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# REACTIONS OF TETRAPHENYLANTIMONY MERCAPTIDES

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## Summary

Reactions of tetraphenylantimony mercaptides, $Ph_4SbSC_6H_4Y$, with electrophilic species in chlorocarbon solutions are reported. With chloromethyl methyl sulphide, allyl halides, sulphenyl halide, acyl halides, halogens, and triphenyltin chloride, ready and complete halide—mercaptide exchanges occur. No allylic rearrangement is found in the reaction with *trans*-$PhCH{=}CHCH_2Br$. In a competition reaction for $ClCH_2SMe$, $Ph_4SbSC_6H_5$ was shown to be only slightly (ca. 1.2 times) more reactive than $Ph_4SbSC_6H_4OMe$-*p*. The initial sulphur-containing product of reaction with *p*-toluenesulphonyl chloride, namely the thiosulphonate, *p*-$MeC_6H_4SO_2SC_6H_4Y$, reacts further with $Ph_4SbSC_6H_4Y$ to produce the disulphide, $(YC_6H_4S)_2$.

Benzoyl peroxide and $Ph_4SbSC_6H_4Y$ provide PhSbOCOPh and disulphide.

## Introduction

Tetraorganoantimony(V) mercaptides, $R_4SbSR'$, have been the object of a few studies, covering such features as exchange equilibria [1], electronic effects [2] and thermal reactions [3,4]. The tetraphenylantimony derivatives [1] have been shown to undergo ready mercaptide exchanges with thiols and other organometallic derivatives, e.g. those of tin and mercury. Both $^{19}F$ NMR and vibrational spectroscopies were used to demonstrate the significant electron-donating effects of the $Ph_4SbS$ unit in $Ph_4SbSC_6H_4Y$ (Y = F and $NO_2$) compounds and to establish the relative donating abilities of various $R_nMS$ groups [2]. Thermal instabilities were indicated in other studies [3,4]. Tetramethylantimony derivatives, $Me_4SbSR'$ (R' = Me, $CH_2Ph$ or Ph) are particularly labile even at ambient temperature, decomposition to $Me_3Sb$ and R'SMe results [3]. The tetraphenylantimony compounds have greater thermal stability [4]. Not only can they be isolated at room temperature, but their melting points (above 100°C) can be determined, although some decomposition results. Complete decomposition however occurs on heating (within hours) either alone or in solution. The thermal decomposition products from $Ph_4SbSC_6H_4Y$ included

$PhSC_6H_4Y$, $Ph_3Sb$, $Ph_2$, $(YC_6H_4S)_2$ and other derived from the free radicals, $Ph^{\cdot}$ and $YC_6H_4S^{\cdot}$.

Despite the thermal instability, it was believed that $Ph_4SbSC_6H_4Y$ would have value in synthesis as sources of mercaptide units under mild and neutral conditions, especially as $Ph_4SbSC_6H_4Y$ are soluble in chlorocarbon solvents. Thus this work was undertaken and this paper reports our findings on reactions of tetraphenylantimony mercaptides. In addition some general features of the mass spectra are given.

## Experimental

The tetraphenylantimony mercaptides, $Ph_4SbSC_6H_4Y$, were recrystallised ($CHCl_3$/hexane) samples from a previous study [4].

$Ph_4SbSC_6H_5$, m.p. 116°C; $^1H$ NMR ($CDCl_3$): δ $Ph_4Sb$ 7.2—7.7(m), $SC_6H_5$ 6.3—6.7(m).

$Ph_4SbSC_6H_4Me$-*p*, m.p. 107—108°C; ν(Sb—S) 328 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ $Ph_4Sb$ 7.2—7.7(m), $SC_6H_4$ 6.29 and 6.39 (*J* 6 Hz), Me 2.00.

$Ph_4SbSC_6H_4OMe$-*p*, m.p. 132°C; ν(Sb—S) 345 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ $Ph_4Sb$ 7.2—7.7(m), $SC_6H_4$ 6.15—6.21 (*J* 6 Hz), OMe 3.56.

$Ph_4SbSC_6H_4OMe$-*o*, m.p. 123°C; ν(Sb—S) 315 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ $Ph_4Sb$ 7.2—7.7(m), $SC_5H_4$ 6.2—6.8(m), OMe 3.35.

