246. *Organic Derivatives of Silicon. Part XLVIII. Steric Effects of the* cyclo*Hexyl Group.*

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The interaction of phenylsilicon trichloride (1 mol.) and *cyclo*hexylmagnesium bromide (1 mol.) (Cusa and Kipping, J., 1932, 2205) led to the formation of much very high-boiling material, but this was a complex mixture of substances containing chlorine and oxygen, and no quaternary hydrocarbon was isolated. Efforts have now been made to prepare tri*cyclo*hexylphenylsilicane by the use of excess of the Grignard reagent, but these were unsuccessful. When no precautions were taken to exclude atmospheric oxygen, the principal product was *cyclo*hexyloxydi*cyclo*hexylphenylsilicane (85—90%), but when the experiment was carried out so far as possible in an atmosphere of nitrogen, there resulted a mixture from which *di*cyclo*hexylphenylsilicane* (40—50%) and cyclo*hexyloxydi*cyclo*hexylphenylsilicane* (15—25%), together with di*cyclo*hexylphenylsilicol and condensation products of *cyclo*hexylphenylsilicanediol, have been isolated.

Dilthey and Edouardoff (*Ber.*, 1904, **37**, 1139) failed to obtain tetraphenylsilicane by the action of an excess of phenylmagnesium bromide on silicon tetrachloride, but this substance is readily produced by the interaction of sodium, chlorobenzene, and silicon tetrachloride in ethereal solution (Polis, *Ber.*, 1885, **18**, 1542); attempts to prepare tri-

*cyclo*hexylphenylsilicane by a similar method failed. It has been found, however, that tetraphenylsilicane is readily produced by the action of phenylmagnesium bromide on silicon tetrachloride or on phenylsilicon trichloride at 160—180°. (Dilthey and Edouardoff, *loc. cit.*, carried out the reaction at 35° and obtained exclusively triphenylsilicol on hydrolysis.)

Now, many other quaternary silicohydrocarbons have been prepared without difficulty with the aid of Grignard reagents (Kipping, J., 1907, **91**, 209, 717; Marsden and Kipping, J., 1908, **93**, 198; Bygden, *Ber.*, 1911, **44**, 2642; 1912, **45**, 709), and the authors have obtained *di*cyclo*hexylphenylethylsilicane* by the action of ethylmagnesium bromide on di*cyclo*hexylphenylsilicyl bromide. It is therefore suggested that failure to prepare tri*cyclo*hexylphenylsilicane is due to steric hindrance. A similar case was recorded by Kipping (J., 1923, **123**, 2598), who found that, although the di-iodide, $Si_4Ph_8I_2$, gives a crystalline diethyl derivative with ethylmagnesium bromide, no corresponding decaphenyl compound is produced by the action of phenylmagnesium bromide.

There is also much evidence from several other sources which indicates that the *cyclo*hexyl group exerts a considerable steric effect. For instance, the action of *cyclo*hexylmagnesium bromide on carbonyl chloride or on hexahydrobenzoic ester gives rise to di- and not to tri-*cyclo*hexylcarbinol (Sabatier and Mailhe, *Compt. rend.*, 1904, **139**, 343; Gray and Marvel, *J. Amer. Chem. Soc.*, 1923, **45**, 2796), and although the hydrogenation of triphenylcarbinol under pressure gives tri*cyclo*hexylmethane, yet no trace of tetra*cyclo*hexylmethane is formed when tetraphenylmethane is treated in the same way (Ipatiew and Dolgow, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1023; 1927, **59**, 1087).

The nitration of phenyl*cyclo*hexane gives an *o*/*p* ratio of 0·61, whereas the corresponding value for diphenyl is 1·13 (Mayes and Turner, J., 1929, 500), a fact which cannot be explained by the theories of aromatic substitution. Le Fèvre (*Nature*, 1933, **131**, 655) has called attention to steric hindrance as an important factor in these problems.

The action of *cyclo*hexylmagnesium bromide on germanium tetrachloride gives tri*cyclo*hexylgermanium chloride, but no tetra*cyclo*hexylgermane can be isolated (Bauer and Burschkies, *Ber.*, 1932, **65**, 956). On the other hand, tetraphenyl-, tetra-*p*-tolyl-, and other quaternary germanes are readily produced by such reactions (Tabern, Orndorff, and Dennis, *J. Amer. Chem. Soc.*, 1925, **47**, 2039). Triphenylgermanium chloride, when hydrolysed, gives rise to the corresponding oxide, the simple germanol being unknown (Morgan and Drew, J., 1925, **127**, 1760); tri*cyclo*hexylgermanium chloride, however, gives the simple germanol and the oxide is unknown (Bauer and Burschkies, *loc. cit.*; cf. di*cyclo*hexylphenylsilicol, Cusa and Kipping, *loc. cit.*).

