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ANTIMONY—SULPHUR BONDED COMPOUNDS

IV *. FURTHER STUDIES ON THE THERMAL DECOMPOSITION OF TETRA-ORGANOANTIMONY MERCAPTIDES **

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Summary

The thermolytic decompositions of Ph_4SbSAr in organic solvents are reported. Solvent-derived products from decompositions in CCl_4 and cyclohexane confirm the free radical nature of the reactions.

Thermal decompositions of Ph_3 (p-MeC_6H_4)$SbSC_6H_4OMe$-p, or Ph (p-MeC_6H_4)$_3SbSC_6H_4X$ (X = p-MeO or H) provide mixed triarylstibines, [$Ph_{3-n}Sb(C_6H_4Me$-$p)_n$ (n = 0, 1, 2 and 3), disulphide ($XC_6H_4SSC_6H_4X$), monosulphides ($PhSC_6H_4X$ and p-$MeC_6H_4SC_6H_4X$), arenes, (PhH and PhMe) and biaryls (Ph_2, PhC_6H_4Me-p and p-$MeC_6H_4C_6H_4Me$-p).

Introduction

Various antimony—sulphur-bonded compounds have been studied, including triaryl thioantimonites [1—3], $Sb(SAr)_3$, trialkyl thioantimonites [4,5], $Sb(SR)_3$, antimony(III) thioacetate [6], $Sb(SCOMe)_3$, organoantimony(III)- [7—9] and organoantimony(V)-sulphur bonded compounds [7,8,10—15].

Wide ranges of reactivities and stabilities of antimony—sulphur bonded compounds have been indicated from these studies. The valency state of antimony and the types of organic and sulphur groups attached to antimony all have important influences on such properties. Antimony trimercaptides, $Sb(SR)_3$ (R = alkyl or aryl), for example, are readily hydrolyzed [2,3b] and oxidised

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[*] For part III see ref. 11.

[**] Dedicated to Professor R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).

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[2,4], especially in solution (to disulphides, RSSR, and antimony-oxygen compounds); in contrast, triorganothioantimonites, such as $Sb(SC_6H_4Me\text{-}p)_3$, are thermally stable in the absence of air to at least 130°C and are photochemically stable at ambient temperature in benzene solution [2]. The aerial oxidation was considered to involve intermediate antimony(V) species, e.g. $OSb^{V}(SR)_3$. While $OSb(SR)_3$ compounds have as yet not been isolated, Mehrotra et al. [4] obtained indications of their presence among the oxidation products from elemental analytical data. Apparently, $SSb(SR)_3$ have been isolated [3b]. The antimony—sulphur bonds in $Sb(SR)_3$, [and in $R'_nSb(SR)_{3-n}$] [18] can be cleaved by a variety of electrophilic reagents, including MeI, $o\text{-}NO_2C_6H_4SCl$, SCl_2 and $(CH_3CO)_2O$, under mild conditions [2].

$$3\,MeI + Sb(SR)_3 \xrightarrow{20^\circ C} 3\,MeI + SbI_3$$

$$3\,o\text{-}NO_2C_6H_4SCl + Sb(SR)_3 \xrightarrow{20^\circ C} 3\,o\text{-}NO_2C_6H_4SSR + SbCl_3$$

$$3\,SCl_2 + 2\,Sb(SR)_3 \xrightarrow{20^\circ C} 3\,RSSSR + 2\,SbCl_3$$

Disulphides, R'SSR', are much less reactive electrophilic reagents than sulphenyl halides, R'S—X, but even these react with $Sb(SR)_3$ at ca. 100—130°C in vacuo [2]. The disulphide reactions lead to exchange of the mercaptide groups with formation of all possible disulphides and antimony(III) trimercaptides.

$$\begin{aligned} Sb(SR)_3 + R'SSR' \xrightarrow{130^\circ C} {} & Sb(SR)_3 + Sb(SR)_2(SR') + Sb(SR)(SR')_2 + Sb(SR')_3 \\ & + R'SSR' + RSSR' + RSSR \end{aligned}$$

The mechanism of this exchange process was considered to involve thermally labile, penta-aryl thioantimonates, $Sb(SR)_5$, formed by oxidative addition, and which decompose via reductive elimination:

$$\begin{tikzcd} Sb^{III}(SR)_3 + R'SSR' \arrow[r, leftrightharpoons] & {[Sb^{V}(SR)_3(SR')_2]} \arrow[d, leftrightharpoons] \arrow[dl, leftrightharpoons] \\ Sb^{III}(SR)(SR')_2 + RSSR & Sb^{III}(SR)_2(SR') + RSSR' \end{tikzcd}$$

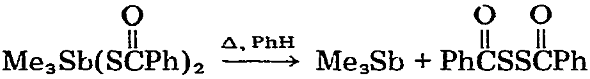
etc.

A series of such exchanges would lead to all possible products; some decomposition occurred at the reaction temperature and it was therefore impossible to establish whether equilibria were set up.

Attempts to make $Sb(SR)_5$ (R = alkyl and aryl) have all failed [3b,4], e.g. reactions of $SbCl_5$ and RSH at ambient temperature provided $Sb(SR)_3$ and RSSR as well as HCl. The instability of $Sb(SR)_5$, at ambient temperature or less, is also shared by some organoantimony(V) mercaptides, for example, by triorganoantimony bismercaptides, $R_3Sb(SR')_2$. Attempts to prepare $R_3Sb(SR')_2$ from Bu_3SnSR' and R_3SbCl_2 at —20°C [19], or from Me_3SbX_2 (X = OEt or Br) and RSH [20] have been unsuccessful [12,19,20]; the organoantimony products isolated are triorganoantimony(III) compounds:

$$2Bu_3SnSR' + Ph_3SbCl_2 \rightarrow Ph_3Sb + 2Bu_3SnCl + R'SSR'$$

In contrast to the thermal instability of simple $R_3Sb(SR')_2$ compounds, Ouchi et al. [15,21] have shown that the antimony—sulphur bonded compounds $R_3Sb(S_2CNR'_2)_2$ (R' = Me, but not Ph), $Me_3Sb(S_2COR)_2$, $Ph_3Sb(SCOR)_2$ and $Ph_3Sb(SCSR)_2$ can be isolated at ambient temperature. However, heating does lead to decomposition [20], e.g.

