TETRAPHENYLANTIMONY MERCAPTIDES, Ph₄SbSAr: THERMAL DECOMPOSITION

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Summary

The products of the thermal decomposition of $Ph_4SbSC_6H_4X$ (X = H, *p*-Me, *p*-OMe, *o*-OMe and *p*-Br) include XC_6H_4SPh, $(XC_6H_4S)_2$, Ph_3Sb, Ph_2 and PhH. Evidence is presented to show that at least a major part of the reaction occurs via free radicals.

Introduction

Various tetraorganoantimony(V) species undergo thermal decomposition [1—4]. While other organoantimony(V) compounds may be formed, e.g. Ar_3-SbO from Ar_4SbOH [1], the majority of such thermolyses are reductive eliminations and lead to organoantimony(III) derivatives, e.g. Ph_3Sb, from Ph_3Me-SbBr [4] and Ph_4SbOR [3], and Me_3Sb from Me_4SbSR [2]. The tetramethylantimony mercaptides are unstable even at room temperature [3]. The tetraphenylantimony analogues are more thermally stable but however do decompose on heating. We wish to report some details of such decompositions.

Results and discussion

Preparation

The tetraphenylantimony mercaptides, $Ph_4SbSC_6H_4X$, were readily prepared by the metathetic reactions of Ph_4SbCl and thiols, XC_6H_4SH, in the presence of NEt_3 at ambient temperatures. The best method of removing unreacted material and other impurities was found to be by precipitating the $Ph_4SbC_6H_4X$ from filtered chloroform solutions on addition of hexane. Chemical analysis and spectra of the solids, prepared in this manner and after extensive drying at room temperature, indicated the presence of small amounts of chloroform. Although the relative amounts of chloroform in the solids could vary slightly

with subsequent reprecipitations from chloroform/hexane solutions, it was not possible to remove the chloroform by prolonged evacuation at ambient temperatures. As evacuation at temperatures higher than ambient would have led to decomposition, the solvated Ph_4SbSAr samples were used as such in the thermolysis study. With these samples, DTA showed a very slightly endothermic shift (starting about 50°C) and a deep exothermic change at about 140°C (heating rate 10°C/min). In calculating the yields of thermolysis products, appropriate allowances were made for the presence of the chloroform in the mercaptide samples.

Previously, Russian workers [5] had prepared Ph_4SbSAr derivatives from Ph_4SbOMe and ArSH in refluxing benzene, followed by recrystallisation from cyclohexane. No mention was made of solvated compounds. As, in our hands, the Ph_4SbSAr compounds suffered considerable decompositions in hot benzene and cyclohexane solutions, we preferred not to use their synthetic method.

Thermal decomposition

While decomposition of neat samples occurred most readily above the melting points (melting points being in the range 105—135°C), decompositions also resulted, but much more slowly, at lower temperatures as shown by gradual changes from yellow microcrystalline materials to yellow-brown oily products.

The products were investigated by GLC, TLC and various spectroscopies. In Table 1 are shown the yields of the major products as determined by GLC for a constant set of reaction conditions. The yields of the disulphides $[(XC_6H_4)_2S_2]$ and Ph_2 are based on two moles of the $Ph_4SbSC_6H_4X$. In addition to these major products, there were a small number of others, all in very low yield. These were not identified, but probably are polynuclear aromatics of the type isolated by TLC. Separations of the dominant products $[(XC_6H_4S)_2,$ $PhSC_6H_4X$, Ph_3Sb and $Ph_2]$ * was also effected by preparative layer chromatography in yields just lower than those calculated from the GLC data. The separated products had physical properties, analyses, etc. in complete agreement with those of authentic samples. In addition, TLC indicated base-line materials, immobile using chlorocarbon solvents, and small quantities of mobile products. The amounts of the latter were only in the order of a few milligrams by weight (<1% of the original material weight) and were shown by mass and ^1H NMR spectra of be organic sulphur compounds of the types $PhSC_6H_3X(SC_6H_4X)$ and $XC_6H_4SC_6H_4SC_6H_4X$ (X = H, Br, OMe and Me).

The base-line TLC fraction proved difficult to remove from both Al_2O_3 and SiO_2; the best extraction of material occurred using $CHCl_3$ on the plates still wet with the eluant ($CHCl_3$/hexane). Analysis and ^1H NMR spectra of the retrieved species indicated phenyl groups, antimony and chlorine but however not SC_6H_4X units. Tetraphenylantimony chloride was at least a part of this recovered product, it being formed either during the thermolysis from the $CHCl_3$ originally present in the $Ph_4SbSC_6H_4X$ sample or subsequently on the plates from reaction of the $CHCl_3$ eluant with other organoantimony compounds, such as Ph_5Sb. Pentaarylantimony compounds are known to react with

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* PhSPh and $(PhS)_2$ could not be separated by TLC. All other pairs of $PhSC_6H_4X$ and $(XC_6H_4S)_2$ were separated.

