed in any previous study of alkyl or aryl derivatives of the tetrachloride.

It was then found that the crude distilled dichloride, and also the non-volatile products, contained compounds which gave hydrogen with alkali; during the original reaction, or the subsequent distillation, therefore, silicon atoms had become directly united.

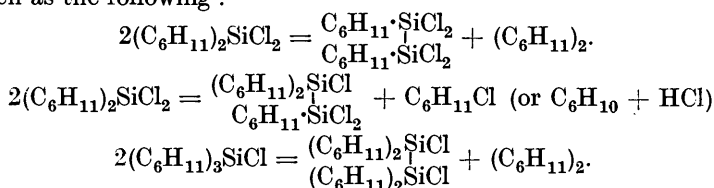
From the volatile products, *cyclohexylsilicon* trichloride was isolated without difficulty; on hydrolysis it gave a non-crystalline material, which consisted of a mixture of at least three condensation products derived from the hydroxide  $C_6H_{11}\cdot Si(OH)_3$ . When dried over sulphuric acid, these different substances gave "*cyclohexylsiliconic acid*" having approximately the composition  $(C_6H_{11}\cdot SiO\cdot OH)_n$ , which was insoluble in all ordinary solvents but gave a soluble crystalline salt with sodium ethoxide; when heated at  $150^\circ$ , the acid underwent further condensation, giving a product having the composition of the "anhydride"  $[(C_6H_{11}\cdot SiO)_2O]_n$ . These results correspond closely with those obtained by Meads and Kipping in their study of the phenyl-, benzyl- and propyl-"siliconic acids" (J., 1914, **105**, 679; 1915, **107**, 459).

The dichloride  $(C_6H_{11})_2SiCl_2$  was not obtained free from *dicyclohexyl*; on hydrolysis it gave a non-crystalline solid, consisting of a mixture of condensation products of  $(C_6H_{11})_2Si(OH)_2$ , soluble in various organic solvents; when precipitated from its ethereal solution with glacial acetic acid, this substance melted at  $140-145^\circ$ , but it underwent further condensation when kept or when heated at  $100^\circ$ , giving an anhydro*dicyclohexylsilicanediol*  $[(C_6H_{11})_2SiO]_7$ . This final condensation product, therefore, is a mixture of compounds of the same order of complexity as those obtained from diethylsilicon dichloride (Martin and Kipping, J., 1909, **95**, 302), which gave an average molecular weight corresponding with  $[SiEt_2O]_7$ .

For the investigation of the non-volatile products of the original interaction, distillation was stopped just below that temperature at which frothing occurred; the residue was treated with ether, which precipitated an insoluble solid. The soluble matter from the ethereal solution gave on hydrolysis a mixture of at least two substances, one insoluble, the other soluble in ether. The former gave analytical data which corresponded with those required for a mixture of condensation products of the hydroxides  $C_6H_{11}\cdot Si(OH)_2$  and  $C_6H_{11}\cdot Si(OH)_2$

$C_6H_{11}\cdot Si(OH)_2$ . The latter seemed to be a tetracyclohexylsilico-  
 $(C_6H_{11})_2Si\cdot OH$   
 ethanediol,  $(C_6H_{11})_2Si\cdot OH$ , which when heated at  $100^\circ$  was con-  
 $(C_6H_{11})_2Si\cdot OH$   
 verted into a condensation product having a molecular weight of  
 about 3000, corresponding with  $[(C_6H_{11})_4Si_2O]_7$ .

From these results it would seem that the interaction of silicon tetrachloride and magnesium cyclohexyl bromide takes place normally, giving cyclohexylsilicic trichloride, dicyclohexylsilicon dichloride and probably some tricyclohexylsilicic chloride. The yield of the dichloride, obtained by distillation, however, is very small and the main portion of the product which has been heated at  $150-180^\circ$  consists of derivatives of silicoethane. Further, the quantity of dicyclohexyl obtained on distillation seems to be greater than that which could have been formed in the preparation of the Grignard reagent under the known conditions. It is inferred, therefore, that some of the original products of the reaction are converted at  $150-180^\circ$  into derivatives of silicoethane by changes such as the following :



This inference is confirmed by the fact that the distilled mixture of dicyclohexyl and dicyclohexylsilicon dichloride gives, when heated, a solid residue similar to that referred to above. Further, since the crude product, before distillation, contains a small proportion of compounds in which silicon atoms are directly united, the formation of silicoethane derivatives occurs to some extent at or below  $100^\circ$ .

