308. *Organic Derivatives of Silicon. Part XLVII.* cyclo*Hexylphenyl and* cyclo*Hexyl Derivatives.*

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When the crude product of the interaction of silicon tetrachloride and *cyclo*hexylmagnesium bromide (2½ mols.) is distilled (35 mm.), it affords only a very small yield of di*cyclo*hexylsilicon dichloride because this compound undergoes decomposition above 150° with the elimination of di*cyclo*hexyl and *cyclo*hexyl chloride and the formation of substances containing linked silicon atoms (Palmer and Kipping, J., 1930, 1020). Some of the simpler silicon compounds in the very complex mixture which is thus formed were shown to be *cyclo*hexyl derivatives of silicon hexachloride, but on hydrolysis they gave only resinous or glue-like mixtures.

As these observations suggested the possibility of a new method of bringing about the direct union of silicon atoms, cyclo*hexylphenylsilicon dichloride* was prepared in the hope that it would behave like the di*cyclo*hexyl derivative and give compounds containing Si–Si links, but which on hydrolysis would afford crystalline substances.

This hope, however, has not been realised. *cyclo*Hexylphenylsilicon dichloride decomposes only to a very slight extent when it is heated and may be distilled even under atmospheric pressure; *di*cyclo*hexylphenylsilicyl chloride* also is unexpectedly stable at high temperatures and gives only a very small proportion of products which evolve hydrogen with alcoholic potash.

cyclo*Hexylphenylsilicanediol*, $C_6H_{11}\cdot SiPh(OH)_2$, like all such diols, readily undergoes condensation, giving glue-like mixtures, but only *trianhydrotris*cyclo*hexylphenylsilicanediol*, $(C_6H_{11}\cdot SiPhO)_3$, was isolated. Cryoscopic determinations of the molecular weight of this compound gave abnormally low values (compare Kipping, J., 1912, **101**, 2125; Pink and Kipping, J., 1923, **123**, 2830). Trianhydrotrisdi*cyclo*hexylsilicanediol also gave anomalous values of the same order (p. 2209).

*Di*cyclo*hexylphenylsilicol*, $(C_6H_{11})_2SiPh\cdot OH$, unlike all other tertiary silicols which have so far been examined, cannot apparently be converted into the corresponding oxide—a possible case of steric hindrance. Since this silicol contains the group $>CH\cdot Si(OH)<$, attempts were made to convert it into an unsaturated compound by the elimination of water, but without success; this result confirms the view (Kipping, J., 1927, 104) that substances containing a Si=C binding are probably incapable of existence.

From the products of the hydrolysis of fractionated *cyclo*hexylphenylsilicon dichloride, a very small proportion of *di*cyclo*hexylsilicanediol* (m. p. 164—165°) was isolated, from which fact it must be concluded that *cyclo*hexylmagnesium bromide may substitute a *cyclo*hexyl for a phenyl group of phenylsilicon trichloride or of *cyclo*hexylphenylsilicon dichloride. Indications of similar displacements have been previously observed (Marsden and Kipping, J., 1908, **93**, 208; Robison and Kipping, *ibid.*, p. 441; Kipping, J., 1907, **91**, 730). The present case offers conclusive evidence that such reactions actually occur, since the phenylsilicon trichloride from which the di*cyclo*hexylsilicanediol was obtained could not have contained any silicon tetrachloride.

*Trianhydrotrisdi*cyclo*hexylsilicanediol*, $[Si(C_6H_{11})_2O]_3$, is obtained by treating di*cyclo*hexylsilicanediol with bromine and by heating di*cyclo*hexylphenylsilicol with nitric acid, or with bromine, in acetic acid solution. It is rather surprising that bromine should bring about an almost quantitative condensation of the diol into the termolecular product, and also that it should displace the phenyl group of the silicol so readily under the given conditions. The rapid displacement of the phenyl group of the silicol by the action of nitric acid is also an unexpected result, since under similar conditions triphenylsilicol is merely converted into the oxide (Lloyd and Kipping, J., 1901, **79**, 455). The yields of *cyclo*hexylphenylsilicon dichloride and di*cyclo*hexylphenylsilicyl chloride from the original interaction are exceptionally poor and, although nearly 50% of the phenylsilicon trichloride is unchanged, a very considerable proportion of the crude material consists of liquids of very high b.p. and of an undistilled resinous solid; these by-products, unlike those obtained by Palmer and Kipping (*loc. cit.*), have relatively small hydrogen values and their nature has not been elucidated.

EXPERIMENTAL.

