CHAPTER 3

CHAPTER 3

SYNTHESIS OF NEW DITHIOCARBOXYLIC ACIDS : POTENTIAL LIGANDS FOR SYNTHESIS OF ORGANOTIN(IV) COMPLEXES.

§ 3.1. INTRODUCTION :

This chapter deals with the synthesis of dithiocarboxylic acids. Houben[1-6] established the method of preparation and synthesis of aliphatic dithioacids, as early as in 1902. The synthesis of dithiocarboxylic acids and their derivatives were carried out much earlier, however, isolation of the salts (almost entirely metal salts), important as intermediate, was first reported by S. Kato and M. Mizuta[7,8] where successful preparation and reaction of some crystalline piperidinium salts of aliphatic dithioacids were reported only recently. Apart from these, a number of trimethyl metal(IVB) esters including tin esters of three different types of acids of the general formulae as

shown here, $RCOMR_3$, $RCSMR_3$, $RCOMR_3$ have been prepared by the
$\quad\quad\quad\quad\quad\quad\quad\; \parallel\quad\quad\;\; \parallel\quad\quad\;\; \parallel$
$\quad\quad\quad\quad\quad\quad\quad\; O\quad\quad\; O\quad\quad\; S$

treatement of the secondary and tertiary amine salts of dithioacids[9-12] with chlorotrimethyl silane[13], —germane[14-15], or —tin, and their IR, UV and NMR spectra recorded. The preparation appeared to be difficult because : a) zinc or lead salts did not react with dithioacids and b) due to the hygroscopic nature of the sodium and potassium salts.[16]

The aromatic dithioacids can also be prepared by the alcoholysis of trimethyl silyl ester of dithioacid in an excellent yield but the same procedure of alcoholysis fail with stannyl ester of dithioacids. Details of about 13 organotin(IV) mono and dithiocarboxylates[17] have been discussed by Kato et.al. in 1975. The ^{1}H NMR data for triphenyltin compounds Ph_3SnX are given below in table 1 which will give some idea about the chemical

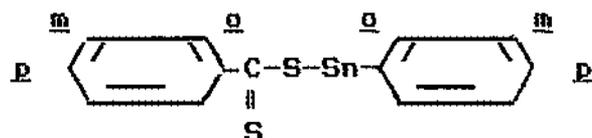shifts (ppm) in these compounds, downfield from internal standard
TMS.

m   o   o   m
p ⬡-C-S-Sn-⬡ p
      ‖
      S

Table 1

Compound	δ_o	δ_m	δ_p	δ_{CH_2}	δ_{CH_3}
PhCS$_2$SnPh$_3$	8.15	7.21	7.43		
PhCOSSnPh$_3$	7.9	7.23	7.44		
PhCH$_2$CS$_2$Sn(∇Cy)$_3$	7.15	7.15	7.15	4.16	
PhCOSSn(∇Cy)$_3$	7.92	7.28	7.37		
(PhCS$_2$)$_2$SnBu$_2$	8.2	7.22	7.45	0.79	
(PhCOS)$_2$SnBu$_2$	7.95	7.27	7.41	0.8	
(PhCS$_2$)$_2$SnMe$_2$	8.2	7.23	7.45		1.37
(PhCOS)$_2$SnMe$_2$	7.92	7.26	7.42	0.66	

The aromatic protons of thiocarboxylate ligand are not
influenced by the alkyl and aryl groups bonded to tin as these
groups are separated by atleast five bonds. The bonding in
organotin(IV) dithiocarboxylate is very much similar to that of
organic dithioacetate and intramolecular coordination of
thiocarbonyl sulfur to group(IVB) metals is small or negligible,
as evident from spectral studies.[17]

§ 3.2. Scope and Objective :

In contrast to the Organotin(IV) carboxylates the corresponding dithiocarboxylates are rather scarce. The organotin-thio compounds, however, have important properties such as thermal stabilisation of PVC[18-19]. Kato and Mizuta[7] reported the synthesis of these types of compounds and their structures. With a view to a systematic study of preparation of organotin(IV) dithiocarboxylates and characterisation of their structures, we have synthesised a number of alkenyl dithiocarboxylic acids which are described here.

There is a large scope for the synthesis of dithiocarboxylic acids of the general formula RCS_2H where R= alkenyl part which are to some extent novel in character and interesting also from the point of view of their structure, stability and their reactivity with different organotin(IV) hydroxide and chlorides. They are isolable as crystaline salt of secondary and tertiary amine[16] as the aliphatic and aromatic dithioacids were found to be stable in organic solvent media but being unstable in open air are converted to resinous products. As far as the knowledge of the author is concerned the literature relating to alkenyl organotin(IV) dithiocarboxylate is absent. Hence the objective of this work is to:

a) synthesise a number of new alkenyl dithiocarboxylic acids

b) to study and characterise them.

c) to study the reaction of the piperidinium salt of these acids with different organotin(IV) chlorides, which are discussed in detail in the chapter 5.

