CHAPTER II

Cleavage of tin-carbon bonds

IIA Introduction

Much of the experimental work in the field of organotin chemistry has been inspired by a desire to understand as fully as possible the reactivity of these compounds. Hundreeds of alkyl tins, especially those with different ligands, were prepared with a view to studying the fission of tin-carbon bond which may be represented as

$$\geqq \mathrm{Sn} - \mathrm{c} \leqq + \mathrm{A{-}B} - \geqq \mathrm{Sn} - \mathrm{A} + \geqq \mathrm{c} - \mathrm{B} \qquad \text{(I)}$$

Although the reactivity of the tin-carbon bond depends on a number of factors, they are susceptible to attack by a wide variety of reagents so that A - B in the above equation may be halogen, mineral acid, carboxylic acid, thiol, phenol, alcohol, metallic or nonmetallic halide, alkali, alkali metal etc.

These reactions are not only of utmost theoretical and practical importence in organotin chemistry, but also has some bearing on the present work. As such a brief discussion on the subject is presented here.

The most frequenly studied reaction of tin-carbon bond is the cleavage by halogen; one or more organic moieties are split off depending upon the condition of the reaction according to the following scheme :

$$R_4Sn + X_2 \rightarrow R_3SnX + RX \quad (2)$$

$$R_3SnX + X_2 \rightarrow R_2SnX + RX \quad (3)$$

$$[X - Cl, Br, I]$$

when unsymmetrical organotin compounds of the type R_3SnR' are treated with one molecular proportion of the reagent, organic groups are usually cleaved from tin in the order (1) :

O - tolyl > p - tolyl > phenyl > benzyl > vinyl > methyl > ethyl > propyl > iso-butyl > iso-amyl > amyl > hexyl > heptyl > octyl.

This series is of practical value in synthetic organotin chemistry since (2) usually predicts correctly the products of cleavage. However predictions are less reliable with $R_2SnR'_2$ type of compounds. Though the sequence have been compiled from reactions using dirrerent cleavage reagents under a variety of conditions, careful examination of the literature reveals a number of contradictions (3), the actual situation being much more complicated.

The mechanism of tin-carbon bond cleavage has been clarified in a series of papers (3-5) by Gielen and co-workers. On the basis of their mechanistic studies these reactions are to be classified essentially as electrophilic substitution at the carbon atom. The geometry of the transition state is however greatly influenced by the solvent and the electrophile which may co-ordinate with the tin atom under proper conditions thereby causing profound variation in the rates. The different types of organotin derivatives are treated separately in the following discussion :-

Tin-carbon bond cleavage in symmetrical tetra alkyl tins

These compounds can be cleaved by a number of electrophiles (1) or radicals (7-8). Among the electrophiles, one may use halogens, halogen acids, tin (IV) halides and also other inorganic halides [eg BX_3(9), $HgCl_2$, $HG_{e}Cl_3$, [illegible]$_3$ (10), PF_5(11)] , Organometallic halides [$RBCl_2$, R_3SnCl (12)] , or oxidants [CrO_3(13)] . Alkyl halides react in presence of tetra alkyl tins to give tri- alkyltin halides (14-15). Halogens can also be used as radical sources (16).

IIB . Electrophilic substitution at a saturated carbon atom

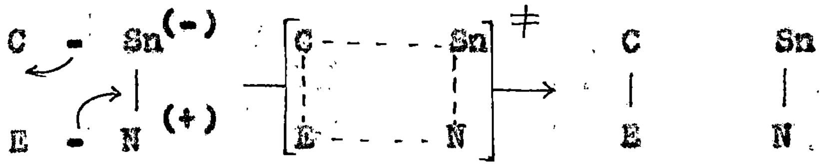
Kienetic studies have shown that tetraalkyltins react with electrophiles [I_2 (17), Br_2 (5), HgX_2 (19-20), CrO_3 (21)] by a complex mechanism (22) which involves a predetermining equilibrium between the organotin substrate and a nucleophile. The step is then followed by the reaction of an electrophile with the activated carbon-tin bond. Depending on the solvent polarity two different situations may be distinguished :

(1) Reaction in "nonpolar" solvents :

In nonpolar media, the most nucleophic species available in the solution is the electrophile E-N itself [X-X(22), H-cl(23), O_2Cr-O(21)] , which may complex with the organotin molecules through the tin atom as follows :

$$C - Sn + N - E \rightleftharpoons C - \overset{(-)}{Sn} - \overset{(+)}{N} - E \qquad (4)$$

The representation is only formal indicating the transfer of electron from N to tin. The complex formed in this equilibrium contains activated C atoms and an enhanced electrophilic species. An intramolecular reaction, which seems thus a reasonable way in which this complex might give reaction products, is observed when the structure of the complex allows such a cyclic transition state. Gielen and Nasielski (44) use the symbol SF 2 (substitution four centred bimolecular) to indicate this mechanism, Abraham and Hill (19) however prefer to call it SEi.



