

Synthesis and Reactions of Tin Tetracarboxylates

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Novel and convenient routes for tin tetracarboxylates have been explored. Tin tetraacetate and tetrapropionate have been obtained in quantitative yields by the interaction between tin tetrathiolate, $\text{Sn}(\text{SR})_4$ ($\text{R} = \text{Et}, \text{Bu}$) and acetic or propionic anhydride. Transacylation reactions of tin tetraacetate with higher mono- and dicarboxylic acids in different stoichiometric ratios have been carried out in refluxing toluene. Mixed tin chloride carboxylates, $\text{SnCl}_n(\text{OAc})_{4-n}$ have been prepared by co-disproportionation between tin tetraacetate and tin tetrachloride.

Introduction

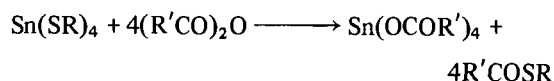
Although the chemistry of organotin(IV) carboxylates has been explored in detail, comparatively little is known about tin tetracarboxylates [1], which may be due to the absence of a facile route for their synthesis. Reactions of carboxylic acids or their metal (sodium, lithium or silver) salts with tin tetrachloride do not appear to proceed to completion and in general, yield the dichlorotin dicarboxylate derivatives [2-4], except in cases of $\text{SnCl}_4/\text{CF}_3\text{COOAg}$ and $\text{SnCl}_4/\text{Me}_2\text{CHCOOAg}$ systems [5]. Henderson and Holliday [6] have synthesized various tin tetracarboxylates by heating tetravinyltin and carboxylic acids in a sealed tube at 110 °C for ~40 hr, but lower reaction temperatures or shorter reaction times resulted in incomplete reaction. Reaction of dibutyltin dicarboxylate with SnBr_4 [7] and solvolysis of SnI_4 in acid anhydrides [8] have also been reported briefly to yield tin tetracarboxylates.

We wish to report a new and convenient route for the synthesis of tin tetracarboxylates from easily available tin tetrathiolates [9] and acid anhydrides.

Results and Discussion

Tin tetraacetate and tetrapropionate have been prepared by the following route:

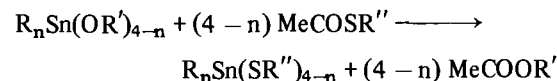
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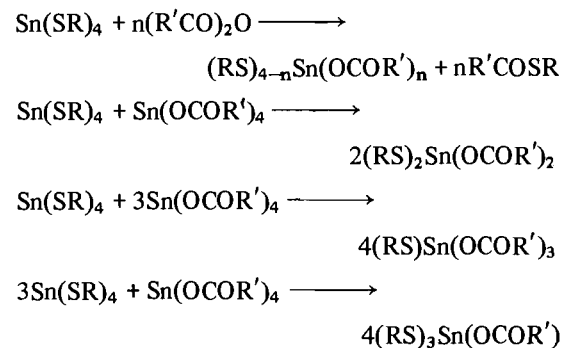
$\text{R} = \text{Et}, \text{Bu}$

$\text{R}' = \text{Me}, \text{Et}$

Quantitative yields of tin tetracarboxylate in these reactions indicate that the backward reaction does not proceed to any appreciable extent. This may be compared with recent findings of Voronkov *et al.* [10] that organotin alkoxides react with thioesters to give organotin thiolates.

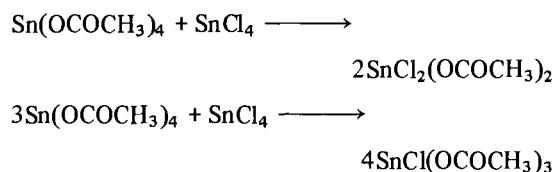


Repeated attempts to synthesize mixed thiolate carboxylate derivatives, $\text{Sn}(\text{SR})_n(\text{OCOR}')_{4-n}$ by a variety of routes (*e.g.*, reactions given below) resulted only in mixtures of products, which could not be separated into their components:

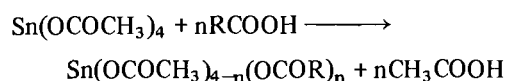


The importance of co-disproportionation reactions for the synthesis of different types of organotin derivatives is well established. However, it seems that such reactions with tin thiolates are rather slow and do not give pure products, expected on the basis of the stoichiometry of the reactants. Thus, although we have earlier been able to obtain butyltin ethoxide carboxylates, $\text{BuSn}(\text{OEt})_n(\text{OCOR}')_{3-n}$, in quantitative yields from $\text{BuSn}(\text{OEt})_3$ and $\text{BuSn}(\text{OCOR}')_3$ [12], the corresponding reactions between $\text{BuSn}(\text{SR})_3$ and $\text{BuSn}(\text{OCOR}')_3$ always resulted in mixtures [13].