An ethereal solution of the Grignard reagent prepared from Mg (48 g.; 2 atoms) and sufficient (480 g.) *cyclo*hexyl bromide to dissolve it in an atmosphere of N at 0° (yield of Grignard compound, about 50%) is slowly added to well-stirred $PhSiCl_3$ (211 g.; 1 mol.) diluted with 3 vols. of C_6H_6 (Kipping and Murray, J., 1927, 2734); a slight development of heat occurs but very little separation of Mg salt takes place, even after 3—4 hrs.' heating on the water-bath. The solvents are therefore evaporated and the residue is heated at 100° to complete the pptn. The product, when free from combined Mg, is distilled (2—3 mm.). $PhSiCl_3$ (about 100 g.) passes over at 60—70°, di*cyclo*hexyl (about 50 g.) at 80—90°, *cyclo*hexylphenylsilicon dichloride (15—20 g.), together with a small proportion of di*cyclo*hexylphenylsilicyl chloride, at 120—150°, a variable quantity (5—20 g.) of the last-named compound at 170—200°, and a very viscous reddish liquid (10—20 g.) at 200—300°. The residue (30—40 g.) does not boil at 300° (1 mm.) and when cold is a pale yellow resin which has a H value of only about 4 c.c. per g. and contains 3—5% of Cl.

cyclo*Hexylphenylsilicon dichloride*, $C_6H_{11}\cdot SiPhCl_2$, is obtained, by further fractionation of the crude product, as a colourless oil, b. p. 123—125°/ 0·5 mm. and 163—165°/4 mm., which fumes only slightly in moist air, acquires a bluish hue on exposure to light, and distils under atm. pressure with only very slight decomp., but neither the residue nor the distillate gives any appreciable quantity of H with Me_2CO and alkali (Found: Cl, 27·5, 27·6. $C_{12}H_{16}Cl_2Si$ requires Cl, 27·4%).

cyclo*Hexylphenylsilicanediol* passes into solution as its K derivative when the dichloride is dropped slowly into ice-cold 5% KOH aq.; an insol. oil is also formed. The diol, pptd. by acids in a cotton wool-like form (yield, about 80%) from the filtered solution, is washed, and repeatedly crystallised from aq. Me_2CO or from light petroleum containing a little Et_2O (Found: Si, 12·8, 12·9. $C_{12}H_{18}O_2Si$ requires Si, 12·8%). The air-dried cryst. powder melts and then effervesces with loss of H_2O at 123—124° when it is heated fairly rapidly. It is readily sol. in many of the common solvents in the cold and also in warm light petroleum, CS_2, and boiling H_2O.

*Trianhydrotris*cyclo*hexylphenylsilicanediol.* — *cyclo*Hexylphenylsilicanediol readily undergoes condensation. When its aq. solution is heated or its Me_2CO solution is treated with HCl aq., or its solutions in caustic alkalis are warmed, it gives oily mixtures, the components of which could not be isolated. When the diol is heated alone in an open vessel at about 150° for 1 hr., the loss in wt. is greater than that (8·1%) calc. for $1H_2O$, owing to the volatilisation of some organic matter, but the resinous residue affords no cryst. material. On hydrolysis with warm alc. KOH these mixtures of condensation products are almost completely converted into K salts of the diol. A cryst. condensation product was isolated by dissolving the diol in cold AcCl and evaporating the solution at room temp.; the glue-like residue, which was miscible with most of the ordinary organic solvents, including light petroleum, fractionated from aq. EtOH, gave about 10% of cryst. *trianhydrotris*cyclo*hexylphenylsilicanediol*,

m. p. 117—118°, the rest of the material remaining in a glue-like form [Found : C, 70·5; H, 7·8; *M*, in camphor, 500, 560. $(C_6H_{11}\cdot SiPhO)_3$ requires C, 70·5; H, 7·8%; *M*, 613]. This compound is relatively sparingly sol. in cold Me_2CO and EtOH, from which it crystallises in needles, but all other solvents which were tried gave glue-like products. It can be distilled unchanged in small quantities and is hydrolysed by alc. KOH.

*Di*cyclo*hexylphenylsilicyl chloride* is obtained in a practically pure state by fractionating the crude product collected from about 170—200°/2—3 mm.; it has b. p. 188—192°/2 mm. and solidifies in long prisms, but is so readily sol. in light petroleum and other anhydrous solvents that it cannot be recrystallised. Freed from traces of oil on porous earthenware, it melts at 45—48° (Found : Cl, 11·6, 11·6. $C_{18}H_{27}ClSi$ requires Cl, 11·55%). It acquires a purple colour on exposure to light, does not fume perceptibly in moist air, and is only slowly hydrolysed by cold H_2O. It distils without appreciable decomp. under atm. pressure; the very small proportion of residue gives H with Me_2CO and alkali, but has only a very low H value.

