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GROUP IVB ORGANOMETALLIC SULPHIDES

VIII *. REACTION OF TRIORGANO-GERMANIUM AND -TIN ARYL SULPHIDES WITH OXIDANTS. SOME REACTIONS OF TRIORGANO-GERMANIUM AND -TIN ARYL *O*-SULPHINATES WITH SULPHUR HALIDES

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Summary

R_3SnSAr are oxidised by H_2O_2, 2,4,4,6-tetrabromocyclohexa-2,5-dienone and $NaIO_4$ (in 1 : 1 ratio) to disulphides, ArSSAr. With $NaIO_4$ as the oxidant, Ph_3SnSAr, gives a complex triphenyltin periodate; however, with the other two oxidants, $(Ph_3Sn)_2O$ is produced. Ph_3GeSAr was oxidised by $NaIO_4$ to $(Ph_3Ge)_2O$ and ArSSAr.

Triorgano-germanium and -tin *O*-sulphinates, $R_3MOSOAr$ react with arenesulphenyl chlorides, ArSCl, giving thiosulphonates, $ArSS(O_2)Ar$, and with sulphur dichloride, producing di(sulphonyl) sulphides $ArS(O_2)SS(O_2)Ar$. Triorganogermanium *p*-toluene sulphonate readily formed by oxidation of the *O*—sulphinate derivative, does not react with arenesulphenyl chlorides.

Introduction

There are few reports of reactions of germanium—sulphur and tin—sulphur bonded species with oxidants. Among these oxidations are the following:

$$Ph_3GeSMe \xrightarrow[(NO_2)_2]{H_2O_2 \text{ or}} (Ph_3Ge)_2O \qquad \text{Ref. 2}$$

$$(Et_3M)_2S \xrightarrow[PhH/\Delta]{(PhCO_2)_2} 2Et_3MOCOPh + S \qquad \text{Ref. 3}$$

$$M = Ge, Sn$$

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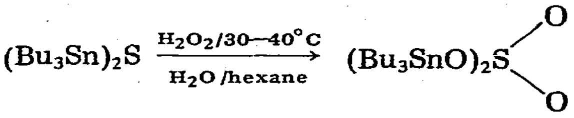
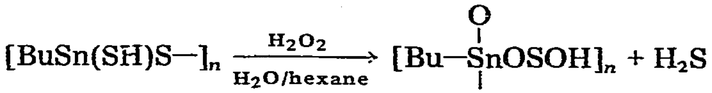


Ref. 4

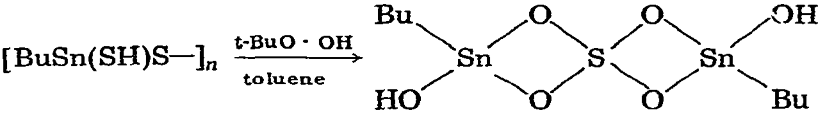
$(Bu_3SnS)_3$...

$(Bu_2SnS)_3 \xrightarrow[H_2O/hexane]{H_2O_2} \{[-OBu_2Sn]_2SO_4\}_n$ Ref. 4



$[BuSn(SH)S-]_n \xrightarrow[H_2O/hexane]{H_2O_2} [Bu-\overset{O}{\underset{|}{\overset{|}{Sn}}}OSOH]_n + H_2S$

Ref. 4



Ref. 5

Oxidations of carbon sulphides, to sulphoxides and sulphones, on the other hand, have been extensively studied and the necessary conditions established for a variety of oxidants [6]. The oxidised products $RS(O)_nR$ contain $\equiv C-\overset{O}{\underset{(O)_{n-1}}{S}}-C\equiv$ (n = 1, 2); since carbon is a borderline class a-b element [7], the isomers, $\equiv C-\overset{(O)_{n-1}}{S}-O-C\equiv$, viz. sulphenate esters [8] (n = 1) and *O*-sulphinates [9] (n = 2), can also be formed. However, preparation of these latter compounds do not include direct oxidation of sulphides but rather reactions of the acids, $RS(O)_{n-1}OH$ or their salts.

