On the Metallo-organic Compounds IX.
Tris-trimethyltin oxonium halide, $((CH_3)_3Sn)_3OX$.

By Taichi HARADA.

(Received September 30, 1940.)

Some time ago the present author⁽¹⁾ discussed on the formation of the compound having the empirical formula⁽²⁾ $((CH_3)_3SnOH)_2Sn(CH_3)_3X$ which is formed by the action of sunlight upon trimethyltin halide containing tetramethyltin as an impurity. The mechanism of the formation of the compound in question is proposed as follows:

$$1.\quad 2(CH_3)_3SnX \rightleftarrows ((CH_3)_3Sn)_2 + X_2$$

$$2.\quad ((CH_3)_3Sn)_2 + \frac{1}{2}O_2 \longrightarrow ((CH_3)_3Sn)_2O$$

$$3.\quad X_2 + (CH_3)_4Sn \longrightarrow (CH)_3SnX + CH_3X$$

$$4.\quad ((CH_3)_3Sn)_2O + (CH_3)_3SnX \longrightarrow ((CH_3)_3Sn)_3OX\,.$$

And then this tris-trimethyltin-oxonium halide readily combines with moisture in the solution and produces the crystalline compound in question.

The crystalline compounds are identical with the compounds formed between 2 molecular proportions of trimethyltin hydroxide and 1 molecular proportion of trimethyltin halides in moist benzene.

If the structures of the compounds were represented in the hydrate form $((CH_3)_3Sn)_3OX+H_2O$, then we might expect that the anhydrous form $((CH_3)_3Sn)_3OX$ would be formed by the direct action of trimethyltin halides upon trimethyltin oxide. However, trimethyltin oxide has not been isolated until very recently. Of course before the isolation, it has been known as an amorphous powder, insoluble in water and all organic solvents, and to be formed by a slow oxidation of the trimethyltin free group in the air⁽³⁾⁽⁴⁾.

Therefore, the direct treatment of the oxide with trimethyltin halide to prepare the oxonium salt $((CH_3)_3Sn)_3OX$ was not carried out. Of recent, the formation and the existence of the oxide as such have been held with doubt. The present author studied the preparation of trimethyltin oxide⁽⁵⁾ and isolated the oxide as a colourless liquid through the following reaction:

$$2(CH_3)_3SnOH + Na = ((CH_3)_3Sn)_2O + NaOH + \frac{1}{2}H_2\,.$$

---

(1) T. Harada, this Bulletin, **2** (1927), 105.

(2) Kraus and T. Harada, *J. Am. Chem. Soc.*, **47** (1925), 2568.

(3) Kraus and Sessions, *ibid.*, **47** (1925), 2629.

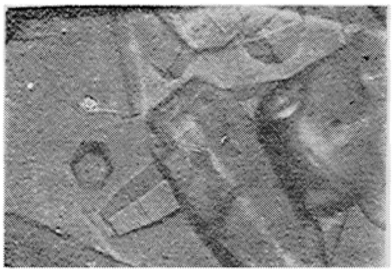
(4) Kraus and Bullard, *ibid.*, **52** (1930), 4057.

(5) T. Harada, to be published shortly in *Sci. Papers Inst. Phys. Chem. Research* (Tokyo).

Trimethyltin oxide readily combines with trimethyltin halide directly or through the medium of a dry solvent to form the oxonium compound, $((CH_3)_3Sn)_3OX$.

Recently Kraus and his student⁽⁴⁾ studied the structure of the complex compound, which might be written as $((CH_3)_3Sn)_3OX+H_2O$ (A) or $((CH_3)_3SnOH)_2Sn(CH_3)_3X$ (B), and investigated whether it is hydrated or not. They described that when the compound is treated with metallic sodium in liquid ammonia, an amount of hydrogen sufficient to correspond to the hydrate formula (A) is not produced. Certainly, the determination of the presence of water in question by the liquid ammonia method is one way of getting some notion regarding the structure of the complex compound since the constituent $(CH_3)_3SnOH$ in the formula (B) does not give an evolution of hydrogen⁽⁶⁾. When the experiment is carefully repeated with the iodide, no hydrogen but a small amount of a hydrocarbon is produced. However, this reason is not strong enough to reject the hydrate formula $((CH_3)_3Sn)_3OX,H_2O$, because if the compound dissociated or reacted with ammonia the amine complex of $(CH_3)_3SnX$ might be formed.

