XVII.—*Organic Derivatives of Silicon. Part XXXII. The Carbon–Silicon Binding.*

By FREDERIC STANLEY KIPPING.

FRESH evidence is continually being obtained by the author that an ethylenic binding between carbon and silicon is either impossible or can only be produced under exceptional conditions. Those reactions which lead to the formation of an olefine seem to be quite inapplicable to the production of the group $>Si{:}C<$.

The loss of one molecule of water from one molecule of a tertiary silicol, $R_2Si(OH){\cdot}CH_2R$, is an unknown change; under conditions which have not yet been fully investigated, such silicon compounds, instead of giving $R_2Si{:}CHR$, pass into the corresponding oxides, $(R_2Si{\cdot}CH_2R)_2O$, as, for example, in the cases of benzylethylpropylsilicol, $SiEtPr(CH_2Ph){\cdot}OH$, and phenyldiethylsilicol, $SiEt_2Ph{\cdot}OH$. Many tertiary alcohols, on the other hand, are readily converted into olefines without any production of the corresponding ether.

Again, the loss of halogen acid from the molecule of a chloride, $R_2SiCl{\cdot}CH_2R$, has never been observed; such compounds can be distilled at relatively high temperatures without appreciable decomposition, as, for example, phenylethylpropylsilicyl chloride and tribenzylsilicyl chloride. This behaviour may be contrasted with that of many analogous carbon compounds which lose a molecule of halogen acid very readily, giving olefines; $CMeEt(CH_2Ph)Br$, for example, cannot be distilled even under low pressure. Similarly, many dichloro-derivatives, R_2SiCl_2, such as dibenzylsilicon dichloride distil at relatively high temperatures without decomposing.

The formation of an unsaturated compound by the action of a Grignard reagent on a tertiary silicyl chloride is also unknown; it has been proved in very many cases that a normal reaction occurs with the formation of a quaternary silicane, and, although by-products are nearly always obtained, these are substances of high boiling point; it is, of course, possible that these by-products are formed by the polymerisation of compounds containing the $Si{:}C$ binding, but no evidence of this has been recorded. Many tertiary halogen derivatives, on the other hand, give rise to olefines (Trotman, J., 1925, **127**, 88) so readily that the formation of a saturated quaternary hydrocarbon either does not take place, or it does so only to a very limited extent.

Experiments with the direct object of producing the group $>Si{:}C<$ seem to have been recorded in one instance only. Schlenk and Renning (*Annalen*, 1912, **394**, 221) treated silicon tetrachloride with magnesium phenyl bromide (2 mols.) in order to form diphenyldichlorosilicane, and then heated the crude product with magnesium methyl iodide (1 mol.) in order to obtain diphenylmethylchlorosilicane; afterwards they decomposed this chloride with water and obtained by distillation a liquid boiling at 266—268°/72 mm. From the results of one combustion and a molecular-weight determination they assigned to this liquid the constitution $SiPh_2{:}CH_2$, although it did not react with bromine or with alkaline permanganate.

Now the known behaviour of certain pure silicols of an analogous structure (see above) casts grave doubt on this supposed conversion of diphenylmethylsilicol into an unsaturated compound.

Further, it is the author's experience that when silicon tetrachloride is treated with magnesium phenyl bromide (2—2½ mols.) the product is always a mixture, no matter how slowly the Grignard reagent is added, or whatever other precautions are taken to ensure the formation of the desired substance only. Consequently, since Schlenk and Renning did not purify either the dichloride, $SiPh_2Cl_2$, or the monochloride, $SiPh_2MeCl$, the final crude product must have been a complex mixture of silicon compounds (with diphenyl), from which it would be no easy task to isolate any component.

Schlenk and Renning's experiments have therefore been repeated, but all endeavours have failed to afford the slightest confirmation of their results.

Further attempts to prepare a compound containing the $>Si{:}C<$ group were then made; tribenzylsilicyl chloride was heated with quinoline or with dimethylaniline with the object of eliminating hydrogen chloride; apparently, however, no such change took place. Tribenzylsilicol, as was previously shown (J., 1909, **95**, 308), is unchanged when it is heated with acetic anhydride; further attempts to convert it into an unsaturated compound by heating it with phosphoric oxide or with zinc chloride have likewise given negative results.

