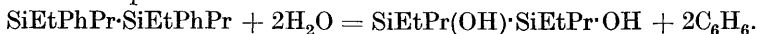


LXIX.—*Organic Derivatives of Silicon. Part XXIV.*
dl-Derivatives of Silicoethane.

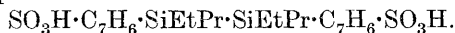
By FREDERIC STANLEY KIPPING.

THE study of the action of sodium on certain mono- and di-halogen derivatives of silicohydrocarbons was commenced some ten years ago, and it was then found that hexaphenylsilicoethane, Si_2Ph_6 , could be obtained from phenylsilicon trichloride, whereas phenylethylsilicon dichloride (T., 1907, 91, 215) gave a product which seemed to be the unsaturated compound, $\text{SiEtPh}:\text{SiEtPh}$ (P., 1911, 27, 143). These observations pointed to the possibility of utilising reactions of this nature for the investigation of organic derivatives of silicon in various directions, and in 1914 further experiments were made with phenylethylpropylsilicyl chloride (T., *loc. cit.*, p. 218), benzylethylpropylsilicyl chloride (T., *loc. cit.*, p. 723), diphenyldichlorosilicane (T., 1912, 101, 2113) and other compounds.

From the first two of these chlorides, the silicohydrocarbons *dl-diphenyldiethylpropylsilicoethane* and *dl-dibenzyl-diethylpropylsilicoethane* were respectively prepared, although the reactions did not take place quantitatively by any means. These two derivatives of silicoethane, $\text{SiH}_3\cdot\text{SiH}_3$, were found to have the general characters of silicohydrocarbons of the type SiR_4 . Thus, they are both colourless liquids at ordinary temperatures, give normal molecular-weight results by the cryoscopic method in benzene solution, and, in small quantities, can be distilled under atmospheric pressure without their undergoing appreciable decomposition. Although their molecules contain linked silicon atoms, both silicohydrocarbons are attacked only very slowly, if at all, by boiling aqueous alkalis, and even when they are warmed with a solution of sodium methoxide in methyl alcohol or acetone, no rapid evolution of hydrogen is observed. It is obvious, therefore, that the grouping $:\text{Si}:\text{Si}:$ is not necessarily unstable towards alkalis and that whether the silicon atoms become separated or not is determined by the nature of the atoms or groups with which they are combined. The behaviour of the two silicohydrocarbons towards concentrated sulphuric acid is widely different, and exactly what might have been anticipated from previous observations with derivatives of silicane. The diphenyl compound, like phenylbenzylethylpropylsilicane (T., 1907, 91, 223), is readily decomposed by the acid, the phenyl group being eliminated as benzene, doubtless in accordance with the equation



The dibenzyl derivative, on the other hand, is sulphonated with very great readiness, just as is benzylethylpropylsilicol (T., 1907, 91, 727) and is no doubt converted into a mixture of the optically isomeric disulphonic acids of the constitution



The preparation of these acids was the most important initial object of this work, because, since the two compounds thus obtained should be optically analogous to *dl*-tartaric acid and *i*-tartaric acid respectively, it was hoped that they could be separated from one another and the *dl*-compound then resolved into its optically active components.

The experiments, however, were not carried further than to show that, from the product of sulphonation, it was possible to obtain brucine and *l*-menthylamine salts of a disulphonic acid of the composition given above. Whether these salts were derivatives of the *dl*- or of the *i*-acid, or even mixtures of the two, was not established. As it will take some time to prepare the material and to make the more extended investigation of these acids which the author has in view, the publication of the results obtained some years ago seems to be desirable.

EXPERIMENTAL.

dl-Diphenyldiethyldiethylpropylsilicoethane, SiEtPrPh SiEtPrPh.

A freshly distilled sample of phenylethylpropylsilicyl chloride (T., 1907, 91, 218) which boiled at about 176–180°/100 mm., was diluted with an approximately equal volume of dried xylene, and a slight excess of the theoretical quantity of sodium added to the solution. No visible reaction occurred until the liquid was heated at its boiling point; the metal then became coated with a blue film, which gradually changed into an almost colourless layer of sodium chloride. The liquid was vigorously shaken from time to time, to detach the crust of sodium chloride from the globules, and after having been boiled intermittently during about twenty hours, a portion of the clear solution was found to be free from combined halogen. The solution was then filtered, the residue washed with a little xylene, and the combined filtrate and washings submitted to distillation.

After most of the xylene had passed over, the pressure was reduced to 50 mm. and the following fractions were collected : 1. A portion which passed over between 165° and 225°, and which formed about 20 per cent. of the whole. 2. A slightly fluorescent liquid collected between 225° and 275°, which formed about 60 per cent. of the whole. 3. A viscous, yellow, oily residue.

The experiment was repeated with another sample of the chloride, but again the crude product distilled over a wide range of temperature, and gave fractions substantially the same as before.