Of the four types of compounds, represented by the formulae, $R_3M(O)_nSR')$ (n = 1,2), only the *O*-sulphinates for M = Ge and Sn are known [9—15]. These have been prepared by sulphur dioxide insertion into organometal bonds and by metathetic reactions of metal sulphinates and organometallic halides. Infrared spectral data generally and a crystal structure determination (specifically for $Me_3SnOS(O)CH_2-C\equiv CH$) [10] clearly indicate the *O*-sulphinate structure. The fact that no sulphoxides or sulphones $[R_{4-m}Sn(S(O)_nR')_m; n = 1, 2]$ of Sn, Ge and Pb are known can be accounted for by the metals significant class a (or hard) character and hence their stronger preference for bonding to oxygen before sulphur. The organometallic *O*-sulphenates, $R_{4-m}M(OSR')_m$, have not been isolated. Such compounds could possibly be formed in oxidation reactions of $R_{4-m}M(SR')_m$, after an initial oxygen atom transfer to the sulphur from the oxidant. Whether these compounds could survive in the oxidation media, in particular in regards to further oxidation or hydrolysis, is problematical. From Stapfer's work [4,5] on ≡Sn—S—Sn≡ bonded species further oxidation was shown, from the products formed, to occur.

It was thought of interest to look at more oxidation reactions of organometal sulphides, in particular of R_3GeSAr and R_3SnAr, a class of sulphides not hitherto oxidised, using limited quantities (1 : 1 molar ratio) of the oxidants. The fates of the ArS units were of particular interest.

Furthermore some reactions of triphenyl-germanium and -tin *p*-toluenesulphinates with sulphur halides are also reported.

Experimental

Mössbauer data were obtained as described previously [1].

Compounds

Triphenyltin *p*-t-butylphenyl sulphide, m.p. 113—115°C (Lit. [1] m.p. 112—115°C), triphenyltin *p*-tolyl sulphide, m.p. 102°C (lit. [1] m.p. 103—105°C), tributyltin *p*-tolyl sulphide, b.p. 190°C/0.1 mmHg (lit. [1] m.p. 190°C/0.1 mmHg) and triphenylgermanium *p*-t-butylphenyl sulphide, m.p. 107°C (lit. [16] m.p. 106—107.5°C) were prepared by published procedures.

Triphenylgermanium p-toluene-sulphinate and -sulphonate. Triphenylgermanium *p*-toluenesulphinate was prepared from $(Ph_3Ge)_2O$ (0.3 g, 0.48 mmol) and *p*-toluenesulphinic acid (0.15 g, 0.96 mmol) in light petroleum/ether, (1 : 1). After refluxing the solution for 20 min, the solvent was removed to leave a solid, m.p. 96—99°C (lit. [9] m.p. 96—97°C). IR: 791s, 1122s (lit. [17] ν_{as}(SOGe) 794, ν(SO) 1126 cm^{-1}).Found: C, 65.2; H, 5.2. $C_{25}H_{22}GeO_2S$ calcd.: C, 65.4; H, 4.8%.

The preparation of $Ph_3GeOS(O)C_6H_4Me$-*p* was also attempted in the following manner. Sodium *p*-toluenesulphinate tetrahydrate (2.0 g, 8 mmol) in water (60 ml) and triphenylgermanium bromide (3.0 g, 8 mmol) in diethyl ether (110 ml) were stirred vigorously overnight. The organic layer was collected, dried with anhydrous sodium sulphate and the solvent removed under reduced pressure to leave a white solid residue, yield 3.3 g. The IR spectrum of this solid indicated this was a mixture of $(Ph_3Ge)_2O$ (ν(GeOGe) 860 cm^{-1}, lit. [18] ν(GeOGe) 858 cm^{-1}) and *p*-toluenesulphinic acid. However, on crystallisation from light petroleum, the white mixture gave white crystals of $Ph_3GeOSOC_6H_4Me$-*p*, m.p. 97°C.

Triphenylgermanium *p*-toluenesulphinate, either on standing in air or on successive crystallisations from light petroleum, oxidised to triphenylgermanium *p*-toluenesulphonate, m.p. 144—147°C. IR spectrum 908s, 1170s, and 1328s cm^{-1} (lit. [19] for $ArSO_3H$ ν(SO) 900, $\nu_s(SO_2)$ 1160, $\nu_{as}(SO_2)$ 1350 cm^{-1}). Found: C, 62.6; H, 4.6; S, 6.9. $C_{25}H_{22}GeO_3S$ calcd.: C, 63.1; H, 4.6; S, 6.7%.