EXPERIMENTAL.

To a solution of purified diphenyldichlorosilicane in ether (5 vols.) an ethereal solution of magnesium methyl iodide (1 mol.) was gradually added. There was very little heat developed, and no deposition of magnesium salt occurred, but after some time the liquid had separated into two liquid layers. The next day the ether was distilled, and the residue heated at about 120° during 2 hours; the magnesium salt had then become crystalline. The silicon compound was extracted from the magnesium salt in the usual way in the absence of moisture and was distilled (25 mm.) without fractionating in order to get rid of magnesium salt; a small proportion of a liquid of high boiling point remained in the residue. The whole distillate was then fractionated (45 mm.); it began to boil at 170°, and from 170° to 185° a large fraction was collected. From 185° to 195° very little came over, but above this temperature a considerable proportion of diphenyldichlorosilicane was collected. The fractions 170—185° and 185—200° were separately redistilled many times, but no liquid of constant boiling point could be obtained. Analyses indicated that the portion boiling at 175—180° consisted chiefly of diphenyldimethylsilicane with some diphenylmethylsilicyl chloride; the latter compound was contained principally in the fraction 180—195°, a colourless, mobile liquid which fumed slightly in moist air.

In order to obtain a silicol the very impure chloride was diluted with light petroleum and shaken with either water or potassium hydroxide solution. The product distilled mainly from about 170—190° (45 mm.), and a little passed over up to about 210°, leaving a very small proportion of liquid of high boiling point, which was probably the oxide, but which could not be obtained in crystals; all attempts to isolate from the main fraction either the pure silicol or the unsaturated compound described by Schlenk and Renning were unsuccessful, and every time the liquid was distilled a very small proportion of the residue of high boiling point was formed. The combined fractions were then repeatedly distilled very slowly under atmospheric pressure; during each operation water was formed and a substance (the oxide) of high boiling point; after five such treatments, the distillate having been dried after each, the whole was put back on to the residue and the liquid was heated just below its boiling point during about 2 hours. Water was again formed and removed. Finally, the liquid was distilled (45 mm.); about 80% of the original preparation passed over from 165—185° and the thermometer then rose very rapidly to about 270°, above which temperature a thick, yellow oil was collected. The lower fraction did not decolorise a dilute chloroform solution of bromine, or an aqueous solution of permanganate; these facts, also observed by Schlenk and Renning with their preparation, afford strong evidence of the absence of unsaturated compounds. The higher fraction slowly deposited crystals of *diphenylmethylsilicyl oxide*, $(SiMePh_2)_2O$, which, freed from oil on porous earthenware, separated from cold alcohol in plates having the outline of a regular hexagon, or of a rhomb, and melting at 51—52° (Found: Si, 13·7. $C_{26}H_{26}OSi_2$ requires Si, 13·7%). This oxide is very readily soluble in ether, light petroleum (b. p. 50—60°), acetone, and other common solvents, from which it usually separates as an oil; it is only sparingly soluble in cold alcohol.

These results show that diphenylmethylsilicol is only very slowly decomposed when it is heated at its boiling point, and that, like other silicols of a similar type, it then gives the oxide. Schlenk and Renning's product, obtained apparently after one distillation only, was doubtless a mixture of diphenyldimethylsilicane, diphenylmethylsilicol, and probably diphenyl, and the results of their single analysis can scarcely establish the existence of a compound containing the $>Si{:}C<$ binding.

A pure specimen of *diphenyldimethylsilicane*, $SiMe_2Ph_2$, was prepared by treating diphenyldichlorosilicane with an excess of magnesium methyl iodide in ethereal solution, and then heating the residue at 150°; after cooling and addition of water, the silicon compound separated as an oil, and, on distillation, was obtained as a colourless, fairly mobile liquid with a faint aromatic odour, b. p. 176—178°/45 mm., and miscible with all organic solvents. It was not easy to estimate the silicon in this compound in the usual way, even using bromine or nitric acid in addition to sulphuric acid, all the results being low; good results, however, were obtained on combustion (Found: C, 79·0; H, 7·6. $C_{14}H_{16}Si$ requires C, 79·2; H, 7·5%).

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, November* 20*th*, 1926.]