$Ph_4SbSC_6H_4Br$-*p*, m.p. 131—132°C; ν(Sb—S) 342 $cm^{-1}$, $^1H$ NMR ($CDCl_3$): δ $Ph_4Sb$ 7.2—7.7(m), $SC_6H_4$ 6.20 and 6.87 (*J* 8 Hz).

$Ph_4SbSC_6H_4NH_2$-*p*, m.p. 138—141°C; ν(Sb—S) 345 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ $Ph_4Sb$ 7.25—7.7(m), $SC_6H_4$ 6.01 and 6.16 (*J* 8 Hz), $NH_2$ 3.26

Triphenyltin *p*-methoxyphenyl mercaptide was prepared [5] from $Ph_3SnCl$ and $HSC_6H_4OMe$-*p* in $CCl_4$ solution in the presence of $Et_3N$, m.p. 74°C (δ OMe 3.64). Anal. Found: C, 61.5; H, 4.4; S, 6.5. $C_{25}H_{22}OSSn$ calcd.: C, 61.3; H, 4.5; S, 6.6%.

Solvents were the best commercial grade and were redistilled prior to use.

*Reagents.* Allyl bromide, cinnamyl bromide, *trans*-β-bromostyrene, benzoyl chloride, *p*-toluenesulphonyl chloride and chloromethyl methyl sulphide were all commercial samples which were either recrystallised or redistilled before use. Benzoyl peroxide, iodine and bromide were used as obtained. 2,4-Dinitrobenzenesulphenyl chloride was prepared from bis(2,4-dinitrophenyl)disulphide and chlorine [6]. *p*-Chlorophenyl-*p*-chlorobenzenethiosulphonate, *p*-$ClC_6H_4SO_2SC_6H_4Cl$-*p*, m.p. 138°C, lit. [7a] 133—135°C; was obtained by oxidation of $(p\text{-}ClC_6H_4S)_2$ with *m*-chloroperbenzoic acid [7b]. Anal. Found: C, 45.2; H, 2.4; S, 20.1. $C_{12}H_8Cl_2O_2S_2$ calcd.: C, 45.1; H, 2.5; S, 20.1%. The following symmetric disulphides were obtained by oxidation of the appropriate thiol with iodine in the presence of base [8] and were shown to have the expected physical properties: $(o\text{-}MeOC_6H_4S)_2$, $(p\text{-}MeOC_6H_4S)_2$ and $(p\text{-}ClC_6H_4S)_2$.

### *Reactions*

*Allyl bromide and $Ph_4SbSC_6H_4OMe$-o.* Allyl bromide (0.046 g, 0.380 mmol) was syringed into the yellow solution of $Ph_4SbSC_6H_4OMe$-*o* (0.216 g, 0.380 mmol) (δ 3.35) in $CDCl_3$ solution (0.4 ml). Reaction was immediate as shown both by $^1H$ NMR (δ 3.80) and visible spectra (colourless solution). Removal of

most of the solvent and addition of hexane led to the precipitation of $Ph_4SbBr$. This was collected by filtration, 0.173 g, 88%, m.p. 213—215°C, lit. [9] m.p. 214—216°C. The filtrate, on evaporation, gave a residue, 0.060 g, which from the mass (*m/e* 180) and NMR spectra was $CH_2{=}CHCH_2SC_6H_4OMe$-*o*. The mass spectrum indicated that a little $PhSC_6H_4OMe$-*o* was also present.

*Cinnamyl bromide and $Ph_4SbSC_6H_4OMe$-o.* Cinnamyl bromide (0.111 g, 0.563 mmol) and $Ph_4SbSC_6H_4OMe$-*o* (0.321 g, 0.465 mmol) were dissolved in $CHCl_3$ (0.5 ml). After 5 minutes, the solvent was removed and warm hexane added to the residue. The precipitate of $Ph_4SbBr$ (0.240 g, 84%) was collected and well washed with hot hexane. The hexane fractions were evaporated to leave solid, $PhCH{=}CHCH_2SC_6H_4OMe$-*o*, which was recrystallised from hexane, 0.125 g, 87%; m.p. 87—88°C, lit. [10] m.p. 88.5—89.5°C. Anal Found: C, 74.8, H, 6.3, S, 12.4. $C_{16}H_{16}OS$ calcd.: C, 75.0; H, 6.2; S, 12.5%. $^1H$ NMR (220 MHz in $CDCl_3$): $PhCH^c{=}CH^bCH_2\ ^aC_6H_4OMe$-*o*: δ $H^a$ 3.68, $H^b$ 4.24, $H^c$ 4.41. $J_{ab}$ 8 Hz, $J_{bc}$ 15 Hz, OMe 3.85, aryl protons centred at 6.84 and 7.26 (multiplets). No evidence for $PhCH(SC_6H_4OMe$-*o*$)CH{=}CH_2$ in the reaction medium was obtained.

