CHAPTER - II

A SHORT REVIEW OF ORGANOTIN ALKOXIDES AND RELATED COMPOUNDS.

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IIE. ORGANOTIN DERIVATIVES OF SOME (ARYLAZO)PHENOLS

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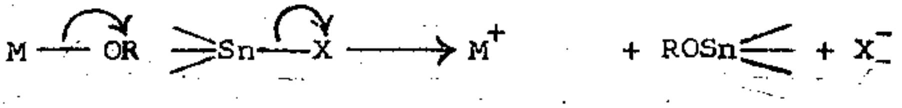
IIA. Introduction

As the present work is a study on the reactions of azophenoxy compounds with organotin compounds, it is desirable that a brief review of the chemistry of organotin alkoxides and related compounds be presented to make the reader familiar with the wide variety of alkoxides, phenoxides and related compounds and their reactions and structures so that a proper assessment of the present work may be made.

IIB. Organotin alkoxides.

The simple organotin alkoxides and phenoxides are usually prepared by nucleophilic substitution by an alcohol or its metal derivatives at a tin centre [equation (1) (M = H, Na etc.]. The best established method is that in which an organotin halide is treated with the sodium alkoxide, often in the parent alcohol as solvent. The sodium chloride which is formed is filtered or centrifuged off and the alkoxide is recovered by distillation or crystallisation [e.g. eqn. (3)].



Eqn.(1)

Alkoxides can be prepared by reaction between an alcohol and an organotin halide in the presence of a base[1] or by a metathetical reaction from an alkali-metal alkoxide[2,3].

$$R_3SnCl + R'ONa \longrightarrow R_3SnOR' + NaCl \qquad \text{Eqn. (2)}$$

$$MeONa + Bu_3SnCl \longrightarrow MeOSnBu_3 + NaCl \qquad \text{Eqn. (3)}$$

The alkoxides are sensitive to moisture and carbon dioxide, and the filtration has to be carried out in the absence of air, which may be tedious if the sodium chloride is finely divided. A more convenient route to the trialkyltin alkoxides, when the alcohol or phenol boils above about 90°C, is the azeotropic dehydration of a mixture of the appropriate alcohol and bis-(trialkyltin) oxide in benzene or toluene[4].

$$(Bu_3Sn)_2O + 2BuO.CH_2.CH_2OH$$

$$\longrightarrow 2\ Bu_3SnO.CH_2.CH_2OBu + H_2O \qquad \text{Eqn. (4)}$$

The water formed can be collected in a Dean and Stark Separator and good yields are obtained after one hour's boiling under reflux[5]. Triethyltin oxide reacts with acetylenic alcohols at room temperature .

$$(Et_3Sn)_2O + 2HOCR_2C{\equiv}CH \longrightarrow 2Et_3SnO.CR_2C{\equiv}CH + H_2O \qquad \text{Eqn. (5)}$$

[R = H or alkyl]

If the mixture is heated and water is removed azeotropically the product reacts further[6,7].

$$(Et_3Sn)_2O + 2Et_3SnOCR_2C{\equiv}CH \longrightarrow 2Et_3SnO.CR_2C{\equiv}C.SnEt_3 + H_2O \qquad \text{Eqn. (6)}$$

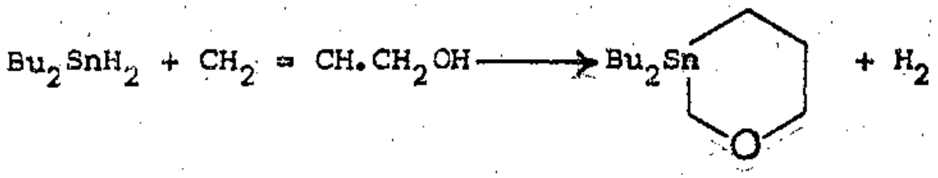
Trialkyltin alkoxides can be obtained in good yields by heating together an oxide and a dialkyl carbonate[5]

$$(R_3Sn)_2O + (R'O)_2CO \longrightarrow 2R_3SnOR' + CO_2 \qquad \text{Eqn (7)}$$

If the alcohol is more volatile, for example if it is methanol then trialkyltin alkoxide can be obtained conveniently[4] by using dialkyl carbonate.

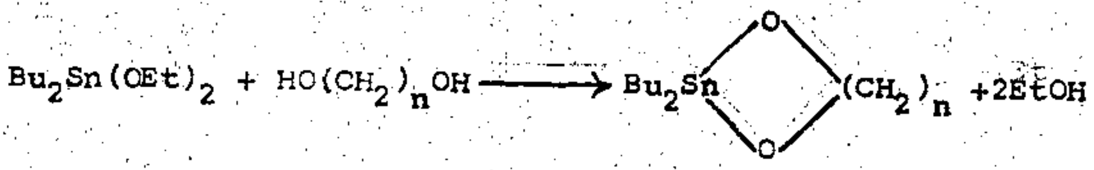
$$\begin{array}{l} (Bu_3Sn)_2O + (MeO)_2CO \longrightarrow Bu_3SnOMe + Bu_3SnO.COOMe \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow -CO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 2Bu_3SnOMe \end{array} \qquad \text{Eqn. (8)}$$

A further process which avoids filtration is the reaction between alkyltin hydrides and alcohols to give alkoxides and molecular hydrogen. This route has been used particularly for preparing cyclic alkoxides[8].



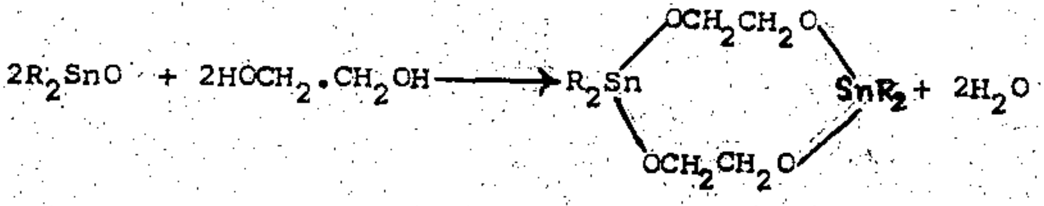
Eqn.(9)

Suitable dialkyltin compounds with glycols give cyclic alkoxides[9] ⎡Mercaptoalcohols such as $HSCH_2.CH_2OH$ react similarly ⎦



Eqn.(10)

(n = 4,5,6) (Ref. 10)

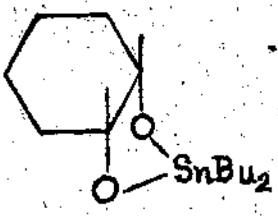


Eqn.(11)

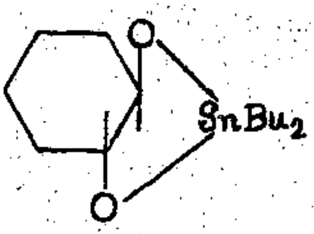
I

(Refs. 11,12)

Although compound I, (R = Bu) has a molecular weight corresponding to the dimeric structure shown, a number of 1,2-glycols can give monomeric cyclic alkoxides, for example, compounds II-IV[10,11]



II



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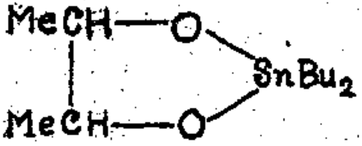
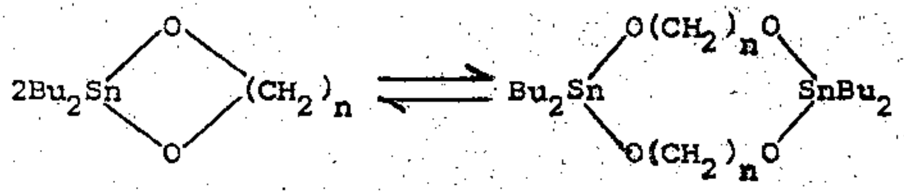
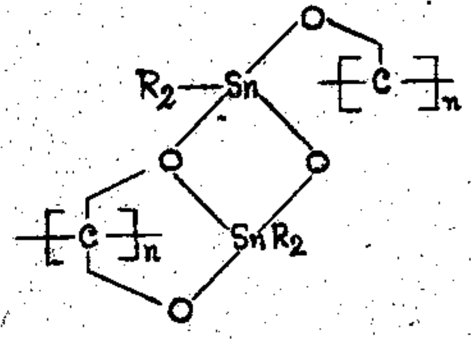


