

CHAPTER 7

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PREPARATION OF ORGANOTIN(IV) COMPOUNDS WITH CARBAZIC ACID.

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§ 7.1. INTRODUCTION.

There are reports on the work on metal complexes of thio-schiff bases^{1-4,9} containing S-alkyl dithiocarbazic acid and S-benzyl dithiocarbazate⁵⁻¹⁰. The thio-schiff base ligand of S-benzyl dithiocarbazate are well known for their antitumor¹¹, antibacterial¹², and antifungal¹³ activities. The dithiocarbazate ligand is of special interest from the point of view of potential ligating behaviour of its nitrogen and donor sulfur atoms. To the best of the knowledge on the part of the author of this dissertation, the literature of organotin(IV) dithiocarbazate is obscure, though works on schiff bases of dithiocarbazate derivative are known. There is a report of studies of copper (II) complexes of a schiff base formed by condensation of 2-hydroxy benzaldehyde with N-methyl-S-benzyl dithiocarbazate, which were characterised by variable temperature magnetic measurements.¹⁴ Ali et.al.² was first to synthesise acetylacetonone schiff bases of S-benzyl dithiocarbazate. Syntheses and structural studies of S-benzyl dithiocarbazate schiff base complexes of organotin(IV) compounds were done by Sharma et.al.¹⁵.

§ 7.2. SCOPE AND OBJECTIVE.

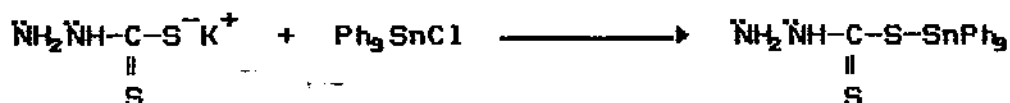
As mentioned earlier, organotin(IV) dithiocarbazates are rich in structural possibilities owing to the presence of both nitrogen and sulfur donor atom in the ligand part. The interest lie in the study of the geometry or environment around tin atom. They are potential biocides also.

Due to a general interest in this class of compounds, attempts were undertaken to prepare a number of organotin(IV)

dithiocarbazates. The objective was first to synthesise dithiocarbazic acids and then to perform reaction of the sodio-salt of the dithiocarbazic acid with a number of organotin(IV) chlorides. Besides, the course of the reaction including its plausible mechanism was also followed.

§ 7.3 EXPERIMENT AND CHARACTERISATION.

The dithiocarbazic acid was prepared and converted to its sodio-salt in situ. Then reactions were carried out with a number of organotin(IV) chlorides following the expected route depicted below:



§ 7.3.1. PREPARATION OF THE LIGAND.

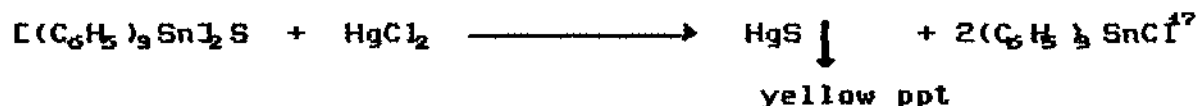
To 2.24gm (40mmol) of KOH in 150ml absolute alcohol, 20ml hydrazine hydrate (70%), (d=1.02, 40.0mmol) was added, followed by dropwise addition of 2.4ml (d=1.262, 39.8mmol) freshly distilled CS₂. The temperature of the reaction mixture was always kept below 20°C. The solid potassium salt was collected and then washed repeatedly with alcohol, to get a white crystalline product, m.p. 75°C to 96°C.⁴⁶

The potassium carbazate, a perfectly white crystalline solid was found to decompose to a red coloured product in few days, when kept in open air even at 0°C but could be preserved in a sealed container kept in a vacuum dessicator.

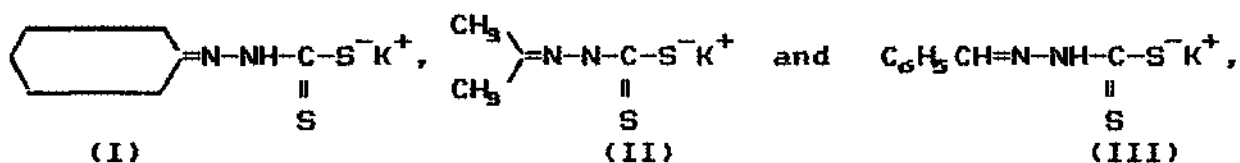
§ 7.3.2. PREPARATION OF ORGANOTIN(IV) COMPLEXES OF CARBAZIC ACID.

The details of the reaction of the sodio-salt of dithiocarbazic acid with Triphenyltin chloride is given below:

0.1gm (0.68mmol) of sodio salt of dithiocarbazic acid was dissolved in dry methanol and was taken in a 50ml round bottomed flask fitted with a pressure equalising dropping funnel containing 0.26gm (0.68mmol) Ph_3SnCl dissolved in 20ml dry methanol from which it was added dropwise under the inert condition of nitrogen and continuous stirring condition. The white needle shaped crystals came out (m.p. 142°C). The elemental detection by sodium fusion test showed the the presence of sulfur and tin in the compound, but nitrogen and halogen as element were absent. The compound was insoluble in water. Elemental and spectral studies proved the compound to be bis(triphenyltin) sulfide. This was also supported by the following observation. 0.017gm mercuric chloride was mixed with 0.0266gm of the product in ether medium and stirred when a yellow precipitate came down heavily. The product was filtered and extracted repeatedly with ether to wash out any triphenyltin chloride formed. The ether extract was taken in a preweighed (8.69123)gm test tube and the ether was evaporated off. The amount of triphenyltin chloride formed was 0.029gm which was stoichiometrically almost accurate to the theoretical yield of 0.028gm. This indicates the product to be bis(triphenyltin) sulfide.