Then the oxide as soon as freed may react with the water and produces trimethyltin hydroxide⁽⁵⁾. If so one might expect that the solution will not give any evolution of hydrogen even though it is treated with 3 atomic proportions of sodium but will form trimethyltin, sodium hydroxide and sodium halide. It is true, however, that the water in the compound in question can not be removed without accompanying decomposition⁽¹⁾. It is also true that once the compound $((CH_3)_3Sn)_3OX$ is dissolved in a moist solvent, the compound $((CH_3)_3SnOH)_2Sn(CH_3)_3X$ is formed. Discussions and conclusions on the compounds of this type and related compounds will be presented in a subsequent paper.⁽⁷⁾



$((CH_3)_3Sn)_3OI$ Crystals in dry petroleum ether

Experimental Part. $((CH_3)_3Sn)_3OI$:—(A) The dry benzene (or petroleum ether) solution of trimethyltin oxide was treated with an excess of trimethyltin iodide. A crystalline precipitate (or crystals) was readily formed. The crystals were washed with dry petroleum ether to remove the iodide and subjected to dry air over P_2O_5 in a desiccator for a few minutes to evaporate the ether, and analyzed for the halogen. It melts at 94°C (uncor.) with slow decomposition.

Subs. 0.4054 g. AgI 0.1503 g. Calc. for $C_9H_{27}OSn_3I$; I, 20.01% Found: 20.04%.

(B) Trimethyltin oxide was treated directly with an excess of

---

(6) T. Harada, this Bulletin, **4** (1929), 266.

(7) T. Harada, to be published shortly in *Sci. Papers Inst. Phys. Chem. Research* (Tokyo).

trimethyltin iodide, and white powder-like crystals⁽⁸⁾ immediately formed with evolution of heat. In this experiment a trace of white insoluble dimethyltin oxide was also formed rendering the compound difficult to purify (free from the oxide) in the original state since the compound is sensitive to moisture when dissolved. The mixed precipitate, therefore, was washed with dry petroleum ether in order to remove the excess trimethyltin iodide and was then dissolved in moist benzene, filtered and finally crystallized as $((CH_3)_3SnOH)_2Sn(CH_3)_3I$.

Subs. 0.2662 g. AgI 0.0945 g. Calc. for $C_9H_{29}O_2Sn_3I$; I, 19.43% Found: 19.20%.

Action of Na on the mixture $((CH_3)_3Sn)_3OI$ and H_2O in liquid ammonia:— About 2.78 g. of $((CH_3)_3Sn)_3OI$ was dissolved in liquid NH_3 and about 0.07 g. of H_2O was added to the solution. The mixture was then treated with an excess of Na giving a permanent light yellow coloration of $(CH_3)_3SnNa$. In this reaction no hydrogen but 7.5 c.c. of an unidentified hydrocarbon gas was produced; while Na if acting on the amount of water used should give 43.5 c.c. of H_2 at the standard condition.

Action of Na on $((CH_3)_3SnOH)_2Sn(CH_3)_3I$ in liquid NH_3:— (A) About 1.96 g. of the sample was dissolved in liquid ammonia and treated with about 0.5 g. of Na. In this experiment 8.6 c.c. of gas was obtained at the standard condition. The gas was not hydrogen but an unidentified hydrocarbon.

However, when this reduction was carried out with the iodide (1 mol proportion) and Na (1 atom proportion) in a relatively large amount of the solvent, a considerable amount of dimethyltin oxide⁽⁹⁾ containing trimethyltin hydroxide was obtained along with trimethyltin. The formation of dimethyltin oxide in this case is due to a decomposition of $(CH_3)_3SnOH$ by the long treatment with liquid NH_3; for the reason that even by simply streaming liquid ammonia upon $(CH_3)_3SnOH$ (in the absence of Na), a considerable amount of an unidentified hydrocarbon gas was shortly evolved leaving dimethyltin iodide.

$((CH_3)_3Sn)_3OBr$:—This compound was prepared as was the corresponding iodide by treating trimethyltin oxide with an excess of trimethyltin bromide in dry petroleum ether; m.p. 88° (uncor.) with a slow decomposition.

Subs. 0.4671 g. AgBr 0.1453 g. Calc. for the formula: Br, 13.60% Found: 13.40%.

In this method, when trimethyltin chloride was used instead of the bromide a colourless liquid separated out simultaneous with the formation of a small amount of $(CH_3)_2SnO$.

---

(8) This was identical with the precipitate formed from the dry benzene solution of $(CH_3)_3Sn$ containing $(CH_3)_3SnI$ by oxidation in dry air (T. Harada, this Bulletin, **2** (1927), 105.).

(9) It was thought that it might be $((CH_3)_3Sn)_2O$ in a previous experiment (T. Harada, this Bulletin, **2** (1927), 105.), for it appeared at that time to be the same substance obtained by a slow oxidation of $(CH_3)_3Sn$ in the air. (Kraus and Sessions, *J. Am. Chem. Soc.*, **47** (1925), 2629.)

Summary.

Tris-trimethyltin-oxonium halide $((CH_3)_3Sn)_3OX$ has been prepared by the direct treatment (or in a dry solvent, for example, dry petroleum ether) of $((CH_3)_3Sn)_2O$ with $(CH_3)_3SnX$ according to the equation: $((CH_3)_3Sn)_2O+Sn(CH_3)_3X=((CH_3)_3Sn)_3OX$.