IV

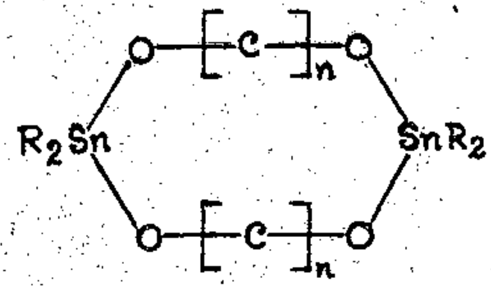
other workers have suggested that in solution, these cyclic compounds exist as an equilibrium mixture of monomer and dimer[10]



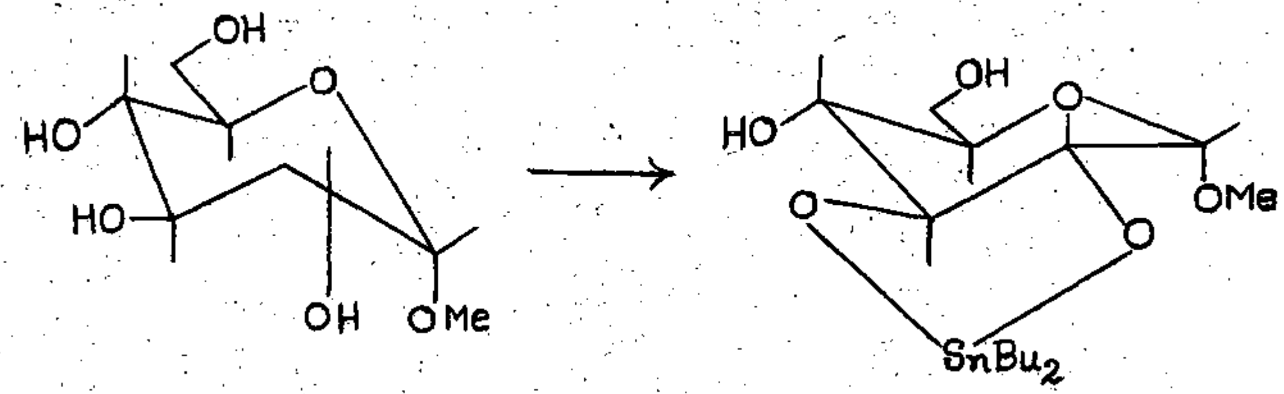
Diols are more reactive towards dialkyltin oxides and triols towards alkyl stannoic acids, than are monohydric alcohols and the cyclic dialkyltin dialkoxides and mono alkyltin trialkoxides can be prepared by azeotropic dehydration. Sometimes the products from diols may exist as both monomers or dimers[13]. IR and NMR data[13] support the structure (V) and the nature of some reaction products[14,15] favours the larger ring (VI). Carbohydrates react in this way to form cyclic dialkoxides, which are useful in organic synthesis. For example methyl-α-D -glucopyranoside gives methyl 2, 3, -O-dibutylstannylene-α-D-glucopyranoside (VII)[16].



V

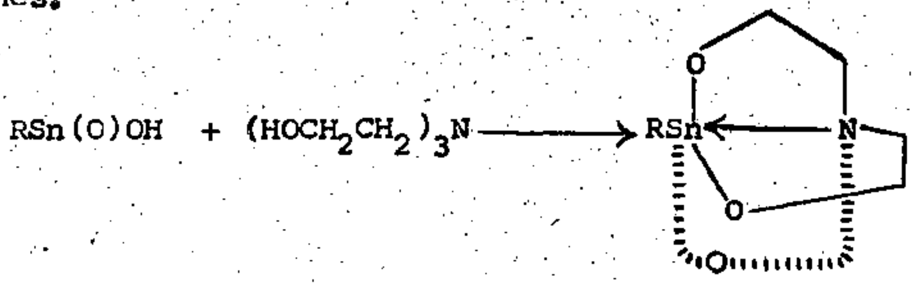


VI



VII

The stannatranes (VIII) which can be formed by azeotropic dehydration of a mixture of stannoic acid and triethanolamine[17] have attracted a lot of attention because of their triptych structures[18] and their analogy with the physiologically active silatranes.



VIII

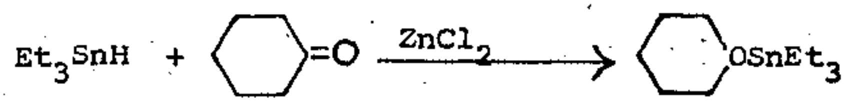
Reactions (4) and (7) are the best for preparing trialkyltin alkoxides. Under the same conditions, dialkyltin oxides react only to the stage of the dialkoxy-tetralkyldistannoxanes $R' - OR_2SnOSnR_2OR'$ and though these decompose thermally to give R_2SnO and $R_2Sn(OR')_2$, the reaction between sodium alkoxides and dihalides still provides the best route to the dialkoxides. In tetralin however, phenols react with dialkyltin oxides to give the diphenoxides $R_2Sn(OAr)_2$ directly[19] and it is possible that the higher boiling alcohols might show a similar reaction.

A number of α-substituted organotin compounds add to the carbonyl groups of aldehydes and ketones to give substituted alkoxides for example[26]

$$Bu_3SnCH_2CN + PhCHO \longrightarrow Bu_3SnO.CHPhCH_2CN \qquad \text{Eqn.(12)}$$

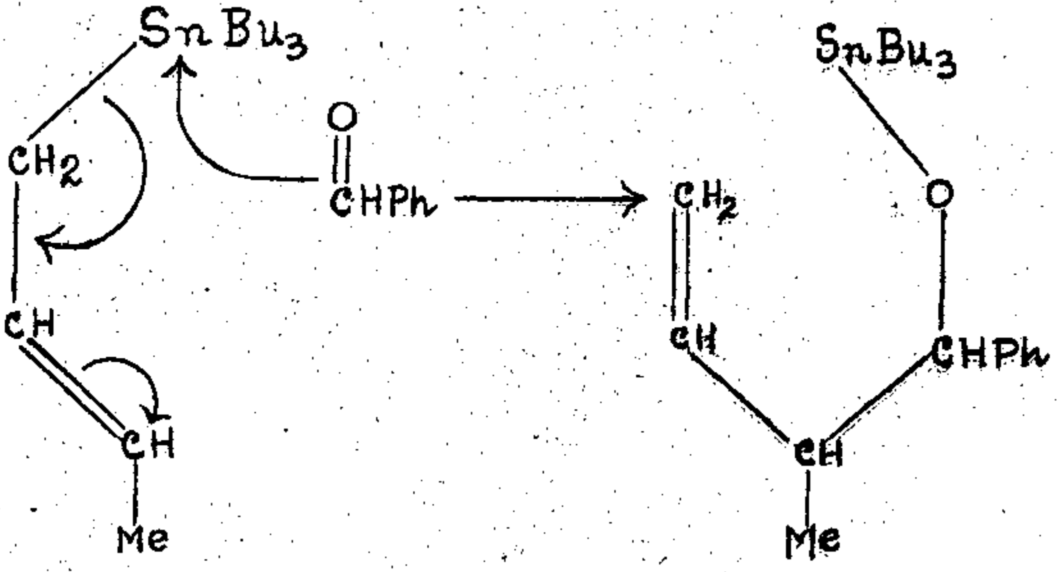
Organotin alkoxides can also be formed by the addition of the Sn-H bond or activated Sn-C, Sn-O or Sn-N bonds to the carbonyl groups of aldehyes and ketones. The Sn-H additions can be catalysed by azobisisobutyronitrile (AIBN) or by zinc chloride, involving attack at oxygen by a radical or an electrophilic tin species respectively[27].

$$Et_3SnH + Me_2CH.CHO \xrightarrow{AIBN} Me_2CH.CH_2.OSnEt_3 \qquad \text{Eqn.(13)}$$



Activated $Sn-CH_2X$ bonds ($X = CN, COMe, COOEt, CONMe_2, CH_2 = CH_2$ (etc) will add to certain aldehydes and ketones[37,38].

Substituted allyl compounds react with aldehydes, probably through a cyclic transition state (IX)[37].

