

Unusual reaction of the salts of dithiocarboxylic acids and carbazic acid with organotin(IV) chlorides

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Piperidinium salts of some dithiocarboxylic acids react with organotin(IV) chlorides to yield organotin(IV) dithiocarbamates instead of the expected dithiocarboxylates whereas the potassium salt of carbazic acid with triphenyltin chloride yields bis(triphenyltin)sulphide. The products have been characterised by spectroscopic methods and possible mechanisms of the apparently unusual reactions are proposed.

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^{1,2}. Kato and Mizuta³ reported the synthesis of these types of compounds and their structures. In a systematic study of preparation of organotin(IV) dithiocarboxylates and characterisation of their structures, we have come across apparently unusual results which we report herein.

Experimental

Dithiocarboxylic acids were prepared by literature methods^{4,5}. Piperidinium salt of dithiobenzoic acid was prepared by dropwise addition of calculated amount of piperidine to an ethereal solution of the dithiocarboxylic acid at 5°C with constant stirring. The piperidinium salt which precipitated on cooling, was filtered off and recrystallised from ether (m.p. 96°C)⁵. The piperidinium salt of the alkenyl dithiocarboxylic acid $\text{Ph}_2\text{C}=\text{C}(\text{Ph})\text{CS}_2^- \text{pipH}^+$ was prepared *in situ* as above and reacted with

appropriate amount of organotin(IV) chlorides. The potassium salt of carbazic acid was prepared by following the literature method⁶.

The organotin halides except $[\text{Ph}_2\text{C}=\text{C}(\text{Ph})]_2\text{SnCl}_2$, were used as procured (Aldrich) after recrystallisation. The new α -bonded α -unsaturated compound, viz., $[\text{Ph}_2\text{C}=\text{C}(\text{Ph})]_2\text{SnCl}_2$, was synthesised by the reaction of $\text{Ph}_2\text{C}=\text{C}(\text{Ph})\text{MgBr}$ with SnCl_4 in appropriate ratio in ether under inert atmosphere. The product (m.p. 259°C) was characterised by elemental and spectroscopic analyses. Equimolar amounts of the piperidinium salt of the dithiocarboxylic acids and the organotin halide, $\text{R}_n\text{SnX}_{4-n}$, both in dry ether, were reacted by dropwise addition of organotin(IV) chloride with constant stirring at 5°C. After the addition was complete, the reaction mixture was allowed to warm-up to room temperature and then refluxed for two hr in an inert atmosphere of nitrogen. The volatiles were removed and the product was recrystallised from the ether extract of the residue. The reaction of potassium salt of carbazic acid with triphenyltin chloride was carried out in methanol or in petroleum ether (60°-80°C) by stirring for 8 hr in 1:1 proportions of the reactants under inert atmosphere. In each case after work-up, bis(triphenyltin)sulphide was isolated as the only product. The dialkenyltin dichloride also reacts with the salt of dithiocarboxylic acid to produce the dithiocarbamates. By this reaction, the first characterised α -bonded α -alkenyltin dithiocarbamate i.e., $[\text{Ph}_2\text{C}=\text{C}(\text{Ph})]_2\text{Sn}[\text{S.CS.N}(\text{CH}_2)_5]_2$, is obtained.

The elemental analysis, IR and PMR spectra of the compounds were carried out at the RSIC, NEHU, Shillong, India. The instruments used were Beckman IR 20 and Varian EM 390. X-ray diffraction analysis of the two compounds (Sl.no. 1 and 3) were carried out at the Department of Chemistry, Trinity College, Dublin, Ireland and the data will be published elsewhere.

A summary of the reaction products and their analytical and spectroscopic data are given in Table I.

Results and discussion

As shown in Table 1, reaction between the piperidinium salt of dithiocarboxylic acids and organotin halides do not yield the desired products, viz, organotin(IV) dithiocarboxylates. On the

