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COMMUNICATION

Disproportionation of triorganotin species, R_3SnX

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Triorganotin compounds, R_3SnX, have found extensive use as a biological agents in such areas as agrochemicals, marine antifoulants and timber preservatives. In contrast, di(R_2SnX_2) and tetra-organotin derivatives (R_4Sn) possess less biological activity than do their triorganotin counterparts. It has been shown that disproportionation of R_3SnX species (i.e. to produce R_2SnX_2 and R_4Sn) can occur especially when X is a chelating or bridging group such as oxide, carboxylate, hydroxy ketone or hydroxyquinoline. This process has implications for the industrial applications and analysis of R_3SnX compounds.

Keywords: Disproportionation, triorganotin compounds

INTRODUCTION

Triorganotin compounds, R_3SnX, have had varied application, particularly as biological agents in such areas as wood preservation, marine antifouling and as agrochemicals.[1] Di- and tetra-organotin species have less bioactivity than do their triorganotin counterparts.[2] It is thus of some importance for applicational purposes that the triorganotin moiety remains intact for as long as possible *in situ*. One such process that affords lower alkylated derivatives is degradation, i.e. cleavage of Sn–C bonds resulting in loss of organic moieties, viz.

$$R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4$$

Another process leading to less bioactive species is disproportionation, i.e. the formation of di- and tetra-organotin products from triorganotin compounds:

$$2R_2SnX \rightarrow R_2SnX_2 + R_4Sn$$

Although there have been numerous observations of degradative processes,[3] the phenomenon of disproportionation is less well understood or documented. In this preliminary paper, we suggest evidence that disproportionation may be more widespread than hitherto realised.

EXPERIMENTAL

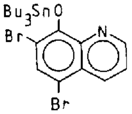
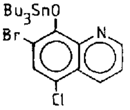
Compounds

The tributyltin carboxylates, $Bu_3SnOCOR$, where $R = C_{11}H_{23}$, C_6H_5, $C_6H_4NO_2-4$, and the tributyltin derivatives of 5,7-dibromo-8-hydroxyquinoline and 5-chloro-7-bromo-8-hydroxyquinoline were prepared by azeotropic dehydration reactions between equimolar quantities of bis(tributylin) oxide and the appropriate carboxylic acid or substituted 8-hydroxyquinoline in refluxing toluene.

NMR spectroscopy

^{119}Sn NMR spectra were recorded on JEOL FX60Q and FX90Q spectrometers at 22.24 MHz and 33.35 MHz respectively, under Nuclear Overhauser suppressed conditions. Field frequency lock for the FX60Q and FX90Q instruments was to external D_2O. Chemical shifts ($\delta\,^{119}Sn$) are relative to Me_4Sn and are accurate to ±0.2 ppm.

Table 1 Disproportionation of triorganotin compounds

Triorganotin compound	Disproportionation conditions	Products	Extent of reaction (%)	Method of study identification	References
$Bu_3SnO_2CC_{11}H_{23}$ $[\delta^{119}Sn = 86.7]^a$	Neat, 60°C, 14 days	$Bu_4Sn[\delta^{119}Sn = -12.5]^a$ $Bu_2Sn(O_2CC_{11}H_{23})_2$ $[\delta^{119}Sn = -137.9]^b$	20	^{119}Sn NMR	This study
Bu_3SnO_2CPh $[\delta^{119}Sn = 110.3]^b$	Neat, 220°C, 30 min	Bu_4Sn $[\delta^{119}Sn = -10.7]^b$ $Bu_2Sn(O_2CPh)_2$ $[\delta^{119}Sn = -137.9]^b$	14	^{119}Sn NMR	This study
$Bu_3SnO_2CC_6H_4NO_2$-p $[\delta^{119}Sn = 127.1]$	Neat, 220°C, 30 min	Bu_4Sn $[\delta^{119}Sn = -11.3]$ $Bu_2Sn(O_2CC_6H_4NO_2\text{-}4)_2$ $[\delta^{119}Sn = -148.0]^a$	80	^{119}Sn NMR	This study
 (Bu_3SnOR) $[\delta^{119}Sn = 60.3]^c$	During synthesis via azeotropic distillation in refluxing PhMe	Bu_4Sn $[\delta^{119}Sn = -11.7]^c$ $Bu_2Sn(OR)_2$ $[\delta^{119}Sn = -251.1]^c$	>5	^{119}Sn NMR	This study
 (Bu_3SnOR^1) $[\delta^{119}Sn = 61.0]^c$	During synthesis via azeotropic distillation in refluxing PhMe	Bu_4Sn $[\delta^{119}Sn = -11.6]^c$ $Bu_2Sn(OR)_2$ $[\delta^{119}Sn = -250.2]^c$	*ca* 5	^{119}Sn NMR	This study
$(Ph_3Sn)_2O$	(i) 290°C (ii) 280°C (iii) 140°C, *in vacuo*, 8 h (iv) refluxing PhMe	Ph_4Sn: Ph_2SnO	Quantitative	Thermal analysis	2 This study 3
$(Me_3Sn)_2O$	190°C	Me_4Sn Me_2SnO	Quantiative	Chemical analysis	5
$Bu_2(H_2C{=}CH)SnOH^d$	RT	Bu_2SnO $Bu_2(H_2C{=}CH)_2Sn$	Quantitative	Chemical analysis	6