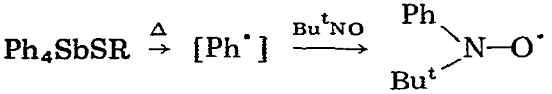


$$Me_3Sb(S\overset{O}{\overset{\|}{C}}Ph)_2 \xrightarrow{\Delta,\ PhH} Me_3Sb + Ph\overset{O}{\overset{\|}{C}}SS\overset{O}{\overset{\|}{C}}Ph$$

Schmidbaur and Mitschke have prepared Me_4SbSR (R = Me, CH_2Ph or Ph) at —70°C [13]; however, decomposition to Me_3Sb and RSMe occurs at room temperature. We have shown that the tetraphenylantimony analogues, Ph_4SbSR, are more thermally stable. Not only can they be isolated at ambient temperature (ca. 20°C) but their melting points, above 100°C, can be determined, although some decomposition results [10]. Complete decomposition occurs on heating, e.g. at 130°C for 2—3 hours, to give a variety of products:

$$Ph_4SbSR \xrightarrow[2\text{—}3\ h]{130^\circ C} Pb_3Sb + RSPh + RSSR + Ph_2 + PhH + ...$$

At least part of the reaction must proceed via free radicals. The nature of the products, e.g. Ph_2, PhH and RSSR, and trapping of $Ph^\bullet$ as phenyl tert-butyl nitroxide, $PhBu^tNO^\bullet$ (identified from its ESR parameters) by nitroso-tert-butane, indicate this:



$$Ph_4SbSR \overset{\Delta}{\rightarrow} [Ph^\bullet] \xrightarrow{Bu^tNO} \begin{matrix} Ph \\ Bu^t \end{matrix}\!\!>N\text{—}O^\bullet$$

Despite the thermal instability of Ph_4SbSAr, several reactions of Ph_4SbSAr have been studied. These include exchange reactions with other organometallic mercaptides [8] and organotin halides [11] as well as reactions with a variety of electrophilic reagents [11]:

$$Ph_4SbSAr + PhHgSAr' \rightarrow Ph_4SbSAr' + PhHgSAr$$

$$Ph_4SbSAr + Bu_3SnCl \rightarrow Ph_4SbCl + Bu_3SnSAr$$

$$Ph_4SbSAr + X_2 \rightarrow 2Ph_4SbX + ArSSAr$$

$X_2 = Br_2$ or I_2

$$Ph_4SbSAr + Ar'SX \rightarrow Ph_4SbX + ArSSAr'$$

$$Ph_4SbSAr + RX \rightarrow Ph_4SbX + RSAr$$

$RX = PhCH{=}CH_2Br$, $PhCOCl$ or $MeSCH_2Cl$

These mild electrophilic reactions show that the tetraphenylantimony mercaptides are good mercaptide transfer agents (very much better than triphenyltin mercaptides).

Several aspects of the thermolyses reactions of R_4SbSR' remained to be investigated. These included thermolyses in solution and the thermolyses of unsymmetrical antimony mercaptides, e.g. RR''_3SbSR'. We now report our findings.

Experimental

Solvents

These were the purest commercially available materials, purified according to standard procedures [22], deoxygenated and dried prior to use.

Preparation of tetraphenylantimony chloride [23]

To a mixture of Ph_3Sb (30 g) and $AlCl_3$ (30 g) was added PhCl (9.5 g). The mixture was refluxed for 24 h and added to ice/water (1 l). This was boiled for $\frac{1}{2}$ h, charcoal added and filtered. A saturated sodium chloride solution (100 ml) was added to the filtrate. After a period, the crystals of Ph_4SbCl were collected, 8.2 g, 20% yield, m.p. 201—203° C; lit. [23], m.p. 202—205° C.

Preparation of tetraphenylantimony mercaptides

To a solution of Ph_4SbCl (5 g, 0.011 mol) in CCl_4 (350 ml) was added a thiol (0.01 mol) in CCl_4 and an excess of Et_3N. After filtering off the precipitate of $Et_3NH^+Cl^-$ the filtrate was washed with water (3 X 100 ml), dried over anhydrous magnesium sulphate and evaporated at ambient temperature. The pale yellow solid mercaptide product was recrystallised two or three times from chloroform/hexane and dried under vacuum at ambient temperatures. The samples prepared by this route contained some $CHCl_3$.
$Ph_4SbSC_6H_4Me$-*p* · 0.25 $CHCl_3$, m.p. 107—108° C. Analysis, Found: C, 64.5; H, 5.0; S, 5.5; Cl, 4.7. Calcd.: C, 64.4; H, 4.7; S, 5.5; Cl, 4.6%.
$Ph_4SbSC_6H_4OMe$-*o* · 0.5 $CHCl_3$, m.p. 121—122° C. Analysis, Found: C, 60.5; H, 4.8; S, 5.3; Cl, 8.1. Calcd.: C, 60.1; H, 4.4; S, 5.1; Cl, 8.5%.
$Ph_4SbSC_6H_4OMe$-*p* · 0.11 $CHCl_3$, m.p. 131—132° C. Analysis, Found: C, 64.8; H, 4.9; S, 5.6; Cl, 2.1. Calcd.: C, 64.2; H, 4.7; S, 5.5; Cl, 2.0%.