*trans-β-Bromostyrene and $Ph_4SbSC_6H_4OMe$-p. trans*-β-Bromostyrene (0.064 g, 0.348 mmol) and $Ph_4SbSC_6H_4OMe$-*p* (0.198 g, 0.348 mmol) were dissolved in $CDCl_3$ (0.5 ml). The slow removal of $Ph_4SbSC_6H_4OMe$-*p* was monitored by $^1H$ NMR spectroscopy. After eight days at ambient temperature, no $Ph_4SbSC_6H_4OMe$-*p* remained. TLC (silica gel G.F.$_{254}$ using $CHCl_3$/hexane (1/9) as eluant) and GLC (Column: $2\frac{1}{2}$% silicone gum rubber (E 301) on Chromosorb G-AW-DMCS 80—100 mesh) confirmed the presence of significant amounts of $PhSC_6H_4OMe$-*p*, $(p\text{-}MeOC_6H_4S)_2$ and $Ph_3Sb$, products of the decomposition of $Ph_4SbSC_6H_4OMe$-*p*. In addition, the substitution products, $Ph_4SbBr$ and *trans*-$PhCH{=}CHSC_6H_4OMe$-*p* were also indicated.

*Benzoyl chloride and $Ph_4SbSC_6H_4OMe$-p.* Addition of benzoyl chloride (0.040 g, 0.285 mmol) by syringe to a solution of $Ph_4SbSC_6H_4OMe$-*p* (0.162 g, 0.285 mmol) in $CDCl_3$ (0.5 ml) produced an immediate reaction as shown by $^1H$ NMR spectroscopy. Removal of the solvent and addition of hot hexane to the oily residue caused the precipitation of $Ph_4SbCl$, 0.106 g, 80%, m.p. 204—206°C lit. [11] m.p. 204—205°C. From the filtrate, on concentration and on cooling, crystalline $PhCOSC_6H_4OMe$-*p* was obtained, 0.059 g, 85%, m.p. 95—96°C, lit. [12] m.p. 97°C; δ OMe 6.24. Anal. Found: C, 68.9; H, 5.1; S, 13.0. $C_{14}H_{12}O_2S$ calcd.: C, 68.8; H, 5.0; S, 13.1%.

*2,4-Dinitrobenzenesulphenyl chloride and $Ph_4SbSC_6H_4OMe$-p.* An instantaneous reaction occurred between $2,4\text{-}(NO_2)_2C_6H_4SCl$ (0.021 g, 0.090 mmol) and $Ph_4SbSC_6H_4OMe$-*p* (0.050 g, 0.089 mmol) (δ OMe 3.56) in $CDCl_3$ solution (0.4 ml). TLC indicated the presence of $2,4\text{-}(NO_2)_2C_6H_3SSC_6H_4OMe$-*p* (δ OMe 3.76). Separation of the major products was brought about by removal of $CDCl_3$ and addition of hexane to cause precipitation of $Ph_4SbCl$, 0.032 g, 80%.

*Iodine and $Ph_4SbSC_6H_4OMe$-o.* The compound, $Ph_4SbSC_6H_4OMe$-*o* (0.137 g, 0.241 mmol) reacted immediately with iodine (0.061, 0.240 mmol) in $CDCl_3$ solution to give $(o\text{-}MeOC_6H_4S)_2$ (δ OMe 3.86). A further quantity of $Ph_4SbSC_6H_4OMe$-*o* (0.137 g, 0.241 mmol) was added to the deep brown coloured solution, with formation of more $(o\text{-}MeOC_6H_4S)_2$. The solvent was removed to leave a residue, from which $Ph_4SbI$ was obtained on addition of hexane. The

$Ph_4SbI$ was collected and well washed with hot hexane, 0.255 g, 95%, m.p. 228—230°C, lit. [13] 225—226°C. The combined hexane fractions were concentrated and on cooling, $(o\text{-}MeOC_6H_4S)_2$, was obtained 0.045 g, 67%, m.p. 120°C, lit. [14], m.p. 119°C. Anal. Found: C, 60.5; H, 5.0; S, 22.9. $C_{14}H_{14}O_2S_2$ calcd.: C, 60.4; H, 5.0; S, 23.0%.