§ 3.3. PREPARATION AND CHARACTERISATION :

§ 3.3.1. SYNTHESIS OF $Ph_2C=C(Ph)CS_2H$:

5.7 gm (17.01 mmol) of triphenyl ethenyl bromide, $Ph_2C=C(Ph)Br$ dissolved in minimum amount of dry ether and taken into a pressure equalising dropping funnel fitted on a three necked round bottomed flask along with a double surface reflux condenser and a nitrogen gas inlet. 0.4gm (16.68 mmol) of dry magnesium was taken into the three necked round bottomed flask containing about 200ml of dry ether. 2-3 drops of ethylene dibromide was added as a catalyst for initiation. The initiation took place within few minutes on warming with hot water externally and after initiation took place the vigourosity of the reaction was maintained by the controlled rate of addition of the triphenyl ethenyl bromide $Ph_2C=C(Ph)Br$ to keep the reaction mixture under continuous refluxing condition . The completion of the reaction was evident from the complete exhaustion of the metallic magnesium. Even after the reaction was apparently over, the refluxation was continued for more than half an hour along with continuous stirring. Then the reaction mixture was allowed to come to room temperature and it was then cooled in ice. 1 ml (16.6 mmol) of freshly distilled carbon disulfide CS_2, taken into the pressure equalising dropping funnel was added dropwise to the Grignard reagent mixture under cold and continuous stirring condition. After the addition was over , the reaction mixture was allowed to come to room temperature gradually while the continuous stirring condition was maintained for overnight. Next day the reaction mixture was again cooled by ice. The decomposition temperature was maintained at a level as low as possible so that

only insignificant amount of hydrogen sulfide escaped. Then the decomposition of the reaction mixture was done using cold 10% hydrocloric acid, the magnesium salt went into solution and two layers separated, the caramine red coloured etheral layer contained most of the acid. The complete decomposition of the magnesium salt was indicated by the complete decolourisation of the aqueous layer. After complete decomposition of the magnesium salt $[(RCS_2)_2Mg$, R= $Ph_2C=C(Ph)-$] into RCS_2H, the etheral layer was separated by using a separating funnel. The aqueous part was repeatedly washed with ether and all the fractions were collected and the total etheral layer part was evaporated to concentrate and then kept at $-18°C$ for two days, when needle shaped reddish brown crystals came out, m.p. 203°C. The crystals gave the positive tests for acidity, and it liberated CO_2 from bicarbonate solution.

Elemental analysis: Found(Calcd.):

C	H	S
76.3	4.58	19.37
(75.90)	(4.80)	(19.27)

IR (cm^{-1}) : 710(vs), 738(m), 772(w), 780(w), 790(w), 800(w), 1040(w), 1085(w), 1210(s), 1560(w), 1580(vw), 1600(w).

$\nu_{C=S} = 1210 cm^{-1}$ (s) $\nu_{C-S} = 710$ (vs)

NMR (δ, ppm) : δ 7.2 - 7.6 (m)

(vide table 2)

§ 3.3.2. Synthesis of $Me_2C=C(Ph)CS_2H$:

1.4 gm (58.33 mmol) of wel-dried magnesium, activated with 4 drops of ethylene dibromide was taken in 200 ml of sodium dried ether. 12.3gm (58.29 mmol) of $Me_2C=C(Ph)Br$ was taken in a pressure equalising dropping funnel fitted on a 500 ml three necked round bottomed flask along with a double surface reflux condenser. The reaction was carried in an inert atmosphere of nitrogen. The bromide was added to magnesium in drops and the initiation took place within few minutes on external warming with hot water. The vigorosity of the reaction mixture was maintained so that the reaction mixture remained in constant refluxing condition by the controlled rate of addition of the bromide. After the addition of the bromide was over the refluxation was continued till all magnesium reacted.

3.51ml (58.2 mmol) of freshly distilled carbon disulfide dissolved in 25ml of dry ether taken in the pressure equalising funnel was added in drops to the Grignard reagent formed, under ice cold condition, along with constant stirring. Then the reaction mixture was allowed to come to room temperature and stirred overnight at room temperature. The reaction mixture was decomposed under ice cold condition with ice cold 10% hydrochloric acid till all the magnesium salt [$(RCS_2)_2Mg$, R= $Me_2C=C(Ph)-$] went into the etheral part with distinct formation of two layers. The water layer was separated with a separating funnel and washed repeatedly with ether till the aqueous part became colourless. The volume of the etheral part was reduced by evaporation and dried over anhydrous magnesium sulphate when approximately 8.5gm (yield ~ 70%) of the desired product was obtained.

Elemental analysis: Found(Calcd.)