Synthesis of tin chloride carboxylate derivatives, however, seems to be facile by the interaction between tin tetracarboxylates and tin tetrachloride. Dichloride diacetate and monochloride triacetate derivatives of tin have been obtained by the following reactions:



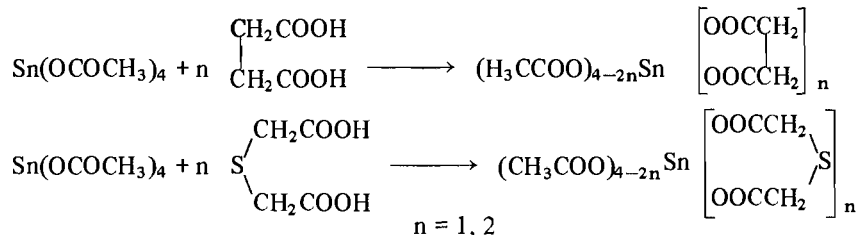
For the preparation of higher tin tetracarboxylates from tin tetraacetate, transacylation reactions can be pushed to completion in refluxing toluene by fractionating out acetic acid in the form of an azeotrope (b.p., 106 °C) with toluene. Transacylation appears to be particularly suited for the synthesis of mixed carboxylate derivatives. Thus, in the reactions of tin tetraacetate with monochloro- and dichloro- acetic, butyric and benzoic acids, stepwise replacement of acetate groups has been demonstrated and the mixed derivatives have been obtained in quantitative yields (95–100%).



(where R = ClCH₂, Cl₂CH, CH₃CH₂CH₂ and C₆H₅; n = 1–4)

It may be mentioned here that similar transacylation reactions between tin tetraacetate and trichloroacetic acid in different molar ratios did not yield any pure products. Evidence for the formation of tin tetrachloride during the reaction was obtained. Facile decomposition of trichloroacetate derivatives of tin [14] has been recorded before also.

Transacylation between tin tetraacetate and succinic and thiodiacetic acids appears to be comparatively slower and requires a longer time even when the acetic acid is removed azeotropically. This may be due to the insolubility of succinic and thiodiacetic acids in toluene. All the compounds obtained from these reactions in 1:1 and 1:2 molar ratios are white solids, which are insoluble in common organic solvents.



Most of the new derivatives have been characterized by their PMR spectra (CDCl₃ or CCl₄). The spec-

trum of tin tetraacetate shows only one singlet at 7.9τ for the acetate protons and the position of this signal remains unaffected in mixed acetate butyrate derivatives, but shifts downfield by 0.1 to 0.2 ppm in mixed chloroacetate, dichloroacetate and benzoate derivatives.

The mixed derivatives with chloroacetic and dichloroacetic acids show CH₂Cl and CHCl₂ protons as singlets at 5.7 and 3.7τ respectively whereas in mixed benzoate derivatives, the aromatic protons appear as multiplets in the region 1.4–2.8τ. In the corresponding butyrate derivatives, a triplet at 7.6τ, a sextet at 8.3τ and again a triplet at 9.05τ are observed which may be assigned to the methylene attached to carboxyl group, the middle methylene and the methyl groups of the butyrate moiety respectively.

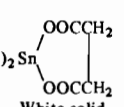
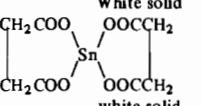
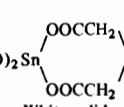
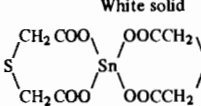
Ebulliometric molecular weight determinations show that the tin tetrabutyrates as well as mixed acetate butyrate derivatives are monomeric in refluxing benzene. Cryoscopic molecular weight measurements for tin tetraacetate and tetrapropionate, reported by Henderson and Holliday [6], are also consistent with their monomeric nature in solution.

All the three possible modes of combination of carboxylic groups (monodentate, bidentate chelating and bridging) have been reported in the structure of organotin carboxylates on the basis of i.r. spectra. The trialkyltin monocarboxylates have been reported to be five coordinate with bridging carboxylic groups, the dialkyltin dicarboxylates are hexacoordinate, with two chelating carboxylic groups and the monoalkyltin tricarboxylates are reported to be heptacoordinate. The tetracarboxylates are, on the other hand, polymeric with the two bridging carboxylic groups, but the bridges tend to break down in dilute solutions, giving monomeric species.

