CCLXV.—A Study of Some Organic Derivatives of Tin as Regards their Relation to the Corresponding Silicon Compounds.

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In spite of the well-established relationship between organic derivatives of silicon and analogous derivatives of carbon, as regards their general behaviour, there are many noteworthy instances in which a silicon compound differs very considerably in certain particulars from the corresponding carbon compound of the same type; consequently, any forecast of the course of a reaction in the case of a compound of the one element, which is based on a knowledge of the behaviour of the corresponding derivative of the other, may be partly or entirely unfulfilled.

It would also seem that a similar lack of success may attend an attempt to predict the reactions of an organic derivative of tin from analogy to those of the corresponding compound of silicon; at any rate, this is one of the lessons that we have been taught by the results of the work described in this paper.

For some time past, intermitted efforts have been made in these laboratories to prepare an asymmetric carbon compound of the same type as that of one of the silicon compounds which has been resolved into its optically active components; if this task could be accomplished, and the *dl*-compound,

$$\underset{\Pr}{\overset{Et}{\rightarrow}} \subset \overset{CH_2 \cdot C_6H_5}{\underset{2}{\leftarrow} C_6H_4 \cdot SO_3H},$$

for example, could be obtained and resolved, a comparison of the optical properties of the active acid with those of the corresponding silicon compound (Challenger and Kipping, Trans., 1910, **97**, 755) might lead to important conclusions.

Hitherto the experiments in this direction have been fruitless; thus, although the preparation of the silicon compound,

SiEtPr(CH₂·C₆H₅)₂,

is a relatively easy matter (Challenger and Kipping, Trans., 1910, **97**, 142), that of dibenzylethylpropylmethane presents far greater difficulties, owing to the fact that substances of the type CR_sX so readily lose the elements of a halogen acid, HX, when the displacement of the halogen by a hydrocarbon radicle is attempted (Kipping and Davies, Trans., 1911, **99**, 300).

The possibility of obtaining a tin compound, analogous to one

of the known optically active derivatives of silicon, was therefore considered, and experiments were instituted on the preparation of a dibenzylethylpropylstannane * of the composition

 $SnEtPr(CH_2 \cdot C_6H_5)_2$,

corresponding with dibenzylethylpropylsilicane, by the following series of reactions:

 $\begin{aligned} & \operatorname{SnCl}_4 + 2\operatorname{MgCl}\cdot\operatorname{CH}_2\cdot\operatorname{C}_6\operatorname{H}_5 = \operatorname{SnCl}_2(\operatorname{CH}_2\cdot\operatorname{C}_6\operatorname{H}_5)_2 + 2\operatorname{MgCl}_2.\\ & \operatorname{SnCl}_2(\operatorname{CH}_2\cdot\operatorname{C}_6\operatorname{H}_5)_2 + \operatorname{MgEtBr} = \operatorname{SnClEt}(\operatorname{CH}_2\cdot\operatorname{C}_6\operatorname{H}_5)_2 + \operatorname{MgClBr}.\\ & \operatorname{SnClEt}(\operatorname{CH}_2\cdot\operatorname{C}_6\operatorname{H}_5)_2 + \operatorname{MgPrBr} = \operatorname{SnEtPr}(\operatorname{CH}_2\cdot\operatorname{C}_6\operatorname{H}_5)_2 + \operatorname{MgClBr}. \end{aligned}$

If this product could be converted into a *dl*-sulphonic acid, analogous to dibenzylethylpropylsilicanesulphonic acid, and the *dl*-tin compound could then be resolved, the desired object would have been attained.