(5)

This complex which contains rather nucleophilic carbon atoms, may also react with another electrophile E - N to give the cleavage of a carbon-tin bond :

$$N - E + C - \overset{(-)}{Sn} - \overset{(+)}{N} - E \longrightarrow C - E + N - \overset{(-)}{Sn} - \overset{(+)}{N} - E \quad (6)$$

A third possibility cannot be excluded : it is the reaction of the electrophilic part of this complex with another organotin molecule :

$$C - \overset{(-)}{Sn} - \overset{(+)}{N} - E + C' - Sn' \longrightarrow C' - E + Sn' - N + C - Sn \quad (7)$$

This mechanistic picture explains a large number of findings such as :

a) The presence of a third over term : The rate of reaction between tetra iso-propyl tin and bromine in chlorobenzene may roughly be described by :

$$- d[X_2]/dt = K_2[R_4\,Sn][X_2] + K_3[R_4Sn][X_2]^2 \quad (8)$$

where the third order term may be considered as due to the existance of reaction (6).

b) The mixing effect : Tetraethyltin reacts 11.7 times faster than tetramethyltin with Br_2 in chlorobenzene. A mixture of tetramethyl and tetraethyltin, reacting with Br_2 in chlorobenzene yields a ratio $[Et\text{-}Br]/[MeBr] = 4.3$. It has been shown (22) that the presence of tetraethyltin influences the reaction of Br_2 with tetramethyltin. This mixing effect is readily explained by reaction (7).

The observed reactivity sequence (24) for halodemetallation of R_4 Sn type compounds in nonpolar solvents is :

$$i\text{-}Pr > Et > Bu \sim Pr > Me.$$

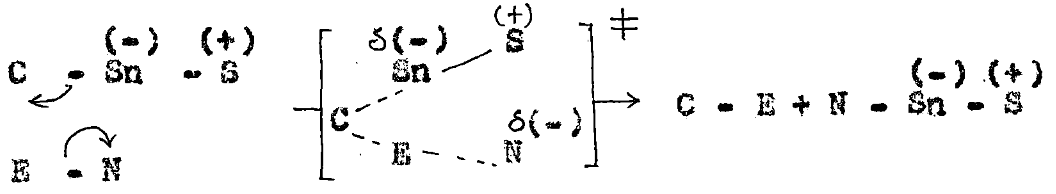
However the rate constants lie close together and deviations from the sequence often occure depending on the experimental conditions.

(ii) Reaction in polar solvent

In this case, the solvent co-ordinates with the metal atom which may be formally represented as :

$$C - Sn + S \rightleftharpoons C - \overset{(-)}{Sn} - \overset{(+)}{S} \qquad (9)$$

Formation of such complex (which may be a true or a collision complex) would increase the electron density at the carbon atom which may be easily attached by an electrophile, yielding an open transition state whose existance has been fairly well established by Abraham and Spalding (20) :


(10)

Co-ordination withthe metal generally does not make the solvent electrophilic enough to compete with the electrophile E - N and to reat either intermolecularly or intramolecularly with a carbon-tin bond and these two steps thus seem to be the only possible reaction. Indeed neither a third order term nor any mixing effect could be detected in nucleophilic solvents such as methanol.

The nucleophilicity of the solvent toward tin, which seems to be the most important factor affecting the polarity of the solvents for electrophilic aliphatic substitution (17) may be estimated by the ability of the medium to complex the tin atom of trimethyl tin chloride (25,44). Using NMR spectroscopy the following sequence has been found :

HMPT > DMSO $\simeq$ DMF > Py > MeOH $\simeq$ i-PrOH >

t - BuOH $\simeq$ MeCOMe $\simeq$ MeCOOMe > DiOxane > MeCN >

MeCOOH > Phcl $\simeq$ CCl_4 $\simeq$ Cyclohexene.

The reactivity sequence observed in polar solvents is :
R = Me > Et > Bu > Pr > i-Pr > t - Bu.

