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CLEAVAGE REACTIONS OF TRIPHENYLANTIMONY WITH DIALKYL (OR ALKYLENYL) DITHIOPHOSPHORIC ACIDS[a]

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ABSTRACT

Triphenylantimony reacts with dialkyl (or alkylenyl) dithiophosphoric acids in 1:1 and 1:2 molar ratio to form complexes of the types $Ph_{3-n}Sb[S_2P(OR)_2]_n$ and $Ph_{3-n}Sb[S_2\overline{POGO}]_n$ (R = Pr-$\underline{n}$, Pr-$\underline{i}$, Bu-$\underline{i}$; G = $-CMe_2CMe_2$, $-CH_2CMe_2CH_2-$, $-CMe_2CH_2CHMe-$, n = 1,2) by the cleavage of antimony-carbon bonds. The complexes are colourless powdery solids, soluble in common organic solvents, monomeric in nature and have been characterized by various physico-chemical and spectroscopic [IR, NMR (^1H, ^{13}C, ^{31}P)] techniques.

INTRODUCTION

The coordination chemistry of O,O'-dialkyl and alkylenyl dithiophosphoric acids has been widely investigated and reviewed[1-3], these compounds show an interesting versatility in their bonding modes [unidentate, bidentate (chelating/bridging), ionic] towards different metals. A survey of the literature reveals that the organoantimony dialkyl[4] (or alkylenyl[5]) dithiophosphates have been synthesized by the reaction of organoantimony halide with the corresponding dithiophosphates. In continuation of our earlier investigations[6-8] of dithio ligands,

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[a] This article is dedicated to the late Prof. G. Srivastava, Department of Chemistry, University of Rajasthan, Jaipur, India.

the present paper describes the preparation of organoantimony dialkyl (or alkylenyl) dithiophosphates by a new synthetic route.

RESULTS AND DISCUSSION

Reactions of triphenylantimony with O,O'-dialkyl (or alkylenyl) dithophosphoric acids in 1:1 and 1:2 molar ratios proceed with cleavage of the antimony carbon bond of Ph_3Sb and yield the corresponding mono- and disubstituted derivatives of the following types:

$$Ph_3Sb + nHS_2P(OR)_2 \xrightarrow{\text{benzene}} Ph_{3-n}Sb[S_2P(OR)_2]_n + n\ PhH \qquad (1)$$

$[R = Pr\text{-}\underline{n},\ Pr\text{-}\underline{i},\ Bu\text{-}\underline{i};\ n = 1,\ 2]$

$$Ph_3Sb + nHS_2\overline{POGO} \xrightarrow[\text{4 hrs.}]{\text{benzene}} Ph_{3-n}Sb[S_2\overline{POGO}]_n + n\ PhH \qquad (2)$$

$[G = -CMe_2CMe_2-,\ -CH_2CMe_2CH_2-,\ -CMe_2CH_2CHMe-;\ n = 1\ ,\ 2]$

The complexes thus obtained are colourless powdery solids, soluble in common organic solvents, monomeric in nature, stable at ambient conditions and may be stored for a long time under an inert atmosphere.

IR Spectra

The IR spectra have been recorded in the region 4000–200 cm^{-1} and show the following characteristic changes.

(i) The absorption band present in the region 2520–2450 cm^{-1} (νS–H)[9] in the parent dithiophosphoric acid disappears completely in the IR spectra of the newly synthesized derivatives which indicates complete deprotonation of the dithiophosphoric acid.

(ii) The appearance of a new, medium intensity absorption band in the regions 460–450 cm^{-1} and 450–425 cm^{-1} for the dialkyl and alkylenyl dithio derivatives, respectively indicates the formation of antimony–sulfur bonds[10].

(iii) The absorption band due to νP=S vibrations shows a noted shift of 20-30 cm^{-1} towards lower frequencies in comparison to the position in the IR spectra of alkyl (or alkylenyl) dithiophosphates which may be due to P=S→Sb coordination.