*Di*cyclo*hexylphenylsilicol*, prepared by adding aq. alkali to an acetone solution of the preceding compound and then evaporating the organic solvent, quickly solidifies and after being washed and dried separates from Et_2O or light petroleum in large, well-defined, transparent prisms, usually hexagonal in outline; m. p. 145—146° (Found : C, 75·3; H, 9·8; Si, 9·5, 9·6; *M*, in camphor, 270—300, in C_6H_6, 287. $C_{18}H_{28}OSi$ requires C, 74·9; H, 9·6; Si, 9·7%; *M*, 288). It dissolves freely in the cold in all the common organic solvents except light petroleum, but is insol. or nearly so in caustic alkali; it distils without appreciable decomp. When the silicol is boiled with AcCl and the reagent is then distilled, there remains an oil which apparently is a mixture of silicol and silicyl chloride; after having been kept during several days in a vac. over caustic alkali the percentage of Cl in the product indicates the presence of about 68% of the chloride. From boiling Ac_2O the silicol crystallises unchanged.

The silicol could not be converted into the oxide by treating it with alkalis, NaOEt, or alc. HCl; when it was heated during many hrs. with Me_2CO and conc. NaOH aq., it gave traces of matter which was sol. in aq. alkali, owing no doubt to the partial elimination of one of the *cyclo*hexyl groups.

*Di*cyclo*hexylsilicanediol*, $(C_6H_{11})_2Si(OH)_2$.—The insol. oil which is formed when redistilled *cyclo*hexylphenylsilicon dichloride is hydrolysed with KOH aq. is washed with H_2O and dissolved in Me_2CO; the solution very slowly deposits a mixture of crystals and glue-like material. The latter is very readily dissolved by cold $CHCl_3$ and the residue then crystallises from AcOEt or light petroleum in prisms or needles, m. p. 164—165°. The matter sol. in $CHCl_3$ is doubtless a complex mixture of the condensation products of *cyclo*hexylphenylsilicanediol and probably contains also corresponding products of the di*cyclo*hexylsilicanediol. The yield of cryst. *di*cyclo*hexylsilicanediol* is only about 0·1 g. from 10 g. of the impure *cyclo*hexylphenylsilicon dichloride (Found : C, 63·2; H, 10·4; *M*, in AcOH, 226. $C_{12}H_{24}O_2Si$ requires C, 63·1; H, 10·5%; *M*, 228).

Di*cyclo*hexylsilicanediol decomposes with efferv. a few degrees above its m. p., giving glue-like condensation products from which a cryst. substance, m. p. 110°, was isolated but not characterised; it is insol. or nearly so in H_2O and in caustic alkali, sparingly sol. in C_6H_6 and $CHCl_3$, and freely in cold EtOH, Me_2CO, or Et_2O. When it is treated with Br in AcOH at 80—90°, trianhydrotrisdi*cyclo*hexylsilicanediol (m. p. 237—239°) is pptd. within a few mins. and the change seems to be complete.

*Trianhydrotrisdi*cyclo*hexylsilicanediol* is obtained when a solution of di*cyclo*hexylphenylsilicol in hot AcOH is treated with a few drops of conc. HNO_3. The solution becomes brown and in a few mins. the termolecular silicon compound is pptd.: this product is also formed, but not so quickly, when the silicol is boiled with HCl in AcOH. It crystallises from Me_2CO–$CHCl_3$ or C_6H_6–light petroleum in transparent rhomboidal plates, m. p. 237—239° after sintering at about 230° (Found: C, 68·5; H, 10·5; Si, 13·5; *M*, in camphor, 530—550. $C_{36}H_{66}O_3Si_3$ requires C, 68·5; H, 10·5; Si, 13·5%; *M*, 631).

This compound is also produced when Br is added to a warm solution of di*cyclo*hexylphenylsilicol in AcOH, a cryst. ppt. being formed almost immediately. The crude product is a mixture, m. p. 200—205°. A considerable proportion of the main component (about 80% of the mixture) can be isolated by fractional crystn. from C_6H_6 and light petroleum; it is thus obtained in rhomboidal plates identical with those described. The two components in the more sol. fractions are not easily separated except by mechanically sorting the rhomboidal plates from the rectangular crystals in the deposit. Quant. expts. show that in AcOH the decomp. of the tertiary silicol by Br is approximately quantitative. This condensation product is not easily hydrolysed by KOH in aq. Me_2CO or EtOH owing to its slight solubility, but when it is heated with pyridine and KOH aq. it is partly converted into di*cyclo*hexylsilicanediol.

The rectangular crystals sorted from those of trianhydrotrisdi*cyclo*hexylsilicanediol were recryst. from C_6H_6 and from AcOEt–$CHCl_3$. Even after several operations the product did not melt sharply, softening at 280° and melting at about 284°. This substance is probably a crystallographic mixture of trianhydrotris- and tetra-anhydrotetrakis-di*cyclo*hexylsilicanediol analogous to that formed from the two corresponding diphenyl compounds (Kipping, J., 1912, **101**, 2139) {Found: C, 68·5; H, 10·5; *M*, in camphor, 712. $[(C_6H_{11})_2SiO]_4$ requires C, 68·5; H, 10·5%; *M*, 841}.

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