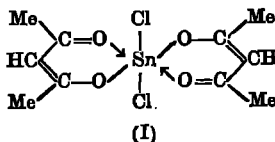


## Reactions of Stannic Chloride with Acetylacetone

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A detailed study has been made of the reaction between stannic chloride and acetylacetone. In the refluxing benzene, the reaction in varying molar ratios yields a light brown crystalline solid, corresponding to  $\text{SnCl}_2(\text{AcAc})_2$  (I) which has been shown to be a simple monomeric, non-conducting compound. In cold, a product, corresponding in analysis to  $\text{SnCl}_4 \cdot \text{HAcAc}$ , is obtained, to which the plausible formula  $[(\text{HAcAc})_2\text{SnCl}_2]_n$  has been assigned. This has been confirmed by its observed conductance in nitrobenzene as well as by the isolation of an identical product by adding stannic chloride to  $[(\text{HAcAc})_2\text{SnCl}_2]\text{Cl}_2$ , obtained by passing hydrogen chloride in a solution of (I).

A light brown crystalline solid, moderately soluble in benzene, with the empirical formula  $\text{SnCl}_2(\text{AcAc})_2$  was reported by Dilthey<sup>1</sup> and by Rosenheim *et al.*<sup>2</sup> by the condensation of acetylacetone with stannic chloride. This has been confirmed in the present study and it has been further shown that the same compound is obtained irrespective of the molar ratios of the reactants in refluxing benzene. This behaviour is different from that of the titanium tetrachloride<sup>3</sup> which affords  $\text{TiCl}_3(\text{AcAc})$  in 1:1 molar reaction. On account of the high m.p. (202-203°) compound (I) was assigned a trimeric formula,  $[\text{Sn}(\text{AcAc})_2]_3 \cdot \text{SnCl}_6$ , by Dilthey<sup>1</sup>. Morgan and Drew<sup>4</sup>, however, found it to be monomeric in boiling benzene. Like the corresponding titanium derivative<sup>3</sup>, compound (I) does not react with acetic acid and ethanol and is recrystallised unchanged from the above solvents as well as from benzene and chloroform. Its monomeric nature has been further confirmed by measuring its molecular weight cryoscopically in benzene. On the basis of the above properties and its very low conductance in nitrobenzene solutions, the following plausible structure, similar to that of the corresponding titanium derivative<sup>5</sup>, is proposed for this derivative:



Morgan and Drew<sup>4</sup> also found the reaction of stannic chloride and acetylacetone in 1:1 molar ratio in chloroform at the room temperature to yield a product with the empirical formula  $\text{SnCl}_4 \cdot \text{HAcAc}$ . This was assumed<sup>4</sup> to be a equimolecular mixture of  $\text{SnCl}_2(\text{AcAc})_2$  and  $\text{H}_2\text{SnCl}_6$ . It is obtained as a white crystalline solid, sparingly soluble in benzene which changes to a light brown colour on keeping. It has been confirmed during the course of this work that the nature of the product (m.p. 151°) remains unaltered under a variety of conditions, viz., (i) ratio of the reactants and (ii) presence or absence of solvents. The

1. Ber., 1902, 36, 929; *Annalen*, 1906, 344, 339.

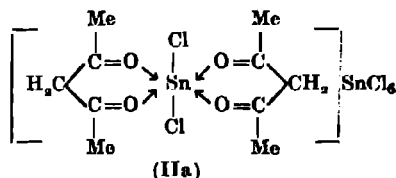
2. Ber., 1902, 36, 1836.

3. Puri *et al.*, *J. Less-common Metals*, 1962, 4, 481.

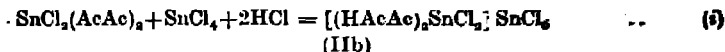
4. *J. Chem. Soc.*, 1924, 373.