Certain stages of the proposed plan were accomplished with comparative facility, although by methods somewhat different from those originally outlined, which were based on previous experience with the corresponding silicon compounds. In the first place, the dibenzylstannic chloride, SnCl₂(CH₂·C₆H₅)₂, with which the work was to commence, could not be conveniently obtained directly from stannic chloride by a process similar to that used in the preparation of dibenzyldichlorosilicane (Robison and Kipping, Trans., 1908, 93, 451), because when stannic chloride was treated with two molecular proportions of magnesium benzyl chloride, the main product was tribenzylstannic chloride, and a considerable quantity of the stannic chloride remained unchanged. It was much simpler, therefore, to prepare the tribenzyl derivative (for which purpose three, instead of two, molecular proportions of magnesium benzyl chloride were used) and then to displace one of the benzylgroups in the product by halogen, than to isolate the small proportion of the dichloride which was formed when two equivalents of the Grignard reagent were employed.

The conversion of the tribenzylstannic chloride into the dibenzyldichloro-derivative was accomplished with the aid of iodine, the reaction taking place in accordance with the following equation:

 $2Sn(CH_2 \cdot C_6H_5)_3Cl + 2I_2 =$

 $\mathbf{Sn}(\mathbf{CH}_2 \cdot \mathbf{C}_6 \mathbf{\overline{H}}_5)_2 \mathbf{Cl}_2 + \mathbf{Sn}(\mathbf{CH}_2 \cdot \mathbf{C}_6 \mathbf{H}_5)_2 \mathbf{I}_2 + 2\mathbf{C}_6 \mathbf{H}_5 \cdot \mathbf{CH}_2 \mathbf{I}.$

The dibenzyldi-iodostannane, which was simultaneously formed, was also transformed into the dichloride through the corresponding oxide.

^{*} The suggestion is here made that the name "stannane" should be used in preference to the rather cumbersome "stannimethane" to denote the unknown hydride, SnH_4 , of which many of the simple tin derivatives may be regarded as derivatives.

Although a very satisfactory yield of dibenzyldichlorostannane was thus obtained, the relative ease with which the tribenzyl derivative could be prepared, and the readiness with which a benzyl group could be displaced by iodine, suggested a modification of the original plan; instead of attempting to substitute first an ethyl and then a propyl group for the two atoms of chlorine in the dichloride, it seemed better to start from tribenzylstannic chloride and try to carry out the series of operations shown by the following equations:

I. $Sn(CH_2 \cdot C_6H_5)_3Cl + MgEtBr = SnEt(CH_2 \cdot C_6H_5)_3 + MgClBr.$

II.
$$\operatorname{SnEt}(\operatorname{CH}_2 \cdot \operatorname{C}_6 \operatorname{H}_5)_3 + \operatorname{I}_{2} = \operatorname{SnEtI}(\operatorname{CH}_2 \cdot \operatorname{C}_6 \operatorname{H}_5)_2 + \operatorname{C}_6 \operatorname{H}_5 \cdot \operatorname{CH}_2 \operatorname{I}.$$

III. $\operatorname{SnEtI}(\operatorname{CH}_2 \cdot \operatorname{C}_6 \operatorname{H}_5)_2 + \operatorname{MgPrBr} = \operatorname{SnEtPr}(\operatorname{CH}_2 \cdot \operatorname{C}_6 \operatorname{H}_5)_2 + \operatorname{MgBrI}.$

That the changes represented by I and III would occur was, of course, very probable, since many compounds of the type SnR_4 have already been prepared by such interactions, but whether or not the substitution expressed by II could be realised was somewhat doubtful. For although the above-mentioned experiments had proved that the benzyl group could be easily eliminated with the aid of iodine, the fact that alkyl groups may be displaced in a similar manner had also been established; moreover, in the case of those compounds which contain two or more different hydrocarbon radicles, it would seem that the course of the reaction cannot be foretold; thus, whereas it was shown by Cahours (Annalen, 1862, 122, 59) that trimethylethylstannane is decomposed by iodine with separation of ethyl iodide, it was found by Pope and Peachey (Proc., 1900, 16, 42) that both trimethylethyland dimethylethylpropyl-stannane are decomposed with the formation of methyl iodide, the alkyl of lower or lowest molecular weight being separated from the tin atom. In the light of these observations, it seemed possible, or even probable, that the action of iodine on tribenzylethylstannane might give rise to tribenzylstannic iodide and ethyl iodide.