TABLE 1

YIELDS OF PRODUCTS OF THE THERMAL DECOMPOSITION OF $Ph_4SbSC_6H_4X$ AT 140°C FOR 3 HOURS [a]

Starting Material ($Ph_4SbSC_6H_4X$) X	Products (%)				
	Ph_3Sb	$(XC_6H_4S)_2$	$PhSC_6H_4X$	Ph_2	PhH
H	99	30	69	21	6
p-Br	96	3	97	3	3
p-OMe	98	28	69	17	13
o-OMe	97	5	92	6	4
p-Me	93	40	50	4	15

[a] Average of 3 experiments
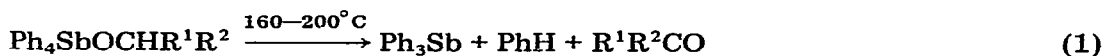
chlorocarbon solvents [6] forming Ar_4SbCl. Some NMR spectral indications of the presence of small quantities of Ph_5Sb among the decomposition products was gained, after careful and prolonged separation from much of the sulphur products using chlorocarbon/hexane solutions. Pentaphenylantimony is itself thermally labile, producing Ph_3Sb and Ph_2; once formed it would withstand the reaction temperatures used (up to 140°C) but not the GLC imput temperatures (>260°C) and would be converted there to Ph_3Sb and Ph_2. Hence the Ph_3Sb yields (as those of Ph_2) obtained by GLC would include that formed from Ph_5Sb.

For all the $Ph_4SbSC_6H_4X$ compounds, listed in Table 1, except X = Me-p, the yields of products varied only slightly (±3%) with the reaction temperature or time. However considerably greater differences were noted for reactions of $Ph_4SbSC_6H_4Me$-p, particularly as the temperature was varied. The reaction time and the particular sample used also had effects on the yields. In these thermolyses of $Ph_4SbSC_6H_4Me$-p, the recovery of antimony as Ph_3Sb generally fell as the thermolysis temperature increased; furthermore at the higher temperatures more $(p$-$MeC_6H_4S)_2$ was produced at the expense of $PhSC_6H_4Me$-p with a slight fall in their combined recovery.

Other mercaptides, $Ph_4SbSC_6H_4X$ (X = NO_2, NH_2), were also studied. However GLC proved not to be too useful in these cases, owing to the products having long retention times and their breakdown at high temperatures. However, it appeared that the thermal decompositions of these two mercaptides followed the same trends as noted for the others.

In a related study, Schmidbauer et al. [2], showed that Me_4SbSR (R = Me, CH_2Ph and Ph), prepared from Me_5Sb and RSH, decomposed at room temperature to Me_3Sb and MeSR. The yields quoted for the decomposition products were in the region of 70%; no mention of other products were given, nor was a mechanism proposed. Razavaev and co-workers [3] reported on the thermal decomposition of Ph_4SbOR. Of interest, it was reported that the decomposition of Ph_4SbOPh (to Ph_3Sb and Ph_2O) was only 68% complete after 3 h at 200°C; this contrasts with the complete decomposition of Ph_4SbSPh and the other mercaptides within 3 h at 140°C. When the R group in Ph_4SbOR contained an alpha hydrogen the decompositions followed eq. 1, for which a radi-

cal mechanism could operate. A radical mechanism (a free radical chain mechanism) was shown by McEwen et al. to operate in the decomposition of Ar_4Sb-OH (the propagating steps are shown in eqs. 2 and 3),

$$Ph_4SbOCHR^1R^2 \xrightarrow{160-200°C} Ph_3Sb + PhH + R^1R^2CO \tag{1}$$

$$Ar_4SbO^{\cdot} \rightarrow Ar_3SbO^{\cdot} + Ar \tag{2}$$

$$Ar^{\cdot} + Ar_4SbOH \rightarrow ArH + Ar_3SbO \tag{3}$$
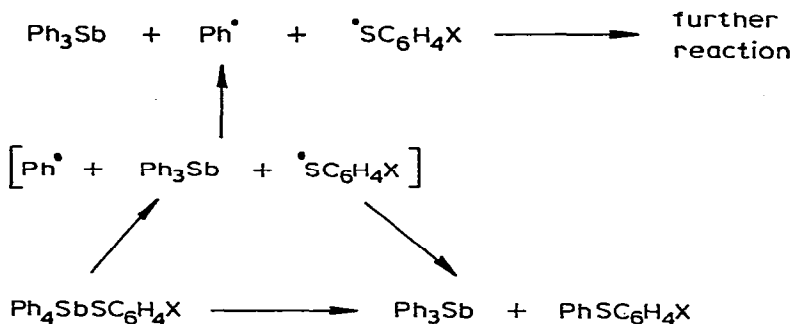
Mechanism of the thermal decomposition of $Ph_4SbSC_6H_4X$

