Monothio-β-diketonates of Phenylantimony(III)

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Bis-*derivatives of phenylantimony(III) with some monothio-β-diketones have been synthesized and characterized as five coordination species by elemental analyses, molecular weight and spectral data. The stereochemistry of the complexes having asymmetrical ligands is discussed.*

Introduction

Although, the β-diketone derivatives of antimony(III), antimony(V) and organoantimony(V) have been extensively studied during the last decade [1–7], the corresponding monothio-β-diketonates do not yet appear to have received attention, except a publication [8] from our laboratories on monothio-β-diketonates of antimony(III).

The present paper describes the synthesis and characterization of a number of monothio-β-diketonates of phenylantimony(III). Attempts have also been made to elucidate their structures on the basis of IR and PMR spectral evidence.

Experimental

Phenyl dichlorostibine was prepared by the method of Long and Jaffe [9]. Monothio-β-diketones were synthesized by Claisen-type condensation of ketones with thionic esters [10]. Phenyl diisopropoxystibine was prepared by the reaction of sodium isopropoxide and phenyl dichlorostibine in refluxing benzene. All reactions were carried out under strictly anhydrous conditions.

Antimony was estimated iodometrically [11] after converting it into antimony(V); sulphur was estimated gravimetrically [12] as barium sulphate. Molecular weights were determined ebullioscopically in refluxing benzene using a Gallenkamp Ebulliometer fitted with a thermistor sensor. IR spectra were recorded as nujol mulls on a model 577 Perkin Elmer spectrophotometer, and PMR spectra were recorded on 60 MHz Perkin Elmer spectrometer, model R12B, in $CDCl_3$ solutions, using TMS as an internal standard.

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Reactions of Phenyl Dichlorostibine with Sodium Salts of Monothio-β-diketones in 1:2 Molar Ratio

Reactions of phenyl dichlorostibine with the sodium salts of a number of monothio-β-diketones (Na(RCSCHCOR'); R = CH_3, R' = C_6H_4–Me-*p*; R = Ph, R' = C_6H_4F-*p*, C_6H_4Cl-*p*, C_6H_4Br-*p* and C_6H_4Me-*p*) were carried out by adding a chloroform solution of the former (0.5 mol) to a suspension of the latter (1.0 mol) in chloroform. The reaction mixtures were stirred for ~4 hours and the sodium chloride formed during the reactions was filtered off. The filtrates, after stripping off the solvent under reduced pressure, gave coloured (yellow to red) solids which were recrystallized from benzene/hexane mixtures.

The experimental results are summarized in Table I.

Results and Discussion

Phenyl dichlorostibine reacts with the sodium salts of monothio-β-diketones (NaL) in 1:2 molar ratio to afford *bis*-derivatives of the type $PhSbL_2$ in quantitative yields, at room temperature:

$$PhSbCl_2 + 2Na(RCSCHCOR') \xrightarrow{CHCl_3} PhSb(RCSCHCOR')_2 + 2NaCl\downarrow$$

Where R = Me; R' = C_6H_4Me-*p*; R = Ph; R' = Ph, C_6H_4F-*p*, C_6H_4Cl-*p*, C_6H_4Br-*p* and C_6H_4Me-*p*.

These *bis*-complexes may also be synthesized by the reactions of phenyl diisopropoxystibine with monothio-β-diketones in 1:2 molar ratios at room temperature, in benzene solutions. The desired product was obtained by leaving the reaction mixture overnight and stripping off the solvent under reduced pressure:

$$PhSb(OPr^i)_2 + 2RCSCH_2COR' \xrightarrow{C_6H_6} PhSb(RCSCHCOR')_2 + 2Pr^iOH$$

R = R' = Ph

All these complexes are found to be non-volatile coloured solids, soluble in common organic solvents and monomeric in refluxing benzene solutions.

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TABLE I. Reactions of $PhSbCl_2$ with Na(RCSCHCOR') in 1:2 Molar Ratios.