A similar reaction occurred between bromine and $Ph_4SbSC_6H_4OMe$-*p* to give high yields of $Ph_4SbBr$ and $(p\text{-}MeOC_6H_4S)_2$, m.p. 119°C, lit. [14], m.p. 119°C.

*Benzoyl peroxide and $Ph_4SbSC_6H_4OMe$-p.* A solution of $Ph_4SbSC_6H_4OMe$-*p* (0.050 g, 0.088 mmol) and $(PhCO_2)_2$ (0.021 g, 0.087 mmol) in benzene was heated for 5 min. GLC indicated the presence of $(p\text{-}MeOC_6H_4S)_2$. The solvent was removed and on addition of hexane, $Ph_4SbOCOPh$ was precipitated, 0.038 g, 77%, m.p. 160°C, lit. [15], m.p. 161—162.5°C.

*p-Toluenesulphonyl chloride and $Ph_4SbSC_6H_4OMe$-o.* An immediate reaction resulted between $p\text{-}MeC_6H_4SO_2Cl$ (0.043 g, 0.226 mmol) and $Ph_4SbSC_6H_4O$-Me-*o* (0.130 g, 0.226 mmol) in $CDCl_3$ solution (0.4 ml). The $^1H$ NMR spectrum indicated several products: δ OMe 3.86 [$(o\text{-}MeOC_6H_4S)_2$] and 3.45 (intensity ratio 6/1); δ Me 2.44, 2.39 and 2.24 (intensity ratio 3/2/3). Mass spectrum (20 eV) indicated the parent ions of $(o\text{-}MeOC_6H_4S)_2$, major product; $o\text{-}MeOC_6H_4$-$SSO_2C_6H_4Me$-*p* and $p\text{-}MeC_6H_4SO_2Cl$ as well as *m/e* cluster due to $Ph_4Sb^+$.

The analogous reaction between $Ph_4SbSC_6H_4OMe$-*p* and $p\text{-}MeC_6H_4SO_2Cl$ (0.195 mmol) led to disulphide, $(p\text{-}MeOC_6H_4S)_2$, as the major product with several *p*-tolyl products, δ Me 2.24, 2.33, 2.36, 2.40 and 2.46.

*p-Chlorophenyl p-chlorobenzenethiosulphonate and $Ph_4SbSC_6H_4OMe$-o.* Reaction between $p\text{-}ClC_6H_4SO_2SC_6H_4Cl$-*p* (0.019 g, 0.0596 mmol) and $Ph_4$-$SbSC_6H_4OMe$-*o* (0.034 g, 0.0597 mmol) in $CDCl_3$ (0.4 ml) was shown by $^1H$ NMR spectroscopy to be immediate, δ OMe change from 3.34 to 3.82. Removal of the solvent and addition of hexane led to the precipitation of $Ph_4$-$SbOSOC_6H_4Cl$-*p*, 0.022 g, 61%, m.p. 105°C dec. From the hexane filtrate, an oily residue was obtained on evaporation. The mass spectrum contained the parent ion of $p\text{-}ClC_6H_4SSC_6OMe$-*o* as well as those of the two symmetric disulphides, $(p\text{-}ClC_6H_4S)_2$ and $(o\text{-}MeOC_6H_4S)_2$.

*Chloromethyl methyl sulphide and $Ph_4SbSC_6H_4OMe$-p.* Reaction of $ClCH_2SMe$ (0.017 g, 0.176 mmol) and $Ph_4SbSC_6H_4OMe$-*p* (0.100 g, 0.176 mmol) in $CDCl_3$ (0.5 ml) was complete within 60 min at 34°C. The removal of solvent and addition of hexane led to the precipitation of $Ph_4SbCl$, 0.071 g, 87%. The hexane was removed from the filtrate to leave an oil, essentially (>99%), $MeSCH_2SC_6H_4OMe$-*p*, 0.047 g, δ MeS 2.17, $SCH_2S$ 3.86, MeO 3.75; mol.wt. Found: 200.0327. $C_9H_{12}OS_2$ cald.: 200.0329. The mass spectrum also indicated the presence of a little $PhSC_6H_4OMe$-*p*: mol.wt. Found: 216.0610. $C_{13}H_{12}OS$ calcd.: 216.0611.

