The Addition of the Sn–O Bond to Aldehydes

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A RAPID exothermic reaction occurs between tributyltin methoxide and an equimolar amount of an aliphatic aldehyde (*e.g.* Me·CHO, Pr·CHO, Bu^t·CHO, Cl_3C·CHO,[1] Br_3C·CHO; but not Ph·CHO) at room temperature.

The adduct (I) which is formed cannot be purified by distillation, because some aldehyde is lost as the reaction is reversible, but reasonably pure adducts can be obtained by carrying out the reaction with a slight excess of aldehyde, then removing the excess under reduced pressure.

$$Bu_3Sn{\cdot}OMe + R{\cdot}CH{=}O \rightleftharpoons \underset{\text{(I)}}{Bu_3Sn{\cdot}O{\cdot}CHR{\cdot}OMe} \qquad (1)$$

Bis(tributyltin) oxide reacts much more slowly with simple aldehydes; overnight, the aldehyde is consumed, but the formation of the adduct (II) is now complicated by a side reaction, probably a Tischenko-type hydrogen transfer. Chloral, however, still reacts exothermically to give the adduct. (II: R = Cl_3C).*

$$Bu_3Sn{\cdot}O{\cdot}SnBu_3 + R{\cdot}CHO \rightleftharpoons \underset{\text{(II)}}{Bu_3Sn{\cdot}O{\cdot}CHR{\cdot}OSnBu_3} \qquad (2)$$

One aldehyde can replace another in the adducts. For example, if chloral is added to the butyraldehyde–methoxide adduct (III), or butyraldehyde to the chloral–methoxide adduct (IV), the approximate equilibrium concentrations (from integrated n.m.r.) shown in equation 3 are rapidly established.

$$\underset{0{\cdot}1}{Cl_3C{\cdot}CHO} + \underset{0{\cdot}1}{\underset{\text{(III)}}{Bu_3Sn{\cdot}O{\cdot}CHPr{\cdot}OMe}} \rightleftharpoons \underset{0{\cdot}9}{\underset{\text{(IV)}}{Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}OMe}} + \underset{0{\cdot}9\text{ mol.}}{Pr{\cdot}CHO} \qquad (3)$$

The 1 : 1 adducts (I) and (II) are of course themselves tin alkoxides, and would be expected to add to a suitably reactive aldehyde, and, by repeating this process, to build up an oligomer or polymer. This behaviour is observed when either the chloral–methoxide or the chloral–oxide adduct is treated with more chloral. For example, the methoxide adduct (IV) will react with a second mole of chloral with a slight evolution of heat, giving, we believe, the adduct (V) in equilibrium with (IV), and, overnight, a large excess (16 mol.) of chloral is converted into polychloral[2] which has

$$\begin{tikzcd}
 & Bu_3Sn{\cdot}OMe + O{=}CH{\cdot}CCl_3 \arrow[r, shift left] & Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}OMe \quad \text{(IV)} \arrow[l, shift left] \arrow[d, shift left, "Cl_3C{\cdot}CHO"] \\
Bu_3Sn{\cdot}(O{\cdot}CH{\cdot}CCl_3)_{n+2}{\cdot}OMe \arrow[rr, shift right] & & Bu_3Sn{\cdot}O{\cdot}CH(CCl_3){\cdot}O{\cdot}CH(CCl_3){\cdot}OMe \quad \text{(V)} \arrow[ll, shift right, "nCCl_3CHO"'] \arrow[u, shift left]
\end{tikzcd} \qquad (4)$$

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*The reaction of bromal is also exothermic, but does not stop at simple addition; this will be discussed in a subsequent publication.

[1] Bloodworth and Davies, *Proc. Chem. Soc.*, **1963**, 264.

[2] Noval and Whalley, *Trans. Faraday Soc.*, **1956**, **55**, 1490.

been obtained as a fine white powder and as a transparent film.

The polymerization has no termination step, and is reversible, and the product is thus a "living" polymer: it can cause the polymerization of more chloral, and, when heated, the bulk of the chloral can be recovered.

This mechanism for the polymerization of an aldehyde by a repeated insertion mechanism has been suggested before,[3] but the basic reaction involved does not appear to have been demonstrated previously.

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[3] Furukawa, Saegusa, and Fujii, *Makromol. Chem.*, 1961, **44—46**, 398.