Experiment showed, however, that the reaction expressed by equation II could be brought about, and dibenzylethylpropylstannane was, in fact, obtained in accordance with the above scheme.

It was at the next stage that the difference between dibenzylethylpropylstannane and dibenzylethylpropylsilicane became sufficiently pronounced to defeat entirely the object of this work. When attempts were made to sulphonate one of the benzyl groups in the tin derivative, a complex reaction occurred, and even when chlorosulphonic acid was used at low temperatures, both the benzyl groups were eliminated, with the formation, among other products, of a salt of ethylpropylstannic oxide. Many sulphonation experiments were made, not only with dibenzylethylpropylstannane, but also with dibenzyldiethylstannane, which was more easily prepared than the ethylpropyl compound; they all ended in failure. These two compounds, apparently, unlike dibenzylethylpropylsilicane, cannot be converted into their monosulphonic derivatives owing to the readiness with which the benzyl group is eliminated.

The union between the benzyl group and the tin atom shows, in fact, the same instability towards sulphuric acid as that between the phenyl group and the silicon atom (Kipping, Trans., 1907, **91**, 212); the union between the benzyl group and the silicon atom, on the other hand, is much more resistant to the action of sulphonating agents, as has been shown by the isolation of several substances containing the group \geq Si·CH₂·C₆H₄·SO₃H. The breakdown of the analogy between dibenzylethylpropylstannane and dibenzylethylpropylsilicane, in so far as concerns their behaviour towards sulphonating agents, brought this work to an abrupt conclusion; it is intended, nevertheless, to utilise some of the compounds which have been cbtained for further experiments on the preparation of some *dl*-derivatives of tin.

EXPERIMENTAL.

Preparation of Tribenzylstannic Chloride, $Sn(CH_2 \cdot C_6H_5)_3Cl$.

Tribenzylstannic chloride was first prepared by Pfeiffer and Schnurmann (*Ber.*, 1904, **37**, 319) by the gradual addition of stannic chloride (1 mol.) to an ice-cold ethereal solution of magnesium benzyl chloride (3 mols.). Under these conditions the yield was very poor, the weight of solid raw material amounting to only 20 per cent. of the theoretical, and that of the pure compound to only about 8 per cent.

Much more satisfactory results are obtained by omitting the preliminary preparation of the solution of the Grignard reagent (compare Kipping and Davies, Trans., 1911, **99**, 296), and carrying out the operation in the following manner: Some ether (about 10 vols.), contained in a flask, is cooled in ice and stannic chloride (100 grams, 1 vol.) is slowly added from a tap funnel; during this operation the mixture is vigorously stirred, and atmospheric moisture is excluded. In this way the solid additive product of ether and stannic chloride which is formed is obtained in a very finely divided condition. Dry magnesium powder (28 grams, 3 atoms) is now added, and a little benzyl chloride is dropped into the mixture from a tap funnel; if the reaction does not start in the course of a few minutes, it is caused to do so by the addition of a

small quantity of magnesium benzyl chloride prepared in a testtube. The rest of the benzyl chloride (150 grams, 3 mols.) is then slowly dropped in, an operation which occupies about two hours, whilst the contents of the flask are vigorously stirred and cooled in ice. When this process is at an end, and the development of heat is no longer noticed, the mixture is heated on a water-bath under a reflux condenser during two hours. The ether is then distilled off, and the product is heated during a further period of two hours at about 100°. When cold, the solid contents of the flask are slowly added to a large volume of water, and the crude tribenzylstannic chloride is separated and washed with water. The preparation is first crystallised from acetone, containing a little water, and then from glacial acetic acid, until its melting point is The yield of pure substance, melting at 143-145°, is constant. about 60 per cent. of the theoretical:

A sample dried over sulphuric acid was analysed:

0.2969 gave 0.0980 AgCl. Cl=8.16.