Table 1—Analytical data

Sl no.	Reactants	Products (M.P.) °C	Found(Calc.)%				ν cm ⁻¹		δ ¹ H _{ppm} (relative area)			
			C	H	N	Sn	C-S	C-N	piperidine H	Aliphatic H	Phenyl H	
							δ _o	δ _{m,p}				
1	L ₁ ⁺ + Ph ₃ SnCl	Ph ₃ Sn.S.CS.pip (140) ^a	58.69 (56.48)	4.67 (4.90)	2.69 (2.74)	21.42 (21.35)	1000	1500	4.1(4)	1.75(6)	nil	7.5(15)
2	L ₁ ⁺ + Ph ₂ SnCl ₂	PhSn(S.CS.pip) ₂ (182) ^a	47.79 (48.57)	4.95 (5.05)	4.89 (4.72)	21.12 (20.05)	996	1507	4.0(8)	1.8(12)	nil	7.3(10)
3	L ₂ ⁺ + Ph ₃ SnCl	Ph ₃ Sn.S.CS.pip (140) ^a	58.69 (56.48)	4.66 (4.90)	2.69 (2.74)	21.41 (21.35)	1000	1504	4.2(4)	1.70(6)	nil	7.6(15)
4	L ₂ ⁺ + Ph ₂ SnCl ₂	Ph ₂ Sn(S.CS.pip) ₂ (182) ^a	47.79 (48.57)	4.95 (5.05)	4.89 (4.72)	21.10 (20.05)	996	1507	4.1(8)	1.75(12)	nil	7.3(10)
5	L ₂ ⁺ + Me ₃ SnCl ₂	Me ₃ Sn(S.CS.pip) ₂ (210) ^a	35.60 (35.80)	5.48 (5.54)	6.35 (5.97)	24.5 (25.35)	1000	1504	4.2(8)	1.75(12)	1.5(6)	nil
6	L ₂ ⁺ + Cy ₃ SnCl	Cy ₃ Sn.S.CS.pip (135) ^a	54.49 (54.55)	8.05 (8.14)	—	22.34 (22.52)	1010	1494	4.2(4)	1.70(6)	1.65(33)	nil
7	L ₂ ⁺ + Bu ₃ SnCl	Bu ₃ Sn.S.CS.pip (liq)	47.75 (45.01)	8.19 (8.22)	—	26.39 (26.42)	1015	1490	4.3(4)	1.75(6)	1.2(27)	nil
8	L ₂ ⁺ + BuSnCl ₃	Bu.Sn(S.CS.pip) ₂ (187) ^a	40.16 (40.25)	5.87 (5.95)	—	17.97 (18.12)	1010	1468	4.0(12)	1.70(18)	1.15(9)	nil
9	L ₂ ⁺ + R ₂ SnCl ₂	R.Sn(S.CS.pip) ₂ (206) ^a	65.5 (65.7)	5.24 (5.27)	2.73 (2.95)	12.57 (12.50)	1015	1467	3.7(8)	1.60(12)	nil	7.6(30)

^aL₁ = Ph₃CS₂⁻.pipH⁺; ^bL₂ = Ph₂C = ClPh.CS₂⁻.pipH⁺

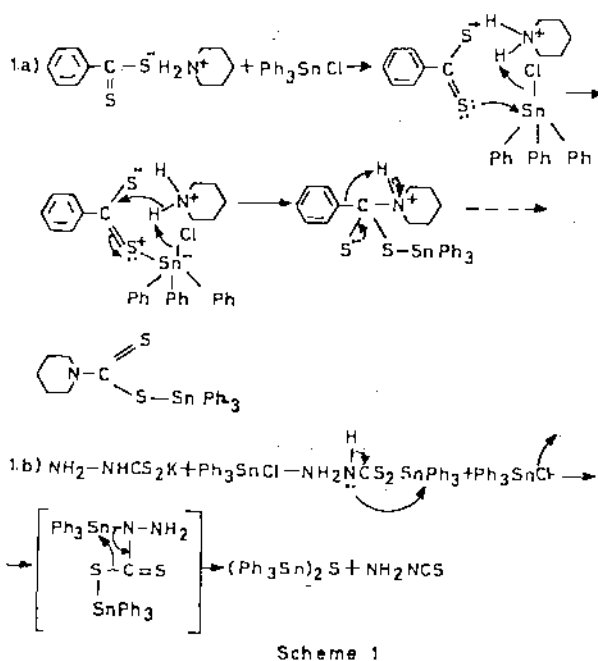
Abbreviations: pip: -N(CH₂)₅; Cy = cyclohexyl; R = Ph₃C = C(Ph)

contrary, the products correspond to the known organotin(IV) dithiocarbamates^{7,8}. The structures of 1 and 3 were in agreement with the data reported earlier for these complexes^{8,9}.

The dithiocarbamate ligand is rather anisobidentate, the stereochemical disposition of tin atom being distorted tetrahedron. There is weak coordination between one sulphur atom and tin presumably due to p-d_π back bonding between the atoms. The structure is exactly similar to the one established earlier by X-ray crystallography⁹ though the method of preparation of the compound Ph₃Sn.S.CS.N(CH₂)₅ was different from the usual one followed for the synthesis of organotin(IV) dithiocarbamates^{7,8}.

The structure of Ph₃Sn.S.CS.N(CH₂)₅ is supported by IR and PMR data (Table 1). Due to appearances of large numbers of peaks of the aromatic rings in the IR, only a few could be ascertained with certainty. The ν_{C=S} and ν_{C=N} appear at ~ 1000 cm⁻¹ and ~ 1500 cm⁻¹, respectively, the regions being typical for these types of compounds. The PMR data of the compounds in CCl₄ and CDCl₃ also support the structure and explain the bonding features. The potassium salt of carbazic acid too reacts with triphenyltin chloride to yield an unusual product instead of the desired triphenyltin carbazate.

A probable mechanism for the formation of dithiocarbamates is depicted in Scheme 1a which involves the initial weak coordination of the lone pair



on sulphur with tin atom followed by formation of the C-N bond and subsequent rearrangement to yield the product. For carbazic acid, the mechanism (Scheme 1b) proposed involves the initial formation of Sn-N bond along with the Sn-S bond followed by rearrangement to the product. Similar mechanism was also proposed by Ishii *et al*¹⁰. Detailed mechanistic studies are in progress.

In view of the results explained in this note, it seems imperative to reexamine the products reported by Kato *et al.*³ and the need to study the structures of those compounds by single crystal X-ray diffraction appears to be essential for the sake of definite conclusions.

It may be pointed out that these reactions are in fact organotin aided reactions by which organic compounds such as thiocarbamic acid derivatives and different isothiocyanates may be synthesised.

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