# CCCLXXXIV.—*Organic Derivatives of Silicon. Part XLV. The Fission of Aromatic* Si—R *Links by Aluminium Chloride.*

By Walter Eric Evison and Frederic Stanley Kipping.

With the object of working out a general method for the production of alkyl derivatives of aromatic silicon compounds, the Friedel and Crafts reaction was tried with diphenylsilicon dichloride.

Aluminium chloride dissolves in the dichloride, giving a red solution, but no evolution of halogen acid occurs even at about 100°. On the addition of ethyl bromide, a reaction starts at the ordinary temperature, and when heat is applied halogen acid is rapidly evolved. Alkyl derivatives of the dichloride are not obtained; the products are silicon tetrachloride, phenylsilicon trichloride, and ethyl derivatives of benzene. Since diphenylsilicon dichloride is stable towards hydrogen chloride at 200°, it was inferred that the dichloride had reacted with the aluminium chloride as follows:

$$\mathrm{SiPh_2Cl_2 + AlCl_3 = PhAlCl_2 + SiPhCl_3;}$$
$$\mathrm{SiPhCl_3 + AlCl_3 = PhAlCl_2 + SiCl_4.}$$

Further experiments confirmed this view. Diphenylsilicon dichloride, heated alone with aluminium chloride at about 70°, gives silicon tetrachloride and a solid, which is decomposed by water, with the formation of benzene and basic aluminium salts, and which, after it has been well washed with light petroleum, gives acetophenone when it is treated with acetyl chloride and then with water.

Other phenyl derivatives of silicon are decomposed by aluminium chloride, probably in an analogous manner. Tetraphenylsilicane, in chloroform solution, is decomposed at the ordinary temperature; at about 50° during 30 minutes at least 80% of the silicon in the original compound is converted into silicon tetrachloride.

Octaphenyl*cyclo*silicotetrane under like conditions is also attacked by aluminium chloride at the ordinary temperature and when the filtered solution is treated with water, it gives a solid, most of which is insoluble in organic solvents. It was hoped that this solid might be an octahydroxy*cyclo*silicotetrane, $\mathrm{Si_4(OH)_8}$, formed by the hydrolysis of an octachloro*cyclo*silicotetrane, but its low hydrogen value indicated that Si·Si links had been severed with the formation, possibly, of silico-oxalic acid.

Trianhydrotrisdiphenylsilicanediol in chloroform solution gives silicon tetrachloride at the ordinary temperature, the oxygen atoms in the Si·O·Si groups being also displaced by chlorine, but a great deal of charring occurs.

The $\mathrm{Si{\cdot}CH_2Ph}$ link also undergoes fission by aluminium chloride, tetrabenzylsilicane giving silicon tetrachloride even at the ordinary temperature.

## EXPERIMENTAL.

*Diphenylsilicon Dichloride, Ethyl Bromide, and Aluminium Chloride.*—Diphenylsilicon dichloride (20 g.; 1 mol.) was treated with anhydrous aluminium chloride (10·5 g.; 1 mol.), which dissolved completely, giving a dark red viscous liquid. Ethyl bromide (40 g.; 5 mols.) was then added in five equal portions in the course of 2 days. The first and the second portion caused a considerable development of heat and a brisk evolution of hydrogen bromide, but the later ones did not cause any notable rise in temperature or other sign of a reaction. The mixture was afterwards warmed gently until the evolution of halogen acid, containing probably some silicon tetrachloride, had ceased; the total amount of the acid, collected in water, was approximately only 2½ mols., although the whole of the ethyl bromide had been changed. This result, and the fact that most of the hydrogen bromide is evolved during the addition of the first 2 mols. of ethyl bromide, seem to show that the supposed phenylaluminium dichloride is converted into ethyl derivatives, which are decomposed by hydrogen bromide during the later stages of the reaction.

The main product had gradually separated into two layers in the course of the reaction; the upper one was colourless and fumed strongly; the lower one was a very viscous, dark red liquid. The upper layer, decanted, began to boil at about 70° and four fractions were collected up to 185°/760 mm.; two others were collected from 100° to 130°/45 mm. Each fraction was separately treated with water; an examination of the products proved that the first four fractions consisted of silicon tetrachloride mixed with an oil which was free from halogen; the two higher fractions consisted of a similar oil, mixed with a small proportion of phenylsilicon trichloride. The lower, dark red layer, treated with water, gave a little silica and phenylsiliconic acid and an oil similar to the products referred to above. The combined portions of oil boiled from 140° to 220° and doubtless consisted of various ethyl derivatives of benzene; the fraction of lowest b. p. on prolonged oxidation with nitric acid afforded benzoic acid, and a higher fraction with alkaline permanganate gave what seemed to be a mixture of benzenedicarboxylic acids.

