CCXXIV.—*isoPropylstannonic Acid and its Derivatives.*

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*iso*PROPYLSTANNONIC ACID, prepared in a similar manner to ethylstannonic acid * (T., 1921, **119**, 758), by the interaction of *iso*-propyl iodide and potassium hydrogen stannite in accordance with the equation $\text{C}_3\text{H}_7\text{I} + \text{KHSnO}_2 = \text{C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OH} + \text{KI}$, is amphoteric, forming salts with bases (most of which are basic) and dissolving in hydrochloric or hydrobromic acid to give the tin *iso*propyl trihaloid.

By boiling with excess of alkali hydroxide solution, the acid is converted into diisopropylstannic oxide :

This reaction recalls the mode of formation of ketones, with which this oxide is analogous but to which it shows very little resemblance in physical and chemical properties. When treated with hydrochloric or hydrobromic acid, it yields the corresponding dihaloid.

The di- and tri-haloid derivatives, $(\text{C}_3\text{H}_7)_2\text{SnX}_2$ and $\text{C}_3\text{H}_7\cdot\text{SnX}_3$, yield double salts with the halogen salts of pyridine. These substances have properties similar to those of the organic stannichlorides (T., 1918, **113**, 715).

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isoPropylstannonic Acid, $\text{C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OH}$.—The potassium hydrogen stannite solution required was made by adding a sufficient quantity

* Called ethylstannic acid in the paper quoted.

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(about 250 c.c.) of 10 per cent. potassium hydroxide to produce a clear solution with 20 grams of stannous chloride, shaken with 60 c.c. of water. *iso*Propyl iodide (22 grams) was then added and the mixture was shaken at intervals during ten days.* When the *isopropyl* iodide had disappeared, the solution was treated with dilute hydrochloric acid until neutral, the gelatinous precipitate of *isopropylstannonic acid* filtered, washed with warm water, and dried on a porous plate (Found: Sn = 59.9; C = 18.0; H = 4.5. $C_3H_8O_2Sn$ requires Sn = 60.0; C = 18.5; H = 4.1 per cent.).

The *isopropylstannonic acid* was an almost white, amorphous substance, which did not melt, but decomposed when strongly heated, leaving a residue of stannic oxide. The acid was anhydrous, and did not gain in weight on exposure to the air. When heated out of contact with the air, it decomposed, giving off *iso*-propyl alcohol, propylene, and a trace of propane. The residue contained stannous and stannic oxides and also a little carbonaceous matter.

The acid was insoluble in water and organic solvents, but dissolved in dilute mineral acids and in sodium or potassium hydroxide.

The *potassium salt*, $C_3H_7\cdot SnO\cdot OK$, was prepared by digesting excess of the acid (5 grams) with 40 c.c. of 10 per cent. potassium hydroxide for several hours on a warm water-bath. After filtration the solution was kept in a desiccator over sulphuric acid until colourless, deliquescent, tabular crystals separated. These were washed with alcohol, drained, and dried between filter-paper (Found: K = 16.9; Sn = 49.6. $C_3H_7O_2KSn$ requires K = 16.7; Sn = 51.0 per cent.). The salt dissolved readily in water, forming a very alkaline solution which became cloudy on keeping and on warming, owing to hydrolysis. With excess of alkali, the solution remained clear.

The *sodium salt* was isolated in the same way as the potassium salt, which it resembled in its properties (Found: Na = 10.3; Sn = 53.7. $C_3H_7O_2NaSn$ requires Na = 10.6; Sn = 54.8 per cent.).

Basic calcium, strontium, and barium salts were obtained as white precipitates by adding excess of a solution of sodium or potassium *isopropylstannionate* to solutions of the metal chlorides. On analysis, the products were found to contain excess of the alkaline earth metal, and less tin, hydrogen, and carbon than the normal salt, $(C_3H_7SnO_2)_2M$, would require. Other basic salts of little interest were also obtained.

* In some experiments the equivalent amount of *isopropyl* bromide was used instead of the iodide, and in others the duration of the reaction was shortened by the addition of alcohol to the reaction mixture, thus making it a nearly homogeneous solution.

Tin Diisopropyl Oxide, $(C_3H_7)_2SnO$.—This substance was most readily formed by heating under reflux for four hours the reaction mixture obtained in the preparation of isopropylstannonic acid. Carbon dioxide was passed through the pale brown solution, and the white precipitate, which, unlike the stannonic acids, was easily filtered and washed, was dried on porous plate in a desiccator over sulphuric acid and solid sodium hydroxide (Found : Sn = 53·6. $C_6H_{14}OSn$ requires Sn = 53·8 per cent.).

Tin diisopropyl oxide is infusible. When heated in air, it yields stannic oxide. It does not dissolve in water, aqueous solutions of alkalis, or in organic solvents, but is soluble in hot hydrochloric and hydrobromic acids, yielding the corresponding tin diisopropyl dihaloids.

The oxide has also been obtained by boiling isopropylstannonic acid with excess of 10 per cent. potassium hydroxide for half an hour. The residue of tin diisopropyl oxide was isolated as described above.

Tin isoPropyl Tribromide, $C_3H_7\cdot SnBr_3$.—Very deliquescent, pale yellow, prismatic tablets of this substance were obtained by allowing a solution of 4 grams of isopropylstannonic acid in 25 c.c. of concentrated hydrobromic acid to evaporate in an evacuated desiccator over sodium hydroxide (Found : Sn = 28·7; Br = 58·9. $C_3H_7Br_3Sn$ requires Br = 59·7; Sn = 29·6 per cent.). It melted at about 112° and was very soluble in water, giving a strongly acid solution. Dry ether did not dissolve it, but it was soluble in the moist solvent, and also in glacial acetic acid; hot benzene and chloroform appeared to dissolve it slightly, but the substance was not recovered in a pure condition on removal of the solvent.