Many analyses of the solid produced during distillation have been made but without any definite results. This product contains only about 1 atom of chlorine to 4 silicon atoms and less than 1 cyclohexyl group to each silicon atom. From the hydrogen values of many samples it must be concluded that the elimination of hydrogen chloride and cyclohexene from the silicoethane derivatives is not accompanied by a further direct combination of silicon atoms, but rather by a fission of some of the  $\equiv Si-Si \leq$  links. Its products of hydrolysis differ but little in composition from the original solid, and when treated with sodium hydroxide solution they give apparently sodium silicate and the sodium salt of "cyclohexylsilicic acid," without the production of any appreciable quantity of a fission product which is insoluble in aqueous alkali.

Until some other *cyclohexyl* derivatives of silicane have been studied, any suggestions as to the natures of these complex products would be of little value; it is hoped that work now in progress may afford some information.

#### EXPERIMENTAL.

*The Grignard Reagent.*—In the preparation of magnesium *cyclohexyl* bromide the yield is never theoretical; \* the best results (yield, 50—60%) were obtained as follows. Into a mixture of magnesium (18 g.) and ether (150 c.c.) containing a crystal of iodine, about 6 c.c. of a mixture of *cyclohexyl* bromide (120 g.) and ether (90 c.c.) are run. As soon as the initial vigorous reaction has somewhat subsided, the remainder of the bromide solution is added during 4—5 hours; the whole is then heated on a water-bath for  $\frac{1}{2}$  hour. Only about 5% of the magnesium remains undissolved and there is no deposition of magnesium salt.

*The Reaction with Silicon Tetrachloride.*—The solution of the Grignard compound ( $2\frac{1}{2}$  mols.) is dropped into an ice-cold, well-stirred solution of silicon tetrachloride (35 g.) in dry ether (50 c.c.). Magnesium halide begins to separate when about  $\frac{1}{3}$  of the reagent has been added, occasionally in the solid form, but more often as a brown or green oil, which in some cases does not crystallise even when, after the addition of all the Grignard reagent, the contents of the flask are heated on a water-bath under reflux during 3 hours. This oil, which passes through filter paper, contains about 60% of ether and probably consists of a saturated solution of ether in an etherate of magnesium chlorobromide of the class of compound described by Menshutkin (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1548).

After having been heated until the deposition of magnesium salt seems to be at an end, the clear ethereal solution gives on evaporation a further quantity of magnesium salt as a purple crystalline mass, the yellowish liquid turning emerald-green; the latter is filtered, the residue washed with ether, and the combined filtrate and washings are again evaporated. These processes must be repeated three or four times before the solution ceases to give a deposit of magnesium halide. The liquid product, which is now light yellow, is submitted to distillation (35 mm.). At first a little *cyclohexene* passes over and then a considerable fraction is collected at 120—135°; this

\* Tschitschibabin (*Ber.*, 1905, **38**, 562) prepared the corresponding chloride in dry hydrogen, with a cooled reaction vessel, and used it to prepare esters, of which the yield was only 40%. Hell and Schaal (*Ber.*, 1907, **40**, 4162) observe that in the preparation of magnesium *cyclohexyl* bromide, the maximum yield of Grignard compound is about 60%; Adams and Noller ("Organic Syntheses," Vol. VI) give 61—65%.

contains *cyclohexylsilicon trichloride* and *cyclohexyl bromide*. The next fraction, collected up to  $150^{\circ}$ , consists almost entirely of *dicyclohexyl* but contains a little *dicyclohexylsilicon dichloride*. The temperature then rises rapidly to  $170$ – $180^{\circ}$  but only a very small quantity of liquid distils, and there is violent frothing, owing doubtless to the evolution of hydrogen chloride, with formation of a bulky solid. When the heating is discontinued, before frothing commences, while the whole contents of the flask are still liquid, the residue is soluble in dry ether with the exception of a small proportion of a yellowish solid, and the products in the ethereal solution, on hydrolysis, give a small proportion of the oxide  $[(C_6H_{11})_2SiO]_n$ , together with compounds containing linked silicon atoms. When, however, the heating is continued, the contents of the flask solidify, no dichloride distils, none can be extracted from the residue, and no diol is obtained by the hydrolysis of either the distillate or the residue.