Preparation of tri(p-tolyl)antimony

Tri(*p*-tolyl)antimony was prepared by a standard procedure [24] from $SbCl_3$ (11.4 g, 0.05 mol), *p*-MeC_6H_4Br (34 g, 0.2 mol) and Mg (5 g, 0.21 mol) in THF (150 ml). The residue was recrystallised from hexane, m.p. 127—128° C. Analysis, Found: C, 64.1; H, 5.2. Calcd. for $C_{21}H_{21}Sb$: C, 63.8; H, 5.3%.

Preparation of tri(p-tolyl)phenylstibonium tetrafluoroborate, Ph(p-$MeC_6H_4)_3$-$SbBF_4$

Benzenediazonium tetrafluoroborate, $PhN_2^+BF_4^-$, was prepared by a literature method [25]. A solution of tri(*p*-tolyl)antimony (13 g, 0.033 mol) in nitrobenzene (60 ml) was added to a solution of benzenediazonium tetrafluoroborate (6.33 g, 0.033 mol) in nitrobenzene (50 ml) [20]. The solution was left overnight. Considerable evolution of gas occurred during this period. The dark solution was washed several times with petroleum ether (60—80° C) (50 ml portions) until a brown solid appeared. A final washing of the dark solid with ether (25 ml) removed much of the coloured impurity, m.p. 144—146° C. ^1H

NMR (60 MHz) (ppm) $CDCl_3$: δ(Aryl) 7.80(s) and 7.63(s), 17H, and δ(Me) 2.50(s), 3H.

Preparation of tri(p-tolyl)phenylstibonium iodide

A solution of tri(*p*-tolyl)phenylstibonium tetrafluoroborate (5 g, 8.95×10^{-3} mole) in acetone was added to a solution of sodium iodide (30 g, 0.2 mol) in acetone. After 10 minutes, the acetone was removed to leave a solid residue. This was taken up in chloroform and water, and shaken with an aqueous solution of sodium thiosulphate. The chloroform layer was collected, dried over magnesium sulphate, and partially decolourised with charcoal. After filtering, the solvent was removed to leave a solid, which was twice recrystallised from petroleum ether (60—80°C), m.p. 152—155°C. ^1H NMR (60 MHz) (ppm) $CDCl_3$: δ (Aryl) 7.46—7.80(m) 17H, and δ (Me) 2.48(s) 3H.

Preparation of tri(p-tolyl)phenylantimony phenylmercaptide

A solution of tri(*p*-tolyl)phenylantimony iodide (20 g, 3.34×10^{-3} mol) in carbon tetrachloride (250 ml) was added to a solution of thiophenol (0.37 g, 3.34×10^{-3} mol) in carbon tetrachloride (20 ml). Excess triethylamine was added to give a precipitate. After filtering off the precipitate of triethylammonium iodide, the filtrate was washed with water (3 × 100 ml) to remove excess Et_3N, dried over anhydrous magnesium sulphate and evaporated at ambient temperature under reduced pressure. The pale yellow mercaptide was recrystallised twice from CH_2Cl_2/petroleum ether, m.p. 113—114°C. Analysis. Found: C, 68.4; H, 5.2; S, 5.5. Calcd. for $C_{33}H_{31}SSb$: C, 68.3; H, 5.3; S, 5.5%. ^1H NMR (60 MHz) (ppm) $CDCl_3$: δ ($PhSbC_6H_4$) 7.0—7.6(m) 17H, δ (SbSPh) 6.3—6.6(m) 5H and δ(Me) 2.33(s) 3H.

Preparation of tri(p-tolyl)phenylantimony p-methoxyphenylmercaptide, $(p\text{-}MeC_6H_4)_3PhSbSC_6H_4OMe\text{-}p$

This was prepared from tris(*p*-tolyl)phenylantimony iodide (2.0 g, 3.34×10^{-3} mol) and *p*-methoxybenzenethiol (0.47 g, 3.34×10^{-3} mol). $(p\text{-}MeC_6H_4)_3$-$PhSbSC_6H_4OMe$-*p*, m.p. 118—120°C. Analysis, Found: C, 66.9; H, 5.7; S, 5.4. Calcd. for $C_{34}H_{33}OSSb$: C, 67.1; H, 5.5; S, 5.3%. ^1H NMR (60 MHz) (ppm) $CDCl_3$: δ($PhSbC_6H_4$) 7.15—7.58(m) 17H, δ($SbSC_6H_4$) 6.30(d, *J* 6 Hz) 4H, δ(OMe) 3.64(s) 3H; δ(Me) 2.36(s) 3H.

Preparation of triphenyl(p-tolyl)stibonium tetrafluorate, $Ph_3(p\text{-}MeC_6H_4)Sb^+BF_4^-$

p-Toluenediazonium tetrafluoroborate, *p*-$MeC_6H_4N_2^+BF_4^-$, was prepared from *p*-$MeC_6H_4NH_2$ according to a published procedure [25]. Nitrobenzene solutions of *p*-$MeC_6H_4N_2^+BF_4^-$ (15.5 g in 50 ml) and Ph_3Sb (26.7 g in 50 ml) were mixed at room temperature. Nitrogen was immediately evolved and the solution left for 24 h. The resulting deep brown solution was repeatedly washed with 50 ml portions of petroleum ether (60—80°C) until solidified. The coloured solid was collected and washed several times with ether (25 ml portions). This produced a pale-coloured solid. Normally this was used as such to prepare the iodide. However, it could be recrystallised from ethyl acetate; m.p. 143°C.