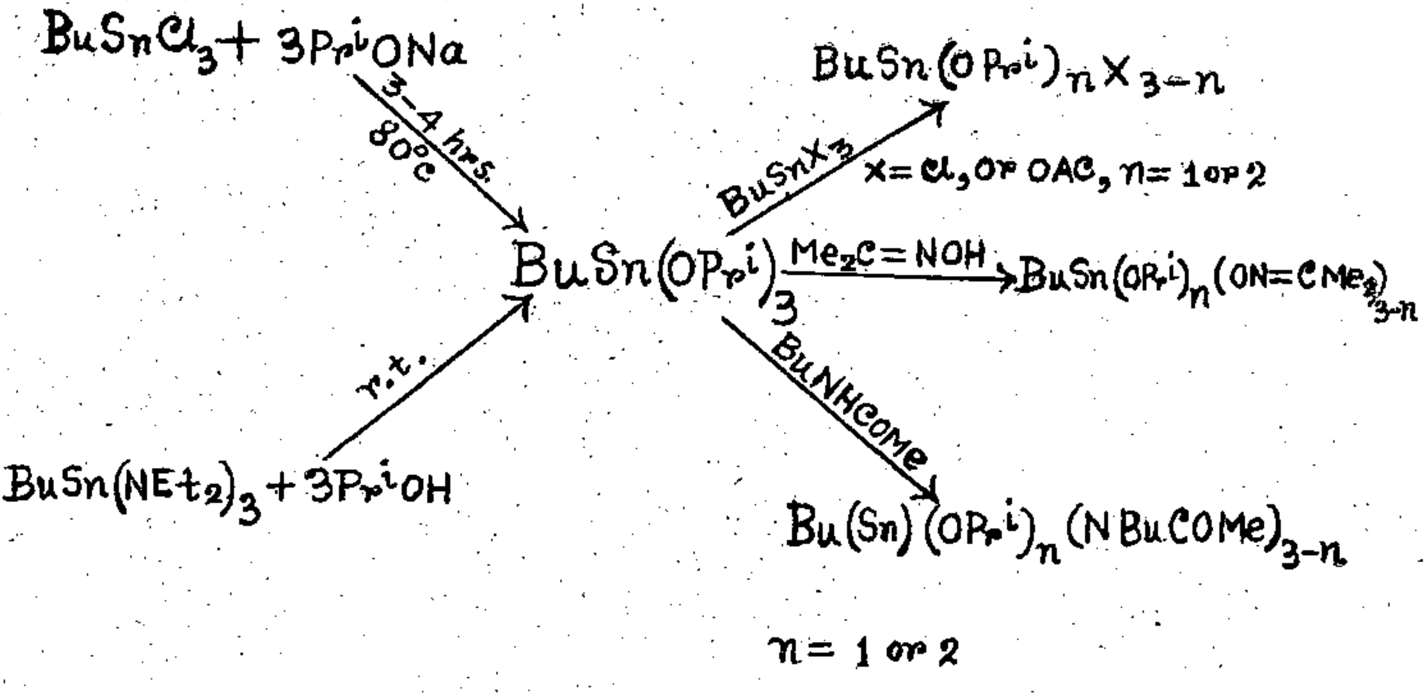


IX

Alkyltin trialkoxides can be formed by heating together the sodium alkoxide and alkyltin trichloride in benzene for 3 or 4 hours[20]. Alternatively the alkyltin tris-(diethylamides) may be subjected to alcoholysis which is rapid and exothermic at room temperature[21,22].

Some reactions by which the trialkoxides may be converted into other alkoxy derivatives are shown in the scheme-1[22].

Scheme - 1



Physical properties of some typical organotin alkoxides are given in Table-1.

Table - 1

Physical properties of some organotin alkoxides and phenoxides[79]

Compound	m.p	b.p	n_D^{20}	d^{20}
$Me_3SnO.Bu$	-	175-6°	1.4575	1.2656
$Et_3SnOCH_2.CH_2OCH = CH_2$	-	90-90.5°/3 mm	1.4810	1.2560
$Pr_3SnO.Me$	-	87-88°/3 mm	-	-
Pr_3SnOPh	-	145-147°/1 mm	1.5284	1.2167
Bu_3SnOMe	-	97-97.5°/0.06 mm	1.4710(25°)	1.1294(1.1690)
Bu_3SnOBu	-	124-128°/3 mm	1.4690	1.0189
Bu_3SnOPh	-	152°/1 mm	1.5171	1.1666
$Bu_2Sn(OMe)_2$	-	126-128°/0.05 mm	1.4852(25°)	-
Ph_3SnOMe	65-66°	-	-	-

Most of the reactions of the organotin oxides and alkoxides involve heterolytic substitution or addition reactions. The utility of these reactions in organic synthesis depends on the modulation of the nucleophilicity of the oxygen by the tin atom : the substitution and addition process often occur in various combinations and these applications have been reviewed[23,24,25].

$$\overset{\delta+}{Sn}\text{——}\overset{\delta-}{O} \qquad \overset{\delta-}{A}\text{——}\overset{\delta+}{B} \rightleftharpoons Sn\text{–}A + O\text{–}B \qquad \text{Eqn.(14)}$$

$$\overset{\delta+}{Sn}\text{——}\overset{\delta-}{O} \qquad \overset{\delta-}{A}=\overset{\delta+}{B} \rightleftharpoons Sn\text{–}A\text{–}B\text{–}O \qquad \text{Eqn.(15)}$$

The alkoxides must be protected from moisture which causes rapid hydrolysis and the readiness with which these compounds participate in both substitution and addition reaction is being increasingly exploited. The versatility of organotin alkoxides to add across unsaturated linkages are provided by the following examples:

$Bu_3SnOMe + PhNCS \longrightarrow Bu_3SnSC(OMe) = NPh$ (Ref. 28) Eqn.(16)

$Bu_3SnOMe + CO_2 \longrightarrow Bu_3SnO.COOMe$ (Ref. 28) Eqn.(17)

$Bu_3SnOMe + SO_2 \longrightarrow Bu_3SnOSOOMe$ (Ref. 28) Eqn.(18)

$Bu_3SnOMe + Cl_3C.CHO \rightarrow Bu_3SnO.CH(OMe)CCl_3$ (Ref. 29) Eqn.(19)

$Et_3SnOMe + CH_2 = CO \rightarrow Et_3SnCH_2COOMe$ (Ref. 30) Eqn.(20)

$Et_3SnO.Et + ArNCO \longrightarrow Et_3SnNArCOOEt$ (Ref. 31,32) Eqn.(21)

$Bu_3SnO.Me + ArN = C = NAr \rightarrow Bu_3SnN(Ar)C(OMe) = NAr$ Eqn.(22)

(Ref. 28)

$$\mathrm{Bu_3SnO.Me + Cl_3C.CN \longrightarrow Bu_3SnN = C(OMe)CCl_3}$$ (Ref. 33) Eqn.(23)

$$\mathrm{Et_3SnO.C \equiv CMe + Cl_3C.CHO \longrightarrow Et_3SnO.CH(CCl_3)OC \equiv CMe}$$ (Ref. 34) Eqn.(24)

The product from addition to the isocyanate will undergo protolysis with an alcohol to give the urethan and the regenerated organotin alkoxide.

$$\mathrm{Et_3SnNArCOOEt + EtOH \longrightarrow ArNHCOOEt + Et_3SnOEt}$$ Eqn.(25)

It can be thus seen that a small amount of an organotin compound can catalyse the reaction between alcohols and isocyanates and this explains the known efficacy of organotin catalysts for the production of polyurethans[31].