*Chloromethyl methyl sulphide and $Ph_4SbSC_6H_4Br$-p.* Equimolar reaction (0.200 mmol) proceeded similarly to above to give $MeSCH_2SC_6H_4Br$-*p*, δ MeS 2.13, $SCH_2S$ 3.90, as the major sulphur containing product.

*Chloromethyl methyl sulphide and $Ph_3SnSC_6H_4OMe$-p.* The reaction between $Ph_3SnSC_6H_4OMe$-*p* (0.096 g, 0.196 mmol) and $ClCH_2SMe$ (0.074 mmol) in $CDCl_3$ (0.4 ml) at 34°C was monitored by $^1H$ NMR spectroscopy. Even after 5 days only 10% reaction had occurred.

*Chloromethyl methyl sulphide and $Ph_3SnSC_6H_4OMe$-p in the presence of*

*$Ph_4SbCl$.* The $^1H$ NMR spectrum of the colourless solution containing $Ph_4SbCl$ (0.101 g, 0.217 mmol) and $Ph_3SnSC_6H_4OMe$-*p* (0.089 g, 0.182 mmol) in $CDCl_3$ (0.4 ml), indicated that no anion exchange had occurred (δ OMe 3.62). Addition of $ClCH_2SMe$ (0.074 mmol) to this solution resulted in the slow formation of *p*-$MeOC_6H_4SCH_2SMe$, ca. 30% after 24 h at 34°C.

*Competition reaction involving chloromethyl methyl sulphide with $Ph_4SbSC_6H_4OMe$-p and $Ph_4SbSC_6H_5$.* To a solution of $Ph_4SbSC_6H_4OMe$-*p* (0.076 g, 0.134 mmol) and $Ph_4SbSC_6H_5$ (0.077 g, 0.143 mmol) in $CDCl_3$ (0.35 ml) at 34°C was added $ClCH_2SMe$ (0.074 mmol). The $^1H$ NMR (220 MHz) spectrum indicated the formation of both $MeSCH_2SC_6H_4OMe$-*p* (δ MeS 2.18, $SCH_2S$ 3.84 and MeO 3.73) and $MeSCH_2SPh$ (δ MeS 2.18, $SCH_2S$ 3.94); the molar ratio of these products being 1.05/1 after the complete consumption of the $ClCH_2SMe$. Sufficient additional $ClCH_2SMe$ was added to react completely with both the antimony mercaptides. The solvent was removed and hexane added to the oily residue to cause precipitation of $Ph_4SbCl$. The mass spectrum of the filtrate indicated that $MeSCH_2SPh$ and $MeSCH_2SC_6H_4OMe$-*p* were the major sulphide products.

## Results and discussion

As mentioned in the Introduction, the tetraphenylantimony mercaptides, $Ph_4SbSC_6H_4Y$, are thermally labile. Heating neat samples or refluxing in solution results in decomposition [4]. Even in chloroform solution at ambient temperature, some decomposition or reaction results but however only slowly, e.g. $Ph_4SbSC_6H_4OMe$-*p* (0.155 g in ca. 0.4 ml) was totally consumed after 14 days. This is sufficiently slow for use to be made of $Ph_4SbSC_6H_4Y$ as mercaptide transfer agents at this temperature. Thus reactions with several electrophilic reagents, e.g. halogens, allylic bromides, chloromethyl methyl sulphide, acyl chlorides and sulphenyl chlorides were shown to lead to high yields of substitution products under essentially mild and neutral conditions. Furthermore, as the separations of products are practically simple, these reactions are all viable synthetic methods. While the majority of the reactions involved $Ph_4SbSC_6H_4OMe$ (*o*- or *p*-), all $Ph_4SbSC_6H_4Y$ are expected to react similarly; this indeed was realised with $ClCH_2SMe$.

