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Demetallation Reactions of Triorganotin Carboxylates with Mercury(II) Salts. Investigations on Reaction Pathways

A. ROY* and A. K. GHOSH

Department of Chemistry, North Bengal University, Darjeeling, India 734430

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The synthesis of new organotin carboxylate polymers by a convenient demetallation route has recently been described by us [1]. We wish to report in this communication, on the basis of chemical evidence, the probable reaction pathways by which these polymeric products are formed.

The general reaction procedure and the organotin carboxylates studied are mentioned elsewhere [1]. In each case the products have been isolated quantitatively and the stoichiometry of the reaction has been determined. All the isolated products (Table) are characterised by chemical analyses and physical data.

Considering the stoichiometries in the reaction between triorganotin carboxylates with mercuric halides the following sequence of reactions may be proposed to account for the products:

A)

1. $nR_3SnOCOR' + nHgX_2 \rightarrow nR_2SnX(OCOR') + nRHgX$
2. $nR_2SnX(OCOR') + nR_3SnOCOR' \rightarrow nR_2Sn(OCOR')_2 + nR_3SnX$
3. $nR_2Sn(OCOR')_2 + nHgX_2 \rightarrow nRSnX(OCOR')_2 + nRHgX$
4. $nRSnX(OCOR')_2 + 2nHOH \rightarrow [RSn(OH)_2OCOR']_n + nHX + nR'COOH$

$$R_3SnOCOR' + HgX_2 + H_2O \rightarrow \frac{1}{2n}[RSn(OH)_2OCOR']_n + \frac{1}{2}R_3SnX + RHgX + \frac{1}{2}HX + \frac{1}{2}R'COOH$$

(Where (i) R = Ph; R' = H; X = Cl, (ii) R = Ph; R' = H, CH_3, CH_2CH_3; X = Br, I and (iii) R = Pr, Bu; R' = CH_3; X = Cl)

However when R = Ph; R' = CH_3, CH_2CH_3 and X = Cl, the reactions take the following course after the 3rd step of the above sequence (A):

B)

4. $nRSnX(OCOR')_2 + nR_3SnOCOR' \rightarrow nRSn(OCOR')_3 + nR_3SnX$
5. $nRSn(OCOR')_3 + nHgX_2 \rightarrow nSnX(OCOR')_3 + nRHgX$
6. $nSnX(OCOR')_3 + 4nHOH \rightarrow [Sn(OH)_4]_n + nHX + 3nR'COOH$

The overall reaction, therefore, is

$$R_3SnOCOR' + HgX_2 + \frac{4}{3}H_2O \rightarrow \frac{1}{3n}[Sn(OH)_4]_n + \frac{2}{3}R_3SnX + RHgX + \frac{1}{3}HX + R'COOH$$

The different types of polymers obtained by the reaction of $HgCl_2$ with different triphenyltin carboxylates are particularly interesting. Thus almost complete demetallation is achieved in the case of triphenyltin acetate and propionate whereas triphenyltin formate produces a polymer which contains at least one phenyl group per tin atom. We suggest two different hydrolysis steps (4th step in A and 6th in B) to account for the products formed. Such a preferential hydrolysis, however, could be attributed to the difference in acid strength of the carboxylic acids of the corresponding organotin carboxylates. With the increase in polarity of the Sn → O bond of organotin carboxylate, contraction of 'd' orbital of the Sn atom will be more pronounced. This enhances the probability of the attack of a nucleophile, *e.g.* H_2O, at the tin atom resulting in carboxylate hydrolysis. The formate having the most polarised Sn → O bond among the series studies, is readily hydrolysed after the 3rd step (A) producing the tin polymer. Hence it may be reasonable to assume that the competition between the $HgCl_2$ and moisture to react with $PhSnCl(OCOR')_2$ would determine the final steps of the reactions. It is more likely, therefore, in the reactions of triphenyltin acetate and propionate with $HgCl_2$ that the reaction of $HgCl_2$ with the intermediate $PhSnCl(OCOR')_2$ precedes the hydrolysis reaction, at least in these two cases.

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*Present address: Department of Chemistry, Trinity College, University of Dublin, Dublin-2, Eire.

TABLE. Isolated Products.