The reaction probably involves combination of an addition followed by a substitution reaction.

$$\mathrm{Bu_3SnOEt + PhN = C = O \longrightarrow Bu_3SnNPhCO_2Et}$$ Eqn.(26)

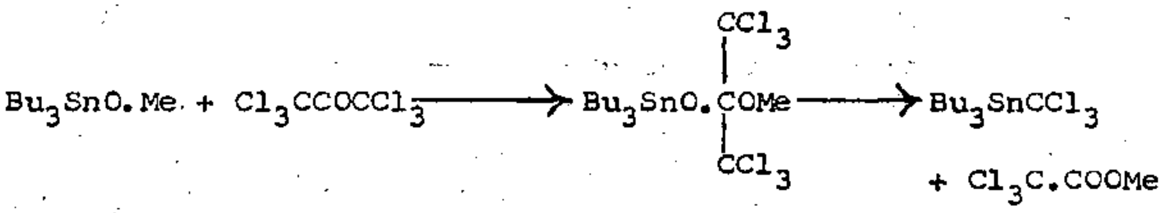
$$\mathrm{Bu_3SnNPhCO_2Et + EtOH \longrightarrow Bu_3SnO.Et + PhNHCO_2Et}$$ Eqn.(27)

$$\mathrm{PhNCO + EtOH \xrightarrow{Sn(IV)} PhNHCO_2Et}$$ Eqn.(28)

Addition to carbonyl compounds occurs with a number of aldehydes and with reactive ketones such as hexachloroacetone. Since the products are themselves alkoxides further additions may occur and in the case of chloral, a polymeric product was obtained[29,35].

$$\mathrm{Bu_3SnOMe + xCl_3CCHO \longrightarrow Bu_3Sn(OCHCCl_3)_xOMe}$$ Eqn.(29)

The product from addition of tributyltin methoxide to hexachloroacetone is unstable and decomposes to give the trichloromethyltin derivative[36].



$$Bu_3SnO.Me + Cl_3CCOCCl_3 \longrightarrow Bu_3SnO.\overset{CCl_3}{\underset{CCl_3}{C}}OMe \longrightarrow Bu_3SnCCl_3 + Cl_3C.COOMe$$

Eqn.(30)

^{119}Sn NMR chemical shift in some butyltin alkoxides shown in Table - 2 , provide some insight into the nature of these alkoxides.

Table - 2

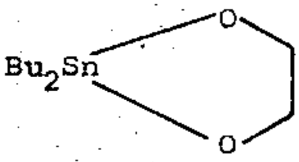
^{119}Sn Chemical Shifts (p.p.m) of Butyltin Alkoxides[a]

R	Bu_3SnOR	$Bu_2Sn(OR)_2$	$BuSn(OR)_3$
Me	+83	-165	-
Et	+86	-161	-428
Pr^n	+87	-159	-414
Pr^i	+76	- 90	-333
Bu^n	+91	-161	-428[b]
Bu^i	+82	-150	-401[c]
Bu^s	+80	- 34	-321
Bu^t	+60	- 34	-200

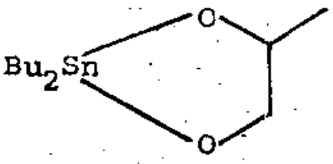
[a] Neat liquids at 25°C, [b] at 38°C, [c] at 66°C

The tributyltin alkoxides all show a high frequency shift and are believed to exist as tetrahedral monomers at room temperature. The dibutyltin dialkoxides are monomeric only when a butyl alkyl group (R = Bu^s or Bu^t) prevents dimerization and the enthalpy of dissociation of the dimers in solution is found to be 60-100 KJ mol^{-1} [39]. The butyltin trialkoxides exhibit a wider range of chemical shifts[22]. Butyltin tributoxide again appears to be monomeric, for steric reasons, but the compounds with similar alkyl groups, showing chemical shifts of about -425 p.p.m., are probably octahedrally six coordinated.

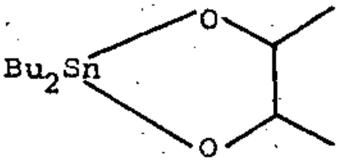
By this chemical shift criterion, the dibutyltin derivatives of the 1,2-diols shown in structure X to XII appears to contain five coordinated tin as in VI[39].



X



XI



XII

^{119}Sn chemical shift (p.p.m) -189

-164

-155 (in $CDCl_3$)

Dialkoxides undergo similar addition reactions to those already discussed for the monoalkoxides and in most cases, 1:1 and 1:2 adducts can be isolated[40].

$$\begin{tikzcd}
Bu_2Sn(OMe)_2 + A = B \arrow[r] & Bu_2Sn(OMe)ABOMe \arrow[d, "A = B"] \\
 & Bu_2Sn(ABOMe)_2
\end{tikzcd}$$

Eqn. (31)

(A = B = isocyanate, isothiocyanate, aldehyde, sulphur dioxide, carbon dioxide, cyanide, carbodiimide). Dibutyltin dimethoxide undergoes a redistribution reaction with a dibutyltin dihalide and the resulting halomethoxide also participates in addition reactions[40,41].

$$Bu_2Sn(OMe)_2 + Bu_2SnCl_2 \longrightarrow 2Bu_2Sn(Cl)OMe$$ Eqn. (32)

$$Bu_2Sn(Cl)OMe + A = B \longrightarrow Bu_2Sn(Cl)ABOMe$$ Eqn. (33)

The dialkoxides react with a variety of compounds, R_2SnX_2 in solution, in a process analogous to the Schlenk equilibrium involving Grignard reagents to give the monoalkoxy compoun ds[41]. The ^{119}Sn NMR spectra show that the methoxide chlorides $R_2Sn(OMe)Cl$ (R = Me or Bu) exist as monomers in dilute solution, but as methoxide-bridged dimers in more concentrated solutions[42].

$$Bu_2SnCl_2 + 2MeONa \longrightarrow Bu_2Sn(OMe)_2 \xrightarrow{Bu_2SnX_2} Bu_2Sn(OMe)X$$

Eqn. (34)

(X = F, Cl, Br, I, SNC, OAc, OSO_2R)

Turning next to substitution reactions, the alkoxides are sensitive to a wide range of protic species; reaction with water has already been mentioned and acetylenes readily displace alkoxyl groups[43].

$$Et_3SnOMe + HC{\equiv}C.CH = CH_2 \longrightarrow Et_3SnC{\equiv}C.CH = CH_2 + MeOH$$ Eqn.(35)

N-Stannylamides are conveniently prepared from alkoxides

$$Et_3SnO.Me + PhNHCOMe \longrightarrow Et_3SnNPhCOMe + MeOH$$ Eqn.(36)

However when the corresponding thioamides are used the products have Sn-S rather than Sn-N bonds[44].

$$Et_3SnOMe + PhNHCSMe \longrightarrow Et_3SnSC(Me) = NPh$$ Eqn.(37)

Alkyl halides and alkoxides react to give ethers and organotin halides.

$$Bu_3SnOMe + CH_2 = CHCH_2Br \longrightarrow Bu_3SnBr + CH_2 = CH.CH_2OMe$$ Eqn.(38)

(Ref. 45)

$$Et_3SnOCH_2.CH_2C{\equiv}CH + MeOCH_2Cl \longrightarrow Et_3SnCl + HC{\equiv}C.CH_2CH_2OCH_2OMe$$ Eqn.(39)

(Ref. 46)

$$R_3SnOCH_2C{\equiv}CSnR_3 + MeI \longrightarrow R_3SnI + R_3SnC{\equiv}C.CH_2OMe$$ Eqn.(40)

(Refs. 47,48,49)

Irradiation with ultraviolet light and the addition of Lewis acids did not increase the yields in these reactions[45]. In a similar manner alkoxyl groups can be transferred to silicon by the use of silyl halides.

$$Bu_3SnOMe + Et_3SiCl \longrightarrow Bu_3SnCl + Et_3SiOMe$$ Eqn.(41) (Ref. 50)

$$R_3SnO.CH_2C{\equiv}CSnR_3 + R'_3SiCl$$
$$\longrightarrow R_3SnCl + R'_3SiOCH_2C{\equiv}CSnR_3$$ Eqn.(42) (Refs. 47, 51)

$$3Bu_3SnOCH = CMe_2 + MeSiCl_3 \longrightarrow MeSi(OCH = CMe_2)_3$$
$$+ 3Bu_3SnCl$$ Eqn.(43) (Ref. 52)

The silyl halides react more readily than the alkyl halides and cooling is often necessary.