Attempts to prepare ethyl derivatives of diphenylsilicon dichloride by this method, but using a very small proportion of aluminium chloride, were unsuccessful.

*Diphenylsilicon Dichloride and Aluminium Chloride.*—Diphenylsilicon dichloride (10 g.; 1 mol.) was treated with aluminium chloride (15 g.; 3 mols.), most of which dissolved, giving a dark red solution, but no evolution of halogen acid occurred. At 70° the mixture began to fume and in the course of about an hour drops of a colourless liquid, which gradually increased in quantity, condensed in the upper portions of the reaction flask. The liquid, decanted from the pasty or solid matter, distilled between 60° and 80° and was proved to be silicon tetrachloride. The residue in the reaction flask, treated with ice, gave an oil, b. p. 70—90°, which proved to be benzene.

Diphenylsilicon dichloride (15 g.) was warmed with aluminium chloride (20 g.) at 70° during about 1 hour only. Light petroleum free from aromatic hydrocarbons was then added, the clear solution decanted, and the residue well washed with light petroleum. This residue, cooled in ice, was treated with acetyl chloride at the ordinary temperature; after 1 hour the solution was poured on ice; the yellow oil which separated was proved to be acetophenone.

*Tetraphenylsilicane and Aluminium Trichloride.*—Tetraphenylsilicane, dissolved in chloroform, was treated with aluminium chloride (about 4½ mols.) and after 12 hours the yellowish-brown solution was distilled on a water-bath. The distillate contained silicon tetrachloride and the weight of silica obtained from it showed that about 80% of the tetraphenylsilicane had been converted into the tetrachloride. The residue in the flask, with water, gave a small quantity of a yellow glue-like solid, probably phenylsiliconic acid, and an appreciable quantity of what seemed to be carbon.

*Octaphenyl*cyclo*silicotetrane and Aluminium Chloride.*—Octaphenyl*cyclo*silicotetrane (Kipping and Sands, J., 1921, **119**, 830), dissolved in chloroform, was treated with aluminium chloride (8½ mols.), and the mixture left during 24 hours at the ordinary temperature. The dark brown solution was then decanted, the residue washed with chloroform, and the combined filtered solutions poured on ice. The yellow pasty product which was precipitated, washed with acetone and with benzene, afforded a yellow powder, the weight of which, when air-dried, was about 25% of that of the silicohydrocarbon used. This product, dried at 130°, charred to some extent when ignited with sulphuric acid and gave 71% of silica; it evolved hydrogen with alkali in the cold and gave a hydrogen value (c.c. per g.) of 144, but as nearly 50% of the powder did not dissolve, it must have contained some compound having a much higher hydrogen value than that of silico-oxalic acid (H.V. 184). As it was evident that Si·Si links had undergone fission, and that in addition a great deal of charring had occurred, no further attempts to prepare the hydroxide, $Si_4(OH)_8$, were made.

*Trianhydrotrisdiphenylsilicanediol and Aluminium Chloride.*—The silicon compound, $(SiPh_2O)_3$, dissolved in chloroform, was treated with rather more than 6 mols. of aluminium chloride. The solution became red but no other change was noted. The mixture was left for a few days at the ordinary temperature, during which time it turned black, and the decanted chloroform solution was then distilled; the distillate fumed strongly and gave silica with water and also a glue-like product soluble in aqueous alkali which no doubt was phenylsiliconic acid. The residue from which the chloroform solution had been decanted contained a considerable quantity of what seemed to be carbon.

*Tetrabenzylsilicane and Aluminium Chloride.*—The silicohydrocarbon, dissolved in chloroform and treated with more than 4 mols. of aluminium chloride, gave a deep red solution which soon began to fume strongly. After 12 hours, the solution, decanted and distilled, gave a considerable proportion of silicon tetrachloride. No tetrabenzylsilicane could be isolated from the residue from which the chloroform had been distilled.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 29th,* 1931.]