From the two main portions (225—275°/50 mm.), by further fractionation under reduced pressure, there was ultimately obtained a colourless liquid boiling at 265—270°/100 mm. This preparation seemed to be a satisfactory specimen of diphenyldiethyldipropylsilicoethane (Found: C = 74.0; H = 9.6; Si = 16.1, 16.0. $C_{22}H_{34}Si_2$ requires C = 74.4; H = 9.7; Si = 15.9 per cent. Cryoscopic determinations in benzene solution gave $M. = 339, 341$. Calc., $M. = 354$.)

The yield of this substance was barely 50 per cent. of the theoretical, and the behaviour of the crude product on distillation was that of a complex mixture. This may have been due to the presence of phenylethylsilicon dichloride and phenylethyldipropylsilicane in the samples of phenylethylpropylsilicyl chloride which were employed, as the preparation of the last-named compound in a state of purity is a matter of considerable difficulty (T., 1907, **91**, 219). It is possible, on the other hand, that the action of the sodium on the monochloride is not restricted to the simple elimination of halogen, as is indicated by the results described below.

dl-Diphenyldiethyldipropylsilicoethane is a rather viscous liquid having a faint pleasant aromatic odour; it is specifically lighter than water and only very slightly volatile in steam. It is sparingly soluble in cold methyl alcohol, but dissolves much more freely in the hot liquid, and it is miscible with acetone and most of the common organic solvents in all proportions. It is readily attacked by bromine water, giving a heavy, volatile oil, which is no doubt bromobenzene, and a non-volatile product, which is probably formed by the condensation of dihydroxydiethyldipropylsilicoethane. It is also rapidly decomposed by concentrated sulphuric acid at 100° with evolution of benzene, in which respect it resembles other silicohydrocarbon derivatives which contain a phenyl group. Unlike most of those compounds which contain silicon atoms in direct combination, diphenyldiethyldipropylsilicoethane seems to be very stable towards hot solutions of alkali hydroxides; this is probably due to some extent to its insolubility in the aqueous solutions, but even when it is warmed with a solution of sodium ethoxide in aqueous acetone, no appreciable evolution of hydrogen is observed.

dl-Dibenzyl-diethyldipropylsilicoethane, $SiEtPr(C_7H_7) \cdot SiEtPr \cdot C_7H_7$.

This compound was prepared from benzylethylpropylsilicyl chloride (T., 1907, **91**, 722) in substantially the same way as the

silicohydrocarbon just described; after having been boiled during about ten hours, the xylene solution gave no reaction for combined halogen.

The crude product seemed to be a complex mixture, and when distilled (30 mm.) about 30 per cent. of the whole passed over between about 135° and 160°. The temperature then rose rapidly and a large fraction (about 55 per cent.) was collected between 160° and 240°, most of which boiled fairly steadily in the neighbourhood of 240°; above this temperature the thermometer again rose rapidly, and about ten per cent. passed over between 240° and 300°, leaving about 5 per cent. of a dark brown residue.

Further fractionation showed that the portion collected from 135° to 160° contained a considerable proportion of dibenzyl, whereas the main product of the reaction consisted principally of a liquid boiling from 240° to 250° (20 mm.). The latter was again distilled and separated into two portions, boiling at 240—244° and 244—248° respectively (20 mm.).

Both these samples seemed to consist of almost pure dibenzyl-diethyldipropylsilicoethane (Found: fraction 240—244°, C = 74·7; H = 9·8; Si = 14·2; fraction 244—248°, C = 75·2; H = 10·0; Si = 14·6. $C_{24}H_{38}Si_2$ requires C = 75·2; H = 10·0; Si = 14·5 per cent. Cryoscopic determinations in benzene solution gave M. = 340 [fraction 240—244°] and M. = 362 [fraction 244—248°]. Calc., M. = 380).

These results indicate that the sample boiling at 244—248°/20 mm. was the better sample, and the true boiling point of the compound is probably within these limits.

Since the benzylethylpropylsiliclyl chloride which was used in the above described experiment was prepared from benzylethylsilicon dichloride and the latter is easily obtained almost free from dibenzyl, the isolation of a considerable quantity of this hydrocarbon seemed to show that its formation had taken place during the interaction of the metal and the monochloride.

dl-Dibenzyl-diethyldipropylsilicoethane is a colourless, moderately mobile liquid having a faint, pleasant smell, and is specifically lighter than water. It is only sparingly soluble in cold methyl alcohol, but is miscible with most of the common organic solvents. Like the compound described above, it is relatively very stable towards aqueous solutions of the alkali hydroxides, and even when it is warmed with a methyl-alcoholic solution of sodium methoxide there is no sign of the evolution of gas. It does not immediately decolorise a dilute solution of bromine in carbon tetrachloride, but after some time the colour is discharged and the solution begins to fume. It is not oxidised to any appreciable

extent when it is left in contact with an acidified solution of potassium dichromate.

Sulphonation of dl-Dibenzyl-diethyl-di-propyl-silicoethane.