Trans-alkoxylations can be effected by heating an alkoxide with excess of another alcohol[53].

$$Bu_3SnOMe + HO(CH_2)_nX \longrightarrow Bu_3SnO(CH_2)_nX + MeOH$$ Eqn.(44)

$(X = Cl, Br; n = 2,3,4)$

An alkoxysilane may also be used[54].

$$Bu_3SnOMe + Me_3SiO.Bu \xrightarrow[40\text{ hr}]{145^\circ C} Bu_3SnO.Bu + Me_3SiOMe$$ Eqn.(45)

A similar reaction occurs under milder condition when an alkoxide is treated with an ester[55].

$$Et_3SnOMe + C_6H_{11}OAc \xrightarrow{25^{o}C} Et_3SnO.C_6H_{11} + MeOAc \qquad \text{Eqn.(46)}$$

IIC. Organotin Enolates

Organotin derivatives of simple enols are usually prepared by treating the acetate of the appropriate enol with a trialkyltin methoxide but the alternative routes have also been used[56-59]. The keto and enol forms exist in metallotropic equilibrium which usually favours the C-isomer.

$$Bu_3SnOMe + MeCOOCH = CHEt \longrightarrow Bu_3SnOCH = CHEt + MeO.COMe \qquad \text{Eqn.(47)}$$

$$Bu_3SnH + MeCOCH = CHMe \longrightarrow Bu_3SnO.CMe = CH.CH_2Me \qquad \text{Eqn.(48)}$$

$$(Me_3Sn)_2S + Hg(CH_2COR)_2 \longrightarrow 2Me_3SnOCR = CH_2 + HgS \qquad \text{Eqn.(49)}$$

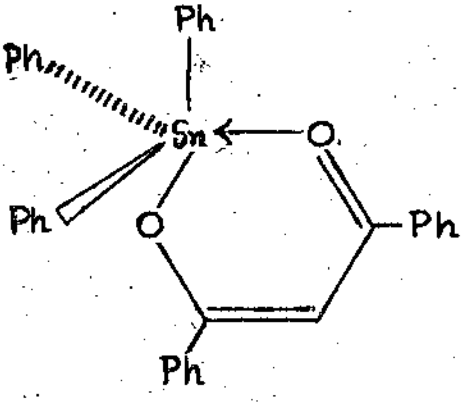
$$Bu_3SnNEt_2 + MeCOBu^t \longrightarrow Bu_3SnO.CBu^t = CH_2 + Et_2NH \qquad \text{Eqn.(50)}$$

$$C = C\text{-}OSnR_3 \rightleftharpoons R_3SnC\text{-}C = O$$

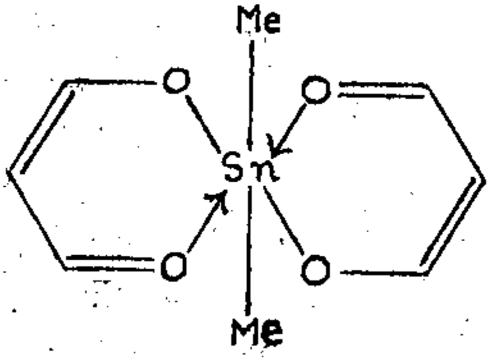
O-isomer C-isomer

The derivatives of 1,3-diones can be prepared from the organotin oxides[60] in a reaction analogous to the preparation of alkoxides. These diones act as bidentate ligands and the structures shown in XIII[61] and XIV[62] have been established by X-ray crystallography.

$$Me_2SnO + 2MeCOCH_2COMe$$
$$\downarrow$$
$$Me_2Sn(OCMe = CHCOMe)_2 + H_2O \qquad \text{Eqn. (51)}$$

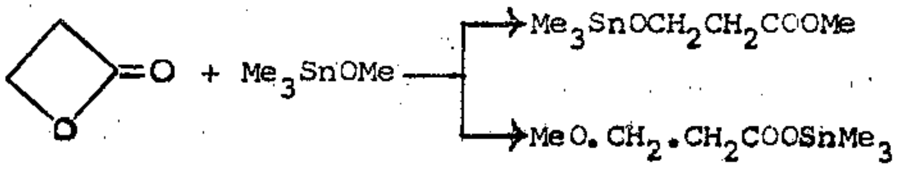


XIII



XIV

The reaction of β-propionolactone with trimethyltin methoxide (and other Me_3SnX compounds) has been studied in detail[63,64]. The dominant product is that resulting from acyl-oxygen bond cleavage XV but the product obtained from alkyl-oxygen bond cleavage XVI can also be detected, the ratio of the products depending upon the polarity of the solvent used



XV

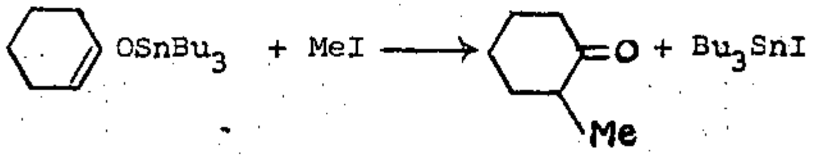
XVI

Stannylated celuloses are prepared by reaction between cellulose (or a derivative) and an organotin alkoxides[65]. When an alkoxide reacts with an enol ester then the O-stannyl derivative of the enol form and/or the C-stannyl derivatives of the keto form is obtained[57,66].

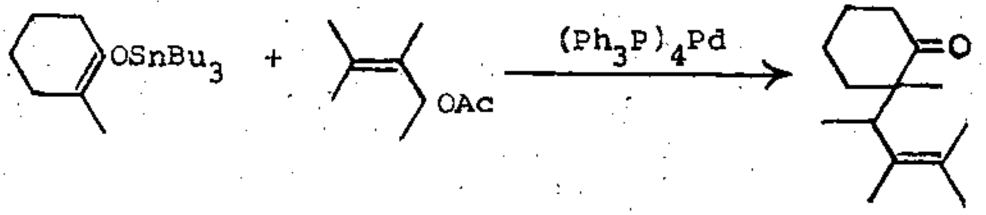
$$RR'C = CR''OAc + Bu_3SnOMe \longrightarrow \left.\begin{array}{r} RR'C = CR''OSnBu_3 \\ RR'C(SnBu_3)CR'' = O \end{array}\right\} + MeOAc$$

Eqn. (52)

Organotin enolates in which the O- and C- bonded isomers are in metallotropic equilibrium react with alkyl halides by C-alkylation[67] and C-allylation can be brought about by allylic acetates in the presence of tetrakis - (triphenylphosphine) palladium (0)[68].



Eqn.(53)



Eqn.(54)

IID. Organotin Phenoxides

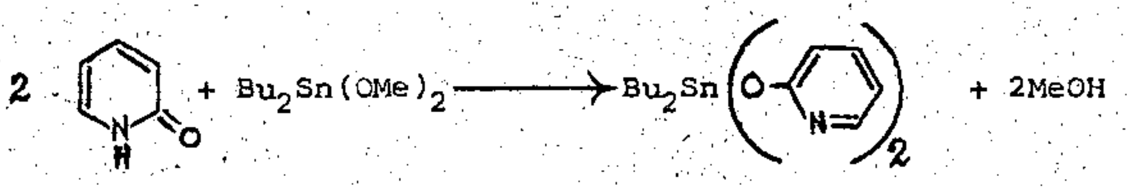
The organotin phenoxides, $R_nSn(OAr)_{4-n}$, are conveniently prepared by reaction between an oxide and a phenol in the same manner as the alkoxides[69].

$$(Bu_3Sn)_2O \; + \; 2O\text{-}PhC_6H_4OH \longrightarrow 2Bu_3SnOC_6H_4Ph\text{-}O \; + \; H_2O \qquad \text{Eqn.(55)}$$

Among other methods, treatment of an organotin chloride with a phenoxide may be used[70].

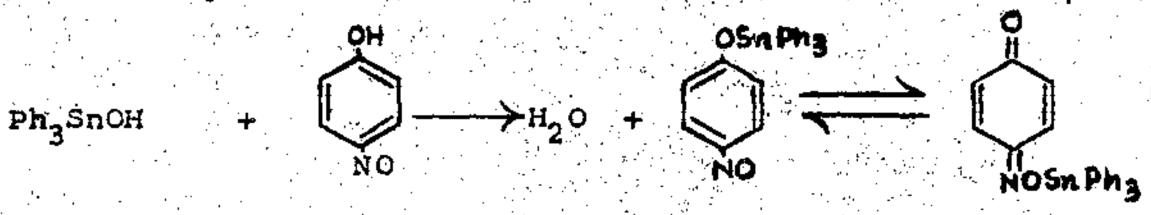
$$Ph_3SnCl + p\text{-}NO_2C_6H_4ONa \longrightarrow p\text{-}NO_2C_6H_4OSnPh_3 + NaCl \qquad \text{Eqn.(56)}$$

Dibutyltin dimethoxide reacts with 2-pyridone as follows[71]



Eqn.(57)

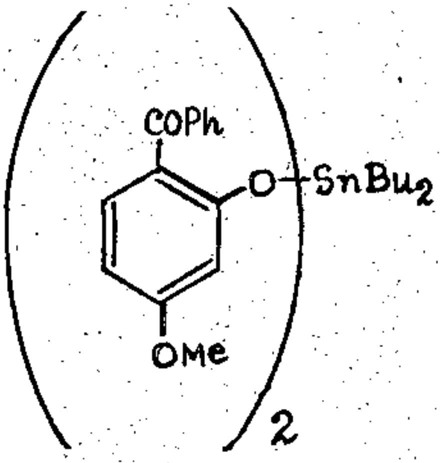
Reaction between triphenyltin hydroxide and p-nitrosophenol gave the p-nitrosophenoxide which, from the infrared and visible spectra of its solutions, was considered to be in equilibrium with the tautomeric quinoxime[72].