In view of the limited facilities available, i.r. spectra of the carboxylate (acetate, butyrate, benzoate, succinate and chloroacetates) derivatives synthesized during this period have been recorded either as Nujol mulls or in the liquid form. These show in general, an absorption around 1700 ± 24 cm⁻¹ characteristic of monodentate carboxylic groups. Further, the i.r. spectra of a number of these derivatives, which are liquids at ambient temperature, showed peaks around 1550 and 1450 cm⁻¹. These appear to indicate bridging chelate carboxylic groups

also, but final assignments do require more detailed investigations.

TABLE I. Transacylation Reaction between Sn(OCOCH₃)₄ and Monochloro, Dichloroacetic, Butyric, Benzoic, Succinic and Thiodiacetic Acids.

S. No.	Sn(OCOCH ₃) ₄ (g)	Carboxylic acid (g)	Molar Ratios of the Reactants	Formula and Nature of the Product	Acetic Acid in Azeotrope Found (g) (Calc.)	Tin (%) Found (Calc.)	Mol. wt. Found (Calc.)
1	2	3	4	5	6	7	8
With Monochloroacetic Acid							
1.	2.03	0.54	1:1	(CH ₃ COO) ₃ SnOOCCH ₂ Cl White solid	0.34 (0.34)	30.78 (30.51)	383.0 ^a (389.0)
2.	1.84	0.98	1:2	(CH ₃ COO) ₂ Sn(OOCCH ₂ Cl) ₂ White solid	0.65 (0.62)	28.12 (28.03)	425.0 ^a (424.0)
3.	1.71	1.36	1:3	(CH ₃ COO)Sn(OOCCH ₂ Cl) ₃ Black solid	0.86 (0.86)	25.87 (25.91)	459 ^a (453)
4.	1.54	1.64	1:4	Sn(OOCCH ₂ Cl) ₄ Black solid	0.92 (1.04)	24.33 (24.11)	490 ^a (493)
With Dichloroacetic Acid							
5.	1.98	0.72	1:1	(CH ₃ COO) ₃ Sn(OOCCHCl ₂) Light yellow powder	0.37 (0.33)	28.28 (28.03)	
6.	2.00	1.45	1:2	(CH ₃ COO) ₂ Sn(OOCCHCl ₂) ₂ Brownish viscous liquid	0.68 (0.68)	24.01 (24.11)	
7.	1.92	2.09	1:3	(CH ₃ COO)Sn(OOCCHCl ₂) ₃ Brownish viscous liquid	0.97 (0.97)	21.29 (21.13)	
8.	1.48	2.15	1:4	Sn(OOCCHCl ₂) ₄ Brownish viscous liquid	0.95 (1.00)	18.98 (18.83)	
With Butyric Acid							
9.	2.23	0.55	1:1	(CH ₃ COO) ₃ SnOOCCH ₂ CH ₂ CH ₃ White solid	0.37 (0.37)	31.31 (31.01)	383 ^b (383)
10.	2.46	1.21	1:2	(CH ₃ COO) ₂ Sn(OOCCH ₂ CH ₂ CH ₃) ₂ White solid	0.83 (0.83)	29.44 (28.91)	456 ^b (411)
11.	2.06	1.54	1:3	(CH ₃ COO)Sn(OOCCH ₂ CH ₂ CH ₃) ₃ Colourless liquid	1.01 (1.04)	27.31 (27.06)	438 (438)
12.	2.08	2.07	1:4	Sn(OOCCH ₂ CH ₂ CH ₃) ₄ Colourless liquid	1.41 (1.41)	25.18 (25.43)	444 (467)
With Benzoic Acid							
13.	2.29	0.79	1:1	(CH ₃ COO) ₃ SnOOC ₆ H ₅ White solid	0.39 (0.39)	28.37 (28.48)	418 ^a (417)
14.	2.01	1.38	1:2	(CH ₃ COO) ₂ Sn(OOC ₆ H ₅) ₂ White solid	0.68 (0.68)	24.61 (24.79)	479 ^a (479)
15.	1.88	1.94	1:3	CH ₃ COOSn(OOC ₆ H ₅) ₃ White solid	0.95 (0.95)	21.91 (21.95)	544 ^a (541)
16.	2.12	2.93	1:4	Sn(OOC ₆ H ₅) ₄ White solid	1.43 (1.43)	19.97 (19.70)	601 ^a (602)
With Succinic Acid							
17.	2.46	0.82	1:1	(CH ₃ COO) ₂ Sn  White solid	0.83 (0.83)	33.46 (33.66)	
18.	1.91	1.26	1:2	Sn  white solid	1.26 (1.28)	33.67 (33.85)	
With Thiodiacetic Acid							
19.	1.94	0.82	1:1	(CH ₃ COO) ₂ Sn  White solid	0.65 (0.65)	24.33 (24.30)	
20.	1.50	1.27	1:2	Sn  White solid	0.98 (1.02)	28.62 (29.44)	

^aMol. wt. was determined in chloroform.^bMol. wt. was determined in benzene.