 $C_{21}H_{21}ClSn$ requires Cl=8.29 per cent.

Tribenzylstannic chloride is very readily soluble in acetone, benzene, or chloroform, less readily so in ether or alcohol, and insoluble in water; it crystallises from boiling glacial acetic acid in fairly well-defined prisms.

Dibenzylstannic Chloride, $SnCl_2(CH_2 \cdot C_6H_5)_2$.

A small quantity of dibenzylstannic chloride may be isolated from the residues obtained in the preparation of the tribenzyl derivative, and by employing two instead of three molecular proportions of magnesium benzyl chloride, the yield of the dibenzyl compound may be increased. Even under the more favourable conditions, however, the main product of the reaction is tribenzylstannic chloride, and a considerable proportion of stannic chloride remains unchanged. It is more convenient, therefore, to prepare the dibenzyl- from the tribenzyl-derivative in the following manner:

Tribenzylstannic chloride (1 mol.) is dissolved in warm carbon tetrachloride, and iodine (1 mol.) is added in small portions at a time to the warm solution, which is vigorously shaken; the reaction represented by the following equation then takes place:

 $2\operatorname{Sn}(\operatorname{CH}_2 \cdot \operatorname{C}_6 \operatorname{H}_5)_3\operatorname{Cl} + 2\operatorname{I}_2 =$

 $\operatorname{Sn}(\operatorname{CH}_2 \cdot \operatorname{C}_6 \operatorname{H}_5)_2 \operatorname{Cl}_2 + \operatorname{Sn}(\operatorname{CH}_2 \cdot \operatorname{C}_6 \operatorname{H}_5)_2 \operatorname{L}_2 + 2\operatorname{C}_6 \operatorname{H}_5 \cdot \operatorname{CH}_2 \operatorname{I}.$

At first the colour of the iodine rapidly disappears, but towards the end of the operation the reaction takes place much more slowly, and it may be necessary to heat the solution in order to complete the change. Direct sunlight also accelerates the change very considerably. When the colour of the iodine has entirely disappeared, the solution is placed aside, and the crystals of dibenzylstannic chloride which are afterwards deposited are collected by the aid of the pump, and washed with a little light petroleum. The substance is then recrystallised from acetone containing a little hydrochloric acid.

The mother liquors, which contain the di-iodide and some dichloride, together with benzyl iodide, are best treated in the following way: The solvent and the benzyl iodide are removed by distillation in a current of steam, and the residue is then well shaken with a concentrated aqueous solution of ammonium hydroxide. The solid dibenzylstannic oxide, which is thus formed, is well washed with water to free it from ammonium salts, and is then dissolved in a mixture of acetone and concentrated hydrochloric acid; from this solution dibenzylstannic chloride is deposited in colourless crystals. The total yield of the chloride is practically theoretical.

A sample dried over sulphuric acid was analysed:

0.1515 gave 0.1170 AgCl. Cl=19.07.

 $C_{14}H_{14}Cl_2Sn$ requires Cl=19.08 per cent.

Dibenzylstannic chloride is readily soluble in acetone, alcohol, ether, carbon tetrachloride, or chloroform, but it is only sparingly soluble in hot light petroleum; it dissolves freely in boiling acetic acid, and separates from the cooled solution in long needles melting at 163—164°.

Dibenzylstannic Iodide, $Sn(CH_2 \cdot C_6H_5)_2I_2$.

The dibenzylstannic iodide which is formed in the preparation of dibenzylstannic chloride by the method just described is more soluble than the dichloride in carbon tetrachloride, and therefore remains in the mother liquors from which the last-named compound has been deposited. If the solvent and the benzyl iodide are removed by distillation in a current of steam, and the residue is then recrystallised, first from alcohol, and then several times from ether and petroleum, the di-iodide is finally obtained in a pure condition.