Tetra*cyclo*hexyltin (Krause and Pohland, *Ber.*, 1924, **57**, 532) and tetra*cyclo*hexyl-lead (Krause, *Ber.*, 1921, **54**, 2060) are formed in poor yields by the action of *cyclo*hexylmagnesium bromide on the tetrachlorides, but the products are relatively unstable.

*cyclo*Hexyloxydi*cyclo*hexylphenylsilicane, $(C_6H_{11})_2SiPh{\cdot}OC_6H_{11}$, unlike phenoxy- (Kipping, J., 1927, 2730) and ethoxy-silicon compounds (Murray and Kipping, *ibid.*, p. 2734), is very stable towards alkalis; it resembles these compounds closely in its other chemical reactions. The formation of this substance in considerable quantities, even when oxygen is excluded so far as possible, may possibly be due to the unavoidable oxidation of the Grignard reagent, a factor the importance of which has recently been emphasised by Goebel and Marvel (*J. Amer. Chem. Soc.*, 1933, **55**, 1693).

The formation of di*cyclo*hexylphenylsilicane, $(C_6H_{11})_2SiPhH$, in the above reaction was entirely unexpected, no corresponding case having been observed in silicon chemistry. Gomberg and Cone (*Ber.*, 1906, **39**, 1461), however, obtained some triphenylmethane by the action of phenylmagnesium bromide on triphenylmethyl chloride. This they ascribed to the formation of triphenylmethylmagnesium bromide, which gave triphenylmethane when treated with water. Although the occurrence of such a reaction has been questioned (Gilman and Jones, *J. Amer. Chem. Soc.*, 1929, **51**, 2841), its assumption seems to be the only satisfactory explanation in the present case.

This substance, unlike triphenyl- (Kipping and Murray, J., 1929, 364) and tribenzylsilicane (Evison and Kipping, J., 1931, 2830), is only very slowly decomposed by alkalis, with evolution of hydrogen. According to Taurke, however (*Ber.*, 1905, **38**, 1665), tri*iso*-amylsilicane is not attacked by aqueous potassium hydroxide.

*Di*cyclo*hexylphenylethylsilicane*, $SiEtPh(C_6H_{11})_2$, when treated with bromine in glacial acetic acid solution, gives rise to ethyl bromide, bromobenzene, and an oil which apparently consists of a mixture of condensation products of di*cyclo*hexylsilicanediol. The stability of the Si–C_6H_{11} linkage towards bromine is not, therefore, a general property of aliphatic, as opposed to aromatic, groups.

EXPERIMENTAL.

cyclo*Hexyloxydi*cyclo*hexylphenylsilicane*.—Phenylsilicon trichloride (10 g.) is added to an ethereal solution of *cyclo*hexylmagnesium bromide (prepared from 100 g. of *cyclo*hexyl bromide), and the mixture heated under reflux for 1 hour; the ether is then evaporated, and the residue heated at 160—180° for a further 3—4 hours. The product, after treatment with dilute hydrochloric acid, is steam-distilled to expel di*cyclo*hexyl and then distilled in a vacuum. The fraction, b. p. 180—220°/0·5 mm. (15 g.), solidifies when cooled, and is freed from traces of oily matter by recrystallisation at 0° from aqueous acetone.

A colourless, crystalline solid, m. p. 103—104°, is thus isolated, which is readily soluble in all the common solvents with the exception of alcohol, acetone, and acetic acid in the cold. It crystallises in large, transparent, hexagonal prisms (Found: C, 78·0, 78·1; H, 10·3, 10·2; *M*, cryoscopic in benzene, 371. $C_{24}H_{38}OSi$ requires C, 77·9; H, 10·3%; *M*, 370). When treated with bromine or with hydrogen bromide in acetic acid, this *substance* is converted into trianhydrotrisdi*cyclo*hexylsilicanediol (Cusa and Kipping, *loc. cit.*), m. p. 237—239°, and when heated in acetyl or benzoyl chloride solution during 30 mins., and the product hydrolysed, it affords di*cyclo*hexylphenylsilicol, m. p. 146°; these reactions serve to establish its constitution. When heated during an hour with acetone and 5% aqueous potassium hydroxide, *cyclo*hexyloxydi*cyclo*hexylphenylsilicane is unchanged.

*Di*cyclo*hexylphenylsilicane*.—Phenylsilicon trichloride (50 g.) is treated with a large excess of *cyclo*hexylmagnesium bromide (from 500 g. of *cyclo*hexyl bromide) under the conditions described above, except that this operation and the preparation of the Grignard reagent are carried out in an atmosphere of dry nitrogen.* The product, after decomposition with dilute hydrochloric acid, is extracted with ether, dried, and distilled under 8 mm. Di*cyclo*hexyl (200 g.) passes over below 120°, and the temperature then rises rapidly to 190°; the fraction, b. p. 190—230°, consists principally of di*cyclo*hexylphenylsilicane (40 g.); that of b. p. 230—260° (20 g.) solidifies when cooled, and consists of *cyclo*hexyloxydi*cyclo*hexylphenylsilicane. A small fraction (10 g.) distils at 260—330° and contains di*cyclo*hexylphenylsilicol and condensation products of *cyclo*hexylphenylsilicanediol.

