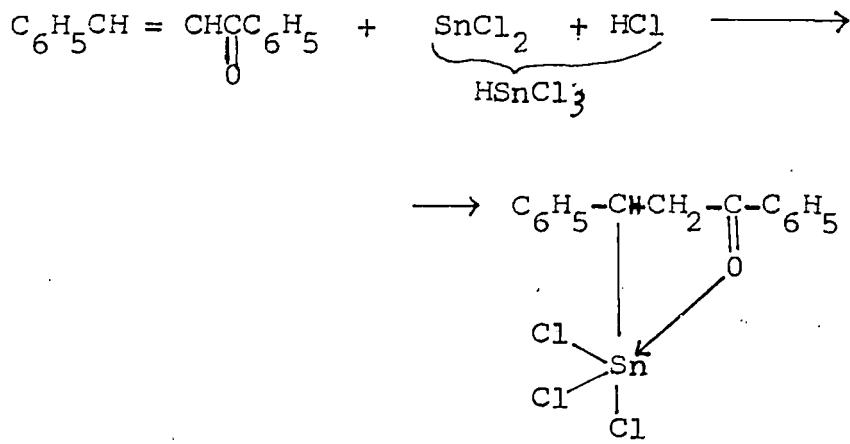


## **SUMMARY**

The thesis is divided into two parts. In the Part I, a brief discussion on organotin chlorides, reported in earlier literatures have been attempted. In recent years the hydroboration and hydrostannation reactions have added a new dimension in the field of organometallic and organic chemistry. Hutton et al have extended these reactions to develop new methods of preparation of a number of "estertin" chlorides. They have found that unsaturated carbonyl compounds react with trichlorostannane compounds react with trichlorostannane or dichlorostannane intermediates in a facile way. In the present investigation aromatic unsaturated carbonyl compounds reacted with trichlorostannane under different experimental conditions.

The reactions of benzylideneacetophenone (chalcone) stannous chloride and hydrogen chloride gas in diethyl-ether were studied at different temperatures. The major reaction under suitable conditions may be indicated as follows.

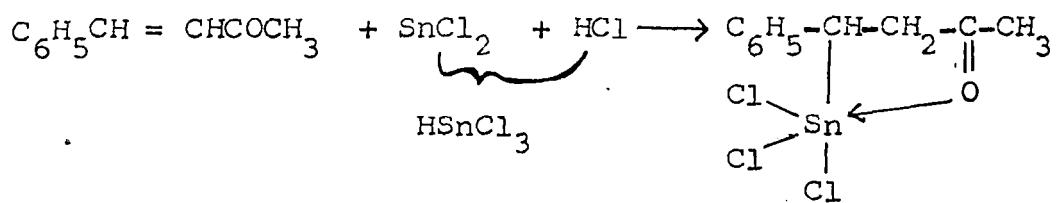


(IV )

The final product was characterised by elemental analyses, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra. The yield of the final product varied with temperature and time of the reactions. Maximum yield ( 30%) of the compound was obtained when the reaction was carried out in the temperature range  $10\text{-}20^\circ\text{C}$  for 2-5 hours. The same product was obtained in a much better yield ( 75%) when chalcone was added to trichlorostannane (prepared separately before adding chalcone) at  $8\text{-}10^\circ\text{C}$  for an hour. The temperature and time of reaction had profound effect on the yield of the compound. On increasing the reaction time or temperature, some uncharacterised gummy materials were found to form in addition to  $\beta$ -benzoyl- $\alpha$ -phenylethyltin trichloride.

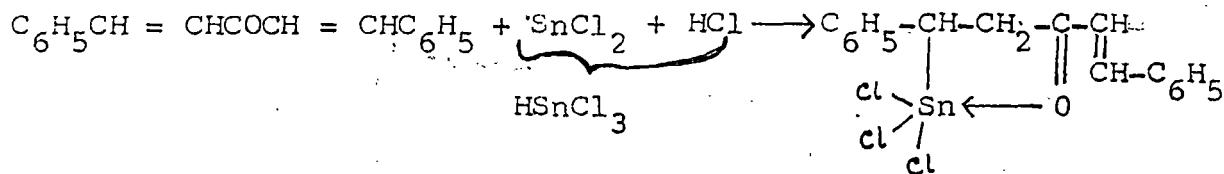
Similarly the reaction between benzylideneacetone, stannous chloride and hydrogen chloride gas yielded very small amount ( 15%) of  $\beta$  -acetyl-  $\alpha$ -phenylethyltin trichloride when the reaction was carried out at  $0^\circ\text{C}$ . The yield was found to decrease with the increase of temperature. The compound could be best obtained (yield 40%) by reacting benzylideneacetone with trichlorostannane (prepared before adding benzylideneacetone) in diethylether medium at  $3\text{-}5^\circ\text{C}$  and keeping the reaction time forty minutes. The reaction was found highly sensitive to temperature and time. Some uncharacterised product (not containing tin) could be isolated along with  $\beta$ -acetyl- $\alpha$ -phenylethyltin trichloride.

