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Difunctional distannoxanes, $XR_2SnOSnR_2X$

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The difunctional distannoxanes, $XR_2SnOSnR_2X$, can be prepared by a number of different routes, and frequently turn up unexpectedly in reactions involving organotin compounds. They show a variety of (usually dimeric) structures, and are mild but effective catalysts for a variety of polar organic reactions. This article gives an overview of their chemistry.

Keywords: difunctional distannoxanes, organotin, catalysis

Introduction

The difunctional distannoxanes, $XR_2SnOSnR_2X$, are stable compounds that are available from a number of different reactions, and frequently are encountered adventitiously when organotin compounds are being handled. They have attracted attention, because of this ubiquity, because they show a wide and interesting variety of (usually dimeric) structures, and because they are very effective catalysts for some condensation reactions.

The many X-ray diffraction studies of these compounds have recently been thoroughly reviewed.[1]

Preparation

The principal ways in which the compounds can be prepared are shown in Scheme 1.[2, 3] The ligand X is frequently halide or carboxylate, though there are many alternatives (F, Cl, Br, I, RCO_2, $ROCO_2$, R_2NCOS, N_3, NCS, HO, RO, ArO, RCOCH=CRO, R_2C=NO, R_3SiO, ROO, NO_3, RS, R_2BO, $(RO)_2BO$, $(RO)_2PSO$, $(RO)_2PS_2$, R_2PO_2, R_2AsO_2, RSO_3, CrO_4, ReO_4: the list continually expands).[3] The organic group R is frequently n-butyl, because the dibutyltin precursors are more readily available and cheaper than the other alkyl- or aryl-tin compounds, and carry little toxic hazard.

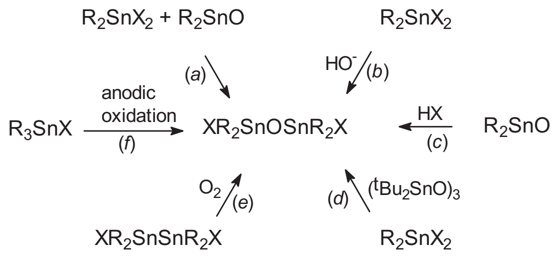
The reaction between R_2SnX_2 and R_2SnO (Scheme 1, reaction *a*) provides an easy, general, route to the difunctional distannoxanes, and dates from the early days of organotin chemistry. From the reaction of ethyl iodide with a tin-sodium alloy, Löwig obtained, in 1852, a compound that he thought was the radical Et_2SnI. In 1858, Strecker showed the compound in fact had the composition $Et_4Sn_2I_2O$, and that it could be obtained from the reaction between diethyltin diiodide and diethyltin oxide, and in 1914, Pfeiffer and Brack[4] showed the generality of the reaction.

Dibutyltin oxide has provided the starting material for many of the distannoxanes; it is an insoluble polymer, but it usually dissolves readily on heating with Bu_2SnX_2 in benzene or toluene, and the compounds $XBu_2SnOSnBu_2X$ can be isolated as air-stable solids, that are usually highly crystalline, and very soluble in non-polar solvents.[5] *e.g.* equation 1.

$$Bu_2SnO + Bu_2Sn(NCS)_2 \xrightarrow[<110\,°C]{PhMe} (SCN)Bu_2SnOSnBu_2(NCS) \qquad (1)$$

The reaction between R_2SnO and R'_2SnX_2 can lead to mixed distannoxanes $XR_2SnOSnR'_2X$ (equation 2).[6]

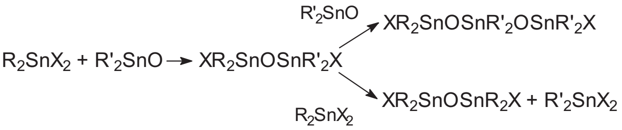
$$Bu^t_2SnO + Pr^i_2SnCl_2 \xrightarrow[\text{reflux, 15 min}]{PhMe} ClBu^t_2SnOSnPr^i_2Cl \qquad (2)$$