A sample dried over sulphuric acid was analysed:

0.3860 gave 0.3261 AgI. I=45.67.

 $C_{14}H_{14}I_2Sn$ requires I=45.75 per cent.

Dibenzylstannic iodide crystallises in long, silky, yellow needles, melting at 86-87°; its behaviour towards solvents is much the

same as that of the dichloride, but, as stated above, the di-iodide is the more soluble in carbon tetrachloride.

Dibenzylstannic iodide may also be obtained by dissolving the oxide in a hot mixture of acetone and hydriodic acid, and then leaving the solution to crystallise.

Dibenzylstannic Bromide, Sn(CH₂·C₆H₅)₂Br₂.

Dibenzylstannic bromide is formed when dibenzylstannic oxide is treated with hydrobromic acid in acetone solution; the product is crystallised from aqueous alcohol, and then from light petroleum; it forms colourless needles, melts at 130°, and resembles the chloride in its behaviour towards solvents, but is more soluble than that compound:

0.2845 gave 0.2316 AgBr. Br = 34.7. $C_{14}H_{14}Br_2Sn$ requires Br = 34.7 per cent.

Dibenzylstannic Acetate, $Sn(CH_2 \cdot C_6H_5)_2(O \cdot CO \cdot CH_3)_2$.

This salt is easily obtained by dissolving the oxide in hot glacial acetic acid; when the solution is cooled or diluted with water, the acetate separates in long, colourless needles, which may be recrystallised from aqueous alcohol.

The sample for analysis was dried over sulphuric acid:

0.1501 gave 0.2833 CO₂ and 0.0644 H₂O. C=51.5; H=4.77. 0.1576 , 0.2964 CO₂ , 0.0686 H₂O. C=51.3; H=4.83.

 $C_{18}H_{20}O_4Sn$ requires C=51.5; H=4.8 per cent.

Dibenzylstannic acetate melts at 136—137°, and is readily soluble in acetone, alcohol, benzene, or chloroform; like the dichloride and other salts of dibenzylstannic oxide, it dissolves slowly in an aqueous solution of potassium hydroxide, giving a product from which the oxide may be precipitated with the aid of carbon dioxide.

Tetrabenzylstannane, $Sn(CH_2 \cdot C_6H_5)_4$.

Tetrabenzylstannane is easily obtained by gradually adding benzyl chloride (4 mols.) to an ethereal solution of stannic chloride (1 mol.) in the presence of powdered magnesium (4 atoms).

The ethereal solution of the stannic chloride is prepared as described above (p. 2556), the reaction is started in the usual manner, and when the whole of the benzyl chloride has been added, the ether is distilled off, and the residue is heated at 100° during two to three hours. The cold mixture is treated with water, and submitted to steam distillation in order to remove any dibenzyl and unchanged benzyl chloride; the solid residue is then separated

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by the aid of the pump, dried on porous earthenware, and dissolved in light petroleum. When this solution is cooled in ice, the tetrabenzyl derivative is deposited in colourless crystals, which are easily purified by recrystallisation from light petroleum.

The sample for analysis was dried over sulphuric acid:

0.2505 gave 0.6364 CO₂ and 0.1316 H₂O. C=69.29; H=5.84. 0.2505 , 0.0803 SnO₂. Sn=25.2.

 $C_{28}H_{28}Sn$ requires C=69.54; H'=5.79; Sn=24.64 per cent.

Tetrabenzylstannane crystallises in well-defined prisms, and melts at $42-43^{\circ}$. It is readily soluble in most of the common organic solvents, with the exception of light petroleum. Like many of the benzyl derivatives of tin, tetrabenzylstannane slowly undergoes atmospheric oxidation, even at the ordinary temperature, with formation of benzaldehyde.

Tribenzylethylstannane, $SnEt(CH_2 \cdot C_6H_5)_3$.