Evidence of a free radical route for at least a part of the decomposition of $Ph_4SbSC_6H_4X$ has been found. Heating (60°C) $Ph_4SbSC_6H_4X$ (X = OMe, Me, Br) solutions in the presence of the spin-trapping agent, t-BuN=O, within the cavity of an ESR spectrometer led to the detection of the free radical t-Bu-(Ph)N—O$^{\cdot}$, i.e. trapping of Ph$^{\cdot}$. The ESR spectrum of t-Bu(Ph)N—O$^{\cdot}$ (a(N) 12.30, a(o-H) 2.05, a(p-H) 2.03, a(m-H) 1.0 G) was identical to that previously reported by Forrester and Calder [7]. No other radicals were detected. While thiyl radicals, ArS$^{\cdot}$, would also react with the spin trapping agent, t-BuN=O to give initially t-Bu(ArS)NO$^{\cdot}$, such nitroxides would not be detected under our reaction conditions (50—80°C). This is due to the thermal lability of radicals of the type R(R'S)N—O$^{\cdot}$, e.g. the half-life of $2,3,5,6-Me_4C_6HH(PhS)N—O^{\cdot}$ is only about 3 s at ambient temperature; they have consequently only been detected at low temperatures [8,9].

As well as this evidence for Ph$^{\cdot}$, some products of the decompositions strongly suggest a radical process, e.g. PhH and Ph_2 (arising from Ph$^{\cdot}$), $(XC_6H_4S)_2$ and the polynuclear sulphur containing species, $(PhSC_6H_3XSC_6H_4X)$ and $XC_6H_4SC_6H_4SC_6H_4X)$ (arising from attack by $C_6H_4S^{\cdot}$ on $PhSC_6H_4X$). From decompositions in refluxing solvents, further pointers to at least a considerable extent of a radical reaction were obtained. Thus the decomposition of Ph_4Sb-SC_6H_4OMe-p in refluxing CCl_4 and in cyclohexane gave p-$MeOC_6H_4CCl_3$ (ca. 20%) and cyclohexyl SC_6H_4OMe-p (ca. 30%), respectively as well as usual products. These reactions will be reported on fully in due course. Davies and Hook [10] have shown that triphenylantimony and benzenethiol (3 equivalents) in benzene solution gives $Ph_2SbSC_6H_5$, in a free radical reaction involving $C_6H_5S^{\cdot}$ (i.e. equations 4 and 5). We found no such products in our thermolysis study.

$$Ph_3Sb + PhS^{\cdot} \rightarrow Ph_2SbSPh + Ph^{\cdot} \tag{4}$$

$$Ph^{\cdot} + PhSH \rightarrow PhH + PhS^{\cdot} \tag{5}$$

The free-radical mechanism we propose for the decomposition of Ph_4SbS-C_6H_4X involves formation of both Ph$^{\cdot}$ and $XC_6H_4S^{\cdot}$ and their subsequent reaction to give $PhSC_6H_4X$, Ph_2, $(XC_6H_4S)_2$, PhH (by hydrogen abstraction) and the other products. Whether the two radicals, Ph$^{\cdot}$ and $XC_6H_4S^{\cdot}$, are formed concurrently or consecutively remains to be answered. The fact that both are present is beyond dispute and we propose that their formation is practically concurrent as shown in Scheme 1. As well as the radical route, a direct route to $PhSC_6H_4X$ can also operate.

SCHEME 1.

$$Ph_3Sb \ + \ Ph^\bullet \ + \ ^\bullet SC_6H_4X \longrightarrow \text{further reaction}$$

$$\left[Ph^\bullet \ + \ Ph_3Sb \ + \ ^\bullet SC_6H_4X \right]$$

$$Ph_4SbSC_6H_4X \longrightarrow Ph_3Sb \ + \ PhSC_6H_4X$$

Experimental

Ph$_4$SbCl was prepared by the reaction of Ph$_3$Sb, PhCl and AlCl$_3$ [11]. Solvents were dried and distilled prior to use.