(iii) Radical substitution at a saturated carbon atom :

Symmetrical tetraalkyltins may also be attacked by radicals. Following mechanistic picture has been proposed for the reaction of these organo-matellic molecules with halogens in chlorobenzene in an inert atmosphere under illumination

$$Br_2 \xrightarrow{h\nu\,(410mm)} 2\ Br. \qquad (11)$$

$$Br\cdot + R_4Sn \longrightarrow \overset{(-)}{R_4Sn} - \overset{(+)}{Br\cdot} \qquad (12$$

$$R\ \overset{(-)}{Sn_4} - \overset{(+)}{Br\cdot} \longrightarrow R_3SnBr + R\cdot \qquad (13)$$

and

$$\overset{(-)}{R_4Sn} - \overset{(+)}{Br.} + R'_4Sn \longrightarrow R_4Sn + R'_3SnBr + R'\cdot \qquad (14)$$

forming a chain with

$$R\cdot + Br_2 \rightarrow R - Br + Br\cdot \qquad (15)$$

Oxygen seems to modify the stoichiometry, the reaction products and thus the mechanism of the analogous reaction of tetraethyltin with iodine (27) is :

$$I_2 \xrightarrow{h\nu\,(430mm)} 2I\cdot \qquad (28)$$

$$I\cdot + Et_4\ Sn \longrightarrow EtI + Et_3\ Sn\cdot \qquad (29)$$

which then reacts :

in the absence of oxygen $Et_3Sn\cdot + I_2 \rightarrow Et_3SnI + I\cdot$ (30)

chain reaction $\phi >> 1$

in presence of oxygen $Et_3Sn\cdot + O_2 \rightarrow Et_3Sn{-}O{-}O\cdot$ (31)

$Et_3Sn{-}O{-}O\cdot \rightarrow$ Stable products (32)

Razuvaev and co-workers (15,28-29) have obtained a considerable body of evidence for the participations of trialkyltin radicals in the photolysis of tetraalkyltins and in the reactions of these derivatives with carbon tetra-chloride initiated by oxygen or by peroxide :

$$R_4\,Sn \longrightarrow R_3\,Sn\cdot + R\cdot \qquad (33)$$

$$R_3\,Sn\cdot + X - C\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix} \quad R_3SnX + \cdot C\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix}$$

IIC . Symmetrical vinylic, acetylenic and aryl derivatives.

Tetravinyl tin reacts more than 20 times faster with iodine than tetraethyl tin but is less reactive than vinyl trialkyltins (30). Little is known about the more reactive symmetrical acetylenic organotin compounds (31). The reactivity of vinylic and acetylenic derivaties is in accordence with the order of bond polarity :

$$Sn - C\ (Øp^3) < Sn - C\ (Øp^3\ ) < Sn - C\ (Øp).$$

Tetraaryltins are also more prove to cleavage than tetraalkyl tins; one or two aryl groups are cleaved off the tin atoms in the cleagave reactions depending on experimental condition.

In carbon tetrachloride bromine gives Ar_2SnBr_2whereas iodine in chloroform at - 40° produces mono-substituted product (1,33 - 34). The most widely used reaction is the disproportionation with $SnCl_4$ which furnish good yields of triaryltin chloride, diaryltin dichloride and aryltin trichloride (1,34,35-39) under proper experimental condition. Sulpher reacts with tetraphenyl tin to yield phenyltin — sulpher polymer chains and diphenyl sulphide; selemium yields only a monoinsertion product (40-42). No mechanistic study has been made on symmetrical tetraaryl tin compounds, the mechanism of aryl-tin bond cleavage has been derived from unsymmetrical compounds.

IID. Unsymmetrical Organotin Compounds

1. Unsymmetrical tetraalkyltins

The kienetic scheme which describes the reaction of symmetrical tetraalkyltins with electrophiles E - N is also valid for the same reaction on mixed tetraalkyltins and can be used to explain most of the experimental data. Only the important difference between this case and the former one are the nonequivalence of the alkyl groups bound to the metal atom in mixed derivatives; this introduces a new parameter : the selectivity, which depends dramatically on experimental conditions.

(i) Reactions in nonpolar solvents :

The reaction of bromine with propyl trimethyltin in chlorobenzene is described by a ratio $K_2(Me)/K_2(Pr) = 60$, showing a rather low selectivity. However the ratio decreases to 4.3 in the presence of tetraethyl tin (22), although it does not vary with concentration of Me_3SnPr. The mixing effect may be ascribed to the following reactions :

$$R\ Sn\ Me_3 + X_2 \rightleftharpoons R\ Me_3\ \overset{-}{Sn} - \overset{+}{X_2} \begin{array}{l} \nearrow RX + X\ Sn\ Me_3 \\ \searrow MeX + X\ Sn\ Me_2\ R \end{array} \qquad (34)$$

$$R'_4\ Sn + X_2 \rightleftharpoons R'_4\ \overset{-}{Sn} - \overset{+}{X_2} \longrightarrow R' - X + R'_3\ SnX \qquad (35)$$

$$R\ Sn\ Me_3 + R'_4\ \overset{-}{Sn} - \overset{+}{X_2} \begin{array}{l} \nearrow RX + X\ Sn\ Me_3 + R'_4\ Sn \\ \searrow MeX + SnMe_2\ R + R'_4\ Sn \end{array} \qquad (36)$$

Since $R'_4\ \overset{-}{Sn} - \overset{+}{X_2}$ would be more electrophilic than X_2, the selectivity of the cleavage would decrease.