The 2/1 $Ph_4SbSC_6H_4Y$/halogen reactions are given in eq. 1. With relatively more halogen, appropriate quantities of $Ph_4SbX_3$ are formed. The first step in

$$2\ Ph_4SbSC_6H_4Y + X_2 \rightarrow 2\ Ph_4SbX + (YC_6H_4S)_2 \quad (1)$$

(X = Br or I)

the reaction is considered to be the formation of a sulphenyl halide and $Ph_4SbX$ (eq. 2). This is followed by reaction of the sulphenyl halide (eq. 3,

$$Ph_4SbSC_6H_4Y + X_2 \rightarrow Ph_4SbX + XSC_6H_4Y \quad (2)$$

Ar′ = $C_6H_4Y$) to give the overall reaction as described in eq. 1. That sulphenyl

$$Ph_4SbSC_6H_4Y + Ar'SX \rightarrow Ph_4SbX + Ar'SSC_6H_4Y \quad (3)$$

halides can react with tetraphenylantimony mercaptides was shown separately,

e.g. with $Ph_4SbSC_6H_4OMe$-*p* and 2,4-$(NO_2)_2C_6H_3SCl$.

The allylic bromide reactions (eq. 4) proceeded without rearrangement; thus the only allylic sulphide obtained in the reaction of $Ph_4SbSC_6H_4OMe$-*o* and

$$Ph_4SbSC_6H_4Y + RCH{=}CHCH_2Br \rightarrow Ph_4SbBr + RCH{=}CHCH_2SC_6H_4Y \quad (4)$$
$$(R = H \text{ or } Ph)$$

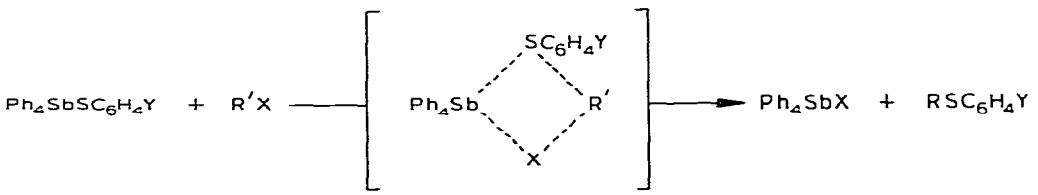
*trans*-$PhCH{=}CHCH_2Br$ was *trans*-$PhCH{=}CHCH_2SC_6H_4OMe$-*p*. The halogen, sulphenyl halide, allylic halide and benzoyl chloride (eq. 5, R = Ph) reactions were apparently instantaneous as indicated both by $^1H$ NMR spectra and by

$$Ph_4SbSC_6H_4Y + RCOCl \rightarrow Ph_4SbCl + RCOSC_6H_4Y \quad (5)$$
$$(R = Ph)$$

colour changes. Those of $ClCH_2SMe$, giving the mixed mercaptals (eq. 6) were slower but generally still required less than 60 min for completion. The yields of the mixed mercaptals were consistently good with all the $Ph_4SbSC_6H_4Y$

$$Ph_4SbSC_6H_4Y + ClCH_2SMe \rightarrow Ph_4SbCl + YC_6H_4SCH_2SMe \quad (6)$$

used. A competition reaction between $Ph_4SbSC_6H_4OMe$-*p* and $Ph_4SbSC_6H_5$ for a deficit of $ClCH_2SMe$ in chloroform solution at 34° C indicated only a minor difference in reactivities (based on products yields), with the $Ph_4SbSC_6H_5$ being ca. 1.2 times more reactive. Significantly the more reactive $Ph_4SbSC_6H_4Y$ had the least electron-releasing Y group. However, the small reactivity difference argues against a mechanism involving the dissociation of $Ph_4SbSC_6H_4Y$ to ion-paired $Ph_4Sb^+ \cdot \overline{SC_6H_4Y}$ as this, it is assumed, would lead to a greater dependence on the electron effects of the Y groups than found. A mechanism involving a four-centred transition state is a possibility as this would have only a small dependence on Y. The lack of allylic rearrangement in the cinnamyl bromide reaction (eqn. 4, R = Ph) could also be accounted for on the basis of this




( R′ = $MeSCH_2$ , R″ = $CH{=}{=}CHCH_2$ etc.)

mechanism. A radical nature to these reactions is not considered probable. The lack of solvent derived products and the lack of allylic rearrangement are among the factors which suggest a non-radical reaction. More work on the mechanism is scheduled and this will be reported in due course.