Preparation of triphenyl(p-tolyl)antimony iodide, $Ph_3(p\text{-}MeC_6H_4)SbI$

Acetone solutions of $Ph_3(p\text{-}MeC_6H_4)Sb^+BF_4^-$ (10 g in 50 ml) and sodium iodide (30 g in 50 ml) were mixed. After leaving for 30 minutes, the solvent was removed and the residue taken up in chloroform and water. The chloroform layer was collected, extracted with sodium metabisulphite, dried over magnesium sulphate and rotatory evaporated. The solid residue was recrystallised from petroleum ether/benzene. $Ph_3(p\text{-}MeC_6H_4)SbI$, m.p. 172—176°C, 8.94 g, 83% yield.

Preparation of triphenyl(p-tolyl)antimony p-methoxyphenyl mercaptide, $Ph_3(p\text{-}MeC_6H_4)SbSC_6H_4OMe\text{-}p$

Triphenyl(*p*-tolyl)antimony iodide (2.5 g, 4.38×10^{-3} mol) was partially dissolved in hot CCl_4 (250 ml). After cooling, *p*-methoxybenzenethiol (0.61 g) in CCl_4 solution and Et_3N (0.6 ml) were successively added. The reaction mixture was stirred for 15 minutes and filtered. The filtrate was washed with water, dried over magnesium sulphate and the solvent removed by rotatory evaporation at ambient temperature. The oily product was repeatedly washed with petroleum ether (25 ml portions) until it solidified. Purification of $Ph_3(p\text{-}MeC_6H_4)SbSC_6H_4OMe\text{-}p$ was achieved by dissolving the solid in the minimum quantity of CH_2Cl_2 and reprecipitating by addition of petroleum ether. The product was collected and as much of the solvent as possible was removed in vacuo at ambient temperature, m.p. 106—107°C. Analysis. Found: C, 65.7; H, 5.0; S, 5.4; Cl, 0.3. Calcd. for $C_{32}H_{29}OSSb$: C, 65.9; H, 5.0; S, 5.5%. The analysis indicated a low chlorine content, due to the presence of a little CH_2Cl_2. ^1H NMR (220 MHz) (ppm) $CDCl_3$; δ(Ph—Sb) 7.56(m) *ortho* and 7.35(m) *meta* and *para*; $\delta(SbC_6H_4Me)$ aryl protons (quartet) 7.16 and 7.35, *J* 6 Hz; $\delta(SbSC_6H_4OMe)$ aryl protons (quartet) 6.18 and 6.27; *J* 6 Hz; δ(OMe) 3.58(s), δ(Me) 2.35(s).

Preparation of bis(p-chlorophenyl)sulphide, $p\text{-}ClC_6H_4SC_6H_4Cl\text{-}p$

p-Chlorobenzenesulphenyl chloride (30 g, 0.17 mol), prepared from *p*-chlorobenzenethiol and chlorine in carbon tetrachloride, was added to chlorobenzene (200 ml) and iron (200 mg) and the mixture refluxed for 1 h. The excess chlorobenzene was removed by distillation to leave a mixture of the monosulphide, $(p\text{-}ClC_6H_4)_2S$, and the disulphide $(p\text{-}ClC_6H_4S)_2$. To this was added a solution of $Na_2S \cdot 9H_2O$ (21 g) and NaOH (7.5 g) in H_2O (50 ml) and EtOH (100 ml). After refluxing for 2 hours, the solution was diluted with H_2O (200 ml) and extracted with Et_2O. The ether layer was collected, dried over magnesium sulphate and evaporated. The crude solid was recrystallised twice from ethyl acetate-methanol; 13 g, 30% yield, m.p. 94—95°C, lit. [27], m.p. 95°C. Analysis. Found: C, 54.4; H, 2.9; S, 12.5; Cl, 27.9. Calcd. for $C_{12}H_8Cl_2S_2$: C, 54.5; H, 3.2; S, 12.6; Cl, 27.9%.

Thermolyses

(i) Neat. A sample of the tetraarylantimony mercaptide (0.2—0.3 g) was sealed in an evacuated tube which was heated to the desired temperature (±2°C) in an oil bath for a given time. After cooling, the tube was opened and the contents carefully washed, using dichloromethane, into a flask containing the GLC

standards (usually bis(p-chlorophenyl)sulphide and bromobenzene). The reaction products were determined by GLC using a Perkin Elmer F11 chromatograph [column 2 m glass O.D. 6 mm: $2\frac{1}{2}$ silicone gum rubber E301 on chromosorb G-AW-DMCS 80—100 mesh]. The product yields were calculated from the peak areas in the chromatogram with the aid of an integrater after due allowance was made for the different response factors. The mixed triarylstibines, $Ph_2(p\text{-}MeC_6H_4)Sb$ and $Ph(p\text{-}MeC_6H_4)_2Sb$ were assumed to have the same response factors as Ph_3Sb and $(p\text{-}MeC_6H_4)_3Sb$, authentic samples of which were available. Confirmation of the presence of the mixed triarylstibines among the reaction products was made by GC-MS. Phenyl p-anisyl sulphide was available from a previous study: the presence of p-tolyl p-anisyl sulphide in the thermolyses products was confirmed by GC-MS; its response factor was assumed to be the same as that of phenyl p-anisyl sulphide. Samples of diaryl disulphides were available from previous studies. A small sample of trichloromethyl p-anisyl sulphide was isolated by TLC (alumina) from one reaction mixture. Biaryls, Ph_2, $(p\text{-}MeC_6H_4)_2$ and $p\text{-}MeC_6H_4Ph$, were all commercial samples. Cyclohexyl p-anisyl sulphide was prepared from cyclohexene and p-methoxybenzenethiol [28], according to a general method.

(ii) In refluxing solutions. Solutions of the mercaptide (about 0.2 g in 15 ml solvent) were refluxed for a given time. Analyses of the products were made as above.

