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# New Synthesis of β-Substituted Alkyltin Halides *via* Halogenostannane Intermediates

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*Summary* β-Substituted ethyltin trihalides and bis-(β-substituted ethyl)tin dihalides can be prepared *via* the *in situ* reaction of αβ-unsaturated carbonyl compounds with active halogenostannane intermediates produced from halogen acids and tin(II) chloride or halogen acids and metallic tin, respectively.

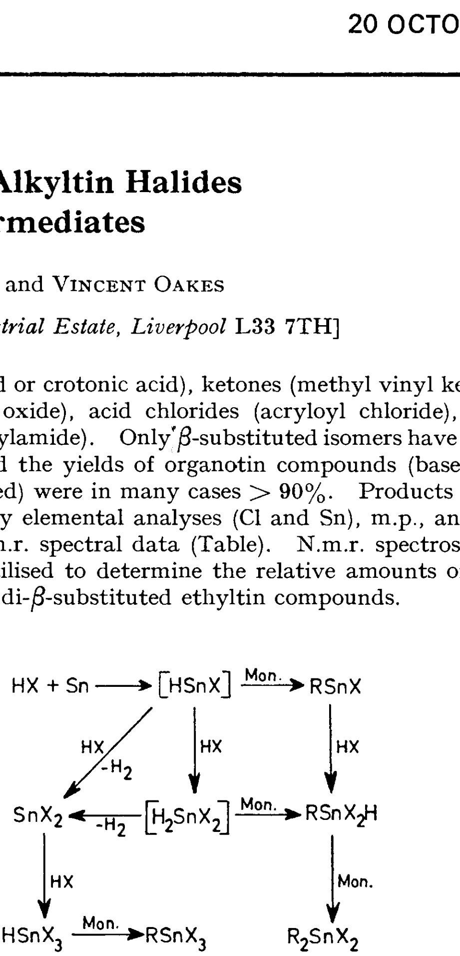
CONVENTIONALLY monoalkyltin trihalides ($RSnX_3$) and dialkyltin dihalides ($R_2SnX_2$) are prepared either by disproportionation of $R_4Sn$ with $SnX_4$ ($R = Bu$, $C_8H_{17}$; $X = Cl$, Br, I) or by the direct reactions of RX with $SnX_2$ and Sn, respectively ($R = Me$, Bu, $C_8H_{17}$; $X = Cl$, Br, I).[1] Alternatively, tetra-alkyltin compounds and trialkyltin halides may be synthesised *via* hydrostannation of olefins with $R_3SnH$ and $R_2SnH.Cl$, respectively.[2] We have now discovered some new hydrostannations applicable to the synthesis of mono- and di-β-substituted alkyltin halides.[3]

We have found that halogen acids react with metallic tin in the presence of αβ-unsaturated carbonyl compounds in hydrocarbon, halogenocarbon, ether, ester, alcohol, or water as solvent to produce, in general, mixtures of mono- and di-β-carbonyl ethyltin halides. This may be represented as reaction (1). αβ-Unsaturated compounds which

$$HX + Sn + R^1R^2C{=}CR^3{-}CR^4{=}O \xrightarrow{-30\text{ to }120\ ^\circ C} X_3SnCR^1R^2{-}CHR^3{-}CR^4{=}O + X_2Sn(CR^1R^2{-}CHR^3{-}CR^4{=}O)_2 \quad (1)$$

($X = Cl$, Br, I)

reacted included esters (*e.g.* methyl acrylate, methyl methacrylate, or methyl crotonate), carboxylic acids (acrylic acid or crotonic acid), ketones (methyl vinyl ketone or mesityl oxide), acid chlorides (acryloyl chloride), and amides (acrylamide). Only β-substituted isomers have been isolated and the yields of organotin compounds (based on Sn consumed) were in many cases > 90%. Products were identified by elemental analyses (Cl and Sn), m.p., and by i.r. and n.m.r. spectral data (Table). N.m.r. spectroscopy was also utilised to determine the relative amounts of the mono- and di-β-substituted ethyltin compounds.