Reactants	Products[a]	Comments
$Ph_3SnOCOH + HgCl_2$	Ph_3SnCl, $PhHgCl$, $[PhSn(OH)_2OCOH]_n$	
$Ph_3SnOCOCH_3 + HgCl_2$	Ph_3SnCl, $PhHgCl$, $[Sn(OH)_4]_n$	With end blocking.
$Ph_3SnOCOCH_2CH_3 + HgCl_2$	Ph_3SnCl, $PhHgCl$, $[Sn(OH)_4]_n$	Organic and Cl groups in polymer
$Pr_3SnOCOCH_3 + HgCl_2$	Pr_3SnCl, $PrHgCl$, $[PrSn(OH)_2OCOCH_3]_n$	Incomplete reaction, 40–50%.
$Bu_3SnOCOCH_3 + HgCl_2$	Bu_3SnCl, $BuHgCl$, $[BuSn(OH)_2OCOCH_3]_n$	Unreacted $HgCl_2$ recovered.
$Cyhex_3SnOCOCH_3 + HgCl_2$		No reaction.
$Ph_3SnOCOR' + HgBr_2$	Ph_3SnBr, $PhHgBr$, $[PhSn(OH)_2OCOR']_n$	
$Ph_2Sn(OCOCH_3)_2 + HgBr_2$	$PhHgBr$, $[PhSn(OH)_2OCOCH_3]_n$	
$[PhSn(OH)_2OCOCH_3]_n + HgBr_2$	$PhHgBr$, $[Sn(OH)_4]_n$	Reaction under refluxing conditions, polymer contains bromine and organic groups as end groups.
$Ph_3SnOCOR' + HgI_2$	Ph_3SnI, $PhHgI$, $[PhSn(OH)_2OCOR']_n$	In polymer, iodine is present as terminal groups. Reactions incomplete, unreacted HgI_2 recovered.
$Ph_3SnOCOCH_3 + Hg(OCOCH_3)_2$	Ph_2Hg, $[PhSn(O)OCOCH_3]_n$	
$Ph_2Sn(OCOCH_3)_2 + PhHgOCOCH_3$	Ph_2Hg, $[PhSn(O)OCOCH_3]_n$	
$R_3SnOCOCH_3 + Hg(OCOCH_3)_2$		No reactions.

[a] Halo and carboxylic acids are also produced according to the reaction schemes (A, B and C). Value of n in polymers is uncertain. R′ = H, CH_3, CH_2CH_3; R = Pr, Bu, Cyclohexyl.

Only one type of polymeric product is isolated with $HgBr_2$ and HgI_2 (Table) irrespective of the nature of carboxylate group present. The less electrophilicity of these two halides probably allows the hydrolysis to go faster after the 3rd step (A). The less acid strength of HgI_2 is further reflected by the recovery of the unreacted halide and triorganotin carboxylates under the same condition of reactions.

The halogen–carboxylate exchange proposed in the 2nd step of the sequence (A) is well documented [2]. By analogy, exchange is also assumed for the 4th step of mechanism (B).

We have carried out reaction of diphenyltin diacetate with mercuric bromide separately. The polymeric product isolated, namely, $[PhSn(OH)_2OCOCH_3]_n$, from this reaction is the same as that obtained from the reaction of $Ph_3SnOCOCH_3$ and $HgBr_2$. This strongly favours the proposed formation and subsequent reaction of $R_2Sn(OCOR')_2$ with HgX_2 as suggested in the 2nd and 3rd reaction steps (A). In addition, it is observed that the polymer $[PhSn(OH)_2OCOR']_n$ does not react with a further mol of $HgBr_2$ at usual room temperature reaction conditions, consistent with the isolation of overall reaction products (A). However, under vigorous refluxing conditions, the tin–carbon bond of the above polymer could be cleaved ultimately producing $[Sn(OH)_4]_n$ following essentially the same course of hydrolysis as in 6th step (B).

The contrasting behaviour of $Hg(OCOCH_3)_2$ towards $Ph_3SnOCOCH_3$ is interesting to note. Reaction of triphenyltin acetate with mercuric acetate produces diphenylmercury (not phenylmercuric acetate) and polymerised phenylstannoic acetate, $[PhSn(O)OCOCH_3]_n$, the formation of which could be explained by the following reaction routes:

C)

1. $nPh_3SnOCOCH_3 + nHg(OCOCH_3)_2 \rightarrow nPh_2Sn(OCOCH_3)_2 + nPhHgOCOCH_3$

2. $nPh_2Sn(OCOCH_3)_2 + nPhHgOCOCH_3 \rightarrow nPhSn(OCOCH_3)_3 + nPh_2Hg$

3. $nPhSn(OCOCH_3)_3 + nHOH \rightarrow [PhSn(O)OCOCH_3]_n + 2nCH_3COOH$

$$Ph_3SnOCOCH_3 + Hg(OCOCH_3)_2 + H_2O \rightarrow \frac{1}{n}[PhSn(O)OCOCH_3]_n + Ph_2Hg + 2CH_3COOH$$

The isolation of polymeric phenylstannoic acetate from an independent reaction run between $Ph_2Sn(OCOCH_3)_2$ and $PhHgOCOCH_3$ is in good agreement with our proposed intermediate formation of $Ph_2Sn(OCOCH_3)_2$ and $PhHgOCOCH_3$ and their subsequent reaction with each other as shown in steps 1 and 2 (C). Isolation of Ph_2Hg obviously shows that $PhHgOCOCH_3$ is a better dearylating agent than the phenylmercuric halides. $PhSn(OCOCH_3)_3$, in presence of moisture, is known to hydrolyse forming polymeric stannoic acetate [3] as proposed in the final step (C).

Finally it may be mentioned that these demetallation reactions of triorganotin carboxylates with $HgCl_2$ depend on the nature of the organic groups bonded to tin (see Table). Based on the amounts of unreacted $HgCl_2$ recovered from each of these reactions it seems that the reactions follow the same trend (*i.e.* Ph $\gg$ Pr $>$ Bu $\ggg$ cyclohexyl) of electrophilic substitution at carbon centre bonded to tin atom [4–6] in polar solvents. However, the possibility of nucleophilic assistance by halogen or carboxylate groups should not be completely ruled out.

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