Table I. Synthetic and Analytical Data of O,O′–Dialkyl (or Alkylenyl) Dithiophosphates of Organoantimony

Reactants, g (mmole)		Molar ratio	Product empirical formula	Yield g/%	Analysis %		Molecular weight
Ph_3Sb	$HS_2P(OR)_2$/ $HS_2\overline{POGO}$ R or G			M.P.°C	Sb found (calcd.)	S found (calcd.)	found (calcd.)
	$Pr\text{-}\underline{n}$		$Ph_2Sb[S_2P(OPr\text{-}\underline{n})_2]$	2.23 (93)	24.62	13.01	472.2
1.73 (4.90)	1.05 (4.90)	1:1	$C_{18}H_{24}O_2PS_2Sb$	118	(24.91)	(13.09)	(488.75)
	$Pr\text{-}\underline{n}$		$PhSb[S_2P(OPr\text{-}\underline{n})_2]_2$	2.11 (98)	19.17	20.34	602.7
1.22 (3.45)	1.49 (6.96)	1:2	$C_{18}H_{33}O_4P_2S_4Sb$	126	(19.48)	(20.48)	(624.75)
	$Pr\text{-}\underline{i}$		$Ph_2Sb[S_2P(OPr\text{-}\underline{i})_2]$	0.92 (91)	24.81	12.98	–
0.73 (2.07)	0.45 (2.10)	1:1	$C_{18}S_{24}O_2PS_2Sb$	119	(24.91)	(13.09)	
	$Pr\text{-}\underline{i}$		$PhSb[S_2P(OPr\text{-}\underline{i})_2]_2$	2.11 (94)	19.23	20.37	–
1.26 (3.57)	1.53 (7.14)	1:2	$C_{18}H_{33}O_4P_2S_4Sb$	125	(19.48)	(20.48)	
	$Bu\text{-}\underline{i}$		$Ph_2Sb[S_2P(OBu\text{-}\underline{i})_2]$	2.03 (89)	23.77	12.26	501.3
1.55 (4.25)	1.06 (4.38)	1:1	$C_{20}H_{28}O_2PS_2Sb$	120	(23.56)	(12.38)	(516.75)
	$Bu\text{-}\underline{i}$		$PhSb[S_2P(OBu\text{-}\underline{i})_2]_2$	2.37 (94)	17.76	18.72	–
1.31 (3.71)	1.79 (7.39)	1:2	$C_{22}H_{41}O_4P_2S_4Sb$	128	(17.88)	(18.80)	
	$-CH_2CMe_2CH_2-$		$Ph_2Sb[S_2\overline{POCH_2CMe_2CH_2O}]$	2.26 (95)	20.85	13.48	456.12
1.77 (5.01)	0.99 (5.03)	1:1	$C_{17}H_{20}O_2PS_2Sb$	136	(20.75)	(13.54)	(472.75)
	$-CH_2CMe_2CH_2-$		$PhSb[S_2\overline{POCH_2CMe_2CH_2O}]_2$	2.16 (91)	20.61	21.53	–
1.42 (4.02)	1.59 (8.03)	1:2	$C_{16}H_{25}O_4P_2S_4Sb$	142	(20.53)	(21.59)	
	$-CMe_2CMe_2-$		$Ph_2Sb[S_2\overline{POCMe_2CMe_2O}]$	1.43 (97)	25.06	13.12	–
1.07 (3.03)	0.63 (2.96)	1:1	$C_{18}H_{22}O_2PS_2Sb$	140	(25.00)	(13.14)	
	$-CMe_2CMe_2-$		$PhSb[S_2\overline{POCMe_2CMe_2O}]_2$	2.62 (91)	19.61	20.58	602.4
1.63 (4.62)	1.96 (9.24)	1:2	$C_{18}H_{29}O_4P_2S_4Sb$	143	(19.59)	(20.60)	(621.35)
	$-CMe_2CH_2CHMe-$		$Ph_2Sb[S_2\overline{POCMe_2CH_2CHMeO}]$	1.08 (89)	25.01	13.04	–
0.88 (2.49)	0.53 (2.49)	1:1	$C_{18}H_{22}O_2PS_2Sb$	138	(25.00)	(13.14)	
	$-CMe_2CH_2CHMe-$		$PhSb[S_2\overline{POCMe_2CH_2CHMeO}]_2$	1.61 (95)	19.61	20.57	–
0.96 (2.72)	1.16 (5.46)	1:2	$C_{18}H_{29}O_4P_2S_4Sb$	146	(19.59)	(20.60)	–