(V)



The above compound  $\beta$ -acetyl- $\alpha$ -phenylethyltin trichloride was also characterised by elemental analyses, IR,  $^1\text{H}$  NMR spectra.

The reaction of dibenzylideneacetone, stannous chloride and hydrogen chloride yielded some complex products. Only in a single experiment, the following product was isolated and characterised by elemental analyses and IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data.



In most cases, one red and another yellow compound could be isolated. Unfortunately these compounds could not be fully characterised so far inspite of our efforts.

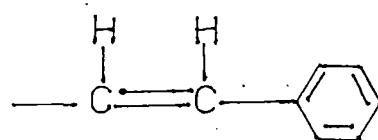
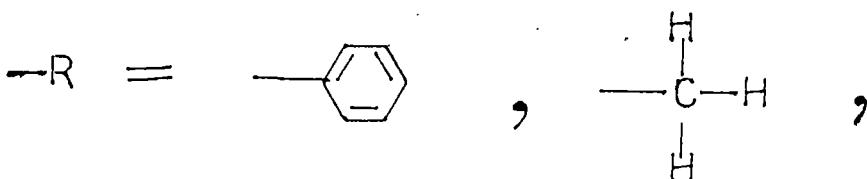
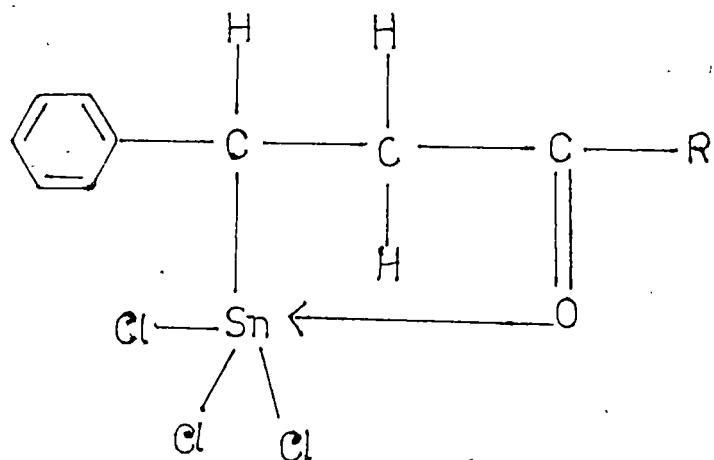
(VI)

Table (a)

Compound	IR ( $\text{cm}^{-1}$ )		$^1\text{H}$	NMR (chemical shift $\delta$ )		$^{119}\text{Sn}$		
	$\nu_{(\text{C=O})}$	$\nu_{(\text{Sn-Cl})}$		$^{13}\text{C}$				
1. $\beta$ -benzoyl- $\alpha$ -phenylethyltin trichloride	1605	$\nu_{\text{as}}$ $\nu_s$	350 310	Methine Methylene Aromatic	3.77 3.85, 4.13 7.0- 8.5	Methine Methylene Aromatic 127.25- 137.11 Carbonyl	43.66 40.74 127.25- 203.03	-154.7
2. $\beta$ -acetyl- $\alpha$ -phenylethyltin trichloride	1645	$\nu_{\text{as}}$ $\nu_s$	330 300	Methyl Methine Methylene	1.7 2.45 2.7- 3.52			
3. $\beta$ -styrylcarbonyl- $\alpha$ -phenylethyltin trichloride	1550	$\nu_{\text{as}}$ $\nu_s$	330 300, 290	Methine Methylene Phenyl and olefinic	1.8 3.6 6.9- 8.25	Methylene Methine Phenyl and olefinic	42.76 43.39 121.71- 152.08 Carbonyl	201.99

(VII)