Scheme 1 Preparation of difunctional distannoxanes

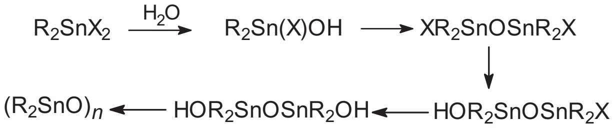
These reactions are special examples of the general exchange of electronegative ligands (here X and $OSnR_2$~) between tin atoms, and result here in the insertion of an $OSnR_2$ unit into an Sn-X bond. This insertion of $OSnR_2$ units can be continued, and R_2SnX_2 reacts with $2R'_2SnO$ to give difunctional trioxanes (equation 3*a*), and thence higher oligomers, but these compounds have received little attention.[7] Conversely, $2R_2SnX_2$ can react, by ligand exchange, with R'_2SnO to give $XR_2SnOSnR_2X$ and R'_2SnX_2 (equation 3*b*). This oxygen-transfer reaction (Scheme 1, reaction *d*), with Bu^t_2SnO (which is a cyclic trimer), has been used by Dakternieks to prepare a number of complex difunctional distannoxanes.[8] Presumably, the other possible products, $XR_2SnOSnBu^t_2X$ and R_2SnX_2, are disfavoured because of steric hindrance in the dimeric form of the distannoxane.

(3*a*)



(3*b*)

The hydrolytic route to the distannoxanes (Scheme 1, reaction *b*) represents one phase of the progressive hydrolysis of R_2SnX_2 to R_2SnO, for which the principal intermediates are represented in equation 4.[3, 9, 10]



(4)

Thus $ClBu_2SnOSnBu_2Cl$ can be prepared in good yield merely by pouring an acetone solution of Bu_2SnCl_2 into water. The hydrolysis can also be carried out in the presence of a tertiary amine or of sodium hydroxide.[5] Controlled hydrolysis with a restricted amount of sodium hydroxide gives the α,ω-dichlorooligostannoxanes, $Cl(Bu_2SnO)_nSnBu_2Cl$, which are identical to the oligomers prepared by reaction 3*a*.[11] Cohydrolysis of R_2SnCl_2 and Me_3SiCl with aqueous ammonia gives the siloxy derivatives $(Me_3SiO)R_2SnOSnR_2(OSiMe_3)$.[12] Hydrolysis of the alkoxide halides $R_2Sn(OR')X$, or carboxylate halides $R_2Sn(OCOR')X$, gives the dihalogenodistannoxanes

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XR$_2$SnOSnR$_2$X rather than the alkoxides, carboxylates, or mixed-ligand compounds.[13]

The monohydroxides R$_4$Sn$_2$X(OH)O can be obtained by further hydrolysis compounds R$_4$Sn$_2$X$_2$O, or, sometimes, from the reaction of R$_2$SnX$_2$ with R$_2$SnO in a moist solvent, and they represent unusual examples of stable alkyltin hydroxides.[9] The dihydroxides R$_4$Sn$_2$(OH)$_2$O usually spontaneously dehydrate to polymeric (R$_2$SnO)$_n$, but they can be isolated if they are sterically stabilised by a bulky group R, as in (HO)[(Me$_3$Si)$_2$CH]$_2$SnOSn[CH(SiMe$_3$)$_2$]$_2$(OH),[14] or HO(PhMe$_2$CCH$_2$)$_2$SnOSn(CH$_2$CMe$_2$Ph)$_2$OH.[15]

Dialkyltin oxides react with the appropriate amount of a strong acid, to give the the difunctional distannoxanes (Scheme 1, reaction *c*), for example, equation 5.[16]

$$R^f_2SnO + 2HCl \longrightarrow ClR^f_2SnOSnR^f_2Cl$$
$$R^f = C_6F_{13}CH_2CH_2 \qquad (5)$$

Carboxylic acids give the dicarboxylates, (R'CO$_2$)R$_2$SnOSnR$_2$(OCOR'), and esters R'CO$_2$R'' give the alkoxy carboxylates, (R''O)R$_2$SnOSnR$_2$(OCOR').[17]

$$Bu_2SnO + OctOCOMe \xrightarrow[25\ min]{200\,^\circ C} (OctO)Bu_2SnOSnBu_2(OCOMe) \qquad (6)$$

Alternatively the difunctional distannoxanes can be prepared from the dialkyltin oxide and a solution of the saturated ammonium salt NH$_4$X (X = F, Cl, Br, OAc) in refluxing dioxane;[18] this reaction probably provides the best route to the fluorides, FR$_2$SnOSnR$_2$F.