(iii) Decomposition in solution at 34°C. Decompositions were also followed by ^1H NMR (60 MHz) spectroscopy in sealed tubes at 34°C. When decomposition was complete (up to 20 days and dependent on concentrations as well as on the antimony compound) the tube was cooled in ice, opened and the contents investigated by GLC.

Results and discussion

The thermolyses of $Ph_4SbSC_6H_4X$ reported earlier were with neat samples and gave as major products Ph_3Sb, disulphide ($XC_6H_4SSC_6H_4X$), monosulphide ($PhSC_6H_4X$), Ph_2 and PhH as detected by GLC and TLC. The relative amount of each product varied with the particular Ph_4SbSAr compound. In addition to these major products, small quantities of more complex aromatic products were also detected by mass spectra, e.g. $PhSC_6H_3X(SC_6H_4X)$ and $XC_6H_4SC_6H_4SC_6H_4X$ ($X = p$-Br, H, p-Me or p-OMe) from thermal decompositions of $Ph_4SbSC_6H_4X$. The trapping of the phenyl free radical, $Ph^\bullet$, by the spin trapping agent, Bu^tNO, and particular products (such as the disulphides, biphenyl and benzene) point to free radical intermediates.

$$\begin{tikzcd}
\text{further reaction} & Ph_3Sb + Ph^\bullet + {}^\bullet SC_6H_4X \arrow[l] \\
Ph_4SbSC_6H_4X \arrow[r, "\Delta"] & {[Ph_3SbPh^\bullet + {}^\bullet SC_6H_4X]} \arrow[u] \arrow[d] \\
 & Ph_3Sb + PhSC_6H_4X
\end{tikzcd}$$

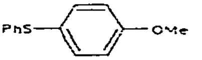
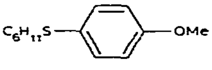
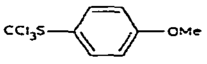
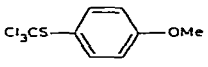
In this study, thermolyses of $Ph_4SbSC_6H_4OMe\text{-}p$ were carried out in refluxing solutions of benzene, chloroform, cyclohexene, cyclohexane and carbon tetrachloride. It was anticipated that carrying out the thermolyses in solution would lead to solvent-derived products, i.e. products obtained by radical attack on the solvent. This was indeed realised for two solvents, carbon tetrachloride and cyclohexane. In carbon tetrachloride solution, some trichloromethyl *p*-anisyl sulphide, $CCl_3SC_6H_4OMe$-*p*, and PhCl were obtained whereas in refluxing cyclohexane solution, cyclohexyl *p*-anisyl sulphide, *cyclo*-$C_6H_{11}SC_6H_4OMe$-*p*, was one of the many products (Table 1). The product mixtures were generally

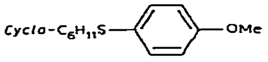
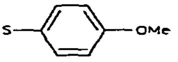
$$\begin{aligned}Ph_4SbSC_6H_4OMe\text{-}p \xrightarrow[\text{cyclohexane}]{\text{refluxing}} & Ph_3Sb + PhSC_6H_4OMe\text{-}p\\ & + cyclo\text{-}C_6H_{11}SC_6H_4OMe\text{-}p\\ & + (p\text{-}MeOC_6H_4S)_2 + Ph_2 + PhH\end{aligned}$$

analyzed by GLC. However, under the GLC conditions employed, *cyclo*-$C_6H_{11}SC_6H_4OMe$-*p*, and $PhSC_6H_4OMe$-*p* had the same retention times. Therefore, to estimate the amount of these two products, GC-MS and NMR spectroscopy were used. The substantial amounts of these solvent-derived products

TABLE 1

PRODUCTS OF DECOMPOSITION OF $Ph_4SbSC_6H_4OMe$-*p* IN SOLUTION [a]

Solvent	Temp. (°C)	Products (%)				
		Ph_3Sb		 [b]	Ph_2 [b]	Others
(i) Refluxing solutions						
PhH	80	95	86	8	4	
C_6D_6	80	97	86	7	—	
$CHCl_3$	64	95	70	19	4	
Cyclohexene		98	80	18	12	
Cyclohexane	81	95	62	5	3	 (31)
CCl_4	78	96	36	22	(<1)	PhCl (33)  (40)
Neat	130	98	69	28	17	
(ii) At 34°C						
$CDCl_3$		95	35	64	—	 (5)
CCl_4		98	47	48		

[a] Yields calculated by GLC and are average of at least three experiments. [b] Based on 1 mol of product per two mol of $Ph_4SbSC_6H_4OMe$-*p*. [c]  and  had the same retention time on GC. Estimation of yields were made by combination of GC-MS and NMR.

indicate that the free radicals play a major part in these reactions. In none of the other solvents used — cyclohexene, benzene, chloroform — was evidence found for radical attack on the solvent. No changes in the proportions of the major products were found between C_6H_6 and C_6D_6. Furthermore, no incorporation of deuterium was found (using mass spectra) in any of the phenyl products — biphenyl and phenyl *p*-anisyl sulphide — of decomposition in C_6D_6.

Considerably slower decompositions occur in solutions ($CDCl_3$ and CCl_4) maintained at 34° C. Reactions of $Ph_4SbC_4H_4X$ (X = *o*-OMe, *p*-OMe, and *p*-Me) could be monitored by ^1H NMR spectroscopy since fortunately the product and reagent SC_6H_4X proton have different chemical shifts. For the *o*-$MeOC_6H_4$-$SSbPh_4$ reactions in particular it was possible to discern distinct products. Some Ph_4SbCl was also obtained, especially in CCl_4 solution. The data in Table 1 show that more disulphide is obtained from decompositions at the lower temperature, 34° C, compared to the situation at reflux. From the brief study, it appeared that the reaction rate for decomposition of $Ph_4SbSC_6H_4OMe$ had almost a zero order dependence on [$Ph_4SbSC_6H_4OMe$], (e.g. see Fig. 1). Relative rates of decompositions, in $CDCl_3$, were found to be $Ph_4SbSC_6H_4OMe$-*o* > $Ph_4SbSC_6H_4OMe$-*p* > $Ph_4SbSC_6H_4Me$-*p*. More work is however necessary to establish the mechanism(s).