On the contrary the presence of trialkyltin halides have two important effects on the reaction of tetraalkyltins with halogens :

a) A decrease of the relative importance of the third order term;

b) An increase of selectivity. $K_2\ (Me) / K_2\ (Pr)$ increases from 6.0 to 7.1 when triethyltin bromide is added to the chlorobenzene solution.

This may be ascribed to the formation of penta co-ordinate species due to association of the trialkyltin halide with the tetraalkyl tin compounds.

The observed reactivity sequence for halodemetallation of Me_3SnR in chlorobenzene is $R = t-Bu > Me \simeq i-Pr > Pr \simeq Bu$ with the rate constants lying quite close together so that halogen in solvents of low polarity does not discriminate well between different alkyl groups. Abraham and Hill (19) has classified the reactions in nonpolar solvent as SEi (substitution, electrophilic, internal) which includes cases lying in between pure SE2 and SE^c (substitution, electrophilic, via co-ordination) mechanism.

The low selectivity observed for the reaction of halogens with mixed tetraalkyltins in nonpolar solvents has been used for qualitative identification of organic groups through the alkyl halides formed as products of the cleavage (43).

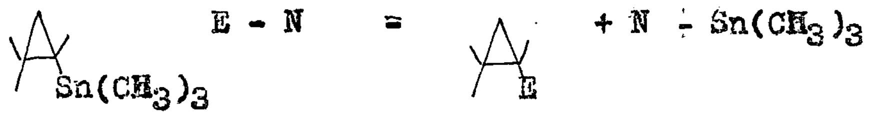
(ii) Reactions in polar solvents

As discussed earlier polar solvents render nucleophilic assistance to the tin atom thereby increasing the polarity of Sn - C bonds. The reactivity sequence observed for cleavage of R group from Me_3SnR or Et_3SnR is $R = Me > Et > Bu \sim Pr > t-Bu$. The spread of the rate constants in a such series is considerable so that there is a high degree of selectivity in halodemetallation reaction in polar solvents. The reactivity of R group in R_3SnR' is also profoundly affected by the nature of the leaving group R_3Sn.

The high degree of selectivity of halodemetallations in methanol has been exploited in the first practicable synthesis of fully unsymmetrically substituted tetra alkyl tin (6,43). The same principle has been utilised for the synthesis of chiral tin compounds (50)

2. Stereochemistry of bimolecular electrophilic substitution at a saturated carbon :

Not many studies have so far been made on the stereochemistry of SE^{2} reactions in organotin compounds. However, the results so far obtained indicate that reactions involving open transition state(SE 20) proceed with complete inversion of configuration (44) as shown by Jensen (45) on the bromodemetallation of sec-butyl trineopentyltin in Methanol. On the contrary SE^{2c} reactions, which go through a cyclic transition state, should occur with retention of configuration (46). Of course, substrates for which the inversion of configuration is unfavourable such as Cis or trans - 2 - methyl-cyclopropyl trimethyltins or (+) - (1-methyl-2,2 diphenyl cycloprop~~y~~yl) - trimethyltin (47) for instance react with retention of configuration even in polar solvents.



(37)

This general hypothesis seems also to be valid for SE^{2} reactions on other organometallic substrates, as shown by Brown (48) who studied the bromodemetallation of tri-exo-norbornyl-boron, which occurs with full retention of configuration in THF whereas the same reaction takes place with full inversion of configuration in the same solvent in the presence of methoxide ion.

3. The reactivity sequence and SE^1 mechanism

The reactivity sequence for the bimolecular replacement of a constant R_3Sn group by an electrophile (iodine or bromine in methanol or in acetic acid (5), HgX_2 in methanol (20) or bromine in chlorobenzene (5) :

$$R' - Sn\,R_3 + E - N \; = \; R' - E + N - SnR_3 \qquad (38)$$

can be described by :

$$R' = C_6H_5 - CH_2 \rangle CH_3 \rangle CH_2 = CH_2 \rangle (CH_3)_2\,CH \rangle (CH_3)_3C.$$