Tribenzylethylstannane is readily formed with development of heat when tribenzylstannic chloride is treated with excess of an ethereal solution of magnesium ethyl bromide, which is slowly added from a tap funnel. When the whole of the Grignard reagent has been run in, the ether is distilled off, and the solid residue is heated at 100° during two to three hours; the product is then cooled and treated with water. The tin compound, which floats at the surface in the form of an oil, is transferred to a separating funnel, and washed first with dilute sulphuric acid and then with water; it is afterwards dissolved in ether and dried with the aid of calcium chloride. When the ethereal solution is allowed to evaporate spontaneously, the tribenzylethylstannane is deposited in glistening plates; it is recrystallised several times from a mixture of alcohol and light petroleum, cooled in ice. An almost theoretical yield of the compound is thus obtained, and its purity is indicated by the following analysis of a sample which had been dried over sulphuric acid:

0.2324 gave 0.0833 SnO₂. Sn = 28.24.

 $C_{23}H_{26}Sn$ requires Sn = 28.25 per cent.

Tribenzylethylstannane separates from alcoholic light petroleum in colourless, tabular crystals, and melts at $31-32^{\circ}$. It is readily soluble in ether, benzene, or chloroform, but is somewhat less soluble in alcohol and sparingly so in light petroleum. It undergoes atmospheric oxidation at the ordinary temperature, and gives benzaldehyde; when heated under atmospheric pressure it is decomposed with separation of tin.

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Dibenzyldiethylstannane, $SnEt_2(CH_2 \cdot C_6H_5)_2$.

Dibenzyldiethylstannane may be prepared by treating dibenzylstannic chloride with excess of magnesium ethyl bromide in ethereal solution. The operation is carried out exactly as described in the case of the tribenzylethyl derivative, and when water has been added the ethereal solution is separated, washed, and dried with calcium chloride. It is then distilled under a pressure of 20 mm., and the portion boiling at 223-224°, which is practically the whole of the crude oil, is collected separately; a very small proportion is decomposed during distillation, with separation of tin:

0.1881 gave 0.4113 CO₂ and 0.1163 H₂O. C=59.63; H-6.87. 0.5073 , 0.2118 SnO₂. Sn=32.9.

 $C_{18}H_{24}Sn$ requires C = 60.1; H = 6.7; Sn = 33.1 per cent.

Dibenzyldiethylstannane is a colourless oil specifically heavier than water, and it does not solidify at the ordinary temperature; it is miscible with all the common organic solvents; when heated under atmospheric pressure it is rapidly decomposed, giving a deposit of tin, and it is readily oxidised on exposure to the air, with formation of benzaldehyde.

Dibenzylethylpropylstannane, $SnEtPr(CH_2 \cdot C_6H_5)_2$.

Dibenzylethylpropylstannane may be obtained from tribenzylethylstannane in the following manner: Tribenzylethylstannane (1 mol.) is dissolved in carbon tetrachloride, and iodine (1 mol.) is added in small portions at a time, when the following reaction takes place:

 $\operatorname{SnEt}(\operatorname{CH}_2\operatorname{Ph})_3 + I_2 = \operatorname{SnEt}(\operatorname{CH}_2\operatorname{Ph})_2I + \operatorname{CH}_2\operatorname{Ph}I.$

The action of the iodine is facilitated by warming the solution or by exposing it to direct sunlight. When the theoretical quantity of the halogen has been added, the solvent and the benzyl iodide are removed with a current of steam, and the crude oily dibenzylethylstannic iodide is extracted with ether. The residue obtained by the evaporation of the dried ethereal solution does not crystallise, and decomposes when it is heated under diminished pressure; it is therefore treated directly with one molecular proportion of magnesium propyl bromide in the usual manner, and, after the ether has been distilled, the residue is heated at about 140° during To the cold product water is added, the oily layer of one hour. dibenzylethylpropylstannane is dissolved in ether, and the washed ethereal extract is dried and evaporated. The product is then distilled under a pressure of 15 mm. The fraction boiling at 220-225° forms about 70 per cent. of the crude product, and is

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pure dibenzylethylpropylstannane, as shown by the following analyses:

0.2221 gave 0.4975 CO₂ and 0.1422 H₂O. C=61.1; H=7.1. 0.2569 , 0.5748 CO₂ , 0.1625 H₂O. C=61.0; H=7.0. $C_{19}H_{26}Sn$ requires C=61.1; H=7.0 per cent.

