

**New Carboxylate Derivatives of Tin Oxinates, Example of Non-bridged or Non-chelated Organotin Carboxylates**

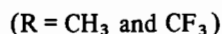
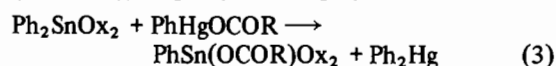
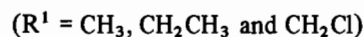
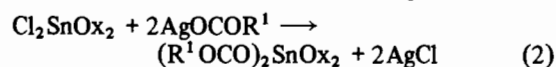
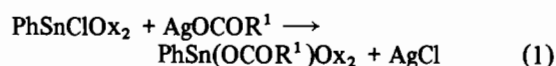
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We wish to report in this letter the syntheses of a new series of unusual carboxylate derivatives of tin oxinates in which the carboxylate groups are not ionic, chelated or bridging

The syntheses involve primarily the conventional halogen-carboxylate exchange (equation 1 and 2) as well as tin-carbon bond cleavage (equation 3) as shown in the following equations



Starting materials were procured or prepared from literature methods and analysed before use. Reactions of  $\text{PhSnClOx}_2$  and  $\text{Cl}_2\text{SnOx}_2$  with silver carboxylates were carried out in refluxing methanol for 3–4 hr, volatiles were removed and the residue was extracted with hot benzene. The yellow analytically pure crystalline compounds were obtained by the benzene extract. In the case of  $\text{Ph}_2\text{SnOx}_2$ , it was reacted with phenylmercuric carboxylates in refluxing benzene (3–4 hr), the solvent was removed and the residue was washed thoroughly with hot petrol (60–80 °C) to remove diphenylmercury,  $\text{Ph}_2\text{Hg}$ . Analytically pure crystalline yellow compound could be obtained after crystallisation from benzene or T H F.

Relevant electronic and infrared spectral data for the compounds are presented in the Table.

It is known that the 320 nm peak of oxine shifts to larger wavelength, 370–430 nm, by chelation to metals [1]. The absorptions at 380 nm in our compounds therefore suggest that all of the oxine groups are chelated in solution. Moreover, the close correspondence of the spectra of these compounds with those of  $\text{Ph}_2\text{SnOx}_2$  [2] and  $\text{PhSn(X)Ox}_2$  [2] (X = Cl, Br, I) indicates a general similarity in their structure involving hexa coordination around the tin atom.

$\nu_{\text{as}}(\text{OCO})$  in triorganotin carboxylates are usually in the range of 1548–1650  $\text{cm}^{-1}$  and the lowering of  $\nu_{\text{as}}(\text{OCO})$  in solid phase has been attributed to the formation of intermolecular coordination [3–5] by the carboxylate groups. In contrast to this,  $\nu_{\text{as}}(\text{OCO})$  in solid carboxylate oxinates are found in the region 1645–1725  $\text{cm}^{-1}$  and are very nearly

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TABLE 1 Relevant Electronic absorptions (in nm) and IR Absorptions (in  $\text{cm}^{-1}$ )

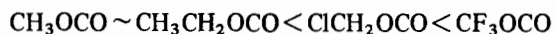
Compound	Mp(°C)	$\lambda_{\text{max}}^{\text{a}}$	$\nu_{\text{as}}(\text{OCO})^{\text{b}}$	$\nu_{\text{as}}(\text{OCO})^{\text{c}}$
$\text{PhSn(OCOCH}_3\text{)Ox}_2$	243–244	259, 380 (3 71)	1645	
$\text{PhSn(OCOCH}_2\text{CH}_3\text{)Ox}_2$	222	259, 380 (3 75)	1645	
$\text{PhSn(OCOCH}_2\text{Cl)Ox}_2$	145	259, 380 (3 74)	1672, 1680	
$\text{PhSn(OCOCF}_3\text{)Ox}_2$	241–242	260, 380 (3 69)	1725	
$(\text{CH}_3\text{OCO})_2\text{SnOx}_2$	286–287	259, 380 (3 72)	1660	
$(\text{CH}_3\text{CH}_2\text{OCO})_2\text{SnOx}_2$	266–267	259, 380 (3 70)	1650	
$(\text{ClCH}_2\text{OCO})_2\text{SnOx}_2$	205–207	259, 380 (3 68)	1690, 1700	
$\text{Ph}_2\text{SnOx}_2^{\text{d,e}}$		260, 380 (3 76)		
$\text{PhSn(Cl)Ox}_2^{\text{d,e}}$		259, 380 (3 71)		
$\text{Cl}_2\text{SnOx}_2^{\text{d,e}}$		245, 385		
$\text{Ph}_3\text{SnOCOCH}_3^{\text{d,f}}$			1548	1640
$\text{Ph}_3\text{SnOCOCH}_2\text{CH}_3^{\text{d,f}}$			1535	1632
$\text{Ph}_3\text{SnOCOCH}_2\text{Cl}^{\text{d,f}}$			1576	1662
$\text{Ph}_3\text{SnOCOCF}_3^{\text{d,f}}$			1650	1722

<sup>a</sup>UV spectra taken in cyclohexane, visible spectra in benzene solution, figures in parentheses indicate  $\log \epsilon_{\text{max}}$  <sup>b</sup> Solid in nujol mull, in  $\text{CHCl}_3$  solution no change in  $\nu_{\text{as}}(\text{OCO})$  was observed for the new oxinates <sup>c</sup>  $\nu_{\text{as}}(\text{OCO})$  in  $\text{CCl}_4$ , taken from ref 3, 5

<sup>d</sup> Data taken for comparison purposes <sup>e</sup> Ref 2 <sup>f</sup> Ref 3, 5

equal to  $\nu_{as}(\text{OCO})$  in the corresponding triorganotin carboxylates in  $\text{CCl}_4$  solution. The large increase in  $\nu_{as}(\text{OCO})$  of triorganotin carboxylates in going from solid to solution phase (by about  $100\text{ cm}^{-1}$ ) has been interpreted in terms of breaking of the intermolecular coordination bonds and consequent formation of molecules with non-bridging (or non-chelated) carboxylate groups (comparable to ester type or carboxylate groups) [4, 5]. The close similarity between  $\nu_{as}(\text{OCO})$  in carboxylate oxinates (even) in solid phase and those in simple carboxylates in solution thus indicates the absence of bridging or chelating carboxylate groups in the former. These compounds, therefore, contain hexacoordinated tin like the corresponding phenyltinhalooxinate, dichlorotindioxinate and diphenyltindioxinate. The reluctance of the carboxylates to form intermolecular bridges in these compounds may be attributed to the comparatively weak donor property of the carboxylate groups as well as the acceptor property of tin atom which has already attained hexacoordination by the presence of chelated oxine groups.

The effect of substitution at the  $\alpha$ -carbon atom of the carboxylate group in the carboxylate oxinates is analogous to that observed in simple carboxylates [5]. Thus  $\nu_{as}(\text{OCO})$  increases in the series:



This trend is, therefore, due mainly to the inductive effect of the substituent groups which raises the  $\nu_{as}(\text{OCO})$ .

The appearance of doublets, namely 1672, 1680 and 1690,  $1700\text{ cm}^{-1}$  in chloroacetate compounds could be considered to be due to the presence of two conformational isomers of the molecules as explained by Cummins [6] and Simons and Graham [7] in the case of triorganotinhaloacetates.

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