A small quantity of the silicohydrocarbon shaken with concentrated sulphuric acid formed a pale yellow emulsion, but when gently warmed on a water-bath during five to ten minutes, this emulsion gave a solution which dissolved completely in cold water. The dilute aqueous solution of the product, neutralised with ammonia, gave on the addition of an aqueous solution of brucine hydrochloride a colourless, pasty precipitate, which, after having been roughly dried, separated from acetone in colourless needles.

A larger quantity of the silicohydrocarbon was shaken with about 3 volumes of concentrated sulphuric acid, and the emulsion left at the ordinary temperature; after some hours, a portion of the liquid, poured into about 10 volumes of water, gave a perfectly clear solution. Like many of the sulphonic acids of silicohydrocarbons, however, the acid was only sparingly soluble in dilute sulphuric acid, and separated as an oil when larger quantities of the sulphonation product were added to a relatively small volume of water. This oil dissolved completely on the addition of a solution of ammonium hydroxide, but when the solution was of a certain concentration, the ammonium salt separated as an oily layer from the aqueous solution of ammonium sulphate.

On the addition of a solution of brucine hydrochloride in slight excess to the neutral solution of the ammonium salt, a pasty, brucine salt was precipitated as before. This precipitate, when dried, was freely soluble in cold acetone, but it could not be obtained in crystals from the solution.

As it was possible that the altered conditions of sulphonation might have given a product different from the first one—an ortho-instead of a para-sulphonic derivative, for example—the first experiment was repeated with a fresh quantity of the silicohydrocarbon, but again the brucine salt was readily soluble in cold acetone and did not separate from the solution in a crystalline form.

The brucine salt from the last two experiments, when fractionally precipitated from its solution in hot chloroform by the addition of benzene, gave a powdery but somewhat gelatinous product, which was no longer readily and completely soluble in acetone. The portion which was insoluble or sparingly soluble in this liquid was further fractionated from a mixture of chloroform, benzene, and acetone, and finally obtained as a colourless powder.

This preparation seemed to be the brucine salt of the disulphonic

acid. An air-dried sample lost 5.1 per cent. of water at 100°, and the anhydrous salt gave Si = 4.0 per cent. The formula $\text{SiEtPr}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, $2\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2\cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 5.1$ per cent. and the anhydrous salt, Si = 4.3 per cent.

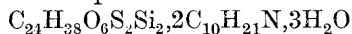
The anhydrous salt was hygroscopic and on exposure to the air seemed to take up $2\text{H}_2\text{O}$.

l-Menthylamine Salt of the Disulphonic Acid.

As the later preparations of the brucine salt did not crystallise well, an aqueous solution of the ammonium salt was treated with an aqueous solution of *l*-menthylamine hydrochloride until no further precipitate was formed. The pasty product was separated by filtration and washed with water, and then some methyl alcohol was poured on the wet filter containing the wet substance. The first portion of the clear solution which came through deposited beautiful, lustrous crystals, but as filtration continued, these became pasty before the operation had been completed, and the addition of water to the filtrate only precipitated a further quantity of a pasty solid. Unfortunately, these lustrous crystals were not obtained again; their precipitation at one stage of the filtration was probably due to the accidental production of a suitable concentration of aqueous methyl alcohol, which may have brought about a separation of the salts of the *dl*- and the *i*-acids, or even a resolution of the former.

The pasty menthylamine salt was separated, roughly dried, and dissolved in boiling acetone; the cold solution deposited a colourless powder, which was further fractionated from a mixture of acetone and methyl alcohol, and finally from wet ethyl acetate.

The salt thus obtained was doubtless the normal *l*-menthylamine salt of *dibenzyl-diethyl-dipropyl-silicoethanedisulphonic acid*. Air-dried samples lost 6.2—6.3 per cent. of water at 100°, and the anhydrous compound gave Si = 6.7 per cent. The formula



requires $\text{H}_2\text{O} = 6.0$ per cent., and the anhydrous salt, Si = 6.7 per cent. The equivalent weight of the salt was also determined by the accurate method previously used in the case of menthylamine sulphobenzylethylpropylsilicyl oxide (T., 1907, 91, 230). The value obtained was $E = 430$, the calculated value for the above formula being $E = 426.4$. This *l*-menthylamine salt was a colourless powder, which under the microscope was seen to consist of fern-like crystals; the anhydrous salt sintered at about 208° and seemed to turn yellow, melting completely at about 220°.

It was readily soluble in cold methyl alcohol, but almost insoluble in dry acetone or ethyl acetate; like so many of the salts of silico-sulphonic acids, its solubility was very much greater in wet than in dry organic solvents, and it dissolved quite readily in both acetone and ethyl acetate in presence of a very small proportion of water. A solution of the sodium salt, prepared from the menthylamine salt, seemed to be quite optically inactive; the solution gave precipitates with solutions of *d*-hydrindamine and *d*-methylhydrindamine hydrochlorides, and it is probable that further experiments will lead to a complete separation of the *dl*- and the *i*-acids and to the resolution of the former.

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