When the crude product is distilled under 3–4 mm. pressure, the first fraction collected below  $120^{\circ}$  contains *dicyclohexyl* and *cyclohexylsilicon trichloride*; the next fraction, from  $140$ – $155^{\circ}$ , contains *dicyclohexyl* and *dicyclohexylsilicon dichloride*; a very small fraction passes over from  $155$ – $180^{\circ}$  and consists principally of the dichloride. At this stage the greenish, very viscous residue is almost entirely soluble in dry ether, but, if heating is continued, frothing occurs and the contents of the flask gradually become solid.

*cycloHexylsilicon Trichloride and "cycloHexylsiliconic Acid."*—The product collected from  $120$ – $135^{\circ}$  (35 mm.), fractionated at atmospheric pressure, afforded a colourless fuming liquid, b. p.  $208$ – $211^{\circ}$  (Found : Cl, 48.6.  $C_6H_{11}Cl_3Si$  requires Cl, 48.9%).

When this *trichloride* is dropped into well-stirred ice-cold water, a white solid is formed, but a considerable proportion of the hydrolysis product remains in solution, and only a small fraction of this dissolved matter can be extracted with ether. The solid, insoluble in water, when freshly precipitated is partly soluble in ether, and the ethereal solution on evaporation gives a colourless glue-like mass which rapidly hardens to a resin and becomes insoluble in ether. The original solid left at the ordinary temperature also becomes wholly insoluble in ether and other solvents; further, it is no longer completely soluble in cold sodium hydroxide solution. The aqueous solution of the original product of hydrolysis gives on evaporation a gelatinous precipitate which dries in the air to a white powder insoluble in water and in ether. Three samples of the preparation insoluble in water and in ether, dried over sulphuric acid during 24 hours and then for an hour at  $100^{\circ}$ , gave Si = 19.2, 19.0, and 19.0 (Calc. for  $C_6H_{11}\cdot SiO\cdot OH$ : Si, 19.4%).

Two such samples were heated first at 100° during 24 hours and then at 150° during 24 hours until constant in weight; the average loss (6.1%) corresponded with that (6.2%) required for  $2C_6H_{11}\cdot SiO\cdot OH = (C_6H_{11}\cdot SiO)_2O + H_2O$  and the heated products gave Si, 20.9 and 20.8 respectively [Calc. for  $(C_6H_{11}\cdot SiO)_2O$  : Si, 20.7%].

“*cycloHexylsiliconic acid*” dissolves slowly in warm 5–10% sodium hydroxide solution, from which it is immediately precipitated at the ordinary temperature or at 0° by ammonium chloride, but only after some time by dilute hydrochloric acid; only a very small proportion of this precipitate is soluble in ether and this rapidly becomes insoluble when it is kept. The insoluble form of the acid does not melt, but chars at a high temperature. When a solution of the sodium salt in 5% caustic soda is boiled, a slight odour of *cyclohexane* can be detected but decomposition is very slow as in the case of other alkylsiliconic acids (Meads and Kipping, J., 1914, **105**, 688). With more concentrated solutions decomposition takes place more rapidly; after having been refluxed during 1 hour the products, precipitated by ammonium chloride and dried at 180–200°, gave the following results: From 8% NaOH, Si = 26.5; 20% NaOH, Si = 30.1; 30% NaOH, Si = 39.1; 40% NaOH, Si = 45.1 [ $(C_6H_{11}\cdot SiO)_2O$  requires Si, 20.7%.  $SiO_2$  requires Si, 46.6%].

The slow evaporation over sulphuric acid of a solution of the acid in alcohol containing the theoretical quantity of sodium ethoxide gave crystals, some cubic, some having a hexagonal outline, which quickly deliquesced and decomposed on being exposed to the air, changing into small globules of a glue-like substance.

*Dicyclohexylsilicon Dichloride and Anhydrodicyclohexylsilicanediol*.—The quantity of *dichloride* in the two crude fractions 140–155° and 155–180° (p. 1024) was so small that the compound could not be isolated; a fraction collected from 140–145° after several distillations gave Cl = 23.9 [ $(C_6H_{11})_2SiCl_2$  requires Cl, 26.7%]. When a portion was heated (760 mm.), a little *dichloride* and *dicyclohexyl* distilled but as heating was continued most of the oil was converted into a glue-like mass, which finally changed to a bulky solid.