Experimental

All glass apparatus with interchangeable joints was used throughout and special precautions were taken to exclude moisture. All reagents and solvents were carefully dried and purified by careful fractionation.

Tin tetrathiolate was prepared by passing dry ammonia into a benzene solution of thiol and tin tetrachloride. Ammonium chloride was filtered and the filtrate was distilled to remove excess of C_6H_6 . The product was finally distilled under reduced pressure, after removing the excess solvent [9].

The propionic and acetic acids were estimated with standard sodium hydroxide solution, using phenolphthalein as indicator.

Tin was estimated directly in a platinum crucible by adding two to three drops of fuming sulphuric and nitric acids, before ignition to SnO_2 .

Volhard's method was employed for estimation of chlorine.

Molecular weights were determined with the semi-micro ebulliometer (Gallenkamp), employing a thermister.

I.r. and n.m.r. spectra were recorded with Perkin-Elmer 337 and R 12 B instruments, respectively.

Synthesis of Tin Tetraacetate

A mixture of tin tetraethanethiolate (14.4 g; 41 mmol) and acetic anhydride (24.3 g; 238 mmol) were heated at 110–120 °C for 3–4 h. On keeping the liquid for 30 mts at room temperature, white needle-shaped crystals were formed (12.7 g; 93%). The solid was filtered, washed with dry ether and dried in *vacuo*. It was further purified by sublimation at 240–250 °/9 mm. *Anal.* Found: Sn, 33.35; $OCOCH_3$, 66.62. Calc. for $C_8H_{12}O_8Sn$: Sn, 33.47; $OCOCH_3$, 66.33%.

In a similar reaction, tin tetrabutaneethiolate (12.7 g; 27 mmol) and acetic anhydride (16.4 g; 161 mmol) also gave tin tetraacetate (9.1 g; 98%). *Anal.* Found: Sn, 33.29; $OCOCH_3$, 66.58%.

Synthesis of Tin Tetrapropionate

The reaction of tin tetrabutaneethiolate (19.0 g; 40 mmol) with propionic anhydride (31.3 g; 241 mmol) was similarly found to give fine white needle-shaped crystals (14.7 g; 89%). *Anal.* Found: Sn, 29.12; $OCOCH_2CH_3$, 71.05. Calc. for $C_{12}H_{20}O_8Sn$: Sn, 28.91; $OCOCH_2CH_3$, 71.11%.

Transacylation Reactions of Tin Tetraacetate with Higher Carboxylic Acids

$Sn(OCOCH_3)_4$ (2.2 g; 6 mmol) and butyric acid (0.55 g; 6 mmol) were mixed in toluene and refluxed for half an hour under a small column. Acetic acid (0.37 g; Calc. for 6 mmol, 0.38 g.) was removed azeotropically. The excess solvent was removed under

reduced pressure (60–65 °C/9 mm) to give a white solid (2.3 g.) which was found on analysis to correspond to tin monobutyrate triacetate (96%). *Anal.* Found: Sn, 31.31; Mol. wt., 383. Calc. for $C_{10}H_{16}O_8Sn$: Sn, 31.01; Mol. wt., 382.0.

Similar reactions were carried out with monochloroacetic, dichloroacetic, benzoic, succinic and thiodiacetic acids in different molar ratios. Results are tabulated in Table I.

Synthesis of Tin Dichloride Diacetate and Tin Monochloride Triacetate

$SnCl_4$ (1.2 g; 5 mmol) and $Sn(OCOCH_3)_4$ (1.7 g; 5 mmol) were mixed in chloroform (35 ml) and refluxed for 3–4 hours. After cooling the clear solution to room temperature and removing the solvent under reduced pressure (35°/5 mm), a white solid (2.9 g; 100%) was finally obtained. *Anal.* Found: Sn, 38.5; Cl, 22.95; $OCOCH_3$, 38.25. Calc. for $C_4H_6O_4Cl_2Sn$: Sn, 38.59; Cl, 23.05; $OCOCH_3$, 38.36%.

A similar reaction between $SnCl_4$ (1.02 g; 4 mmol) and $Sn(OCOCH_3)_4$ (4.2 g; 12 mmol) in chloroform (35 ml) yielded a white solid (4.7 g; 90.9%) corresponding in analysis to $SnCl(OOCCH_3)_3$. *Anal.* Found: Sn, 35.79; Cl, 10.94; $OCOCH_3$, 53.36. Calc. for $C_6H_9O_6ClSn$: Sn, 35.84; Cl, 10.7; $OCOCH_3$, 53.43%.

Acknowledgement

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