When HX is a weak acid, the reaction with R$_2$SnO can be conveniently carried out by azeotropic dehydration with an excess of HX in benzene or toluene. In boiling benzene (80 °C), phenols react to give the diphenoxides, (ArO)R$_2$SnOSnR$_2$(OAr),[19] and hydroperoxides give the diperoxides, (R'OO)R$_2$SnOSnR$_2$(OOR')[20] whereas in tetralin (207 °C), phenols give the compounds R$_2$Sn(OAr)$_2$.[21] In boiling benzene, primary alcohols give the dialkoxides, (R'O)R$_2$SnOSnR$_2$(OR'), but secondary alcohols do not react in boiling benzene or toluene (111 °C).[22]

The aerobic oxidation of the distannanes XR$_2$SnSnR$_2$X to the distannoxanes XR$_2$SnOSnR$_2$X (Scheme 1, reaction 5) is seldom used as a preparative method, but it represents one of the examples of the distannoxanes being formed adventitiously, and initially led to the two classes of compounds being confused.[23] However, it does enable distannanes to be used as air-activated catalysts (X = RCO$_2$) for curing silicone polymers and for preparing polyurethanes (see below).

The interesting cathodic oxidation of R$_3$SnCl in ethanol to ClR$_2$SnOSnR$_2$Cl or ClR$_2$SnOSnR$_2$OH (Scheme 1, Reaction *f*) was published in 1979, but appears not to have been followed up. Presumably, the radical cation R$_3$SnCl$^{\bullet+}$ is formed, and this then loses the R$^\bullet$ radical to give the cation R$_2$SnCl$^+$, which is quenched by the alcohol solvent to give R$_2$SnCl(OEt), and this is hydrolysed during the working up procedure.[24]

Structures

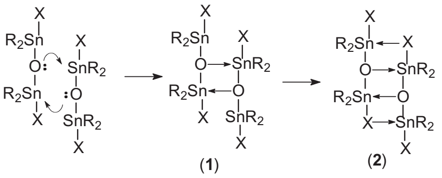
The distannoxanes XR$_2$SnOSnR$_2$X are monomeric in the solid state only when the groups R are very bulky {(HO)[(Me$_3$Si)$_2$CH]$_2$SnOSn[CH(SiMe$_3$)$_2$]$_2$(OH),[14] ClAr$_2$SnSnAr$_2$Cl [Ar = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$],[25] (NO$_3$)MeRSnOSnMeR(NO$_3$) [R = (Me$_3$C)$_3$C][26]}. In all other cases, they exhibit their character as both Lewis acids and Lewis bases by dimerising to give an SnOSnO 4-membered ring, as in shown in formula **1**; the ligand X on the endocyclic tin then usually coordinates to the exocylic tin, as shown in formula **2**, to form two more 4-membered rings if X is mondentate, or two new five or six membered rings if X is bidentate. All four tin atoms are thus rendered 5-coordinate, and the molecule has the structure of a reversed micelle as shown in formulae **3**, with a polar core and hydrocarbon outer shell. The structures of well over one hundred of these compounds have been determined by X-ray diffraction. Some typical structures are illustrated in formulae **4**,[27] **5**,[28] **6**,[29] **7**,[30] and **8**.[6] It is convenient to describe these structures by a shorthand denoting the size of the rings, for example compound **4** as 4–**4**–4, **5** as 6–**4**–6, **6** as 6–6–**4**–6–6, **7** as 4–**4**–4, and **8** as 4–4–**4**–4–4. The 4–**4**–4 structures are referred to as ladders.

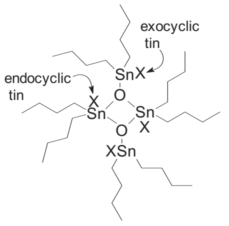
Presumably this associated structure contributes to the thermodynamic stability of these compounds, and their ubiquity in organotin chemistry; it also renders reactions of these distannoxanes very susceptible to steric effects, and permits steric selectivity when they are used as catalysts.