5. Puri and Mehrotra, *J. Less-common Metals*, 1961, 3, 247.

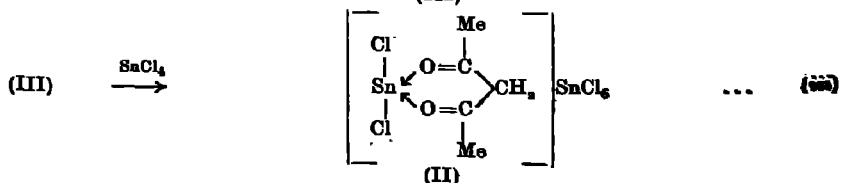
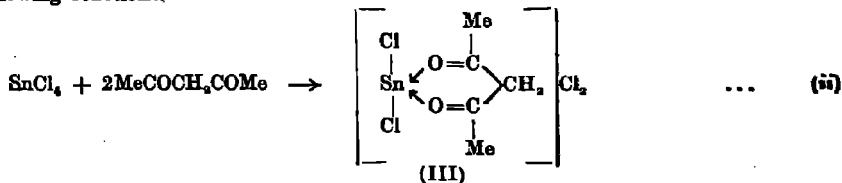
product has been further found to remain unchanged in composition even when heated under reduced pressure (0.1 mm) at 55–60°. If it were a mixture of  $\text{SnCl}_2(\text{AcAc})_2$  and  $\text{H}_2\text{SnCl}_6$ , as suggested above, the latter component could be expected to be volatilised under these conditions. The fact that  $\text{H}_2\text{SnCl}_6$  actually behaves like this was verified by evacuating a solution of stannic chloride in benzene, saturated with  $\text{HCl}$  gas, when it was found to leave no residue. The product also could not be a simple addition product of  $\text{SnCl}_4$  and  $\text{HAcAc}$ , as  $\text{SnCl}_4$  itself (a covalent compound with  $sp^3$  hybridisation) does not show any conductance in nitrobenzene. In view of the above, the 1:1 reaction product may have the formulation (IIa):



The above formulation has been confirmed by its molar conductance of about 22 mhos in nitrobenzene (Table IV). It has been further supported by the observation that the same compound (m.p. 152°; molar conductance 22; Table IV) is obtained by passing  $\text{HCl}$  gas in a 1:1 mixture of  $\text{SnCl}_2(\text{AcAc})_2$  and  $\text{SnCl}_4$  in benzene:



The identity of (IIa) and (IIb) is further confirmed by mixed m.p. of 151–53°. Although compound (IIa) is stable under reduced pressure in the solid state, it appears that on refluxing in solvents, the decomposition goes to completion in benzene according to the reverse of the reaction (i), but remains incomplete in lower boiling chloroform. As it has been found during the course of this work that  $\text{SnCl}_2(\text{AcAc})_2$  has a negligible conductance (Table IV) in nitrobenzene and that the molar conductance of  $\text{H}_2\text{SnCl}_6$  is about 9.6 mhos, the conductance of a simple equimolecular mixture of these two should have been the same (9.6 mhos) as that of  $\text{H}_2\text{SnCl}_6$  (against the value of about 22 mhos, observed for both IIa and IIb). All these facts lend support to the assumed formula (II) for this derivative. The most plausible way in which compound (II) could be formed may be represented by the following reactions:



The proposed mechanism appears to be supported by isolation of a compound, almost corresponding in analysis to compound (III), by slow addition of  $\text{SnCl}_4$  to a large excess of well-cooled acetylacetone. To substantiate the above idea, the intermediate product (III) was obtained indirectly by  $\text{SnCl}_4(\text{AcAc})_2$  and  $\text{HCl}$  gas reaction in benzene as a deep red, highly viscous liquid, insoluble in benzene. Its molar conductance (Table IV) was observed approximately half of (II). This reacted with  $\text{SnCl}_4$ , furnishing (II), though the reaction appeared to be slow due to the insoluble nature of compound (III).

## EXPERIMENTAL

Glass apparatus with interchangeable joints was used. Extreme care was taken to exclude moisture. Fractionations were carried out in a column, 30" long, packed with raschig rings and fitted to a total-condensation variable take-off stillhead.

Stannic chloride was prepared by passing dry chlorine gas over tin metal (A.R.) and was refluxed over thionyl chloride for several hours. It was then fractionated before use. Benzene (B.D.H.) was allowed to stand over sodium wire, refluxed over sodium, distilled, and finally dried azeotropically with ethanol. Acetylacetone (Riedel) and chloroform (E. Merck) were dried by refluxing over aluminium isopropoxide, followed by careful fractionation.  $\text{HCl}$  gas was generated by dropping  $\text{H}_2\text{SO}_4$  (A.R., conc.) over ammonium chloride (A.R.) and was dried by bubbling through  $\text{H}_2\text{SO}_4$  (A.R.). Nitrobenzene was redistilled (208°) immediately before use.

The sample was dissolved in  $\text{HNO}_3$  (conc.) and the solution was neutralised by ammonia, using methyl orange as an indicator. Before filtration ammonium nitrate was added for coagulation and the precipitate was ignited to  $\text{SnO}_2$ . Chloride was estimated gravimetrically in the filtrate.