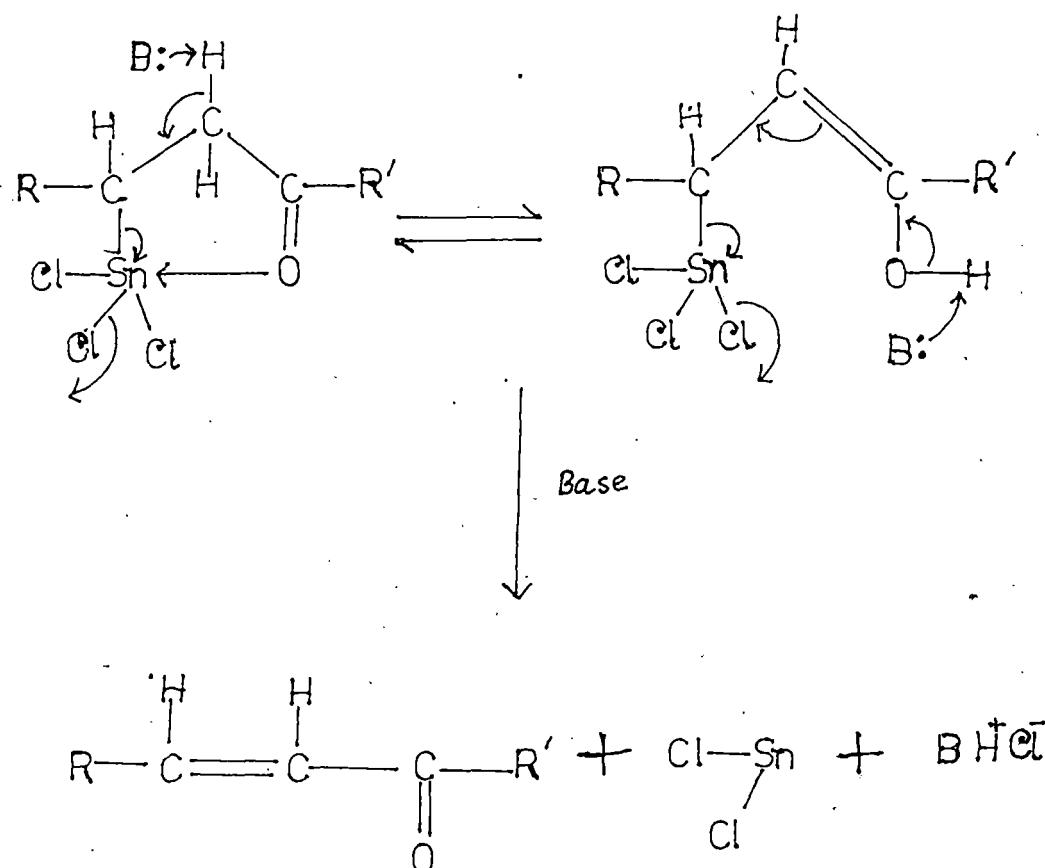
Some of these chlorides showed strong acidic character in non-aqueous solvents. The structural aspects of these compounds have been suggested on the basis of the available data.



In the Part II of this thesis, the Lewis acidity of different organotin compounds <sup>S</sup> have been reviewed.

Moreover, a survey of tin-carbon bond fission of different organotin compounds <sup>S</sup> have been attempted.

The Lewis acidities of some of these new organotin chlorides along with  $\beta$ -carboethoxyethyltin trichloride were investigated. Organotin chlorides generally show strong Lewis acid characters. But  $\beta$ -benzoyl- $\alpha$ -phenylethyltin trichloride when reacted with Lewis bases, showed clear evidence of tin-carbon bond fission instead of adduct or complex formation. The fission of tin-carbon bond can be indicated by the following course of reaction.



$$R = C_6H_5 \quad ; \quad R' = C_6H_5, CH_3$$

## (IX)

The results obtained with different bases can be summarised as follows.

Table (b)

(A) Fission of tin-carbon bond observed in the reaction of organotin chloride and base

Organotin compound	Base	pKa of base
(I) $\beta$ -benzoyl- $\alpha$ -phenyl ethyltin trichloride	Bipyridyl	4.50
	Aniline	4.87
	Pyridine	5.23
	Phenanthroline	5.58
	$\beta$ -picoline	5.70
	$\gamma$ -picoline	5.99
	$\alpha$ -picoline	6.00
	Triethanolamine	7.76
	8-hydroxyquinoline	9.81
	Triethylamine	10.75
(II) $\beta$ -acetyl- $\alpha$ -phenyl ethyltin trichloride	Same set of bases were used as in case of $\beta$ -benzoyl- $\alpha$ -phenylethyltin trichloride.	
	1:3 diamino propane	10.55

(X)  
Table (c)

(B) Formation of adduct or chelate compound of organotin chloride with base.

Organotin compound	Base	pKa (Base)
$\beta$ -carboethoxyethyltin trichloride	Bipyridyl	4.50
	Pyridine	5.23
	Isoquinoline	5.40
	Phenanthroline	5.58
	$\beta$ -picoline	5.70
	$\gamma$ -picoline	5.99
	Triphenyl phosphine	-
	8-hydroxyquinoline	9.81

Unlike  $\beta$ -benzoyl- $\alpha$ -phenylethyltin trichloride and  $\beta$ -acetyl- $\alpha$ -phenylethyltin trichloride,  $\beta$ -carboethoxyethyltin trichloride gave a number of adducts and did not give any indication of tin-carbon bond fission unless very strong bases were used. Attempts have been made to give some explanation of such tin-carbon bond fission.