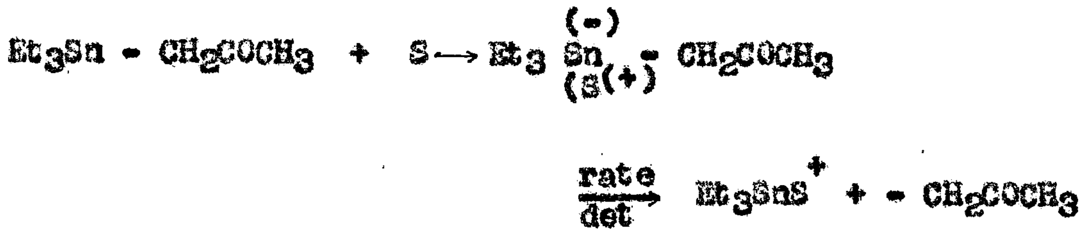
This sequence, generally associated with SE 1 reaction, shows that that the stabilization of the partial negative charge appearing on the different carbon atoms after this first complexation step

$$N + R_3SnR' \rightleftharpoons R_3R'\overset{-}{Sn} - \overset{+}{N} \qquad (39)$$

plays a very important role. Electron-attracting substituents accelerate the substitution reaction and it is reasonable to expect that strong electron-attracting substituents could sufficiently stabilize the incipient carbanion so that the complexation would be no longer dependent on the attack of the electrophile on the carbon atom, giving then a monomolecular electrophilic substitution. However, it has not yet been possible to find an aliphatic electrophilic substitution with a first-order rate equation.

The reaction of benzyltrimethyltin with iodine in methanol is a second order reaction, but poorly electrophilic reagents do not react with this organotin molecule if a strong nucleophile is present. Eaborn (49) has indeed shown that the reaction of m-chlorobenzyltrimethyltin with water in ethanol yields m-chlorotoluene and is catalysed by hydroxyl ion. The electrophile is unfortunately present in large excess and it is thus impossible to determine whether it has to be included in the transition state or not. Nevertheless the nucleophilic catalysis is once more important and kinetic results suggest that there is a considerable negative charge on the separating benzyl group in the transition state. This reaction might be an example of a monomolecular electrophilic substitution SE ^{1} at a saturated carbon atom.

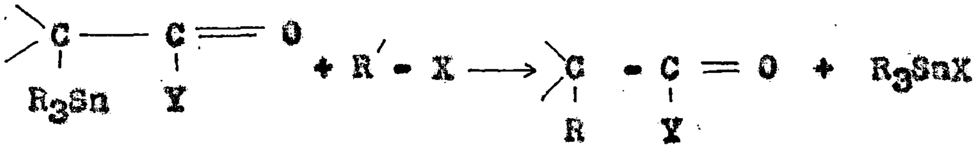
Triethylstammyl acetone (44) reacts very fast with iodine in polar solvents (like methanol, DMSO) is probably SE^1 reaction, but is not confirmed



$$Et_3Sn - CH_2COCH_3 + S \longrightarrow Et_3\overset{(-)}{\underset{(S(+)}{Sn}} - CH_2COCH_3 \xrightarrow[det]{rate} Et_3SnS^{+} + {}^{-}CH_2COCH_3$$

(40)

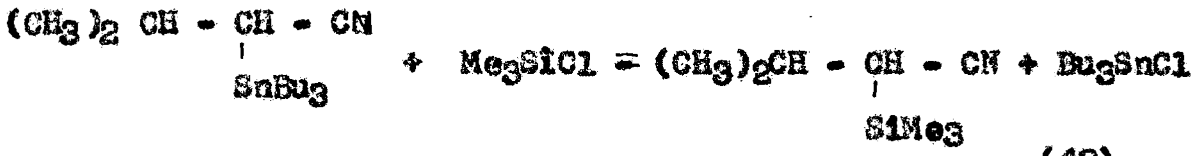
The high reactivity of α - functionally substituted organotin compounds could be ascribed also to a possible monomolecular mechanism. Trialkylstannylacetone or the corresponding ester or nitrile react with poorly electrophilic reagents such as benzylhalides



(41)

$Y = CH_3$ or OR''

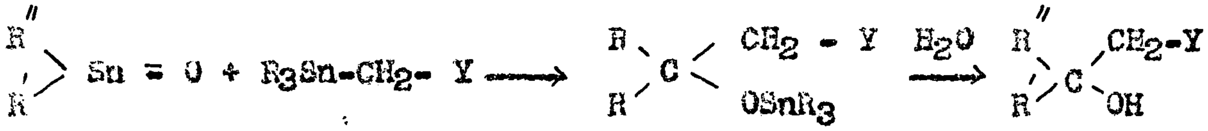
or with trimethyl silicon chloride (61) :



$$(CH_3)_2\,CH - \underset{SnBu_3}{CH} - CN + Me_3SiCl = (CH_3)_2CH - \underset{SiMe_3}{CH} - CN + Bu_3SnCl$$

(42)

Reformatsky - type reactions can also be made with those derivatives showing that aldehydes and ketones are electrophilic enough to cleave the C - Sn bonds of these functionally substituted organotin derivatives. The formation of corresponding β- triorganostannoxy derivatives :



(43)

is almost quantitative and the products formed are very pure. This is therefore, an especially facile organometallic method of functional chain extension (52).