In the mixed distannoxanes, (R$_2$Bu$^t_2$Sn$_2$Cl$_2$O)$_2$, R = Me, Bu,[6] or Me$_3$SiCH$_2$,[30] [(Me$_3$SiCH$_2$)$_2$Bu$^t_2$Sn$_2$(OH)$_2$O]$_2$ (**7**), or [(Me$_3$SiCH$_2$)$_2$Bu$^t_2$Sn$_2$Cl(OH)O]$_2$,[30] the bulky t-butyl groups are located on the exocyclic tin atoms, but it is surprising that in [ClPr$^i_2$SnOSnMe$_2$Cl]$_2$, the larger isopropyl groups are bonded to the endocyclic tin atoms.[31] The crystal structures and the reactions of the *t*-butyl compounds imply that they are better represented as the cyclic dimer (R$_2$SnO)$_2$ which is stabilised by coordination by two Bu$^t_2$SnCl$_2$ molecules, as in formula **8**.[6]

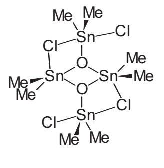
In the distannoxanes, XR$_2$SnOSnR$_2$X', with mixed ligands X, the stronger of the two ligands is found bonded to the endocylic tin atoms, as in **7** and **9**.[32]

In recent years, Dakterniek's group have prepared a number of bridged bis- and tris-4–**4**–4-distannoxanes such as **10**,[33] usually by the reaction of the corresponding dichlorides,


(**1**) (**2**)


exocyclic tin
endocyclic tin

(**3**)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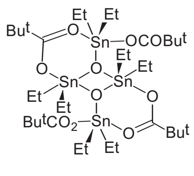
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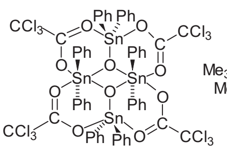
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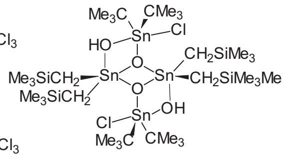
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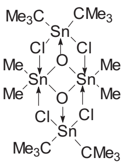
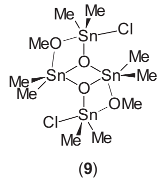
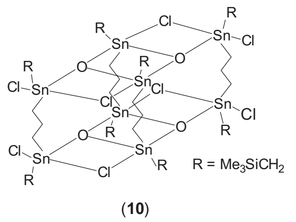

(**8**)


(**9**)


R = Me$_3$SiCH$_2$

(**10**)

$Cl_2RSn–[S]–SnRCl_2$, where [S] is a spacer group such as $(CH_2)_3$ or $(CH_2)_3O(CH_2)_3$, with $Bu^t{}_2SnO$ (Scheme 1, reaction *d*).[34] The aim has been, in part, a search for special catalytic properties. A list of these compounds is given in ref. 1.

Physical properties

The structures of the dimeric distannoxanes as reversed micelles, with a hydrocarbon outer shell, cause them usually to be rather waxy solids that, (unless R is methyl or phenyl), are readily soluble in non-polar solvents. Fluorous distannoxanes such as $XR_2SnOSnR_2X$, where X = $C_6F_{13}CH_2CH_2$, on the other hand, have a fluorocarbon outer shell, and have large partition coefficients in favour of fluorocarbon rather than hydrocarbon solvents.[35]

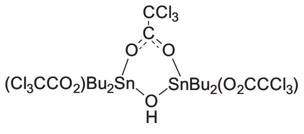
The dimeric structures are usually preserved in solution at room temperature, and this causes the endocylic and exocyclic R_2Sn groups to be inequivalent and to show separate ^{119}Sn NMR signals in the (high field) region for 5- or 6-coordinate tin, with ^{117}Sn coupling with ^{119}Sn. The signal at higher field (larger negative number for δSn) can be taken to represent the endocylic tin atom. There is some evidence, however, for dissociation. For example, in solution at 40 °C, the compound $(Me_3SiO)Et_2SnOSnEt_2(OSiMe_3)$ shows ^{119}Sn NMR signals at –166.8 and –183.8 for the dimer, but also at –47.4 (14%) for 4-coordinate tin in the monomer, and $(Me_3SiO)(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)_2(OSiMe_3)$, with δSn 8.9, is monomeric in solution {and in equilibrium with its progenitors $(Me_3SiCH_2)_2Sn(OSiMe_3)_2$ and $[(Me_3SiCH_2)_2SnO]_3$}.[12]

Examples of structures, melting points and ^{119}Sn chemical shifts are given in Table 1.