Pyridine isoPropylstannibromide, $C_3H_7\cdot SnBr_3\cdot 2C_5H_5N\cdot 2HBr$.—Tin isopropyl tribromide (2·5 grams) and pyridine hydrobromide (2 grams) were dissolved together in 50 c.c. of dilute hydrobromic acid. The solution was slightly concentrated on the water-bath, and, on cooling, deposited pale yellow, nacreous plates (Found : Sn = 16·5; Br = 55·9. $C_{13}H_{19}N_2Br_5Sn$ requires Br = 55·4; Sn = 16·5 per cent.). The substance crystallised unchanged from dilute hydrobromic acid, and did not melt at 300° . It was soluble in water and showed the properties of organic stannichlorides (compare T., 1918, 113, 715).

Pyridine isoPropylstannichloride, $C_3H_7\cdot SnCl_3\cdot 2C_5H_5N\cdot 2HCl$.—Attempts to isolate tin isopropyl trichloride, $C_3H_7\cdot SnCl_3$, from hydrochloric acid solutions of isopropylstannonic acid have been unsuccessful. The double pyridine chloride has, however, been obtained by dissolving 3 grams of isopropylstannonic acid in 25 c.c. of concentrated hydrochloric acid and adding 1·8 grams of pyridine

hydrochloride together with 25 c.c. of water. This solution yielded colourless, sword-shaped crystals, which were recrystallised from dilute hydrochloric acid and dried between filter-paper (Found : Cl = 35.1; Sn = 24.0. $C_{13}H_{19}N_2Cl_5Sn$ requires Cl = 35.4; Sn = 23.9 per cent.).

Pyridine isopropylstannichloride did not melt at 300°; it dissolved in warm water with slight hydrolysis. The acidified solution gave a yellow precipitate when treated with ammonium sulphide.

When *isopropylstannonic acid* was acted upon by concentrated hydriodic acid, a clear solution was not obtained. Benzene extracted a pale yellow, crystalline solid from the reaction products. This gave no carbon dioxide or water when ignited with pure copper oxide. The substance melted at 144° and proved to be stannic iodide. Crystals of potassium stanni-iodide, K_2SnI_6 , were obtained when *isopropylstannonic acid* was heated with potassium iodide and hydriodic acid.

With pyridine, the only product of interaction of the acid and hydriodic acid which separated was pyridine tri-iodide, C_5H_5N, HI_3 , in brown needles.

Tin Diisopropyl Dichloride, $(C_3H_7)_2SnCl_2$.—Tin diisopropyl oxide (5 grams) was dissolved in 25 c.c. of hot concentrated hydrochloric acid. After cooling in a desiccator, this solution gave almost colourless, transparent crystals, which were recrystallised from benzene, in which they dissolved but sparingly in the cold (Found : Cl = 26.1; Sn = 43.4. $C_6H_{14}Cl_2Sn$ requires Cl = 25.7; Sn = 43.1 per cent.).

Tin diisopropyl dichloride melted at 80–84°, and was soluble in water, alcohol, hot benzene, and hot glacial acetic acid. The chief product of hydrolysis obtained when the aqueous solution was boiled, was the hydroxy-chloride, since, after filtration and washing, it dissolved in hot dilute nitric acid. The solution gave a copious precipitate of silver chloride with silver nitrate solution.

Tin diisopropyl dichloride was deliquescent. When heated, it emitted the strong odour of the tin trialkyl haloids, which suggested that it decomposed in accordance with the equation

This matter is being investigated further.

Pyridine diisopropylstannichloride, $(C_3H_7)_2SnCl_2, 2C_5H_5N, 2HCl$.—This double salt was prepared by dissolving together 2 grams of pyridine hydrochloride and 2 grams of tin diisopropyl dichloride in 25 c.c. of hot dilute hydrochloric acid. On cooling, colourless crystals separated (Found : Cl = 28.3; Sn = 24.6. $C_{16}H_{26}N_2Cl_4Sn$ requires Cl = 28.0; Sn = 23.5 per cent.). The compound began

to darken without melting at 270° . It dissolved in water with slight hydrolysis, producing, as in the case of all these double salts, a distinctly acid solution.

Tin Diisopropyl Dibromide, $(C_3H_7)_2SnBr_2$.—This was obtained by dissolving tin diisopropyl oxide in hot hydrobromic acid. The solution deposited pale yellow, hygroscopic crystals after remaining for several days in a desiccator over solid sodium hydroxide (Found : Br = 43.0; Sn = 31.1. $C_6H_{14}Br_2Sn$ requires Br = 43.8; Sn = 32.6 per cent.).

Tin diisopropyl dibromide decomposed on addition of cold water, in which it dissolved at first. Moist alcohol, acetone, and benzene all dissolved it slightly, but it was insoluble in other organic solvents. It melted at about 54° .

Pyridine Diisopropylstannibromide, $(C_3H_7)_2SnBr_2 \cdot 2C_5H_5N \cdot 2HBr$.—About 2 grams of tin diisopropyl dibromide and 2 grams of pyridine hydrobromide were dissolved together in 20 c.c. of hot dilute hydrobromic acid. The solution deposited very pale yellow platelets (Found : Br = 48.8; Sn = 16.3. $C_{16}H_{26}N_2Br_4Sn$ requires Br = 49.6; Sn = 16.4 per cent.). The salt dissolved in water with slight hydrolysis. On heating, it began to darken at 230° and decomposed at a somewhat higher temperature.

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