The same reaction was carried out with the different hydrazone derivatives of the potassium salt of dithiocarbazic acid viz.,



but all ending into the isolation of the same bis(triphenyltin) sulfide, $[(\text{C}_6\text{H}_5)_3\text{Sn}]_2\text{S}$.

The reaction condition was then varied to prevent the above possibility of decomposition so that the desired product could be isolated.

The same reaction in the same stoichiometric proportions of the reactants were carried out in another run in heterogeneous condition in petroleum ether. The Ph_3SnCl was soluble in petroleum ether while the potassium salt was not. The solution of Ph_3SnCl was added dropwise from pressure equalising funnel to the potassium salt of dithiocarbazic acid taken in a 100ml round bottomed flask. The reaction mixture was stirred for more than 16 hours, when a clear distinct precipitate was found to be formed. This was filtered off to collect the precipitate and the filtrate part was also preserved. The filtrate i.e. petroleum ether soluble part was kept at -18°C for two days as such. -A white precipitate (m.p. 125°C) was found to form at the bottom of the conical flask. The compound was detected to have nitrogen, sulfur and tin as elements by sodium fusion test. This compound on reaction with HgCl_2 did not provide mercuric sulphide. The compound was found to decompose very quickly to a sticky mass which in turn was converted to a high melting solid (m.p. $>240^\circ\text{C}$) when kept in open

air. On the basis of tin analysis and IR spectra, the above compound was suggested to have the following formula: $\text{NH}_2\text{NHCS}_2\text{SnPh}_3$.

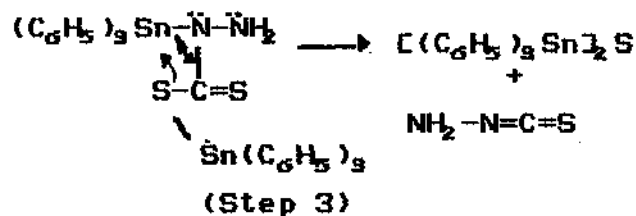
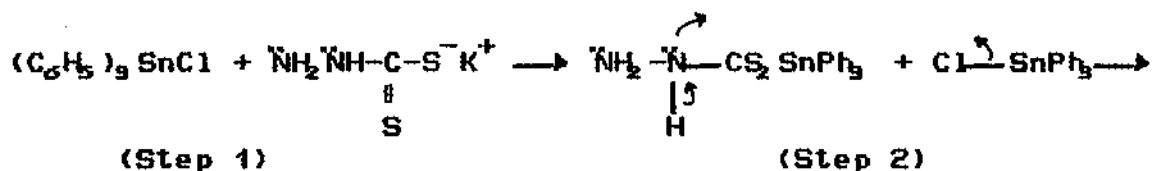
§ 7.4. RESULTS AND DISCUSSION.

This difference in the course of the reaction of Ph_3SnCl with potassium salt of dithiocarbazic acid in homogeneous and heterogeneous media could only be explained by the effect of difference in polarity of the solvent on the mechanism of the reaction. The instability of the product did not allow us the C,H elemental analysis of it but tin was analysed gravimetrically and only IR spectra was possible to record. ^1H NMR spectra was also not possible to record due to instability of the compound. The results are tabulated below:

Compound	% Sn	IR spectra (cm^{-1}) ²⁹		
		$\nu_{\text{N-H}}$	$\nu_{\text{C=S}}$	$\nu_{\text{C-N}}$
$\begin{array}{c} \text{NH}_2\text{NH-C-S K}^- + \\ \\ \text{S} \end{array}$		3400(m, b) 1610(w)	1100(s)	1575(w)
$\begin{array}{c} \text{NH}_2\text{NH-C-S-SnPh}_3 \\ \\ \text{S} \end{array}$	25.9 (26.0)	3400(m, b) 1610(w)	1070(s)	1560(w)

The IR band of $\nu_{\text{C=S}}$ shifts by 30cm^{-1} from 1100cm^{-1} in the ligand to 1070cm^{-1} in tin ester, i.e. to a value of lower wave number indicating that sulfur atom did not coordinate to tin.²¹ The band for $\nu_{\text{C-N}}$ at 1575cm^{-1} in ligand is shifted to a lower value of 1560cm^{-1} in tin ester possibly indicating the nitrogen atom takes part in coordination.²²

The formation of bis(triphenyltin) sulfide, $[(C_6H_5)_3Sn]_2S$ could be explained by the following mechanism.¹⁸



Now when the reaction was carried out in heterogeneous medium, the nonpolarity of the solvent petroleum ether might have some inhibitory effect on the reaction mechanism shown above. The readiness with which decomposition occurs could only be explained by the low thermo-chemical energy of $Sn-N^{10}$ which also explains why the product was too unstable to isolate²⁰. Non polarity of the solvent probably favours the formation of the product in situ. The study to establish the reaction mechanism and its effect on solvent polarity is in progress.

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