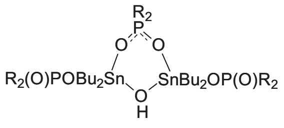
Reactions

The principal reactions of the difunctional distannoxanes are shown in Scheme 2. Their formation from R_2SnX_2 is reversible (reaction *a*). The compounds $(Me_3SiO)R_2SnOSnR_2(OSiMe_3)$, when the groups R are bulky (CH_2SiMe_3 or Bu^t), are in equilibrium in solution with their progenitors $(R_2SnO)_3$ and $R_2Sn(OSiMe_3)_2$,[12] and the dialkyltin dialkoxides, $R_2Sn(OR')_2$, can be prepared by distillation of $(R'O)R_2SnOSnR_2(OR')$ (from the alcohol and dialkyltin oxide) under reduced pressure.[22] The dichlorides, $ClR_2SnOSnR_2Cl$, react with bipyridyl to give R_2SnCl_2 (Scheme 2, reaction *b*), and, when R = Et, the second product has been identified, not as Et_2SnO, but as the bipyridyl complex of the oligomer $ClEt_2SnOSnEt_2OSnEt_2Cl$ (reaction *c*).[5, 41]

Acids, HY, react to give the compounds R_2SnXY, but, when Y is a bidentate ligand [carboxylate (**11**)[42] or phosphinate (**12**)[43]], an adduct may be formed in which the oxygen atom is protonated and Y bridges both tin atoms.



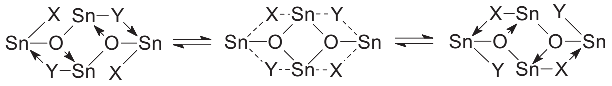
(**11**)



(**12**)

Hydrolysis of the distannoxanes, $XR_2SnOSnR_2X$, gives the hydroxy compounds $(HO)R_2SnOSnR_2X$ (equation 4 and Scheme 2, reaction *d*), which, on recrystallisation from alcohols, R'OH, give the alkoxy compounds $(R'O)R_2SnOSnR_2X$. This nucleophilic exchange of ligands, X, is a general process (Scheme 2, reaction *f*). The dichlorides react with silver acetate to give the diacetates,[33] or with potassium fluoride to give the difluorides,[41] the diacetates react with hydroperoxides to give the di(alkylperoxy) compounds,[20] and, in the air, the alkoxides are hydrolysed back to the hydroxy compounds.

Exchange of the ligands X and Y between the compounds $XR_2SnOSnR_2X$ and $YR_2SnOSnR_2Y$ is rapid on the NMR time-scale, to give the distannoxanes $XR_2SnOSnR_2Y$ with mixed functionality (Scheme 2, reaction *f*).[44, 45] When X and Y are AcO and Cl, or Br and Cl, twenty ^{119}Sn NMR signals can be observed for the five dimers $(X{\sim}X)_2$, $(Y{\sim}Y)_2$, $(X{\sim}Y)_2$, $(X{\sim}X)(X{\sim}Y)_2$, $(X{\sim}Y)(Y{\sim}Y)_2$, which is consistent with the rapid exchange of ligands between *endo* and *exo* tin sites on the NMR time-scale (*e.g.* equation 7), which reduces the number of possible observable isomers.[46, 47] A similar exchange of the Me_3SiO groups between the *endo* and *exo* tin atoms occurs in the dimers $[(Me_3SiO)R_2SnOSnR_2(OSiMe_3)]_2$, which, in solution, show NMR signals for only one type of siloxy group.[12]



