

### 316. *Some Organic Derivatives of Hexachlorodisiloxane.*

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Methyl, ethyl, and phenyl derivatives of hexachlorodisiloxane have been prepared by reaction of the oxychloride with the corresponding Grignard reagent in ethereal solution. Hydrolysis of monochloropentaethylidisiloxane gave a stable monomeric hydroxy-compound.

DESPITE the preparation of a large number of organic monosilicon chlorides by Kipping and his co-workers and others, no attempt has been made to prepare organic silicon oxychlorides. In view of the predominance of the Si-O-Si linkage in the "silicone" polymers, it was of interest to prepare certain simple organic silicon oxychlorides and to examine their properties. In this paper the reactions between hexachlorodisiloxane, the simplest silicon oxychloride known, and methylmagnesium chloride and ethyl- and phenyl-magnesium bromides are described. The mono-, di-, tri- tetra-, and penta-ethyl and the dimethyl and diphenyl derivatives of the oxychloride have been isolated.

All the organodisiloxane *chlorides* isolated were colourless mobile liquids with melting points below room temperature, which hydrolysed readily with water. The products of hydrolysis from  $\text{Si}_2\text{OCl}_5\text{Et}$ ,  $\text{Si}_2\text{OCl}_4\text{Et}_2$ ,  $\text{Si}_2\text{OCl}_4\text{Me}_2$ , and  $\text{Si}_2\text{OCl}_4\text{Ph}_2$  were white solids, whilst  $\text{Si}_2\text{OCl}_3\text{Et}_3$  gave a translucent viscous liquid, which polymerised further on standing to a rubber-like solid. The products obtained by the hydrolysis of  $\text{Si}_2\text{OCl}_2\text{Et}_4$  and  $\text{Si}_2\text{OClEt}_5$  were liquids which were readily soluble in ether. From the products of hydrolysis of  $\text{Si}_2\text{OClEt}_5$  it was possible to isolate in theoretical yield a monohydroxy-derivative, which was a stable liquid with a smell reminiscent of that of camphor. These hydrolysis experiments, which were qualitative, indicated a small decrease in the ease of hydrolysis as the number of substituent organic groups was increased.

The action upon diethyltetrachlorodisiloxane of ammonium fluoride or potassium hydrogen difluoride led to formation of ethylsilicon trifluoride, which was fully characterised, together with a residue of polymerised material. This result, which illustrates the instability of the Si-O-Si bond to fluorination, is in agreement with recent work by Booth and Osten (*J. Amer. Chem. Soc.*, 1945, **67**, 1092), who obtained a large yield of silicon tetrafluoride in the reaction between hexachlorodisiloxane and antimony trifluoride. The same point has been demonstrated by Emeléus and Wilkins, who prepared ethylsilicon trifluoride by the action of sulphuric acid on a mixture of ethylsiliconic acid and calcium fluoride (*J.*, 1944, 454). Experiments on the fluorination of the other alkyl and aryl derivatives described in this paper have not so far been made, but some at least might be expected to yield stable fluoro-derivatives.

The photochemical chlorination of tetrachlorodiethylidisiloxane gave a theoretical yield of the fully chlorinated derivative. Thermal chlorination of the same compound at 150–200° resulted in the formation of a small quantity of hexachloroethane, indicating that some fission of the Si-C bond had occurred. The action of alkali on the fully chlorinated material from the photochemical reaction leads to fission of the C-Si bond and the subsequent formation of tetrachloroethylene, obtained from the initial hydrolysis product, pentachloroethane, by loss of hydrogen chloride. This is in agreement with the known reaction of chloroalkylmonosilicon chlorides with alkali.