IIB. Unsymmetrical vinylic and acetylenic derivatives :

a) Electrophilic substitution at an olefinic carbon atom

1) Stereochemistry of bimolecular electrophilic substitution reactions at an olefinic carbon atom : retention of configuration : The reaction of the type :

$$\rangle C = \overset{|}{C} - MR_n + E - N = \rangle C = \overset{|}{C} - E + N{-}MR_n \qquad (44)$$

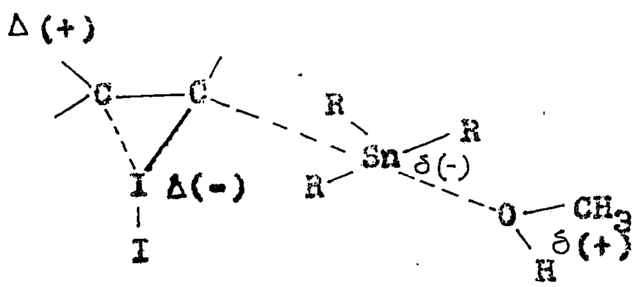
Occurs generally with retention of configuration, in agreement with the rule stated in 1948 by Nesmeyanov and Borisov (53).

Cis-or trans-dipropenyltin dichloride react with $HgX_2$to give pure cis-or trans-propenyl-mercury chloride respectively (53).

Tetrapropnyltin also reats with retention of configuration with butyllithium (54) and phenyllithium (55).

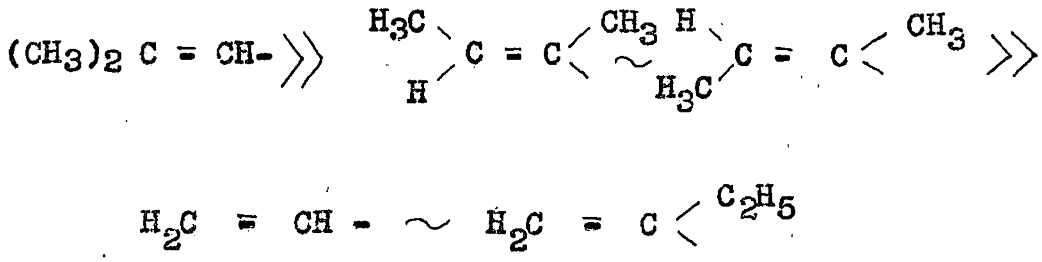
Cis-or trans - 2 - butenyltrimethyltin react with iodine in methanol also with retention of configuration (30).

(ii) Mechanism of bimolecular electrophilic substitution at an olefinic carbon atom : The rates of reaction of a series of vinylic organotin compounds with iodine suggests that the transition state must bear a rather localised positive charge centered around the -carbon atom. A fully dipolar structure involving a complete breakdown of the bond should be disregarded since this would lead to free rotation around the central C - C bond. A highly polar transition state :



is suggested (30) in order to interpret the reactivity sequences (a) and (b) :

(a)



$$(CH_3)_2C=CH- \gg \begin{matrix}H_3C\\H\end{matrix}\rangle C=C\langle\begin{matrix}CH_3\\ \\ \end{matrix} \sim \begin{matrix}H\\H_3C\end{matrix}\rangle C=C\langle\begin{matrix}CH_3\\ \\ \end{matrix} \gg$$

$$H_2C=CH- \sim H_2C=C\langle\begin{matrix}C_2H_5\\ \\ \end{matrix}$$

(b) $R = CH_3 \sim C_2H_5 > nC_4H_9 > iso\ C_3H_7$

and the observed salt effect and the retention of configuration of vinyl group.

(b) Electrophilic substitution at an acetylenic C atom : The high polarity of alkynyl - tin bonds facilitates both electrophilic attack at the carbon atom and nucleophilic attack on the tin atom (56 - 58) making $Sn - C \equiv C -$ bonds extremely labile. Thus Cu^{++} and Ag^{+} break $Sn - C \equiv C$ bonds (56) while $R_3Sn - C \equiv C - CH_2 - CH_2 - O - CH = CH_2$ reacts easily with butanol with the cleavage of $Sn - C \equiv C$ bond (58).