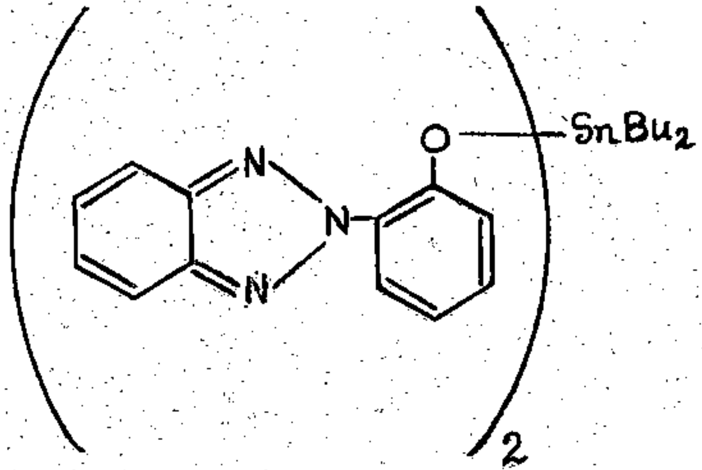
Eqn.(58)

The crystalline product consisted solely of the quinoxime form.

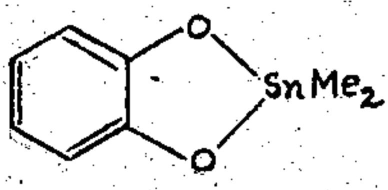
The phenoxides like the alkoxides are generally sensitive to moisture but compounds derived from more acidic phenols (e.g. nitrophenols) are less readily hydrolysed[70,73]. High thermal stability is a property of a number of phenoxides for example compounds XVII[74] and XVIII[75] and also of compounds derived from dihydric phenols such as XIX and XX[76].



XVII



XVIII



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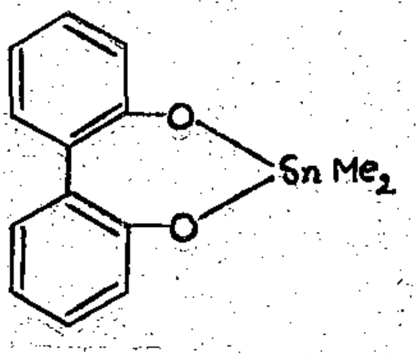
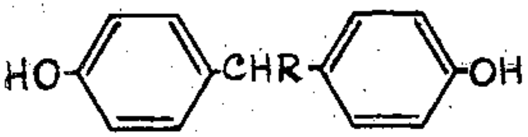


XX

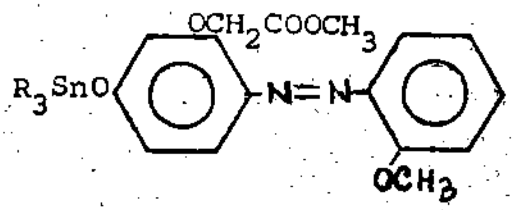
A polymeric phenoxide, having repeating unit $-OSnPh_2OC_6H_4-$ was prepared from diphenyltin dichloride and the dipotassium salt of hydroquinone[77]. A number of polymeric products have also been made by heating together in toluene, dialkyl tin oxides and dihydric phenols of the type XXI[78].



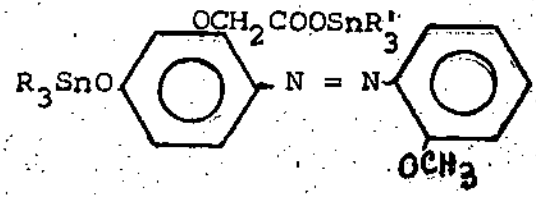
XXI

IIE. Organotin derivative of some (Arylazo) phenols

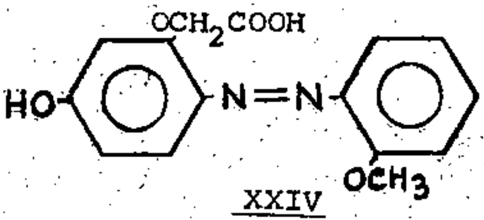
Although no attempt on the synthesis of organotin derivatives of (arylazo) phenols has been yet reported, Sengupta[80] reported the stannylation of the -OH group in 2-(2'-methoxy benzene azo)5-hydroxy phenoxy methyl acetate and the corresponding acid leading to the formation of the compounds XXII and XXIII. Interestingly, stannylation of the -OH group invariably occurred whenever any attempt to substitute the proton of the -COOH group in XXIV by organotin group was made.



XXII

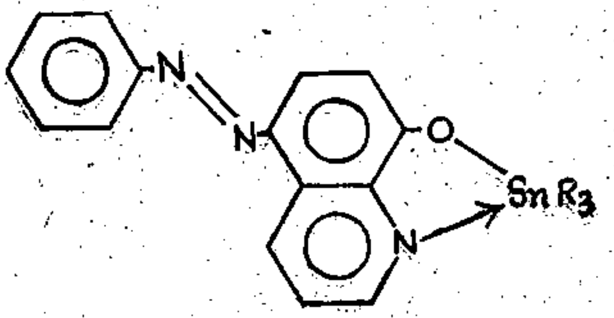


XXIII

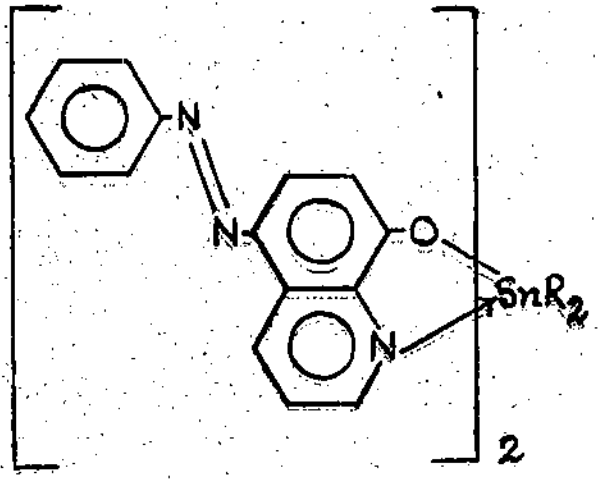


XXIV

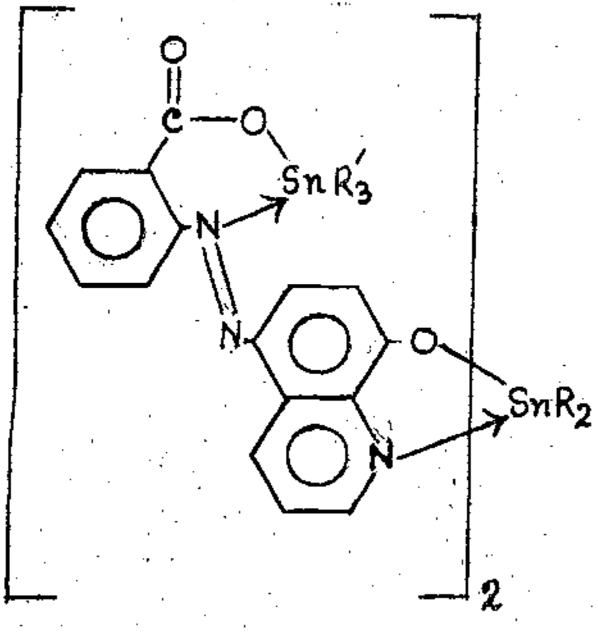
Another group of organotin compounds involving Aryl-O-Sn bond is the organotin derivatives of 5-phenylazo-8-quinolinol and 5-(2'-carboxy phenyl) azo-8-quinolinol XXV, XXVI, XXVII, XXVIII have been reported[81].