Sr. no.	Reactants (g)					NaCl Found (Calcd.) g	Physical state (m.p.) °C	Analysis (%) Found (Calcd.)		Mol. Wt. Found (Calcd.)
	$PhSbCl_2$	Sodium	R	R'	Ligand			Sb	S	
1	0.76	0.14	Ph	Ph	1.38	0.28 (0.34)	Orange-solid (140, d)	17.48 (17.99)	9.28 (9.46)	652 (677)
2	0.45	0.08	Ph	C_6H_4Br-*p*	1.10	0.18 (0.20)	Orange-red solid (145)	14.34 (14.59)	7.32 (7.67)	–
3	0.53	0.10	Ph	C_6H_4Cl-*p*	1.11	0.22 (0.23)	Red solid (124)	16.25 (16.33)	8.40 (8.58)	713 (746)
4	0.42	0.08	Ph	C_6H_4F-*p*	0.82	0.16 (0.18)	Orange-yellow solid (120)	16.97 (17.08)	8.75 (8.98)	–
5	0.42	0.07	Me	C_6H_4Me-*p*	0.60	0.16 (0.18)	Yellow-solid (115, d)	21.30 (20.97)	10.82 (11.02)	–
6	0.48	0.10	Ph	C_6H_4Me-*p*	0.93	0.19 (0.21)	Orange-solid (149, d)	17.09 (17.28)	8.92 (9.08)	–

TABLE II. Spectral Studies in Phenylantimony *bis*-(Monothio-β-diketonates).

Complex	IR frequencies (cm^{-1})						PMR chemical shifts (δ, ppm)		
	$\nu C{=}O$	$\nu C{=}C$	$\nu C{=}S$	$\nu Sb{-}O$	$\nu Sb{-}C$	$\nu Sb{-}S$	Methyl	Methine	Aromatic
$PhSb(PhCSCHCOPh)_2$	1590s	1560m	1240m	560m	445w	355w	–	7.10(s)	7.15–8.20(m)
$PhSb(PhCSCHCOC_6H_4Cl$-*p*$)_2$*	1600m	1550s	1220s	570m	460w	380w	–	7.24(s)	7.28–8.08(m)
$PhSb(MeCSCHCOC_6H_4Me$-*p*$)_2$	1585s	1560s	1265s	615s	445s	–	2.35(s) 2.40(d)	7.00(s)	7.10–8.10(m)
$PhSb(PhCSCHCOC_6H_4Me$-*p*$)_2$	1585s	1550s	1262s	565m	480s	390w	2.42(s)	7.00(s)	7.05–8.18(m)

*As KBr pellet; s = sharp, m = medium and w = weak; (s) = singlet, (d) = doublet and (m) = multiplet.

A comparison of the IR spectra of the free monothio-β-diketones and the corresponding complexes shows the disappearance of a broad band (2700–2100 cm^{-1}) present in the ligands due to the intramolecularly bonded thiol group [13, 14]. The bands in the region 1600–1580 cm^{-1} are attributed to the coordinated carbonyl group ($\nu C{=}O$), indicating the chelating nature of the ligands [14, 15]. New bands observed in the region 620–560, 480–440 and 390–355 cm^{-1} may be assigned to the ν_{Sb-O} [16], ν_{Sb-C} [17] and ν_{Sb-S} [16] stretching vibrations, respectively. Absorption bands due to $\nu_{C=S}$ have been observed in the region 1270–1220 cm^{-1} [18].

The chelating nature of the ligands and the monomeric behaviour of the complexes in solutions suggest a coordination number of five for the central antimony atom.

The most plausible geometry for these complexes appears to be a square–pyramid, in which the phenyl group possesses the apical position (*cf.* the X-ray structure of $PhAs(S_2CNEt_2)_2$ [19]). In the PMR spectra of these complexes the presence of a single, sharp resonance due to methine protons also supports this structure [20]. However, the stereochemically-active lone pair of electrons, present on the central antimony atom [21], would lead to a pseudooctahedral geometry.

The complexes containing unsymmetrical ligands ($R \neq R'$), may exist in *cis*- and *trans*-geometrical forms (Fig. 1), of which only the trans-isomer has a two fold axis of symmetry:

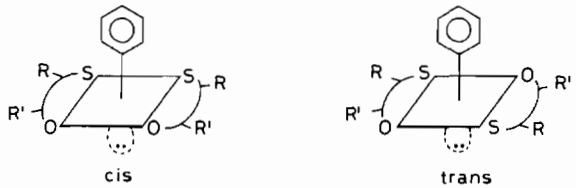

Fig. 1. *cis*- and *trans*-geometrical forms of PhSb-(RCSCHCOR')$_2$ complexes.

The PMR spectrum of the *trans*-isomer (when R = CH_3 and $R \neq R'$) should give rise to a single resonance due to methyl protons, whereas the *cis*-isomer would exhibit double resonances. The PMR spectrum of $PhSb(MeCSCHCOC_6H_4Me\text{-}p)_2$ shows a double resonance due to MeCS protons, indicating a *cis*-configuration for these complexes. However, the possibility of a mixture of *cis*- and *trans*-isomers cannot be ruled out.

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