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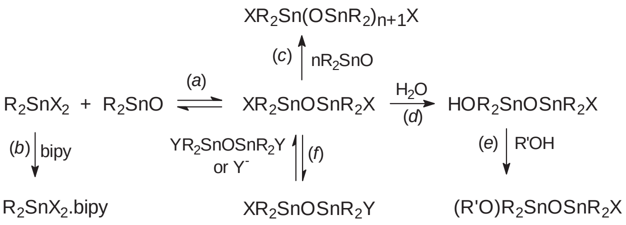


Scheme 2 Reactions of the difunctional distannoxanes

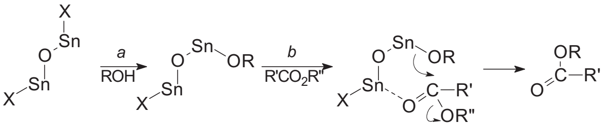
Table 1 Dimeric distannoxanes, $(XR_2SnOSnR_2X)_2$

$[XR_2SnOSnR_2X]_2$	Structure	M.p./°C	$\delta^{119}Sn$	Ref.
$[ClMe_2SnOSnMe_2Cl]_2$	4–**4**–4	>280	–62.6, –114.4	36
$[(Me_3SiO)Me_2SnOSnMe_2(OSiMe_3)]_2$	4–**4**–4	167–168	–136.3, –155.8	12
$[BrEt_2SnOSnEt_2Br]_2$	4–**4**–4	176–178	–79.3, –128.9	36
$[(ClBu_2SnOSnBu_2Cl)]_2$	4–**4**–4	111–112	–91.4, –140.3	36
$[(AcO)Bu_2SnOSnBu_2(OAc)]_2$	4–**4**–6–6	206–210	–171.4, –184.6	36
$[(PhO)Bu_2SnOSnBu_2(OPh)]_2$	4–**4**–4	134	–176.8, –177.4	37
$[(TfO)Bu_2SnOSnBu_2(OH)]_2$	4–**4**–4	75–76	–137, –170	38
$[ClBu_2SnOSnBu^t{}_2Cl]_2$	4–4–**4**–4–4	178–181	–150.7, –157.6	6
$[FCy_2SnOSnCy_2F]_2$	4-**4**-4	>295dec	–212.0, –237.6	36
$[IOct_2SnOSnOct_2I]_2$		90–95	–169.9, –174.6	36
$[ClPh_2SnOSnPh_2Cl]_2$	4–**4**–4	194–196		39
$[ClR^f{}_2SnOSnR^fCl]_2$ [a]	4-**4**-4	90–91	–178.3, –202.5	40
10	4–**4**–4 [b]	304–305	–96.1, –132.9	8
$(HO)R_2SnOSnR_2(OH)$ [c]	Monomer		17.45	14

[a] $R^f = C_6F_{13}CH_2CH_2$; [b]Double ladder; [c]$R = (Me_3Si)_2CH$.

Catalysis

A variety of polar organic reactions are catalysed by organotin oxides, and the difunctional distannoxanes are often particularly effective.[48] Much of the work in this field has been carried out by Otera's research group.[49] Some general mechanistic principles that affect these reactions can be recognised. Stannyl groups can enhance the nucleophilicity of an OH group by stannylation (equation 8, reaction *a*), and/or increase the electrophilicity of a group by acting as a Lewis acid (equation 8, reaction *b*); in the difunctional distannoxanes, with two stannyl groups in close juxtaposition, these two effects may operate in concert, and this principle is illustrated for a transesterification reaction in equation 8. The micellar structure of the distannoxanes may also be important in increasing the local concentration of polar molecules in the region of the polar core. Given these various factors and the complicated structures of the distannoxanes, it is not surprising that the detailed mechanism of the catalysis is seldom understood.



(8)

When dialkyltin oxides are used as the catalyst in these systems, they dissolve during the reaction, and may operate through the alkoxides, $(R'O)R_2SnOSnR_2(OR')$ or $(R'O)R_2SnOSnR_2(OH)$, which can be formed by reaction with alcohols (Scheme 1, reaction *c*), or through the alkoxide carboxylates, $(R'O)R_2SnOSnR_2(OCOR'')$, which can be formed by reaction with esters (equation 6).