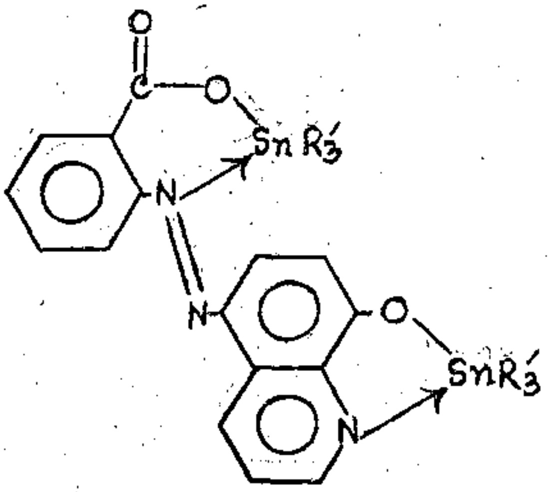
XXV



XXVI



XXVII



XXVIII

IIF. Stannoxides of other elements

The Chemistry of the metallostannoxanes has been reviewed[82], the most important compounds in this class are the stannosiloxanes containing the grouping $\equiv$Sn - O-Si$\equiv$. Although a number of compounds for example $Me_3SiOSnR_3$ (R = Pr, Bu) have been prepared by cohydrolysis of the mixed halides[83,84], the alkali metal oxides are more generally used for laboratory synthesis[85].

$$\begin{tikzcd} Me_3SiOLi + Me_3SnCl \arrow[r] & LiCl + Me_3SiO.Sn.Me_3 \\ & Me_3SnOLi + Me_3SiCl \arrow[u] \end{tikzcd}$$

Eqn. (59)

The reaction of stannylamines with protic species is the basis of many preparative procedures and can be applied to the preparation of Stannosiloxanes[86].

$$R''_3SiOH + R_3SnNR'_2 \longrightarrow R_3SnOSiR''_3 + R'_2NH \qquad \text{Eqn.(60)}$$

Benzene, toluene or ligroin solutions of organotin oxides and hydroxides react with hydroxy-silanes and germanes to give water and the stannosiloxanes or stannogermoxanes[87].

$$(Ph_3Sn)_2O + 2Me_3SiOH \longrightarrow 2Ph_3SnOSiMe_3 + H_2O \qquad \text{Eqn.(61)}$$

$$(Bu_3Sn)_2O + Ph_2Si(OH)_2 \longrightarrow Ph_2Si(OSnBu_3)_2 + H_2O \qquad \text{Eqn.(62)}$$

$$BuSnO.OH + 3Ph_3SiOH \longrightarrow BuSn(OSiPh_3)_3 + H_2O \qquad \text{Eqn.(63)}$$

On treatment with a Grignard reagent the stannosiloxanes are alkylated at the tin atom, for example $Et_3SnO.SiEt_3$ on treatment with EtMgBr gives eventually, $Et_4Sn + Et_3SiOH$[88].

Much of the work in this area has been directed at obtaining modified organopolysiloxanes in which there has been partial replacement of silicon by tin. Although such polymeric compounds have been made[89] their stabilities and physical properties are inferior to those of the organopolysiloxanes[90].

Reaction between metallic or organometallic halides and organotin oxides is a general method of preparing organohalogenostannometalloxanes[91].

$$M{-}X + R_2SnO \longrightarrow MOSnR_2X \qquad \text{Eqn.(64)}$$

Reaction between diethyl cadmium and triethyl tin hydroxide gave impure $Et_3SnOCdEt$[92]: compounds containing Sn-O-P linkages have been made[93].

$$Bu_3SnCl + Bu_2POK \longrightarrow Bu_2POSnBu_3 + KCl \qquad \text{Eqn.(65)}$$

Some stannoxyzirconium alkoxides have also been isolated[94].

$$Zr(OBu)_4 + Bu_3SnOAc \longrightarrow Bu_3SnO.Zr(OBu)_3 + AcOBu \qquad \text{Eqn.(66)}$$

Table -9

Physical properties of some Stannoxides[79]

Compound	m.p.	b.p.	n_D^{20}	d^{20}
$Me_3SnOSiMe_3$	-	144°	-	-
$Me_3SnOSiEt_3$	-	49°/1 mm	-	-
$Et_3SnOSiMe_3$	-	99°/20 mm	-	-
$Et_3SnOSiEt_3$	-	114-115°/4 mm	1.4635	1.1149
$Et_3SnO.GePh_3$	-	167-169°/0.04 mm	-	-
$Bu_3SnOPBu_2$	-	165-167°/1 mm	-	-
$Bu_3SnOZr(OBu)_3$	-	-	1.4892	1.2020(24°)
$Et_2Si(OSnBu\text{-}i_3)_2$	-	203°/3 mm	1.4800	1.1443
$Ph_3SnO.SiMe_3$	-	140°/0.1 mm	-	-
$Ph_3SnO.SiPh_3$	139-140°	-	-	-
$Ph_2Si(OSnPh_3)_2$	94.5-96.5°	-	-	-

REFERENCES

1. M.F. Shostakovskii, A.S. Atavin, E.P. Vyalykh, B.A. Trofimov — Zh. Obshch. Khim. 1965, 35, 751 (Chem. Abs. 1965, 62, 6514a)
2. A.S. Atavin, R.I. Dubova, N.P. Vasil'ev — Zh. obshch. khim, 1966, 36, 1506 (Chem. Abs. 1966, 65, 16956a)
3. G.F. Rubinchik, Z.M. Manulkin — Zh. Obshch. Khim, 1968, 38, 841 (Chem. Abs., 1968, 69, 77394)
4. A.G. Davies, D.C. Kleinschmidt, P.R. Palan and S.C. Vasishtha — J. Chem. Soc. Chem. Commun., 1971, 3972.
5. A.G. Davies, P.R. Palan and S.C. Vasishtha — Chem. and Ind., 1967, 229.
6. I. Gverdtsiteli and S.V. Adamiya — Soobshch. Akad. Nauk-Gruz. S.S.R., 1967, 47, 55 (Chem. Abs. 1968, 68, 29817)
7. M.F. Shostakovskii, V.M. Vlasov, R.G. Mirskov and V.N. Petrova — Zh. Obshch. Khim., 1965, 35, 47 (Chem. Abs. 1965, 62, 13169a)
8. M. Massol, J. Barrau, J. Satge and B. Bouyssieres — J. Organomet. Chem., 1974, 80, 47.
9. D. Sukhani, V.D. Gupta and R.C. Mehrotra — Aust. J. Chem., 1968, 21, 1175.
10. R.C. Mehrotra and V.D. Gupta — J. Organomet. Chem., 1965, 4, 145.

11. W.J. Considine, J. Organomet. Chem., 1966, 5, 263.

12. M.G. Voronkov and I. Romadane, Khim. Geterotsikl. Soedin, 1966, 892 (Chem. Abs. 1967, 67, 32751v)

13. J.C. Pommier and J. Valade, J. Organomet. Chem. 1968, 12, 443.

14. A. Shanzer and N. Mayer-Shochet, J. Chem. Soc. Chem. Commun., 1980, 176.

15. A. Shanzer and E. Berman, J. Chem. Soc. Chem. Commun., 1980, 259.

16. R.M. Munava and H.H. Szmant, J. Org. Chem., 1976, 41, 1832.

17. A.G. Davies, L. Smith and P.J. Smith, J. Organomet. Chem., 1972, 39, 279.

18. A. Tzschach, K. Ponicke, L. Korecz and K. Burger, J. Organomet. Chem., 1973, 59, 199.

19. R.G. Rees and A.F. Weble, J. Organomet. Chem., 1968, 12, 239.

20. D.P. Gaur, G. Srivastava and R.C. Mehrotra, J. Organomet. Chem., 1973, 63, 221.

21. J. Lorberth and M.R. Kula, Chem. Ber., 1964, 97, 3444.

22. J.D. Kennedy, W. McFarlane, P.J. Smith, R.F.M. White and L. Smith, J. Chem. Soc. Perkin Trans., 1973, 2, 1785.

23. A.G. Davies, Synthesis, 1969, 56.

24. J.C. Pommier and M. Pereyre — Adv. Chem. Ser., 1976, 157, 82.

25. J.C. Pommier and M. Pereyre — J. Organomet. Chem., 1976, 1, 161.

26. J.G. Noltes, H.M.J.C. Creemer and G.J.M. Vanderkerk — J. Organomet. Chem., 1968, 11, 21.

27. W.P. Neumann and E. Heymann — Liebigs Ann. Chem., 1965, 11, 683.

28. A.J. Bloodworth, A.G. Davies and S.C.Vasishtha — J. Chem. Soc. Chem. Commun., 1967, 1309.

29. A.G. Davies and W.R. Symes — J. Chem. Soc. Chem. Commun., 1967, 1009.

30. V.V. Khrapov, V.I. Gol'danskii, A.K. Prokof'ev, V.ya. Rochev and R.G. Kostyanovskii — Izv. Akad. Nauk. - S.S.S.R. Ser. Khim., 1968, 1261 (Chem. Abs. 1968, 69, 96850)