The reactions (eq. 1—6) all led to the simple substitution products. By contrast, reactions with *p*-toluenesulphonyl chloride, although as rapid, were more complex. The reaction of $Ph_4SbSC_6H_4OMe$-*o* did not lead solely to the substitution product, *o*-$MeOC_6H_4SSO_2C_6H_4Me$-*p*, although its presence among the

products was indicated in the mass spectrum. The $^1$H NMR spectrum showed two MeO-containing products (ratio 6/1); the major one being the disulphide, ($o$-$MeOC_6H_4S)_2$, δ MeO 3.86, and the other having δ MeO 3.45 probably due to the thiosulphonate, $o$-$MeOC_6H_4SO_2SC_6H_4Me$-$p$. Three $p$-$MeC_6H_4$ absorptions (δ 2.26, 2.40 and 2.46) were also indicated. A complex situation also arose in the reaction of $Ph_4SbSC_6H_4OMe$-$p$; several $p$-$MeC_6H_4$ absorptions were observed in the NMR spectrum (δ 2.24, 2.33, 2.36, 2.40 and 2.46) but only one δ MeO (3.77), that due to the disulphide ($p$-$MeOC_6H_4S)_2$, was observed. The formation of the disulphides are rationalized by reactions 7 and 8. Confirmation of a

$$Ph_4SbSC_6H_4OMe + p\text{-}MeC_6H_4SO_2Cl \rightarrow Ph_4SbCl + p\text{-}MeC_6H_4SO_2SC_6H_4OMe \quad (7)$$

$$Ph_4SbSC_6H_4OMe + p\text{-}MeC_6H_4SO_2SC_6H_4OMe \rightarrow Ph_4SbOS(O)C_6H_4Me\text{-}p + (p\text{-}MeC_6H_4S)_2 \quad (8)$$

rapid reaction between a thiosulphonate ($p$-$ClC_6H_4SO_2SC_6H_4Cl$-$p$) and $Ph_4SbSC_6H_4OMe$-$o$ was made independently. There have been several reports of formation of disulphides, RSSR′, from thiosulphonates, R″$SO_2$SR′, on reactions with thiols, RSH (especially in the presence of bases), and also their alkali metal salts, RSM [16]. Such reactions occur by nucleophilic attack on the divalent sulphur in the thiosulphonates. Our organoantimony findings adds to these reports. The natures of various methyl, i.e. $p$-tolyl, containing compounds were not fully investigated. However, there is no shortage of candidates for these products, e.g. unreacted $p$-$MeC_6H_4SO_2Cl$ (δ Me 2.46), the $O$-sulphinate, $Ph_4SbOS(O)C_6H_4Me$-$p$, and the products of its reaction with $p$-$MeC_6H_4SO_2Cl$ [the bis-sulphone ($p$-$MeC_6H_4SO_2)_2$] and with air [$Ph_4SbOS(O)_2C_6H_4Me$-$p$]. Oxidation of antimony sulphinates has in fact been reported [17]. On keeping the solutions, without vigorous attempts to exclude either moisture or air, further changes among the $p$-tolyl containing products occurred.

*trans*-β-Bromostyrene, *trans*-PhCH=CHBr, was insufficiently reactive towards $Ph_4SbSC_6H_4OMe$-$p$ for reaction to be a useful synthesis of *trans*-PhCH=$CHSC_6H_4OMe$-$p$. While some *trans*-PhCH=$CHSC_6H_4OMe$-$p$ was indeed formed, much of the $Ph_4SbSC_6H_4OMe$-$p$ (>50%) had decomposed during the eight days of the reaction at room temperature. It is clear that *trans*-PhCH=CHBr is at the lower limit of reactivity for useful synthesis.