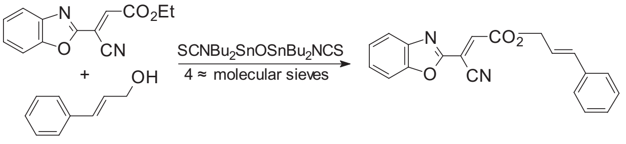
In the presence of a distannoxane catalyst, primary alcohols react with acids to give good yields of esters under mild conditions (equation 9).[50] Succinic acid and propylene glycol in decalin at 190 °C give the polyester with number-average molecular weight of 147,000.[51] Molecular sieves can be used to absorb the water that is formed (equation 10).[52] Esterification can also be carried out with equimolar amount of acid and alcohol, and a fluorous distannoxane catalyst (see above) in perfluorohexanes (F72); yields are often quantitative, and the catalyst can be recovered from the F72 layer.[35]

Enol esters can act as the acylating agents, and the reaction is selective for primary alcohols rather than for secondary alcohols or phenols (equation 11).[53]

$$\mathrm{PrCO_2H + BuOH \xrightarrow[\text{no solvent, 80 °C, 24 h}]{SCNBu_2SnOSnBu_2OH} PrCO_2Bu + H_2O}$$

acid :alcohol:catalyst = 1:30:0.1

(9)



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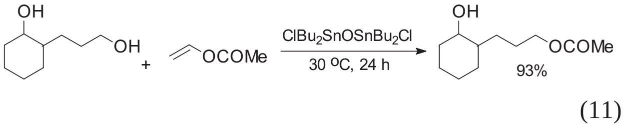
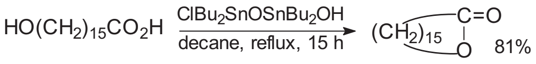


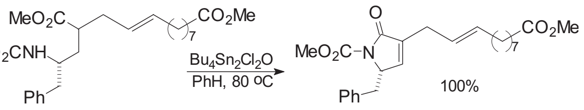
(11)

Lactonisation can similarly be catalysed by distannoxanes; an example is given in equation 12.[54]



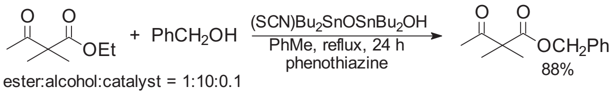
(12)

The equivalent reaction of amidation[55] has been used in the ring-closing synthesis of 3-pyrrolinones (equation 13).



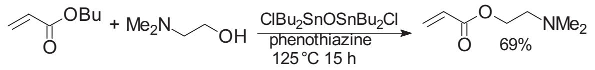
(13)

Transesterification[56] can be carried out by heating a mixture of the ester and alcohol in the presence of a distannoxane. Examples are given in equations 14[57] and 15.[58]



ester:alcohol:catalyst = 1:10:0.1

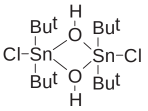
(14)



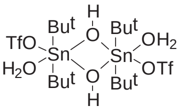
ester:alcohol:catalyst:phenothiazine = 1:1.75:0.0015:0.0016

(15)

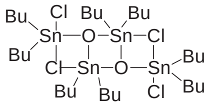
A number of organotin oxides and hydroxides were screened for the deacetylation of acetyl-protected hydroxyl groups. Under standard conditions, the compounds **13** – **15** behaved best, in the sequence **13** > **14** > **15**; because of the steric hindrance presented by the large t-butyl groups, the hydroxide chloride, **13**, does not readily dehydrate to the distannoxane $(ClBu^t_2SnOSnBu^t_2Cl)_2$. Conditions for a typical reaction are shown in equation 16.[59]



(**13**)



(**14**)



(**15**)

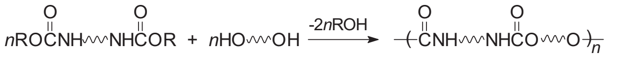
$$\mathrm{PhCH_2CH_2OAc \xrightarrow[\text{30 °C, 19 h}]{MeOH,\ \mathbf{13}} PhCH_2CH_2OH}$$

ester:MeOH:catalyst = 1 mmol:5 ml:0.01 mmol

(16)