Table II. IR Spectral Data of O,O'–Dialkyl (or Alkylenyl) Dithiophosphates of Antimony

Compound	ν(P)-O-C	νP-O-(C)	Ring Vibrations	νP=S	νP–S	νSb–S
$Ph_2Sb(S_2P(OPr\text{-}\underline{n})_2]$	1030 br	820 s	–	675 vs	520 vs	460 m
$PhSb[S_2P(OPr\text{-}\underline{n})_2]_2$	1040 br	835 m	–	630 vs	520 vs	460 w
$Ph_2Sb[S_2P(OPr\text{-}\underline{i})_2]$	1030 br	825 s	–	620 vs	515 vs	450 w
$PhSb[S_2P(OPr\text{-}\underline{i})_2]_2$	1035 br	835 s	–	650 s	530 vs	455 w
$Ph_2Sb[S_2P(OBu\text{-}\underline{i})_2]$	1040 br	830 s	–	620 s	525 vs	455 w
$PhSb[S_2P(OBu\text{-}\underline{i})_2]_2$	1045 br	840 s	–	645 s	535 vs	450 w
$Ph_2Sb[S_2\overline{POCH_2CMe_2CH_2O}]$	1020 s	790 vs	960 s	660 m	510 vs	430 m
$PhSb[S_2\overline{POCH_2CMe_2CH_2O}]_2$	1025 m	785 s	960 s	675 m	510 s	425 m
$Ph_2Sb[S_2\overline{POCMe_2CMe_2O}]$	1000 br	825 s	960 s	665 m	540 s	445 m
$PhSb[S_2\overline{POCMe_2CMe_2O}]_2$	1015 m	840 s	955 s	670 m	535 s	440 m
$Ph_2Sb[S_2\overline{POCMe_2CH_2CHMeO}]$	1050 s	875 s	970 m	690 vs	525 s	445 s
$PhSb[S_2\overline{POCMe_2CH_2CHMeO}]_2$	1055 s	860 s	960 s	675 s	540 s	450 s

vs = very strong, s = strong, m = medium, br = broad, w = weak

PMR Spectra

The PMR spectra of these derivatives show characteristic resonance signals due to glycoxy, alkoxy and phenyl protons. A singlet observed at 3.1–3.5 ppm in the parent dithiophosphoric acids is found to be absent in the spectra of the corresponding newly synthesized complexes, thus indicating the deprotonation of the dithiophosphoric acids[9].

^{13}C NMR Spectra

^{13}C NMR spectra of some representative complexes have been recorded. The signals for alkyl and alkoxy carbons show an upfield shift in comparison to their position in the corresponding ligands. The spectra of the diphenylantimony

