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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

$$\mathrm{PhSnClOx_2 + AgOCOR^1 \longrightarrow PhSn(OCOR^1)Ox_2 + AgCl} \qquad (1)$$

$$\mathrm{Cl_2SnOx_2 + 2AgOCOR^1 \longrightarrow (R^1OCO)_2SnOx_2 + 2AgCl} \qquad (2)$$

($R^1 = CH_3$, CH_2CH_3 and CH_2Cl)

$$\mathrm{Ph_2SnOx_2 + PhHgOCOR \longrightarrow PhSn(OCOR)Ox_2 + Ph_2Hg} \qquad (3)$$

($R = CH_3$ and CF_3)

Starting materials were procured or prepared from literature methods and analysed before use Reactions of $PhSnClOx_2$ and Cl_2SnOx_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 Ph_2SnOx_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, Ph_2Hg 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 Ph_2SnOx_2 [2] and $PhSn(X)Ox_2$ [2] (X = Cl,Br,I) indicates a general similarity in their structure involving hexa coordination around the tin atom

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

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

Compound	Mp(°C)	λ_{max} [a]	$\nu_{as}(OCO)$ [b]	$\nu_{as}(OCO)$ [c]
$PhSn(OCOCH_3)Ox_2$	243–244	259, 380 (3 71)	1645	
$PhSn(OCOCH_2CH_3)Ox_2$	222	259, 380 (3 75)	1645	
$PhSn(OCOCH_2Cl)Ox_2$	145	259, 380 (3 74)	1672, 1680	
$PhSn(OCOCF_3)Ox_2$	241–242	260, 380 (3 69)	1725	
$(CH_3OCO)_2SnOx_2$	286–287	259, 380 (3 72)	1660	
$(CH_3CH_2OCO)_2SnOx_2$	266–267	259, 380 (3 70)	1650	
$(ClCH_2OCO)_2SnOx_2$	205–207	259, 380 (3 68)	1690, 1700	
Ph_2SnOx_2 [d,e]		260, 380 (3 76)		
$PhSn(Cl)Ox_2$ [d,e]		259, 380 (3 71)		
Cl_2SnOx_2 [d,e]		245, 385		
$Ph_3SnOCOCH_3$ [d,f]			1548	1640
$Ph_3SnOCOCH_2CH_3$ [d,f]			1535	1632
$Ph_3SnOCOCH_2Cl$ [d,f]			1576	1662
$Ph_3SnOCOCF_3$ [d,f]			1650	1722

[a] UV spectra taken in cyclohexane, visible spectra in benzene solution, figures in parentheses indicate log ε max [b] Solid in nujol mull, in $CHCl_3$ solution no change in $\nu_{as}(OCO)$ was observed for the new oxinates [c] $\nu_{as}(OCO)$ in CCl_4, taken from ref 3,5 [d] Data taken for comparison purposes [e] Ref 2 [f] Ref 3, 5

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*Present address Department of Chemistry, Trinity College, University of Dublin, Dublin 2, EIRE equal to ν_{as}(OCO) in the corresponding triorganotin carboxylates in CCl_4 solution. The large increase in ν_{as}(OCO) of triorganotin carboxylates in going from solid to solution phase (by about 100 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 ν_{as}(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 α-carbon atom of the carboxylate group in the carboxylate oxinates is analogous to that observed in simple carboxylates [5]. Thus ν_{as}(OCO) increases in the series:

$$CH_3OCO \sim CH_3CH_2OCO < ClCH_2OCO < CF_3OCO$$

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

The appearance of doublets, namely 1672, 1680 and 1690, 1700 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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