*Dicyclohexylsilicanediol* was obtained by hydrolysing the crude *dichloride* and then separating the *dicyclohexyl* by distillation in steam. It was more conveniently prepared by hydrolysing the oil which remains when distillation is stopped as soon as *trichloride* ceases to pass over. The pasty product, freed from *dicyclohexyl*, is a pale yellow, dough-like mass most of which dissolves in ether, leaving a pale yellow solid quite insoluble in that solvent. The latter gives hydrogen with caustic soda and is described later.

The ethereal solution is agitated with dilute caustic soda solution until hydrogen evolution ceases, washed with water, and evaporated; the pale glue-like residue when left in the air changes into a brittle resin, which softens at about 200°, gradually liquefies at higher temperatures, and then chars. When glacial acetic acid or alcohol is added to a cold ethereal solution of the glue-like substance, a white, apparently amorphous, granular solid is precipitated under certain conditions; this product melts indefinitely at 145—150° and, when left during about  $\frac{1}{2}$  hour in the acid solution, becomes a glue-like mass; when kept during a day or two, it changes into the resinous form, which decomposes at 200—250°.

The precipitated powder was dried in the air and at 100° until constant in weight; four different samples gave Si = 13.3; 13.0; 13.2; 13.4 [Calc. for  $\{(C_6H_{11})_2SiO\}_n$  : Si, 13.3%]. Cryoscopic determinations gave (a) in benzene, *M*, 1438 and 1481; (b) in camphor, *M*, 1450 and 1460.

These results show that the simple diol is unstable; the physically different preparations mentioned above are doubtless mixtures of condensation products like those obtained from other diols and the fact that the average molecular weight is as high as 1455 points to the presence of very complex compounds corresponding with some of those obtained from diphenylsilicanediol (Kipping and Murray, J., 1928, 1427).

*Derivatives of Silicoethane.*—The very viscous, dark green residue which is obtained when the distillation of the crude product is discontinued at about 180° is treated with dry ether, which precipitates a small quantity of yellowish solid. The filtered solution gives on evaporation a very thick oil, which when heated under reduced or atmospheric pressure is converted into a yellow solid with evolution of hydrogen chloride, giving a distillate consisting of *cyclohexene*, *dicyclohexyl*, and a small proportion of some compound which evolves hydrogen with aqueous alkalis; the crude oil was analysed (Found: Cl, 21.4%; 1 g. gave 52 c.c. of hydrogen. Two other preparations gave hydrogen values of 51.2 and 52.7 respectively). These results are considered later (p. 1028).

The oil hydrolysed with cold water gives a creamy mass which hardens to a crisp solid. A very variable quantity, sometimes as much as 40%, of this product is soluble in ether and the proportion seems to depend on the stage at which distillation has been stopped. The insoluble portion is a granular infusible powder insoluble in all the solvents which were tried. Three different preparations were dried at 100° and analysed (Found: Si, 19.0, 18.8, and 17.3% respectively). They all evolved hydrogen with caustic alkalis and gave respectively the following values: 70, 69, and 67.4 [Calc. for

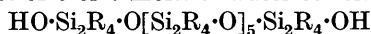
$\text{C}_6\text{H}_{11}\cdot\text{SiO}$  : Si, 22%; hydrogen value 80. Calc. for  $\frac{\text{C}_6\text{H}_{11}\cdot\text{SiO}}{(\text{C}_6\text{H}_{11})_2\text{Si}\cdot\text{OH}}$  :  
 $\text{C}_6\text{H}_{11}\cdot\text{SiO}$   
 Si, 16.9%; hydrogen value 66].

These results agree with the view that the ether-soluble residue from the distillation contains a mixture of di- and tri-*cyclohexyl* derivatives of silicon hexachloride and that this insoluble substance is a mixture of the condensation products formed when they are hydrolysed. The proportions of the two chlorides would no doubt depend on the temperature at which distillation had ceased and the composition of the mixed products of hydrolysis would vary accordingly.