Table III. ^{1}H and ^{31}P NMR Spectral Data of the Complexes

Compound	Chemical shift (ppm)	
	^{1}H	^{31}P
$Ph_2Sb(S_2P(OPr\text{•}\underline{n})_2]$	1.11, t, 6H (CH_3); 1.75, q, 4H (CH_2); 4.13 q, 4H (OCH_2); 7.06–7.53, m, 10H (C_6H_5)	92.88
$PhSb[S_2P(OPr\text{•}\underline{n})_2]_2$	1.07, t, 12H (CH_3); 1.75, q, 8H (CH_2): 4.13, q, 8H (OCH_2); 7.15–7.47, m, 5H (C_6H_5)	93.15
$Ph_2Sb[S_2P(OPr\text{•}\underline{i})_2]$	1.01, d, 12H (CH_3); 3.89–4.20, m, 2H (OCH); 7.12–7.37, m, 10H (C_6H_5)	88.44
$PhSb[S_2P(OPr\text{•}\underline{i})_2]_2$	0.91, d, 24H (CH_3); 3.91–4.17, m, 4H (OCH); 7.08–7.36, m, 5H (C_6H_5)	89.92
$Ph_2Sb[S_2P(OBu\text{•}\underline{i})_2]$	0.95, d, 12H (CH_3); 1.75–2.19, m, 2H (CH); 3.06, q, 4H (OCH_2); 7.15–7.53, m, 10H (C_6H_5)	93.02
$PhSb[S_2P(OBu\text{-}\underline{i})_2]_2$	0.95, d, 24H (CH_3); 2.09–2.32, m, 4H (CH); 3.87, q, 8H (OCH_2); 7.18–7.46, m, 5H (C_6H_5)	93.29
$Ph_2Sb[S_2\overline{POCH_2CMe_2CH_2O}]$	0.97, s, 6H (CH_3); 3.98, q, 4H (OCH_2); 7.06–7.67, m, 10H (C_6H_5)	90.86
$PhSb[S_2\overline{POCH_2CMe_2CH_2O}]_2$	1.01, s, 12H (CH_3); 4.1, q, 8H (OCH_2); 7.31–7.66, m, 5H (C_6H_5)	91.13
$Ph_2Sb[S_2\overline{POCMe_2CMe_2O}]$	1.38, s, 12H (CH_3); 7.18–7.79, m, 10H (C_6H_5)	105.78
$PhSb[S_2\overline{POCMe_2CMe_2O}]_2$	1.30, s, 24H (CH_3); 7.15–7.57, m, 5H (C_6H_5)	106.22
$Ph_2Sb[S_2\overline{POCMe_2CH_2CHMeO}]$	1.24–1.71, m, 11H (CH_2+CH_3); 4.74–4.99 m, 1H (OCH): 7.28–7.79, m, 10H (C_6H_5)	89.47
$PhSb[S_2\overline{POCMe_2CH_2CHMeO}]_2$	–	90.13

complexes show 2-bond coupling with phosphorus. In the spectra of all the complexes, four signals for the phenyl group carbons have been observed in the region 121.98–141.43 for the $C_{(ipso)}$, $C_{(ortho)}$, $C_{(meta)}$ and $C_{(para)}$ atoms. The corrected chemical shift values [$\delta = C_{(p)} - C_{(m)}$] are negative for these complexes. This shows the electron releasing ability from metal to the phenyl ring through $d\pi - p\pi$ conjugation[11].

^{31}P NMR Spectra

Proton decoupled ^{31}P NMR spectra observed in the region 84.44–106.22 ppm show the deshielding of the phosphorus atom to the extent of about 5–12 ppm from the parent dithio acids. This is indicative of a bidentate mode of bonding of the ligand moiety in these complexes.[12]

Due to the non-availability of suitable crystals, the authentic structure of the complexes synthesized by us could not be determined by X-ray crystallography, however, on the basis of spectroscopic studies, a trigonal bipyramidal geometry for these complexes has been suggested.

Mechanistic Aspects

The cleavage of phenyl groups from triphenylantimony by dithiophosphoric acids shows the following unusual features.

(A) The cleavage of second phenyl group is faster than the first one.

The phenyl cleavage reaction is an example of a typical addition elimination reaction. Protons furnished by the dithiophosphate moiety attack the phenyl ring and a sigma (σ) complex is formed. This is followed by the nucleophilic attack of the dithiophosphate anion on antimony, accompanied by the cleavage of an antimony-carbon bond, as shown in Fig. 1. The observed results indicate that step (iii) seems to be the rate determining step in the reaction process. After the replacement of one phenyl group from tri organoantimony, some contribution is made by the dithiophosphate moiety to the formation of backbonding with d orbitals which results in a weakening of the Sb–C bond and thus explains the faster displacement of the second phenyl group as shown in Fig. 2.