### I. Reactions between Stannic Chloride and Acetylacetone at the Room Temperature

Acetylacetone was added dropwise to freshly distilled stannic chloride (either alone or in presence of benzene or chloroform). An exothermic reaction took place and a white crystalline solid immediately separated. After filtration and washing with benzene, the solid was finally dried under reduced pressure (20-23°/0.1-0.5 mm). The results are recorded in Table I (for reactions in absence of solvents) and Table II (for reactions in presence of solvents). As is evident, the analysis of the solid corresponds to the empirical formula  $\text{SnCl}_4 \cdot \text{HAcAc}$  (calc. Sn, 32.9%; Cl, 39.32%).

TABLE I

$\text{SnCl}_4$ .	Acetylacetone.	Molar ratio.	Yield.	Found.	
				%Sn.	%Cl.
3.21 g.	1.23 g.	1 : 1	4.41 g.	33.15	38.95
2.80	2.15	1 : 2	3.25	33.00	39.15
3.70	5.69	1 : 4	3.16	32.51	39.71

TABLE II

SnCl <sub>4</sub> .	Acetylacetone.	Molar ratio.	Solvent.	Yield.	Found.	
					%Sn.	%Cl
3.46 g.	1.33 g.	1:1	20 g. (C <sub>6</sub> H <sub>6</sub> )	4.63 g.	33.00	39.11
2.69	2.21	1:2	25 "	3.07	32.80	39.22
4.00	6.16	1:4	25 "	4.31	32.10	39.59
2.43	0.94	1:1	24 (CHCl <sub>3</sub> )	3.32	32.91	39.33
2.99	2.28	1:2	20 "	2.24	32.56	39.00
4.72	7.30	1:4	20 "	4.02	32.71	38.80

## II. Effect of Heat on the Derivative SnCl<sub>4</sub>.AcAcH

(a). *In Absence of Solvent.*—Compound (IIa) (1.054 g.) was heated at 55-60°/0.1 mm. There was no loss in total weight. (Found: Sn, 33.10; Cl, 39.00. Calc. for SnCl<sub>4</sub>.AcAcH: Sn, 32.91; Cl, 39.32%).

(b). *In Presence of Benzene.*—The above derivative (3.80 g.) was taken in benzene (40 g.). On refluxing (bath 100-10°) the solid dissolved and heating was continued till evolution of HCl had ceased. The excess solvent was distilled and the product was dried under reduced pressure (35°/0.5 mm). A light brown crystalline solid (2.0 g.) was obtained. [Found: Sn, 30.41; Cl, 18.10. Calc. for SnCl<sub>2</sub>(AcAc)<sub>2</sub>: Sn, 30.60; Cl, 18.28%].

(c). *In Presence of Chloroform.*—The above derivative (4.61 g.) was heated under reflux in chloroform (45 g.) till evolution of HCl had stopped. Excess of the solvent was distilled and the contents were dried under reduced pressure (40°/0.5 mm). A yellowish white crystalline solid (2.41 g.) was obtained. [Found: Sn, 31.19%; Cl, 24.40%; ratio Sn: Cl, 1:2.51].

## III. Reactions of Stannic Chloride and Acetylacetone in Refluxing Benzene and Chloroform

The acetylacetone was added to stannic chloride in presence of the solvent when a white solid separated as in reaction (I). On refluxing, the solid redissolved slowly and HCl gas evolved. Refluxing was continued till no further evolution of HCl was observed. The excess solvent was then distilled and the product was dried (30-50°) under reduced pressure (0.5-1.0 mm). The analyses of all the products (Table III) correspond to SnCl<sub>2</sub>(AcAc)<sub>2</sub> (calc. Sn, 30.60%; Cl, 18.28%).

TABLE III

SnCl <sub>4</sub> .	Acetylacetone.	Molar ratio.	Solvent.	Refluxed for.	Yield.	Found.	
						%Sn.	%Cl.
2.31 g.	0.89 g.	1:1	40 g. (C <sub>6</sub> H <sub>6</sub> )	46 hrs.	1.70 g.	30.70	18.50
6.60	5.20	1:2	48 "	10	7.50	30.64	18.28
3.32	5.09	1:4	50 "	9	3.29	30.70	18.28
6.60	5.30	1:2	45 (CHCl <sub>3</sub> )	13	7.15	30.60	18.28
6.10	9.30	1:4	55 "	13	6.10	30.63	18.28

M.W. found, 406; calc., 387.8.