C	H	S
63.35	5.58	30.66
(63.46)	(5.76)	(30.76)

IR (cm^{-1})   : 640(s), 710(vs), 760(vs), 850(s), 880(s), 920(w), 1030(m), 1070(s), 1210(w), 1215(s), 1244(m), 1372(m), 1380(m), 14450(s), 1600(w), 1650(w).

$\nu_{C=S}$ = 1215cm^{-1}(s) ν_{C-S} = 710cm^{-1} (vs)

NMR (δ, ppm) : δ 1.8(3H), δ 2.1(3H), δ 7.2 – 7.6 (5H)

(vide table 2)

§ 3.3.3. SYNTHESIS OF $Me_2C=C(H)CS_2H$:

2gm of metallic lithium (289.85 mmol) were cut into thin pieces and taken into a 500ml three necked round bottomed flask containing 150ml sodium dried ether. The three necked flask was fitted with a pressure equalising funnel and a double surface reflux condenser and a nitrogen gas inlet. 19.60gm (145 mmol) of isobutenyl bromide $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$>C=CH-Br taken in the pressure equalising funnel was added in drops to metallic lithium. The reaction was initiated by external warming with hot water in few seconds and the rate of addition of the bromide was adjusted to such a level that the reaction mixture remained in continuous refluxing condition without external heating any more. The completion of lithiation was indicated by the complete exhaustion of lithium along with the development of greyish black colour.

To this lithiated salt, calculated amount 11gm (145.18 mmol) of freshly distilled carbon disulfide CS_2 was slowly added under ice-cold condition along with continuous stirring. After the

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addition was over, the reaction mixture was allowed to come to room temperature and the stirring was continued overnight. Then the reaction mixture was decomposed under ice cold condition with ice cold 10% hydrochloric acid till all the lithiated salt [RCS_2Li, R= Me_2C=CH-] went in to the etheral part with distinct formation of two layers. The water layer was separated with a separating funnel and washed repeatedly with ether till the aqueous part became colourless. The volume of the etheral part was reduced by evaporation and dried over anhydrous magnesium sulphate when approximately 11.5gm (yield 58.67 %) of the product was obtained.

Elemental analysis: Found(Calcd.)

C	H	S
45.1	5.98	47.9
(45.4)	(6.06)	(48.48)

IR (cm^{-1})   :   530(m), 580(s),   640(s), 700(s),   750(vs), 800(m),850(s), 870(s), 920(w),   1030(m),   1070(s),   1210(w), 1215(vs), 1240(m), 1372(m), 1380(m), 1450(s), 1600(w), 1650(w).

$\nu_{C=S}$ = 1215cm^{-1}(vs) ν_{C-S} = 700cm^{-1} (s)

NMR (δ, ppm) : δ 2.1(3H), δ 1.7(3H), δ 1.3(1H).

(vide table 2)

§ 3.4. RESULTS AND DISCUSSION :

All the melting points are uncorrected. Solvents were distilled from appropiate drying agents and stored under the inert atmosphere of nitrogen. ^{1}H NMR spectra were recorded at the VA-EM-390 NMR spectrophotometer operating at 90 MHz, using tetra methyl silane as internal standard. IR spectra were recorded using the Perkin-Elmer 1720X FT-IR spectrophotometer, Beckman IR-20 and Pye-Unicam SP-300s spectrophotometers.

The most important chromophoric group in these cases is $\nu_{>C=S}$. The strong to very strong bands in the range of 1210-1220 cm^{-1} was tentatively assigned for >C=S chromophoric group. The results fit well with those found for other reported dithioacids in literatures.[16-17]

The study of proton chemical shifts of the synthesised dithiocarboxylic acids, provide information concerning their structure. The results of ^{1}H NMR spectral studies are tabulated below in Table 1 .

Table 2

^{1}H NMR spectral data:

Compound	Chemical shift(δ ppm)		
	Aromatic Protons	Methyl Protons	Ethenyl Protons
$Ph_2C=C(Ph)CS_2H$	7.2-7.6(m)	.....	.....
$Me_2C=C(Ph)CS_2H$	7.2-7.6(5H,m)	1.8(3H,s) 2.1(6H,s)	.....
$Me_2C=C(H)CS_2H$	.....	2.1(3H,s) 1.7(6H,s)	1.3(1H,s) .....

So from the above examination and study of the spectral data of IR and ^{1}H NMR listed in table 1, it may be concluded that the alkenyl dithiocarboxylic acids can also be synthesised using the Grignard method. The aromatic protons appeared as complex multiplet in the range as expected from the literatures, and calculation of number of different types of protons from integration fully conform with the structure.

The aim of synthesising these acids is to study the reaction of the piperidinium salt of these acids with a number of organotin(IV) chlorides including the newly synthesised ones described in details in chapter 4.

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