We next turned out attention to mixed tetraorganoantimony mercaptides, $Ph_3MeSbSC_6H_4OMe$-*p* (I), Ph_3(*p*-MeC_6H_4)$SbSC_6H_4OMe$-*p* (II), Ph(*p*-MeC_6H_4)$_3$-$SbSC_6H_4OMe$-*p* (III) and Ph(*p*-MeC_6H_4)$_3SbSPh$ (IV).

Compound I was particularly labile; all attempts to isolate it at 20° C from the reaction of Ph_3MeSbI (prepared according to ref. 29) and HSC_6H_4OMe-*p* in the presence of excess Et_3N failed. The formation of stoichiometric $Et_3NH^+I^-$ indicated that the metathetic reaction had gone completely but the identifica-

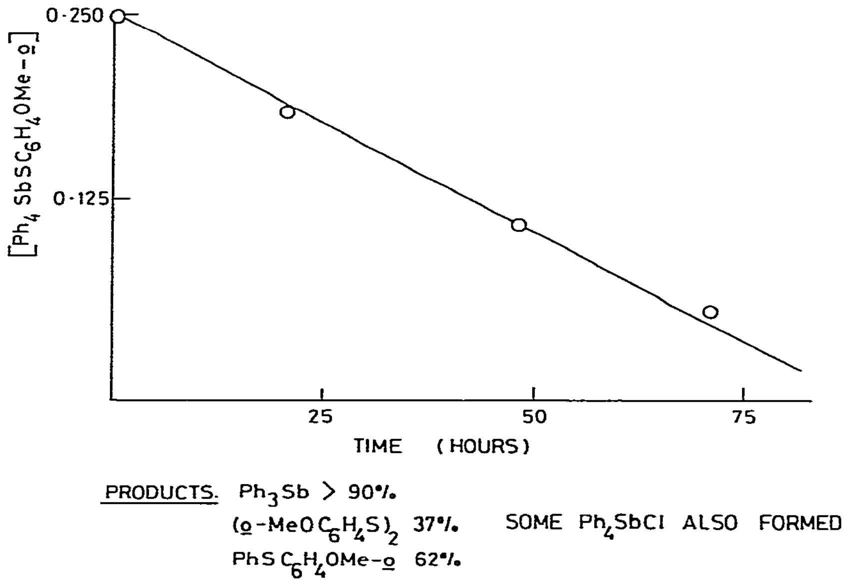


Fig. 1. Decomposition of $Ph_4SbSC_6H_4OMe$-*o*. $[Ph_4SbSC_6H_4OMe\text{-}o]_{initial} = 0.246\,M$.

tion of $MeSC_6H_4OMe$-*p* in very high yield pointed to the decomposition of I. Some disulphide, $(p\text{-}MeOC_6H_4S)_2$ was also detected. The source of this is ambiguous. There is no way of conclusively showing that it was one of the decomposition products of I: it may have been formed on oxidation of the thiol (a facile process in the presence of a base) or even may have been present as an impurity in the samples of the thiol used. Significantly no $PhSC_6H_4OMe$-*p* was detected. This shows that loss of methyl from I is very much more favoured than loss of phenyl, a situation paralleled in the decomposition of $Ph_3MeSbBr$ in MeCN solution [30].

$$\begin{array}{lc} \mathrm{Ph_3MeSbI + HSC_6H_4OMe}\text{-}p \xrightarrow[\mathrm{Et_3N}]{\mathrm{CCl_4}} & [\mathrm{Ph_3MeSbSC_6H_4OMe}\text{-}p] \\ & \downarrow \\ & \mathrm{Ph_3Sb + MeSC_6H_4OMe}\text{-}p \end{array}$$

Particularly complex arrays of products were obtained from thermolyses of compounds II, III or IV. For each $Ar_3Ar'SbSAr''$ compound, the products included the triarylstibines: Ar_3Sb, Ar_2SbAr', $ArSbAr'_2$ and $SbAr'_3$, the disulphide, $Ar''SSAr''$, the monosulphides: $ArSAr''$ and $Ar'SAr''$, mononuclear aromatics; ArH and Ar'H and biaryls: ArAr', Ar'Ar' and ArAr and for decomposition in CCl_4 products derived from the solvent: ArCl, Ar'Cl and CCl_3SAr''. In all, four different conditions were used, i.e. (i) direct injection into the chromatograph (injection port temperature 250° C, oven temperature 190° C), (ii) thermolyses of neat samples at 130° C, (iii) refluxing in solvents and (iv) decomposition in solution at 34° C. As data in Table 2 clearly indicate, the