$R = -CR^1R^2{-}CHR^3{-}CR^4{=}O$; Mon. $= R^1R^2C{=}CR^3{-}CR^4{=}O$

SCHEME

Pure β-carbonyl ethyltin trihalides can also be prepared by a similar reaction between HX and $SnX_2$ in the presence of the αβ-unsaturated carbonyl compounds. This reaction, performed under the same conditions as reaction (1) may be represented as equation (2). As far as we can tell the $SnX_2$

TABLE

M.p., i.r., and n.m.r. data for $\beta$-substituted alkyltin chlorides

| Compound | M.p. /°C | $\nu$(C=O)[a] /$\pm$ 2 cm$^{-1}$ | Chemical shifts ($\tau$)[b] CH$_2$ ($\alpha$) | CH$_2$ ($\beta$) | | Coupling constants[c]/Hz $J$(Sn–H$_\alpha$) | $J$(Sn–H$_\beta$) |
|---|---|---|---|---|---|---|---|
| $Cl_3SnCH_2CH_2CO_2Me$ .. .. .. | 69 | 1660 | 7·73 | 7·01 | 6·03(OMe) | 102 | 186 |
| $Cl_2Sn(CH_2CH_2CO_2Me)_2$ .. .. | 135 | 1677 | 8·07 | 7·07 | 6·18(OMe) | 98 | 150 |
| $Cl_3SnCH_2CH_2CO_2H$ .. .. .. | 123—127 | 1665 | 7·80 | 6·92 | −1·25(CO$_2$H) | *ca.* 88 | 207 |
| $Cl_2Sn(CH_2CH_2CO_2H)_2$ .. .. | 157 | 1676 | 8·25 | 7·08 | −1·04(CO$_2$H) | 104 | 135 |
| $Cl_3SnCMe_2CH_2COMe$ .. .. | 123 | 1665 | — | 6·85(CH$_2$)<br>8·77(CH$_3$) | 7·43(COMe) | — | 210(CH$_2$)<br>204(Me) |
| $Cl_2Sn(CMe_2CH_2COMe)_2$ .. .. | 158 | 1671 | — | 7·01(CH$_2$)<br>8·57(CH$_3$) | 7·07(COMe) | — | 138(CH$_2$)<br>129(Me) |
| $Cl_2Sn(CH_2CH_2CONH_2)_2$ .. .. | 240—250 | 1669 | 8·65 | 7·36 | 1·53(NH$_2$)[d]<br>1·75 | 114 | 141 |

[a] Spectra recorded as Nujol mulls. [b] Spectra recorded in CDCl$_3$ solution. [c] The reported values are the mean of the $^{117}$Sn–H and the $^{119}$Sn–H coupling constants. [d] The NH$_2$ signal appears as a doublet.

$$\mathrm{HX + SnX_2 + R^1R^2C{=}CR^3{-}CR^4{=}O \xrightarrow{-30\text{ to }120\ ^\circ C} X_3Sn{-}CR^1R^2{-}CHR^3{-}CR^4{=}O} \tag{2}$$

($X = Cl, Br, I$)

consumed in these reactions is quantitatively converted into organotin compounds. M.p. and spectroscopic data for a number of these compounds are also presented in the Table. Low $\nu$ (C=O) values are observed for all compounds in the Table suggesting that carbonyl co-ordination to tin occurs.[4] This is probably intra- rather than inter-molecular in origin since the spectra are unaffected by dilution in toluene or ethereal solvents.

HCl and SnCl$_2$ are known to interact in Et$_2$O to give solvated trichlorostannane.[5] The formation of $X_3SnCR^1R^2–CHR^3–CR^4{=}O$ from HX, SnX$_2$, and $R^1R^2C{=}CR^3–CR^4{=}O$ can, therefore, be explained by the hydrostannation of the latter with HSnX$_3$. That this reaction can be performed in non-polar solvents, such as hexane, is significant and suggests that HSnX$_3$ may also be stabilised by interaction with the monomer; the formation of $X_3Sn^{\delta-}H^{\delta+} \leftarrow (O{=}CR^4–CR^3{=}CR^1R^2)_n$ ($n = 1$ or 2) is indicated. Production of $X_3Sn–CR^1R^2–CHR^3–CR^4{=}O$ from HX, Sn, and $R^1R^2C{=}CR^3–CR^4{=}O$ merely represents the *in situ* formation of SnX$_2$. An explanation for the formation of the corresponding di-$\beta$-carbonyl ethyltin dihalides is at present speculative. However, the primary reaction must be the interaction of HX with Sn to give the divalent tin species [HSnX]. Monomer (Mon.) solvation of this species may again be important. The possible reactions of this species are outlined in the Scheme. Divalent organotin species such as RSnX ($R = Bu$ or $C_8H_{17}$) have been previously suggested as reaction intermediates[6] and it is possible that in RSnX intramolecular carbonyl co-ordination imparts some stability to these species.

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