In order completely to separate di*cyclo*hexylphenylsilicane from the *cyclo*hexyloxy-compound, repeated fractionation is necessary. After many distillations, a fraction of b. p. 180—185°/4 mm. can be isolated which is practically pure (Found: C, 79·5; H, 10·5; Si, 10·1; H.V.† 76·2. $C_{18}H_{28}Si$ requires C, 79·3; H, 10·3; Si, 10·3%; H.V., 82). *Di*cyclo*hexylphenylsilicane* is an oily liquid with a pleasant odour, which does not solidify when cooled in a freezing mixture or when kept at 0° for many weeks. It is miscible with all the common solvents with the exception of alcohol and acetic acid in the cold, and can be distilled under atmospheric pressure without decomposition (b. p. 340—345°). When treated with 20% aqueous potassium hydroxide and an organic solvent (acetone, alcohol, pyridine, or piperidine), it is *very* slowly decomposed, giving di*cyclo*hexylphenylsilicol with evolution of hydrogen.

Di*cyclo*hexylphenylsilicane can be readily converted into the silicol by the action of oxidising agents, *e.g.*, ammoniacal silver nitrate or potassium permanganate in acetic acid. It reacts instantly with bromine in carbon tetrachloride solution with evolution of hydrogen bromide, giving rise to di*cyclo*hexylphenylsilicyl bromide (not isolated in the crystalline condition) which yields di*cyclo*hexylphenylsilicol when hydrolysed. As this reaction takes place rapidly in the cold (conditions under which fission of the Si–Ph linkage by bromine takes place only very slowly),

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* Commercial nitrogen which has been passed through alkaline pyrogallol (two bottles), alkaline sodium hydrosulphite (two bottles), concentrated sulphuric acid (two bottles), and finally up a tower containing calcium chloride.

† H.V. = hydrogen value, *i.e.*, volume of hydrogen in c.c. liberated per g. of substance on treatment with bases and an organic solvent (see Kipping and Sands, J., 1921, **119**, 848). This low experimental value may be attributed to the occurrence of atmospheric oxidation during the prolonged treatment which is necessary.

di*cyclo*hexylphenylsilicane can be conveniently estimated by titration with bromine in carbon tetrachloride solution by using either starch–iodide paper externally or, more accurately, by adding an excess of halogen and back-titrating. In this way the fraction of b. p. 180—185°/4 mm. was found to contain 98·7% of di*cyclo*hexylphenylsilicane.

This silicane does not react readily with iodine in solution, but when the two substances are warmed together without a solvent, hydrogen iodide is evolved and the dark, sticky product, when hydrolysed, gives di*cyclo*hexylphenylsilicol.

*Di*cyclo*hexylphenylethylsilicane.*—The above silicane (5 g.) is dissolved in light petroleum, and a solution of dry bromine in the same solvent is added in slight excess. The solvent is then distilled, and the oily residue heated to expel hydrogen bromide; ethylmagnesium bromide in excess is then added, and the mixture heated under reflux for 1 hour. There being no separation of magnesium halide, the ether is distilled, and the residue heated at 160—180° for 3 hours. The product is decomposed with ice–water, a little hydrochloric acid added, and the whole extracted with ether, washed, dried, and distilled under atmospheric pressure. The resulting liquid (b. p. *ca.* 370°) is colourless when freshly distilled but rapidly acquires a greenish fluorescence when exposed to light. It is miscible with most of the common solvents with the exception of alcohol and acetic acid (Found : C, 80·3; H, 10·7; Si, 9·3. $C_{20}H_{32}Si$ requires C, 80·0; H, 10·7; Si, 9·3%).

When this *di*cyclo*hexylphenylethylsilicane* is heated with an excess of bromine in acetic acid for 2—3 mins., the product being neutralised with 20% aqueous potassium hydroxide and then steam-distilled, ethyl bromide and bromobenzene pass over and the residual oil consists of a mixture of condensation products of di*cyclo*hexylsilicanediol (Found : C, 68·4; H, 10·3. Calc. for $C_{12}H_{22}OSi$: C, 68·6; H, 10·5%).

Preparation of Tetraphenylsilicane.—Silicon tetrachloride (5 g.; 1 mol.) is added to an ethereal solution of phenylmagnesium bromide from 20 g. of bromobenzene (*ca.* 4·5 mols.). The mixture is heated under reflux for 1 hour, the ether being then distilled, and the residue heated at 160—180° for 3—4 hours. The product, decomposed with dilute hydrochloric acid, is steam-distilled to expel diphenyl, and the pasty residue is extracted with acetone, which removes small quantities of triphenylsilicol and the other by-products. The remainder (6—7 g.) is completely soluble in hot benzene, from which it crystallises in small, glistening needles, m. p. 233—234°, identical with tetraphenylsilicane produced by Polis's method (*loc. cit.*).

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