Structural isomerism should be possible in the di-, tri-, and tetra-substituted derivatives of

hexachlorodisiloxane. This point has not been fully studied, but in the case of the diethyl derivative,  $\text{Si}_2\text{OCl}_4\text{Et}_2$ , the action of ammonium fluoride yields only ethylsilicon trifluoride, which indicates that one ethyl group is attached to each silicon atom. No fission of the C-Si bond was observed during this reaction. The preparation of hexa-alkyl- and -aryl-disiloxanes was attempted by Schumb, Ackerman, and Saffer (*J. Amer. Chem. Soc.*, 1938, **60**, 2486) by applying the Wurtz reaction to hexachlorodisiloxane and the alkyl or aryl halides. These experiments yielded, however, only the fully substituted monosilicon derivatives in good yield. Using the Grignard reaction with phenylmagnesium bromide, Schumb and Saffer (*ibid.*, 1939, **61**, 363) obtained a 40% yield of hexaphenyldisiloxane. The corresponding reaction using hexabromodisiloxane yielded small amounts of the monosilicon derivative, triphenylsilanol. In the experiments described here no products of low molecular weight corresponding to monosilicon derivatives were detected. Yields of the desired products were relatively high, but in every case a residue consisting of material of high molecular weight was obtained.

#### EXPERIMENTAL.

*Analysis.*—The determination of the percentage of chlorine and silicon present in the compounds obtained was carried out by Gillian, Liebhopsky, and Wimslow's method (*J. Amer. Chem. Soc.*, 1941, **63**, 801). Owing to the low volatility of the derivatives of  $\text{Si}_2\text{OCl}_4$ , it was possible to weigh the sample out in a small gelatin ampoule and then to bring it into reaction with A.R. sodium peroxide in a Parr microbomb. The quantity of sample weighed out varied with the percentage of chlorine in the compounds under analysis, from about 90 mg. of  $\text{Si}_2\text{OCl}_4\text{Et}$  to about 150 mg. of  $\text{Si}_2\text{OCl}_4\text{Et}_2$ .

*Hexachlorodisiloxane.*—Four methods were investigated for this preparation: (i) the reaction between a chlorine-oxygen mixture and elemental silicon at temperatures between 700° and 800°; (ii) the reaction between silicon tetrachloride and oxygen at 900–950°; (iii) the oxidation of silicochloroform by means of solid oxidising agents at temperatures from 200° to 400°; (iv) the partial hydrolysis of silicon tetrachloride in ethereal solution. Method (iii) resulted mainly in the complete oxidation of the silico-chloroform, leading to formation of silicon and hydrogen chloride. Small yields of  $\text{Si}_2\text{OCl}_4$  were obtained by method (iv), but the main portion of the products consisted of higher oxychlorides. Methods (i) and (ii) gave results which were suitable for the preparation of  $\text{Si}_2\text{OCl}_4$  in large quantities. The reaction between silicon tetrachloride and oxygen had the additional merit of being capable of adaptation for use as a continuous process. Dry oxygen was passed at the rate of 2–4 l./hr. through silicon tetrachloride kept about 10° below its b. p. The mixture of silicon tetrachloride and oxygen thus produced passed through the furnace tube maintained at 900–950°. The products together with excess of silicon tetrachloride were condensed by means of two water-cooled, double-surface condensers, and the condensed liquid was returned to the silicon tetrachloride boiler. The b. p. of the silicon tetrachloride increased as the experiment proceeded, and after 2–5 days the apparatus was shut down and the silicon tetrachloride fractionated. Hexachlorodisiloxane, b. p. 137–138°, was collected. A small residue of higher oxychlorides was obtained.

*The Reaction of Hexachlorodisiloxane with a Grignard Reagent.*—In all the experiments the same general method was employed. Variations in the reaction conditions are noted in the separate details of each experiment. The Grignard reagent was prepared from the organic halide by the usual method. A solution of the chloro-compound in anhydrous ether was placed in a three-necked flask (1 g.-mol. of  $\text{Si}_2\text{OCl}_4$  being dissolved in approx. 1 l. of ether), fitted with a stirrer, a spiral double-surface condenser, and tap-funnel. The Grignard solution was filtered through glass-wool into the tap-funnel to remove excess of magnesium, and then run slowly into the well-stirred solution of the halide. Precipitation of magnesium chlorobromide began at once. When the addition was complete, the solution was refluxed for 3–6 hours to ensure completion of the reaction. The reaction mixture was allowed to cool, and the chlorobromide filtered off rapidly through a large Büchner funnel. The residue on the filter was well washed with anhydrous ether. Removal of the ether was carried out by distillation, and the residue was then fractionated. Arrangements were made, by means of drying tubes containing silica gel, to exclude moisture from the reaction vessel, distillation columns, and other apparatus in which the halides were handled. All apparatus was thoroughly dried before use.