$Cl - C \equiv C - SnMe$ reacts instantaneously with water (59). Tricyclohexyltin halides are electrophilic enough to cleave the acetylenic carbon - tin bonds of bis- (trimethyl stannyl) butadiyne (60 - 62). Bromine cleaves diethyl (triethyl - stannyl ethynyl) phosphonate $Et_3Sn - C\equiv C - P(O)(OEt)_2$ (58). Aldehydes and ketones are able to cleave the Sn - C bond of $C_6H_5 - C\equiv C - SnEt_3$. Chloral (63) and cyclohexanone (64) also react with these compounds.

In the presence of bases, $R_3Sn - C\equiv C - CH_3$ is isomerized into the allenic and propergylic compounds (65).

$$R_3Sn - C\equiv C - CH_3 \overset{B}{\rightleftharpoons} R_3Sn - CH=C=CH_2 \overset{B}{\rightleftharpoons} R_3Sn - CH_2 - C\equiv CH \qquad (45)$$

IIF. Unsymmetrical aromatic derivatives

As would be expected from bond polarity aryl - tin bond is more reactive than alkyl - tin bond consequently aryl - tin bond is first to be broken whenever both types of groups are bonded to tin (1).

It has been found that dry HCl in methanol or even in benzene, cleaves only one aryl group (44), whereas halogenation has to be carefully controlled to achieve the same result (33). The most general sequence for electrophilic Sn - C bond c~~e~~leavage is thus :

$$\text{allyl} \gg \text{aryl, vinyl} > \text{alkyl.}$$

However, free radical and alkyl or aryllithum induced cleavage (44) may follow other sequences.

It should be stressed that no reaction involving C - Sn bond cleavage could reasonably be regarded either as a purely electrophilic substitution at the carbon atom or as a nucleophilic displacement at the tin atom. Kinetic studies can, however, be used to determine whether a given reaction is closer to an electrophilic substitution or a nucleophilic displacement.

Where kinetic or mechanistic studies are not available, the situation is obscure and no decision can be reached, as in the insertion reactions of S or Se in a carbon - tin bond of tetraphenyltin (40 - 42) or in the pyrolytic bimolecular elimination of trimethyl iodide from iodobenzene and hindered phenyltrimethyltins (68).

a) Electrophilic substitution at an aromatic C atom. Aryl' trialkyltins have been cleaved under a variety of conditions, and kienetic results are available for iodine in carbon tetrachloride (69), in methanol (70 - 74), in chlorobenzene and cyclohexane (44), for HCl (76) and bromine (77) in methanol, for $HClO_4$ in methanol - water (78 - 79), for mercurie acetate in tetrahydrofuran (80) and for the solvolysis in acetic acid (81). Iododestannylation in nonpolar solvents like carbon tetrachloride, cyclohexane etc. is second order with respect to the electrophile, the cleavage is therefore believed to occur by participation, in the rate determining step, of iodine - aryl stannane complex with a second iodine molecule (69). The second iodine molecule probably acts as a nucleophile on the tin atom since very small amount of methanol added to cyclohexane strongly increases the rate and progressively restore a first order reaction with respect to halogen (44). Despite this a reasonably good correlation between the rates and substitution constants (69) has been observed. With mercuric acetate in THF (80) there is linear correlation of log ($^{K}/Ko$ Vs σ rather than σ^{+} as in classical aromatic substitution, suggesting that a localised σ complex is a poor approximation to the true transition state. On the other hand, halodemetallation in more polar solvents like methanol and acetic acid is strictly first order with respect to the electrophile; the cleavage can be regarded as a simple aromatic substitution. The rate constants also reasonably correlate with σ^{+} substituent constants.

The rate of cleavage is also affected by the size of the leaving group, the rate being decreased as the size of the alkyl group increases (71). This has been attributed to a steric inhibition opposing the attack by the entering electrophile (73). Ortho effects show up as a delicate balance between retardation of electrophilic attack and acceleration by steric decompression :

when the leaving group is - $Sn(CH_3)_3$, two orthomethyl groups have no special influence at all, but with bulkier - $Sn(n\ C_3H_7)_3$ group, the two ortho methyls induce a slight rate enhancement because of the relief of the overcrowding in the starting material (74). This steric acceleration is, however, much less pronounced here than in the case of analogous silicon compounds (83,84), the difference between Si and Sn derivatives is due to longer C - Sn bond which holds the interacting groups further apart. Because of its negligible effect on the electronic properties of the aromatic systems (72,86 - 87) trialkyltin group may be used to study electrophilic substitution on the aromatic carbon atom.