TABLE 2

THERMAL DECOMPOSITIONS OF $Ar_3Ar'SbSAr''$

Conditions	Relative amounts of triarylantimony products [a]		
	Ph_3Sb	$Ph_2(p\text{-}MeC_6H_4)Sb$ [b]	$Ph(p\text{-}MeC_6H_4)_2Sb$
(a) $Ph_3(p\text{-}MeC_6H_4)SbSC_6H_4OMe\text{-}p$			
Direct injection [c]	1.00	2.31	0.16
Neat, 140°C/3 h [d]	1.00	1.34	0.37
Refluxing CCl_4 solution, 3 h	1.00	2.40	0.22
34°C, $CDCl_3$ solution, several days	1.00	2.00	0.23
(b) $Ph(p\text{-}MeC_6H_4)_3SbSC_6H_4OMe\text{-}p$			
Direct injection [c]	0.02	0.50	1.02
Neat, 140°C, 3 h [d]	0.02	0.27	1.27
Refluxing CCl_4 solution, 3 h	—	0.53	1.63
(c) $Ph(p\text{-}MeC_6H_4)_3SbSPh$			
Neat, 140°C, 3 h	0.013	0.21	1.30
Refluxing CCl_4 solution, 3 h	trace	0.11	1.42

[a] From GLC data. [b] $(p\text{-}MeOC_6H_4S)_2$ has the same retention time as $Ph_2(p\text{-}MeC_6H_4)Sb$. [c] Direct injection input temperature 250°C; oven temperature 190°C. [d] Also detected were $(p\text{-}MeC_6H_4)_2$, $p\text{-}MeC_6H_4Ph$ and Ph_2 as well as PhH and PhMe. [e] PhSSPh in yields of <4%.

proportions of triarylstibine and monosulphide products depend on the conditions employed.

The products clearly signify the involvement of free radicals, Ph$^\bullet$, p-MeC$_6$H$_4^\bullet$ and $^\bullet$SC$_6$H$_4$X in the thermolyses of Ph$_n$(p-MeC$_6$H$_4$)$_{4-n}$SbSC$_6$H$_4$X (n = 1 or 3). The variety of monosulphide and arene products are those anticipated from earlier work on the simple Ph$_4$SbSC$_6$H$_4$X species; the formation of all possible mixed triarylstibines was unexpected. It was thought for example that from Ph(p-MeC$_6$H$_4$)$_3$SbSC$_6$H$_4$X, (p-MeC$_6$H$_4$)$_3$Sb and Ph(p-MeC$_6$H$_4$)$_2$Sb would be the only triarylstibine products. There are several possibilities for the formation of Ph$_2$(p-MeC$_6$H$_4$)Sb and Ph$_3$Sb: e.g. that the sample of Ph(p-MeC$_6$H$_4$)$_3$Sb-SC$_6$H$_4$X, while analyzing correctly, was in fact a mixture of Ph$_n$(p-MeC$_6$H$_4$)$_{4-n}$-SbSC$_6$H$_4$X having an overall average value of n = 1, i.e. that some aryl scrambling had occurred during the formation of compounds II, III and IV. From a mixture of Ph$_n$(p-MeC$_6$H$_4$)$_{4-n}$SbSC$_6$H$_4$X (n = 0, 1, 2, 3 and 4) it can be conceived that all triarylstibines would be formed.

$$\underset{(n=0,1,2,3\text{ or }4)}{\mathrm{Ph}_n(p\text{-MeC}_6\mathrm{H}_4)_{4-n}\mathrm{SbSC}_6\mathrm{H}_4\mathrm{X}} \xrightarrow{\Delta} \underset{(n=1,2,3\text{ or }4)}{\mathrm{Ph}_{n-1}(p\text{-MeC}_6\mathrm{H}_4)_{4-n}\mathrm{Sb}}$$

$$+ \underset{(n=0,1,2\text{ or }3)}{\mathrm{Ph}_n(p\text{-MeC}_6\mathrm{H}_4)_{3-n}\mathrm{Sb}}$$

The reaction sequence leading to the tetraorganoantimony mercaptide is shown in Scheme 1. The most likely of the three reaction steps in the whole sequence

	Relative amounts of sulphur products [a]		
(p-MeC$_6$H$_4$)$_3$Sb	PhSC$_6$H$_4$OMe-p	p-MeC$_6$H$_4$SC$_6$H$_4$OMe-p	Others
trace	2.89	1.00	—
0.03	3.45	1.00	—
—	3.55	1.00	Cl$_3$CSC$_6$H$_4$OMe-p (1.92)
trace	3.10	1.00	—
1.00	0.35	1.00	—
1.00	0.34	1.00	—
1.00	0.37	1.00	Cl$_3$CSC$_6$H$_4$OMe-p (2.20)
1.00	0.36	1.00	PhSSPh [e]
1.00	0.36	1.00	CCl$_3$SC$_6$H$_5$; PhSSPh [e] (1.97)

SCHEME 1

$$\begin{tikzcd}
\mathrm{Ar_3Sb + Ar'N_2^+BF_4^-} \arrow[r, "\text{(i) PhNO}_2"] & \mathrm{[Ar_3Ar'Sb^+\,BF_4^-]} \arrow[d, "\text{(ii) I}^-"] \\
\mathrm{Ar_3Ar'SbSAr''} & \mathrm{Ar_3Ar'SbI} \arrow[l, "\text{(iii) HSAr}''", "\mathrm{Et_3N}"']
\end{tikzcd}$$

to produce aryl scrambled products is step (i). There is a report of scrambling of organic groups in mixed pentaorganoantimony compounds [31]. Meinema and Noltes [31] showed by ^{1}H NMR spectroscopy that a mixture of methylethylantimony(V) compounds arises from reaction of Me_3SbCl_2 and Et_2Mg or Et_3SbCl_2 and MeLi. ^{1}H NMR spectra clearly showed the presence of the individual pentaalkylantimony components in the mixture. The formation of mixtures was attributed to nucleophilic substitution of alkyl groups on antimony by alkyl-lithium or -magnesium compounds via hexacoordinate antimony intermediates. Such [hexaorganoantimony(V)]$^-$M$^+$ species are clearly not formed in the $Ar_3Sb/Ar'N_2^+BF_4^-$ reactions. However other hexacoordinate antimony(V) intermediates may be formed, and these could provide routes for some scrambling of the organic groups.