*Monoethylpentachlorodisiloxane.*—116 G. (0.875 g.-mol.) of ethylmagnesium bromide were treated with 200 g. (0.7 g.-mol.) of  $\text{Si}_2\text{OCl}_4$ . The products after separation were fractionated several times under reduced pressure, a 13' column packed with Fenske spirals being used. 47 G. (0.17 g.-mol.) of pure monoethylpentachlorodisiloxane were obtained (b. p. 60.0–61.5°/17 mm., 163–164°/757 mm.); yields, crude 40%, pure 24% (Found: Cl, 63.6; Si, 19.9; C, 8.9; H, 1.9.  $\text{Si}_2\text{OCl}_4\text{Et}$  requires Cl, 63.7; Si, 20.1; C, 8.7; H, 1.8%).

*Diethyltetrachlorodisiloxane.*—333 G. (2.5 g.-mols.) of ethylmagnesium bromide were treated with 285 g. (1 g.-mol.) of  $\text{Si}_2\text{OCl}_4$ . 236 G. (87%) of crude product were obtained, from which 75 g. (0.28 g.-mol., 28%) of pure diethyltetrachlorodisiloxane were collected (b. p. 72.5°/12 mm., 186–187°/757 mm.) by fractionation under reduced pressure through a modified Widmer column, packed with Monel-metal gauze spirals and utilising a partial condensation vapour take-off head (Found: Cl, 52.3; Si, 20.6; C, 17.9; H, 3.7.  $\text{Si}_2\text{OCl}_4\text{Et}_2$  requires Cl, 52.1; Si, 20.6; C, 17.7; H, 3.7%).

*Triethyltrichlorodisiloxane.*—498 G. (3.75 g.-mols.) of ethylmagnesium bromide were caused to react with 285 g. (1 g.-mol.) of  $\text{Si}_2\text{OCl}_4$ . 231 G. (85%) of crude product were obtained, from which, by repeated fractionation under reduced pressure by means of the column described in the previous preparation, it was possible to isolate 78 g. (0.295 g.-mol., 29.5%) of pure triethyltrichlorodisiloxane (b. p. 72.5–73.5°/7 mm., 202–203°/757 mm.) (Found: Cl, 40.0; Si, 21.5; C, 26.8; H, 5.7.  $\text{Si}_2\text{OCl}_4\text{Et}_3$  requires Cl, 40.0; Si, 21.1; C, 27.1; H, 5.7%).

*Tetraethyldichlorodisiloxane.*—An attempt to prepare the pentaethylmonochloro-compound by

reaction of 1 g.-mol. of  $\text{Si}_2\text{OCl}_6$  with 5 g.-mols. of ethylmagnesium bromide led to the isolation of *tetraethylchlorodisiloxane*. When 6.25 g.-mols. of the Grignard reagent were used, difficulty was experienced in separating the product owing to the bulk of the magnesium chlorobromide, and this bulk of inert product probably accounts for the reaction ceasing at the tetra-substituted stage. 194 G. (78%) of crude tetraethyl compound were obtained, which after repeated fractionation gave 29 g. (0.11 g.-mol., 11%) of pure product (b. p. 96—98°/13 mm., 215—216°/757 mm.) (Found: Cl, 27.4; Si, 20.9; C, 36.9; H, 7.4.  $\text{Si}_2\text{OCl}_2\text{Et}_4$  requires Cl, 27.4; Si, 21.6; C, 37.0; H, 7.8%). 12 G. of a fraction consisting mainly of pentaethyl compound were obtained.