Though mechanistic or kinetic studies are not available many other electrophilic substitutions, such as the redistribution with tin tetrahalides (88 - 89), reaction with $C_6H_5PCl_2$ (90), BCl_3(88) or BBr_3 (91) have found interesting synthetic uses.

b) Nucleophilic displacement at the tin atom.

Substituted phenyltrimethyltins react with sodium methoxide in methanol to yield trimethyltin methoxide and the corresponding substituted benzene. The kinetics of this reaction have been studied by Eaborn (92), the substituent effects roughly parallel the results for the base catalysed hydrogen exchange reaction in aromatic hydrocarbons, suggesting that the transition states bear some resemblance to analogous phenyl carbanions.

Perhalo aryltins undergo facile base catalysed cleavages. Thus $(C_6F_5)_4Sn$ is cleaved by KOH as easily as by HCl (93); $C_6F_5Sn(CH_3)_3$ solvolyzes in aqueous methanol, but a trace of acid completely inhibits the reaction (94); crystallization of $C_6H_5Sn(CH_3)_3$ in ethanol contains some KF gives pentafluorobenzene and trimethyl tin fluoride (95).

Reactions of phenyl tin chlorides with chelating agents such as 8-hydroxyquinoline etc. in DMSO (18,96-97,26) at elevated temperatures in which Benzene is formed through tin-phenyl bond cleavage probably proceed through nucleophilic attach at the tin. Other examples include the cleavage of carboranyl - tin bond by KOH (32), or the very fast solvolysis of 2-pyridyltrimethyl tin in hydroxylic solvents (85).

Bis (triphenyl tin) oxide, when ~~st~~irred with CdI_2 in diethyl ether, slowly breaks into polymeric diphenyl stannoxane, $(Ph_2SnO)_x$, and benzene (75), apparently by the action of water present in the solvent. Interestingly, CdI_2 does not take part in the overall reaction. This reaction probably goes through a nucleophilic attack by water at the tin atom which may be rendered sufficiently electronegative through withdrawal of electron density by the formation of complex of the type $(Ph_3Sn)_2O - CdI_2$. This is supported by the fact that similar cleavage cannot be induced by CdI_2 in triphenyl tin oxinate or triphenyl tin carboxylates (82) which contain already pentaco-ordinated tin atom.

As would be expected nucleophilic displacement at the tin atom is facilitated by electron withdrawing group. The reactivity sequence for the nucleophilic attack is :

Ethynyl, fluorenyl $\rangle$ aryl $\rangle$ saturated alkyl.

On the basis of preceding discussion the following generalisation may be made concerning the reactivity of tin-carbon bond :

(1) The reactivity of the tin-carbon bond increases with its polarity. Since the polarity is dependent on the hybridisation of the bonded carbon atom, the reactivity sequence is :

$$C(SP) - Sn \rangle C(SP^2) - Sn \rangle C(SP^3) - Sn.$$

(2) The mechanism of electrophilic destannylation is strongly influenced by the solvent - polarity. Highly polar solvents like methanol and acetic acid favour the formation of open transition state (S_E2) and the reaction generally proceeds through inversion

of configuration at the carbon atom, while nonpolar or weakly polar media generally favour the formation of cyclic transition state (SF^2 or SE^i), retention of configuration being the normal feature.

(3) The reactivity sequence for destannylation in methanol or acetic acid for the group R in R'_3SnR is R = Me $>$ Et $>$ Bu $\sim$ Pr $>$ i - Pr $>$ t - Bu. High degree of selectivity is possible in these solvents and may be therefore used for the synthesis of unsymmetrical tin derivatives.

(4) No definite reactivity sequence exists for nonpolar solvents; usually the rate constants lie close together resulting in a very poor selectivity for the alkyl groups.

(5) Under favourable conditions tin-carbon bond cleavage through nucleophilic displacement at the tin atom may also occure, but it is less common than electrophilic substitution at the carbon atom. The nucleophilic attack at the tin atom is facilitated by electron withdrawing groups.

On the basis of "isolated molecule approximation", Majee and Gupta has proposed two theoretical reactivity parameters, viz; the

Z - index and bond polarisability index (66,9899) for the interpretation and correlation of the reactivity of organometallic compounds. The experimental rate constants in a large number of cases have been shown to corretale fairly well with their calculated reactivity indices. The effect of C - M (M = Si, Ge, Sn, Pb) bond energy on its reactivity and the large spread in rate constants have also been interpreted by Majee. In a more recent study Majee has proposed a new approach to the interpretation of the metal-carbon bond cleavage reactions using the concept of isovalent hybridisation which is capable of explaining almost all the experimental features including stereochemistry at the reaction centre (67).

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