Jousseaume found that, in the (symmetrical) reaction between ethanol and ethyl acetate, the catalysts $(AcO)Bu_2SnOSnBu_2(OAc)$, $(AcO)Bu_2SnOSnBu_2(OMe)$, and $(MeO)Bu_2SnOSnBu_2(OMe)$, were recovered as $(AcO)Bu_2SnOSnBu_2(OEt)$, but $ClBu_2SnOSnBu_2Cl$, which was the most effective catalyst, was recovered unchanged. Thus, whereas the first three catalysts appear to operate through transfer of the alkoxy group, the dichloro catalyst seems to behave as a simple Lewis acid.[60]

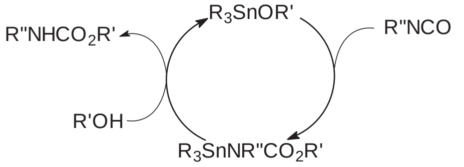
For the application of coatings, polyurethanes are often prepared by the transcarbamoylation route (equation 17), which avoids the handling of toxic and very reactive isocyanates.



$$n\mathrm{ROC(=O)NH{\sim}NHC(=O)OR} + n\mathrm{HO{\sim}OH} \xrightarrow{-2n\mathrm{ROH}} -\!\!(\mathrm{C(=O)NH{\sim}NHC(=O)O{\sim}O})_n\!\!-$$

(17)

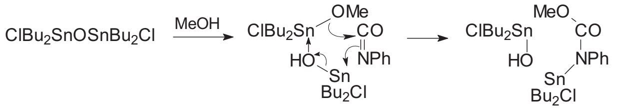
The difunctional distannoxanes are effective catalysts for the reaction.[61] 1,3-Dichlorotetrabutyldistannoxane can be recovered unchanged at the end of the reaction, and is



Scheme 3 Alkoxystannylation of isocyanates

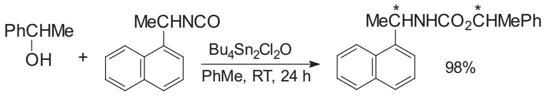
therefore suggested to act again as a Lewis acid rather than as an alkoxide carrier.[62]

The alternative route to urethanes and polyurethanes involves the addition of alcohols to isocyanates, and again the reaction is catalysed by organotin compounds. It is generally accepted that the organotin compounds first react with the alcohol to give the alkoxides, which rapidly add to the isocyanates to give the *N*-stannylcarbamates, and these in turn react rapidly with the alcohol to give the urethane and regenerate the catalyst (Scheme 3).[63] Houghton's detailed model of the reaction when a distannoxane is the catalyst, is shown in equation 18.[64]



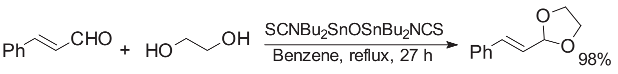
(18)

The mild conditions of the reaction are appropriate for the preparation of the diasterioisomeric urethanes for determining, by GLC or NMR, the optical purity of chiral alcohols (equation 19).[65]



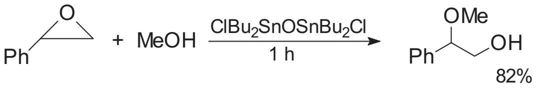
(19)

The distannanes XR_2SnSnR_2X ($X = R'CO_2$) have been patented as air-activated latent catalysts for the manufacture of polyurethanes and silicone polymers. Mixtures of the catalysts and monomers or prepolymers are stable in the pot, but on exposure to air the distannanes are oxidised to the distannoxanes (Scheme 1, reaction *e*), and the polymerisation is initiated.[66, 67] The distannoxanes catalyse the formation of acetals from aldehydes and ketones; $SCNBu_2SnOSnBu_2NCS$ is effective at 0.3 – 0.5 mol%, and can be used with unsaturated aldehydes (equation 20), which usually offer difficulties.[68, 69]



(20)

Epoxides undergo regio- and stereo-selective ring opening when they are treated with alcohols in the presence of dichlorotetrabutyldistannoxane (equation 21), but good yields are obtained only when an equivalent amount of the distannoxane is used.[70, 71]



(21)

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