31. A.J. Bloodworth and A.G. Davies — J. Chem. Soc. Chem. Commun., 1965, 5238.

32. A.J. Bloodworth and A.G. Davies — J. Chem. Soc. Chem. Commun., 1965, 6859.

33. U.S. Patent — Chem. Abs. 1968, 68, 49775.

34. U.S.S.R. Patent — Chem. Abs. 1966, 65, 12240a.

35. U.S. Patent — Chem. Abs. 1968, 68, 105364.

36. A.G. Davies and W.R. Symes — J. Organomet. Chem., 1966, 5, 394.

37. C. Servens and M. Pereyre — J. Organomet. Chem., 1971, 26, C4.

38. E.W. Abel and R.J. Rowby J. Organomet. Chem., 1975, 84, 199.

39. P.J. Smith, R.F.M. White, and L. Smith J. Organomet. Chem., 1972, 40, 341.

40. A.G. Davies and P.G. Harrison J. Chem. Soc. Chem. Commun., 1967, 1313.

41. A.G. Davies and P.G. Harrison J. Chem. Soc. Chem. Commun., 1967, 298.

42. A.C. Chapman, A.G. Davies, P.G. Harrison and W. McFarlane J. Chem. Soc. Chem. Commun., 1970, 821.

43. French Patent Chem. Abs. 1966, 65, 8962f.

44. J.G. Noltes Recl. Trav. Chim. Pays-Bas., 1965, 84, 799.

45. J.C. Pommier and J. Valade Compt. Rend. 1965, 260, 4549.

46. M. Devaud Rev. Chim. Miner. 1967, 4, 921 (Chem. Abs. 1968, 69, 87122).

47. M.F. Shostakovskii, R.G. Mirskov, V.M. Vlasov and S.H.L. Tarpischev Zh. Obshch. Khim., 1967, 37, 1738.

48. M.F. Shostakovskii, V.M. Vlasov and R.G. Mirskov Zh. Obshch. Khim., 1965, 35, 1121. (Chem. Abs. 1965, 62, 6513c).

49. U.S.S.R. Patent Chem. Abs. 1966, 64, 5138d.

50. J.C. Pommier, M. Pereyre and J. Valade Compt. Rend., 1965, 260, 6397.

51. U.S.S.R. Patent Chem. Abs. 1966, 64, 3602e.

52. B. Bellegarde, M. Pereyre and J. Valade Compt. Rend. Ser. C., 1967, 264, 340.

53. J.C. Pommier, B. Delmont and J. Valade — Tetrahedron Lett., 1967, 5289.

54. M. Pereyre, B. Bellegarde and J. Valade — Compt. Rend. Ser. C., 1967, 265, 939.

55. S.V. Ponomarev, Yu. I. Baukov, O.V. Dudikina, I.V. Petrosyan and L.I. Petrovskaya — Zh. Obshch. Khim., 1967, 37, 2204.

56. A.N. Nesmeyanov, I.F. Lutsenko and S.V. Ponomarev — Dokl. Akad. Nauk SSSR, 1959, 124, 1073. (Chem. Abs. 1959, 53, 14984a).

57. M. Pereyre, B. Bellegarde, I. Mendelsohn and J. Valade — J. Organomet. Chem. 1968, 11, 97.

58. I.F. Lutsenko, Yu. I. Baukov and I. Yu. Belaven — J. Organomet. Chem. 1970, 24, 359.

59. Y. Odie and M. Pereyre — J. Organomet. Chem. 1973, 55, 273.

60. M.M. McGrady and R.S. Tobias — J. Am. Chem. Soc., 1965, 87, 1909.

61. G.M. Bancroft, B.W. Davies, N.C. Payne and T.K. Sham — J. Chem. Soc. Dalton Trans., 1975, 973.

62. G.A. Miller and E.O. Schlemper — Inorg. Chem., 1973, 12, 677.

63. K. Itoh, Y. Kato and Y. Ishii — J. Org. Chem., 1969, 34, 459.

64. K. Itoh, S. Kobayashi, S. Sakai and Y. Ishii — J. Organomet. Chem., 1967, 10, 451.

65. U.S.S.R. Patent — Chem. Abs. 1968, 68, 41235.

66. S.V. Ponomarev, B.Y. Rogachev and I.F. Lutsenko — Zh. Obshch. Khim. 1966, 36, 1348. (Chem. Abs. 1966, 65, 16998c).

67. Y. Odic and M. Pereyre — J. Organomet. Chem., 1973, 55, 273.

68. B.M. Trost and E. Keinan — Tetrahedron Lett., 1980, 2591.

69. Japanese Patent — Chem. Abs. 1968, 68, 49777 .

70. T.G. Brilkina, M.K. Safonova and N.A. Sikolov — Zh. Obshch. Khim., 1966, 36, 2202.

71. French Patent — Chem. Abs. 1968, 68, 13178.

72. A.N. Nesmeyanov, L.Al'Fonso, D.N. Karavtsov and B.V. Loshkin — Izv. Akad. Nauk S.S.S.R. Ser. Khim. 1968, 296. (Chem. Abs. 1968, 69, 52238).

73. French Patent — Chem. Abs. 1965, 63, 14904d.

74. French Patent — Chem. Abs. 1967, 67, 32782f.

75. French Patent — Chem. Abs. 1967, 67, 54265s.

76. H.J. Emeleus and J.J. Zuckerman — J. Organomet. Chem. 1964, 1, 328.

77. U.S. Patent — Chem. Abs. 1965, 63, 5774d.

78. U.S. Patent — Chem. Abs. 1966, 64, 5138h.

79. R.C. Pollar — The Chemistry of Organotin Compounds, Academic Press, New York (1970).

80. A. Sengupta — Ph.D. Thesis, N.B.U. 1981.

81. T.S. Basu Baul, T.K. Chattopadhyay and B. Majee — Polyhedron, 1983, 2, 635.

82. P.G. Harrison — Organomet. Chem. Revs., Sect. A., 1969, 4, 379.

83. R. Okawara and K. Sugita — J. Am. Chem. Soc., 1961, 83, 4480.

84. R. Okawara, D.G. White, K. Fujitani and H. Sato — J. Am. Chem. Soc., 1961, 83, 1342.

85. H. Schmidbauer and H. Hussek — J. Organomet. Chem., 1964, 1, 244.

86. K. Jones and M.F. Lappert — Organomet. Chem. Rev., 1966, 1, 67.

87. A.G. Davies, P.G. Harrison and T.A.G. Silk — Chem. and Ind., 1968, 949.

88. M.F. Shostakovskii, N.V. Komarov, A.M. Sklyanova and A.V. Suvorova — Dokl. Akad. Nauk S.S.S.R., 1967, 176, 356.

89. K.A. Andrianov, T.N. Ganina and E.T. Khrustaleva — Izv. Akad. Nauk S.SS.R., Otd. Khim. Nauk 1956, 798 (Chem. Abs. 1957, 51, 3487).

90. A.D. Delman, A.A. Stein, B.B. Simms and R.J. Katzenstein — J. Polymer Sci. Pt. A-1, 1966, 4, 2307.

91. A.G. Davies and P.G. Harrison — J. Organomet. Chem. 1967, 10, 31.

92. V.N. Pankratova and L.P. Stepovik — Zh. Obshch. Khim. 1968, 38, 844.

93. K. Issleib and B. Walther — Angew. Chem. Int. Ed. Engl. 1967, 6, 88.

94. U.S. Patent — Chem. Abs. 1968, 68, 50618.