That this insoluble product contains linked silicon atoms is proved by its behaviour towards alkalis; that it contains both  $\text{R}_2\text{Si} <$  and  $\text{RSi} \leq$  groups is proved by the fact that after fission has occurred the alkaline solution contains in suspension a glue-like substance, soluble in ether, which has all the (rather indefinite) properties of the oxide  $(\text{C}_6\text{H}_{11})_2\text{SiO}$ . The alkaline solution treated with acids gives a precipitate of "*cyclohexylsiliconic acid*."

The product of hydrolysis which is soluble in ether was obtained as a glue-like mass by the evaporation of the solution. It dissolved freely in ether but was less readily soluble in acetone, from which it separated again in a glue-like form. As it might have contained a small proportion of the oxide,  $(\text{C}_6\text{H}_{11})_2\text{SiO}$ , it was fractionally extracted with cold acetone, in which the latter is readily soluble, and then dried over sulphuric acid until constant in weight (sample I); the last acetone extract was evaporated and the residue dried in like manner (sample II) [Found: (I) Si, 13.2%; hydrogen value, 53. (II) Si, 12.4%; hydrogen value, 50. Calc. for  $(\text{C}_6\text{H}_{11})_4\text{Si}_2(\text{OH})_2$ : Si, 13.3%; hydrogen value, 53.5]. That the compound contains the group  $\text{SiR}_2$  was proved by the fact that, when it was treated with aqueous alkali until hydrogen ceased to be evolved, it did not dissolve but gave a product which behaved in all respects like the oxide and contained 12.1% of silicon (Calc. for  $\text{SiR}_2\text{O}$ : Si, 12.3%).

The less soluble portion (I) of this tetracyclohexyl derivative was dissolved in ether, and a little alcohol added to the solution. There was an immediate precipitate of a colourless infusible solid, which, dried over sulphuric acid until constant in weight, gave a hydrogen value of 56.5 and *M* (cryoscopic) in benzene 2980 and in camphor 2900. This product was still soluble in ether, acetone and other solvents, but it could not be obtained in crystals. These results indicate that 7 mols. of the dihydroxide have undergone condensation with the loss of 6 or 7 mols. of water to form



or the closed-chain compound  $[\text{Si}_2\text{R}_4\text{O}]_7$ .



The analytical data given above for the original oily residue (p. 1026) and the results of the investigation of its products of hydrolysis accord with the view that the oil consists principally of the two compounds  $\text{SiR}_2\text{Cl}\cdot\text{SiR}_2\text{Cl}$  and  $\text{SiR}_2\text{Cl}\cdot\text{SiRCl}_2$  with a very variable proportion of  $\text{SiRCl}_2\cdot\text{SiRCl}_2$ .

*The insoluble residue.* The yellow porous infusible solid which remains when the distillation of the crude original product is continued until liquid ceases to pass over, is not present in the original oil; during its formation, hydrogen chloride, *cyclohexene* and *dicyclohexyl* are produced. As it was insoluble in all organic solvents which were tried, it was directly analysed, 6 different preparations being used. The percentage of silicon ranged from 22.9 to 25.5 and the hydrogen values from 45—52.5; a chlorine determination, in one sample only, gave  $\text{Cl} = 9.0\%$ . It is noteworthy that the hydrogen values are no greater than that of the oil from which it has been formed, in spite of the loss of halogen and hydrocarbon radicals.

When left in contact with aqueous alcohol during many hours and then washed, crushed and dried, the solid gave a cream-coloured powder, insoluble in all the common solvents. Several preparations were analysed, but, as was to be expected in view of the small proportion of halogen which was displaced by hydroxyl, the silicon percentages and the hydrogen values were practically the same as those of the non-hydrolysed solid. The only other evidence as to the nature of this product was obtained by warming the solid with acetone and sodium hydroxide until hydrogen ceased to be evolved; with the exception of a small and variable proportion of glue-like matter, the solid was thus converted into products soluble in aqueous alkali, and these were fractionally precipitated by passing carbon dioxide into the solution. The three precipitates thus obtained, when dried, contained 29.5, 22.3 and 19.8% of silicon respectively; since  $\text{C}_6\text{H}_{11}\cdot\text{SiO}\cdot\text{OH}$  requires Si, 19.4% and the sodium hydroxide solution was not sufficiently strong to decompose the silicic acid, it must be concluded that some of the silicon atoms in the solid are not combined with *cyclohexyl* groups.

UNIVERSITY COLLEGE, NOTTINGHAM.

[Received, March 8th, 1930.]

---