*Pentaethylmonochlorodisiloxane*.—The preparation of this compound was carried out in two stages. The triethyl compound was first prepared as described above, the crude material being isolated and analysed for replaceable chlorine. An amount of ethylmagnesium bromide (366 g., 2.75 g.-mols.) was prepared sufficient to reduce the content of the replaceable chlorine in 293 g. of triethyl compound to that corresponding to  $\text{Si}_2\text{OClEt}_3$ , together with the usual 25% excess of Grignard reagent over the halide. Reaction was slower than when the unsubstituted chloride was used and it was necessary to reflux the mixture overnight. 237 G. of crude material were obtained, from which it was possible after repeated fractionations under reduced pressure to obtain 34 g. (0.135 g.-mol., 12.5%) of pure *pentaethyl* compound (b. p. 86—88°/1 mm., 226—227°/757 mm.) (Found: Cl, 13.9; C, 48.1; H, 10.5.  $\text{Si}_2\text{OClEt}_3$  requires Cl, 14.0; C, 47.5; H, 10.0%).

*Dimethyltetrachlorodisiloxane*.—17 G. (0.1 g.-mol.) of methylmagnesium iodide and 179 g. (2.4 g.-mols.) of methylmagnesium chloride, prepared according to Schmalz (J. pr. Chem., 1924, 103, 88), were treated with 285 g. (1 g.-mol.) of  $\text{Si}_2\text{OCl}_4$ . Reaction proceeded vigorously and the vessel had to be cooled during the early stages of the preparation. 203 G. of crude material were obtained. By using a 28" column filled with Monel-metal gauze spirals and fitted with a heater jacket and utilising a total condensation partial take-off head, 137 g. (0.56 g.-mol., 56%) of pure *dimethyltetrachlorodisiloxane* were obtained (b. p. 67—69°/57 mm., 143—144°/757 mm.) (Found: Cl, 57.5; Si, 23.2; C, 10.2; H, 2.5.  $\text{Si}_2\text{OCl}_4\text{Me}_2$  requires Cl, 58.1; Si, 23.1; C, 9.9; H, 2.5%). The pure material was colourless but became pink in contact with air.

*Diphenyltetrachlorodisiloxane*.—520 G. (2.85 g.-mols.) of phenylmagnesium bromide reacted with 285 g. (1 g.-mol.) of  $\text{Si}_2\text{OCl}_4$ . The crude product was separated from the small quantity of diphenyl obtained by fractionation through a 9" Fenske column, fitted with a heater jacket and utilising a total condensation partial take-off head. Further fractionation using the 28" Monel-gauze spiral column used in the previous preparation led to the isolation of 64 g. (0.175 g.-mol., 17.5%) of pure *compound* (b. p. 114—115°/1 mm., 319—320°/757 mm.) (Found: Cl, 38.6; Si, 15.1; C, 39.2; H, 2.6.  $\text{Si}_2\text{OCl}_4\text{Ph}_2$  requires Cl, 38.5; Si, 15.2; C, 39.2; H, 2.7%). The pure material was colourless but on storage became pale yellow.

*Pentaethylchlorodisiloxanol*.—3 G. of pentaethylchlorodisiloxane were dissolved in 15 ml. of ether and a solution containing 2 g. of sodium hydrogen carbonate dissolved in 10 ml. of water added. A steady evolution of carbon dioxide occurred for 2 hours. The solution was refluxed for a further 3 hours until the evolution ceased. The solution was extracted with portions of ether, the resulting ethereal solution was separated and dried ( $\text{CaCl}_2$ ) overnight. The ether was removed by distillation, and the product distilled under reduced pressure. 2.5 G. (100%) of the *siloxanol* were obtained (b. p. 96—98°/1 mm.) [Found: C, 51.4; H, 11.1; M (Rast), 215.  $\text{Si}_2\text{OEt}_5\text{OH}$  requires C, 51.3; H, 11.1% M, 232].

*Photochemical Chlorination of Diethyltetrachlorodisiloxane*.—Dry chlorine was passed into 32.2 g. of the disiloxane contained in a quartz test-tube irradiated by U.V. light from a mercury-vapour lamp. After 66 hours the increase in weight was 40.5 g. [Calc. for formation of  $\text{Si}_2\text{OCl}_4(\text{C}_2\text{Cl}_5)_2$ : 40.8 g.]. The bulk of the *bispentachloroethyltetrachlorodisiloxane* distilled within the range 178—183°/1 mm. and consisted of a colourless viscous liquid with a faint smell [Found: Cl, 81.1; M (Rast), ~ 650.  $\text{C}_4\text{OCl}_4\text{Si}_2$  requires Cl, 80.6%; M, 617].

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