Preparation of Ph$_4$SbSC$_6$H$_4$X. The following procedure was adopted. To Ph$_4$SbCl (2 g, 4.66 mmol) dissolved in CCl$_4$ (250 ml) was added the thiol, XC$_6$H$_4$SH (4.66 mmol) dissolved in CCl$_4$ (20 ml) and an excess of Et$_3$N. After filtering off the precipitate of Et$_3$N · HCl, the filtrate was washed with water (3 × 100 ml) to remove excess Et$_3$N and any remaining Et$_3$N · HCl, dried using anhydrous MgSO$_4$ and then evaporated at ambient temperature. The pale yellow solid mercaptide was recrystallised twice from dry CHCl$_3$/hexane solution, with cooling, if necessary, and dried under vacuum at ambient temperature. The samples prepared by this route contained CHCl$_3$; the analyses of the samples used in the thermal decompositions are listed in Table 2.

Standard compounds for GLC and TLC. Disulphides, (XC$_6$H$_4$S)$_2$, were produced by oxidation of the corresponding thiols, using iodine and base [12]. Phenyl aryl sulphides were obtained from the thermolysis of Ph$_4$SbSC$_6$H$_4$X and

TABLE 2

ANALYSES AND THE MELTING POINTS OF TETRAPHENYLANTIMONY MERCAPTIDES

Compound Ph$_4$SbSC$_6$H$_4$X.nCHCl$_3$		Analyses Found (Calc.) (%)				m.p. ($^\circ$C)
X	n	C	H	S	Cl	
H	0.06	66.5 (66.1)	4.6 (4.6)	5.9 (5.9)	1.1 (1.1)	116
p-MeO	0.11	65.3 (64.2)	4.9 (4.7)	5.6 (5.5)	2.1 (2.0)	132
o-MeO	0.5	60.6 (60.1)	4.8 (4.4)	5.6 (5.1)	8.1 (8.5)	122—123
p-Me	0.25	64.6 (64.4)	5.1 (4.7)	5.5 (5.5)	5.0 (4.6)	106—108
p-Br	0.12	57.3 (57.2)	3.8 (3.8)	5.2 (5.1)	2.6 [a] (2.1)	132—134

[a] Br 12.7 (12.6)

were shown to have correct analyses and properties consistent with those published [13]. Di-(*p*-Chlorophenyl) sulphide was a gift from Dr. D.R. Hogg.

Thermolysis. A sample of the mercaptide (0.3 g) was sealed in an evacuated glass tube and heated in an oil bath, whose temperature could be regulated to $\pm 2°C$. After cooling, the tube was opened and the reaction products investigated by GLC and/or TLC.

GLC. The reaction products were carefully washed, using small quantities, of methylene chloride into a flask containing the reference compounds, $(p\text{-}ClC_6H_4)_2S$ (for determination of yields of $(XC_6H_4S)_2$, $PhSC_6H_4X$, Ph_3Sb and Ph_2) and PhBr (for determination of PhH). The product yields were calculated from the peak areas in the chromatogram, with the aid of an integrator, after due allowances were made for the quite different response factors. Conditions: Instrument Perkin Elmer F11: Columns 2 m glass (O.D. 6 mm): $2\frac{1}{2}\%$ silicone gum rubber E 301 on chromosorb G-AW-DMCS 80—100 mesh.

TLC. The products were separated on silica gel GF 254 plates using $CHCl_3$/hexane (1/9) as the eluant. The separated products [Ph_2, Ph_3Sb, $(XC_6H_4S)_2$ and XC_6H_4SPh] were readily extracted from the plates using $CHCl_3$ and identifications were confirmed by a combination of mass and ^1H NMR spectra, analyses and comparisons with authentic samples. Small amounts of other mobile products were also present; thus from the decompositions of $Ph_4SbSC_6H_4OMe\text{-}p$, a product (ca. 3 mg) was obtained with m/e 354.0746 (Calculated for $C_{20}H_{18}$-O_2S_2 354.0748). The small quantity prevented a well-resolved ^1H NMR spectrum being obtained; however two different methoxy groups were present and the ratio of aryl : methoxy protons = 12 : 6. The brown base-line material was best extracted from wet plates and analyses of the crude materials (C, H, Sb and Cl present; S absent) and ^1H NMR spectra (aryl protons only) obtained. Crystallisation from $CHCl_3$/hexane gave Ph_4SbCl, m.p. 200°C (lit. value 202—205°C [14]).

ESR. Solutions of $Ph_4SC_6H_4X\text{-}p$ (X = OMe and Me) in degassed $CHCl_3$ or CH_2Cl_2/$CHCl_3$ containing t-BuN=O were heated (up to 60°C) in tubes maintained within the cavity of the ESR spectrometer. The spectrum of Ph(t-Bu)-N—O· was obtained [a(N) 12.30, a(o-H) 2.05, a(m-H) 2.03, a(m-H) 1.06], identical to that published [7].

Acknowledgements

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