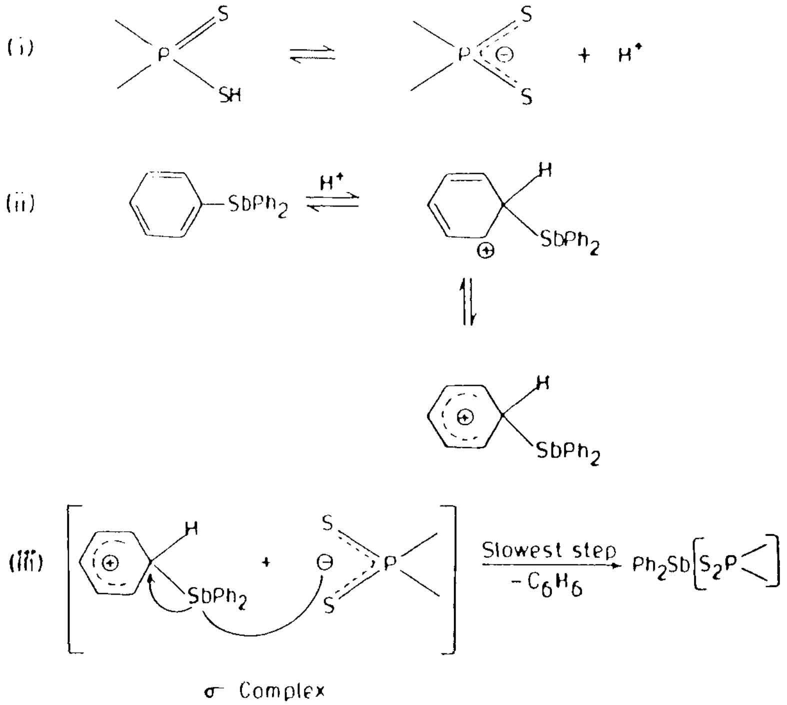

Fig. 1. Mechanism of Phenyl Cleavage Reaction in $SbPh_3$

(B) The stoppage of the reaction after the cleavage of the second phenyl group.

After the displacement of two phenyl groups from triphenylantimony, the resulting species becomes so sterically hindered that it remains no longer vulnerable to nucleophilic attack by another dithiophosphate moiety and, hence, further substitution of phenyl groups does not occur.

(C) Attempts have been unsuccessful for the corresponding reaction with triphenylarsine.

The presence of $d_\pi - p_\pi$ bonding between p_π orbitals of the phenyl ring and vacant d_π orbitals of the metal has been postulated to explain the difference in the reactivities of the different triphenyl derivatives of Group V elements. Because of smaller differences in the energy level of p and d orbitals, $d_\pi - p_\pi$

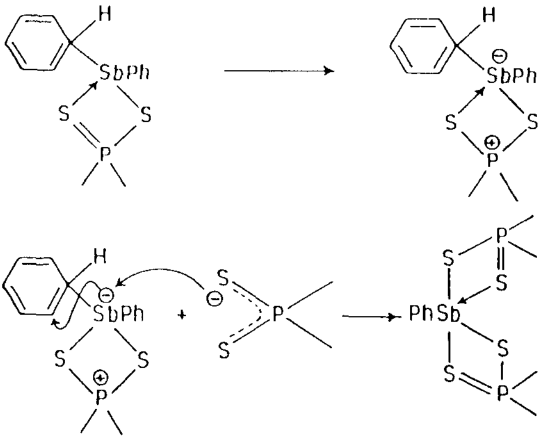

Fig. 2. Mechanism of Phenyl Cleavage Reaction in SbPh$_2$S$_2$P<

bonding is much more effective in triphenylarsine than that in triphenylstibine which makes the C–As bond much stronger than the C–Sb bond and, hence, Ph$_3$As fails to react in the above corresponding reactions.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture from the experimental set-up. Dialkyl and alkylenyl dithiophosphoric acid were synthesized by the method reported in the literature.[9] Antimony and sulfur were determined by an oxidation method[13] on Messenger's method[13], respectively. IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. NMR spectra were recorded on a JEOL FX 90 Q spectrophotometer using TMS (for ^1H and ^{13}C) or 85% H_3PO_4 (for ^{31}P) as external references. Molecular weights were determined on a Knaur vapour pressure osmometer in chloroform.

Reaction of Triphenylantimony with Di-n-propyl Dithiophosphoric Acid in 1:1 Molar Ratio.

A mixture of di-n-propyl dithiophosphoric acid (1.05 g, 4.90 mmole) and triphenylantimony (1.73 g, 4.90 mmole) in benzene (30 mL) in 1:1 molar ratio was refluxed for ∽4 hrs. Upon the removal of the solvent in vacuo the desired product was obtained (2.23 g; 93%) as a powdery solid. The product was purified by washing it 3-4 times with n-hexane and recrystallized from benzene/petroleum ether mixture (1:4).

For the sake of brevity the synthetic and analytical results of the other complexes are summarised in Table 1.

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