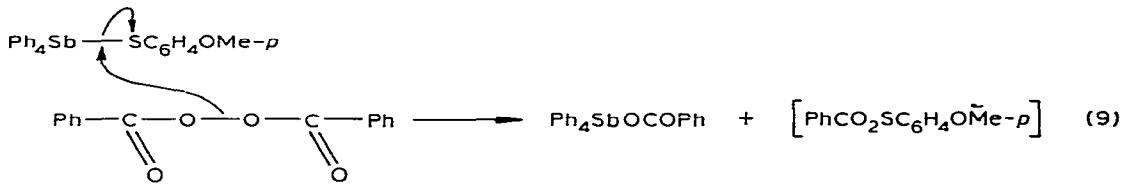
The organoantimony product isolated from the reaction of benzoyl peroxide with $Ph_4SbSC_6H_4OMe$-$p$, after a brief period of heating in benzene solution, was $Ph_4SbOCOPh$ and not $Ph_5Sb$. Some disulphide, ($p$-$MeC_6H_4S)_2$, was also detected by GLC and TLC. Benzoyl peroxide [18] can act as a nucleophile or as a radical source:

$$(PhCO_2)_2 \xrightarrow{\Delta} PhCO_2^{\bullet} \rightarrow Ph^{\bullet}$$

The formation of $Ph_4SbOCOPh$ can be accounted for by both a nucleophilic attack on antimony (e.g. eq. 9) or by trapping of the initial radical, $PhCO_2^{\bullet}$ (eq. 10). If $PhCO_2 \cdot O_2CPh$ is acting as a radical source, then $Ph_4SbSC_6H_4OMe$-$p$ clearly exhibits a considerable reactivity towards radicals in order to react with the initially produced radical, $PhCO_2^{\bullet}$.

Anion exchange equilibria involving organometallic mercaptides of antimony and tin have been demonstrated [1]. We have now shown that complete anion

exchange apparently occurs between $Ph_3SnCl$ and $Ph_4SbSC_6H_4OMe$-*p* in




$$Ph_4SbSC_6H_4OMe\text{-}p + PhCO_2 \rightarrow Ph_4SbO_2CPh + [p\text{-}MeOC_6H_4S^{\cdot}] \quad (10)$$

$CDCl_3$ solution as indicated by NMR spectroscopy (eq. 11). No exchange in the opposite direction could be detected by NMR, although there is some kinetic evidence for such an exchange.

$$Ph_3SnCl + Ph_4SbSC_6H_4OMe\text{-}p \rightarrow Ph_3SnSC_6H_4OMe\text{-}p + Ph_4SbCl \quad (11)$$

The compound, $Ph_3SnSC_6H_4OMe$-*p*, which is completely stable in chloroform solution at room temperature, reacts only very slowly with $ClCH_2SMe$, only ca. 10% reaction after 5 days at 34°C. However, in the presence of $Ph_4SbCl$ (mol ratio of $Ph_3SnSC_6H_4OMe\text{-}p/Ph_4SbCl > 1$), a considerably faster formation of *p*-$MeOC_6H_4SCH_2Me$ resulted. This catalytic effect must arise from an equilibrium process giving rise to kinetically significant but undetectable amounts (by NMR) of the more reactive, $Ph_4SbSC_6H_4OMe\text{-}p$.

*Spectral properties of $Ph_4SbSC_6H_4Y$.* The mass spectra of $Ph_4SbSC_6H_4Y$ were recorded at 20 and 70 eV. Owing to the necessarily high imput temperatures, some of the material will thermally decompose and so the mass spectra will consist of fragmentations induced by electrons and those resulting from thermolysis. The compounds, $Ph_3Sb$, $YC_6H_4SSC_6H_4Y$, $YC_6H_4SPh$ and $Ph_2$, arise in part or entirely by thermal means. In addition to *m/e* due to these species and their fragmentation products (e.g. $Ph_3Sb^+$, $Ph_2Sb^+$, $PhSb^+$), additional ions of interest are generally (i) $Ph_nSbSC_6H_4Y^+$ ($n$ = 1 or 2), (ii) $Ph_4Sb^+$ and (iii) $Sb_4^+$ and also $Sb_3^+$ and $Sb_2^+$. Antimony aggregates have been detected in the mass spectra of other organoantimony compounds [17]. More specifically, polynuclear aromatic compounds, $PhSC_6H_3Y(Ph)^+$ or $PhC_5H_4SC_6H_4Y^+$ (Y = H or OMe) were detected. No molecular ion was detected even at 20 eV.

We have assigned a weak band in the region of ca. 320—343 $cm^{-1}$ to the Sb—S stretching frequency in the trigonal bipyramidal $Ph_4SbSC_6H_4Y$. According to Okawara and coworkers [18], calculations based on Gordy's rule [18] give the frequency of Sb—S single bond as 337 $cm^{-1}$.

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