Dibenzylethylpropylstannane does not solidify even at 0° ; it oxidises in the air at the ordinary temperature with the formation of benzaldehyde, and when heated under atmospheric pressure it decomposes, giving a deposit of tin. It is miscible with all the ordinary solvents.

Attempts to Obtain a Monosulphonic Derivative of Dibenzylethylpropyl- and of Dibenzyldiethyl-stannane.

On the addition of dibenzyldiethylstannane to concentrated sulphuric acid cooled in ice, the oil slowly dissolves, and when the slightly coloured liquid is poured into ice-cold water, a clear solution is obtained; this solution, however, has the unpleasant odour of the diethylstannic salts, and when treated with excess of a solution of ammonium hydroxide it gives a large quantity of a white precipitate. This precipitate is diethylstannic oxide; on treatment with hydrochloric acid, it passes into solution, forming diethylstannic chloride, which may be extracted with ether, and finally obtained in crystals melting at 80-81°. A sample of the dichloride thus obtained was mixed with some diethylstannic chloride from another source, and the melting point of the mixture was the same as that of the separate preparations. An examination of the ammoniacal solution, from which the diethylstannic oxide had been separated, failed to reveal the presence of any sulphonic acid containing tin, and, judging from the quantity of diethylstannic oxide which had been formed, it was obvious that normal sulphonation had not taken place.

On the addition of chlorosulphonic acid, diluted with carbon tetrachloride, to dibenzyldiethylstannane dissolved in the same solvent and cooled in a freezing mixture, a certain amount of charring is observed, and a brown oil is deposited, but no evolution of hydrogen chloride occurs. If when one molecular proportion of the chlorosulphonic acid has been added the solution is filtered from suspended oil and then allowed to evaporate at the ordinary temperature, crystals of diethylstannic chloride are deposited. The oil which separates from the carbon tetrachloride solution also consists principally of a salt of diethylstannic oxide; when treated with water, it gives a solution which shows the reactions of a sulphate, and with ammonium hydroxide it gives diethylstannic oxide, which is readily identified by converting it into the corresponding dichloride.

Although most of the attempts to prepare a sulphonic derivative were made with dibenzyldiethylstannane, some experiments were also carried out with dibenzylethylpropylstannane; the behaviour of the latter, however, was in all respects analogous to that of the diethyl derivative, inasmuch as it was decomposed with formation of a salt of ethylpropylstannic oxide.

Ethylpropylstannic Chloride, SnEtPrCl₂.

Ethylpropylstannic chloride was obtained from the products of the action of concentrated sulphuric acid and chlorosulphonic acid on dibenzylethylpropylstannane. When the aqueous solution of the product of sulphonation was treated with ammonium hydroxide it gave a white precipitate, which was separated by filtration, and dissolved in hydrochloric acid; the acid solution was then extracted with ether, and the extract evaporated. In this way the dichloride was obtained in needles having an unpleasant odour, resembling that of the diethylstannic salts.

Ethylpropylstannic chloride crystallises well from light petroleum, in which it is only sparingly soluble in the cold, and melts at 57-58°; it is readily soluble in ether, alcohol, or water. A chlorine estimation was made by boiling the substance with excess of ammonium hydroxide, filtering from the precipitated ethylpropylstannic oxide, and then estimating the halogen in the filtrate by precipitation with silver nitrate and nitric acid:

0.5439 gave 0.5925 AgCl. Cl=27.1.

 $C_5H_{12}Cl_2Sn$ requires Cl = 27.1 per cent.

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