IV. *Reaction of HCl gas on a Mixture of Stannic Chloride and Dichlorodiacetylacetone of Tin in Equimolar Proportion*

(a). In a benzene solution (50 g.) of stannic chloride (1.88 g.) and  $\text{SnCl}_2(\text{AcAc})_2$  (2.80 g.) dry HCl gas was passed. Noticeable heat was produced. After about 15 minutes a light brown solid began to separate. The passing of the gas was discontinued after 8 hours, when the supernatant benzene became colorless. The solvent was removed under reduced pressure (25°/1.0 mm). A light brown solid (4.99 g.) was obtained. {Found: Sn, 32.89; Cl, 39.30. Calc. for  $[\text{Sn}(\text{AcAcH})_2\text{Cl}_2]\text{SnCl}_2$ : Sn, 32.91; Cl, 39.32%}.

(b). *Reaction of  $\text{SnCl}_2(\text{AcAc})_2$  with HCl gas in Benzene.*—In a benzene solution (40 g.) of  $\text{SnCl}_2(\text{AcAc})_2$  (2.61 g.) dry HCl gas was passed (18 hours) till the supernatant benzene became colorless. A deep red, highly viscous liquid settled at the bottom. Noticeable heat was produced in the reaction. Excess of the solvent was removed at the pump and a deep red, highly viscous liquid (3.06 g.) was obtained. {Found: Sn, 24.52; Cl, 30.05; Sn:Cl, 1:4.10. Calc. for  $[\text{Sn}(\text{AcAcH})_2\text{Cl}_2]\text{Cl}_2$ : Sn, 25.76; Cl, 30.77%}.

Stannic chloride (3.30 g., 10*M*) was added to the above product (0.51 g.) and the mixture was allowed to stand for about 4 hours with occasional vigorous shaking. The reaction mixture was dried under reduced pressure (35°/0.5 mm) when a brown solid (0.60 g.) was obtained. {Found: Sn, 32.80; Cl, 39.19; Sn:Cl, 1:4.0. Calc. for  $[\text{Sn}(\text{AcAcH})_2\text{Cl}_2]\text{SnCl}_2$ : Sn, 32.91; Cl, 39.32%}.

V. *Reaction of Stannic Chloride with Acetylacetone in Large Excess*

Stannic chloride (1.90 g.) was added dropwise with vigorous shaking after each addition into acetylacetone (20 g.), kept in a freezing mixture (−15°). The addition of the first few drops was marked by appearance of a white crystalline solid which dissolved immediately. The volatile solvent was removed under reduced pressure (25–30°/0.1–0.2 mm). A light brown solid (3.11 g.) was obtained. [Found: Sn, 24.81%; Cl, 28.20%; Sn:Cl, 1:3.80].

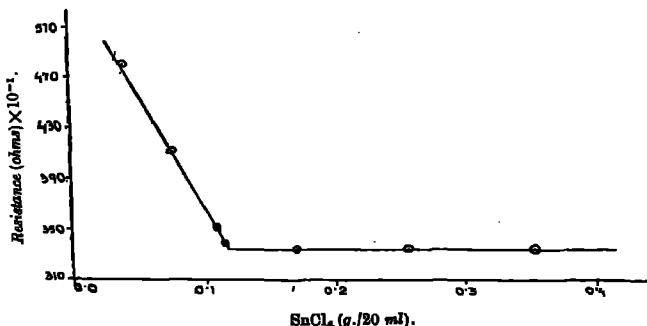


FIG. 1. In 0.046*N*-HCl in nitrobenzene.

*Measurement of Conductance in Nitrobenzene*

The conductances of various derivatives in dry nitrobenzene were measured on an Electronic magic eye conductance apparatus; a Kohlrausch type fixed parallel-plate cell was

used. The molar conductance of  $H_2SnCl_6$  was calculated as about 9.6 mhos. The results are recorded in Table IV from the titration of  $HCl$  with  $SnCl_4$  (Fig. 1).

TABLE IV

$[Sn(AcAcH)_2Cl_2]SnCl_6$ (IIa)		$[Sn(AcAcH)_2Cl_2]SnCl_6$ (IIb)		$SnCl_2(AcAc)_2$ (I)		$[Sn(AcAcH)_2Cl_2]Cl_4$ (III)	
*Conc.	Molar con- duc. at 23°	*Conc.	Molar con- duc. at 24°	*Conc.	Molar con- duc. at 20°	*Conc.	Molar con- duc. at 30°
1.419	21.9	1.890	21.8	6.70	0.395	5.04	9.60
1.974	20.8	2.229	22.8	3.02	0.587	13.60	10.40
2.467	22.9	2.790	22.3	5.60	0.369	5.63	10.00
2.728	21.5	3.105	21.0	4.16	0.547	5.81	10.78
1.419	21.9	..	..	10.20	0.370	..	..

\* Conc. in moles  $\times 10^3$ .

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