Another explanation, and one we prefer, for the formation of the scrambled products is that the scrambling occurs during the thermolyses as a result of free radical reactions (S_H2) involving aryl radicals and triarylstibines:

$$Ar'^{\bullet} + Ar_3Sb \rightarrow Ar'Ar_2Sb + Ar'^{\bullet}$$

In support of this proposal we offer the following evidence. Heating a solution containing Ph_3Sb and $(p\text{-}MeC_6H_4)_3Sb$ in either chloroform or peroxide-free tetrahydrofuran shows no exchange by GLC. However, direct injection into the chromatograph of a solution of Ph_3Sb, $(p\text{-}MeC_6H_4)_3Sb$ and a free radical initiator in peroxide-free tetrahydrofuran shows exchange. Initiators which have proved to be successful are azobisisobutyryl nitrile, AIBN, and lauroyl peroxide. However, the greatest exchange occurred in solution using an old sample of tetrahydrofuran, which contained peroxides. A long chain length has to be assumed from the extent of the exchange for the amount of peroxide or radical initiator added.

$$\text{Radical initiator} \rightarrow R^{\bullet}$$

$$R^{\bullet} + Ar_3Sb \rightarrow Ar_2SbR + Ar^{\bullet}$$

$$Ar^{\bullet} + Ar'_3Sb \rightarrow ArAr'_2Sb + Ar'^{\bullet}$$

etc.

There are a number of known S_H2 reactions involving Group V metals, e.g. thiols with Ph_3Sb [3e] (Scheme 2). In addition, alkoxy radicals will react [32]

SCHEME 2

$$RS^{\bullet} + Ph_3Sb \rightarrow RSSb(Ph_2) + Ph^{\bullet}$$

$$Ph^{\bullet} + RSH \rightarrow RS^{\bullet} + PhH$$

TABLE 3

THERMAL DECOMPOSITION OF $Ar_3Ar'SbX$: DIRECT INJECTION INTO GAS CHROMATOGRAPH [a]

Compound	Relative amounts of triarylantimony compounds			
	Ph_3Sb	$Ph_2(p\text{-}MeC_6H_4)Sb$	$Ph(p\text{-}MeC_6H_4)_2Sb$	$(p\text{-}MeC_6H_4)_3Sb$
$Ph_3(p\text{-}MeC_6H_4)SbBF_4$	1.00	1.23	0.25	—
$Ph_3(p\text{-}MeC_6H_4)SbI$	1.00	3.2	0.07	—
$Ph_3(p\text{-}MeC_6H_4)SbSC_6H_4OMe\text{-}p$	1.00	2.31	0.16	—
$Ph(p\text{-}MeC_6H_4)_3SbBF_4$	0.01	0.16	1.67	1.00
$Ph(p\text{-}MeC_6H_4)_3SbI$	0.02	0.06	1.94	1.00
$Ph(p\text{-}MeC_6H_4)_3SbSC_6H_4OMe\text{-}p$	0.01	0.16	1.02	1.00

---

[a] Injection temperature 250°C; column temperature 190°C.

with Ph_3As.

$$Bu^tO^{\bullet} + Ph_3As \rightarrow Bu^tOAsPh_2 + Ph^{\bullet}$$

From both $Ph_3(p\text{-}MeC_6H_4)SbSC_6H_4OMe\text{-}p$ and $Ph(p\text{-}MeC_6H_4)_3SbSC_6H_4\text{-}OMe\text{-}p$ thermolyses, there appears to be a slight preference for cleavage of the Ph—Sb bond than the p-MeC_6H_4—Sb bond, by factors between 1.00 to 1.18. Such calculations are approximate due to the number of products but do indicate the small differences in reactivity — differences which are expected to be small for radical cleavages. The thermolysis of $(XC_6H_4)Ph_3SbOH$ in xylene is a free radical reaction [33] (Scheme 3). For this reaction the relative reactivity of the two aryl—antimony bonds was calculated from the yields of [PhX] and [PhH]. The ratio of [PhMe] : [PhH] was 13 : 31, which gives, after allowance for the statistical factor, relative departure aptitudes of p-$MeC_6H_4^{\bullet}$ and $Ph^{\bullet}$ of 1 : 1.2.

SCHEME 3

$$(XC_6H_4)Ph_3SbO \begin{cases} \rightarrow (XC_6H_4)Ph_2Sb{=}O + Ph^{\bullet} \\ \rightarrow Ph_3Sb{=}O + XC_6H_4^{\bullet} \end{cases}$$

$$Ar^{\bullet} + (XC_6H_4)Ph_3SbOH \rightarrow ArH + (XC_6H_4)Ph_3SbO^{\bullet}$$

$$(Ar = Ph \text{ or } XC_6H_4)$$

However, only small differences in reactivity [34] were observed in the nucleophilic cleavage of Ph—Sb and p-MeC_6H_4—Sb bonds from pentaarylantimony compounds by alcohol. The ratio of [PhH] to [PhMe] produced in solvolysis of $Ph_4SbC_6H_4Me\text{-}p$ in 2-octanol at 50°C was 4.3 ± 1 while at 65.0 the ratio is 3.3 ± 0.2. When the statistical factor is considered, the reactivity of the two bonds can be clearly seen to be similar. Hence small differences in

$$ArSbAr'_4 + ROH \rightarrow ROSbAr'_4 + ArH$$

reactivities cannot be merely used as diagnosis of the reaction type.

In Table 3 are displayed data for the decomposition of various tetraorganoantimony(V) salts resulting from direct injection into the chromatograph. It can be seen that the nature of the salt influences the product distribution.

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1 Parts I, II and III are considered to be refs. 2, 10 and 11, respectively.

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