[a] Measured in PhMe. [b] Measured in $CDCl_3$. [c] Neat. [d] Probably via the oxide.

Thermal Analysis

This was carried out using a Stanton Redcroft. STA-780 simultaneous thermal analyser.

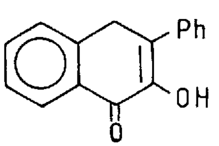
RESULTS AND DISCUSSION

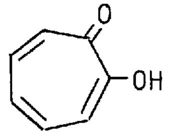
There are a limited number of reports of confirmed disproportionations of R_3SnX derivatives scattered throughout the literature;[4–8] in other cases, detection of one of the two products [R_4Sn or R_2SnX_2] has led to suggestsions that this process had occurred.[9–11] In addition, it has recently been demonstrated that on impregnation into *Pinus sylvestris* sapwood, $(Bu_3Sn)_2O$ is rapidly converted[12] into tributyltin carboxylates ($Bu_3SnOCO.R$), and that these subsequently undergo disproportionation[13] *in situ* at 60°C to form Bu_4Sn and $Bu_2Sn(OCO.R)_2$. The presence of these compounds was positively confirmed by ^{119}Sn NMR spectroscopy.

Furthermore, Bu_4Sn, so produced, is not persistent in timber and is lost by volatilization.

Table 1 shows additional examples from our work and from the literature of verified disproportionation reactions, i.e. where both di-(R_2SnX_2) and tetra-organotin species (R_4Sn) have been identified. It can be seen from this table that, in some cases, this process occurs under relatively mild conditions.

Disproportionations have also been suspected for reactions in which only one of the potential products has been detected. An example is the formation of $R_2Sn(Of)_2$, from the azeotropic dehydration reaction in refluxing toluene between R_3SnOH and HOf (I; HOf = 3-hydroxyflavone).[14]


(I)


(II)

The ease of disproportionation is in the sequence R = Me > Bu > cyclohexyl > neophyl > Ph. The formation of Me_4Sn (as detected by ^1H NMR spectroscopy) from reactions between Me_3SnSPh and $(NC)_2C{=}C(CN)_2$ in CH_2Cl_2 solution at room temperature can also be interpreted as occurring via such a process.[15] A more elaborate disproportionation is the reported complete scrambling of $Me_3(CH_2{=}CHCH_2)Sn$ in the presence of $BF_3.OEt_2$ at low temperatures to $\Sigma^4_{n=0} = Me_n(CH_2CH{=}CH_2)_{4-n}Sn$, as detected by ^{13}C and ^{119}Sn NMR spectroscopy.[16]

It is of interest that many, but not all, of the disproportionations of R_3SnX are achieved when X is a chelating and/or a bridging group, e.g. —O—, —O_2CR or alkoxy ketone.

The facile disproportionation of triorganotin derivatives of chelating ligands may also be of some consequence in speciation studies of organotin species, i.e. in aqueous media. Frequently, chelating ligands, such as tropolone (**II**), are used to aid the extractions of the organotins from aqueous to organic media.[17] Any disproportionation which may arise will at the very least lead to erroneous conclusions.

That disproportionations do occur cannot be disputed, nor can the adverse effects of such reactions. Whether enough heed has been paid to this process is not certain. The range and scope of disproportionations certainly needs investigation and we are now carrying out a study on the kinetic and thermodynamic effects that influence them.

CONCLUSIONS

It has been shown that disproportionations of triorganotin derivatives, R_3SnX, can occur when X is a chelating or bridging group such as oxide, carboxylate, hydroxy ketone or hydroxyquinoline. As a consequence, the range and scope of such a process needs further investigation since the implications for the commercial applications, and indeed analysis of organotin compounds, are wide-ranging.

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