Triphenylgermanium *p*-toluenesulphonate, m.p. 146—150°C was prepared directly from $(Ph_3Ge)_2O$ (0.5 g, 0.8 mmol) and *p*-$MeC_6H_4SO_3H.H_2O$ (0.3 g, 1.6 mmol) in diethyl ether on refluxing. After removal of the solvent, the residue was recrystallised from $CHCl_3$ and light petroleum.

Triphenyltin and tributyltin *p*-toluenesulphinates were obtained from addition of an equimolar amount of the triorganotin chloride (in ether) to the sodium *p*-toluenesulphinate tetrahydrate in water. $Ph_3SnOS(O)C_6H_4Me$-*p*, m.p. 216—220°C (crystallised from benzene/light petroleum), yield 2.5 g, 93%. IR spectrum 950 cm^{-1}. Found: C, 59.5; H, 4.9; S, 6.6. $C_{25}H_{22}O_2SSn$ calcd.: C, 59.4; H, 4.4; S, 6.4%. $Bu_3SnOS(O)C_6H_4Me$-*p*, b.p. 175—180°C/0.2 mmHg, yield 14.5 g, 94%. IR spectrum 970 cm^{-1}.

p-Toluenesulphinic acid. To sodium *p*-toluenesulphinate (20 g, 0.11 mol) in water (100 ml) was added hydrochloric acid (6 *N*, 19 ml) to precipitate *p*-toleunesulphinic acid. This was collected, washed rapidly several times, with small portions of ice-cold water, dried under vacuum and recrystallised from diethyl ether/light petroleum, m.p. 83—85°C (lit. [20] m.p. 85°C).

2,4,4,6-Tetrabromocyclohexa-2,5-dienone. Bromine (16 g, 0.1 mol) in glacial acetic acid (100 ml) was added dropwise to a solution of 2,4,6-tribromophenol (33.1 g, 0.1 mol) and sodium acetate (8.2 g, 0.1 mol) in glacial acetic acid (200 ml) at room temperature. The mixture was stirred for 30 min, then poured onto ice to precipitate the lemon-yellow coloured 2,4,4,6-tetrabromocyclohexa-2,5-dienone, which was recrystallised from chloroform, m.p. 125°C dec. (lit. [21] m.p. 124°C dec).

Other oxidants. Hydrogen peroxide and sodium metaperiodate were commercial samples. Fremy's salt was a gift from Dr. M. Moir.

Other reagents. o-Nitrobenzenesulphenyl chloride was prepared as described by chlorination of bis(*o*-nitrophenyl) disulphide in carbon tetrachloride, m.p. 74°C (lit. [22] m.p. 75°C). Sulphur dichloride was a redistilled commercial sample.

Solvents. All organic solvents were of the highest commercial grade available and were distilled prior to use.

Oxidation reactions

Sodium metaperiodate and triphenylgermanium p-t-butylphenyl sulphide. Triphenylgermanium *p*-t-butylphenyl sulphide (1.0 g, 2.3 mmol), dissolved in dioxane (30 ml), and a solution of sodium metaperiodate (0.4 g, 2.3 mmol) in distilled water (30 ml) were mixed, and stirred at room temperature for two days, giving a yellow solution and a white precipitate. The solid was collected by filtration and dissolved in dichloromethane. The dichloromethane solution was dried with anhydrous sodium sulphate and the solvent from the filtrate evaporated under reduced pressure. Light petroleum was added to the resulting white solid, the white insoluble crystals of bis(triphenylgermanium) oxide collected by filtration and recrystallised from light petroleum (b.p. 60—80°C), m.p. 176—179°C (lit. [23] m.p. 183—184°C), yield 0.45 g. The IR spectrum had bands at 860 cm^{-1} s (lit. [18] ν(GeO) 858 cm^{-1}). From the filtrate, by evaporation of the light petroleum under reduced pressure then recrystallisation from ethanol, bis(*p*-t-butylphenyl) disulphide was obtained, m.p. 85—87°C (lit. [21] m.p. 89°C), yield 0.25 g, 72%.

Sodium metaperiodate and triphenyltin p-t-butylphenyl sulphide. To a solution of triphenyltin *p*-t-butylphenyl sulphide (10.0 g, 0.195 mol) in dioxane (200 ml) was added sodium metaperiodate (4.5 g, 0.02 mol) dissolved in water (200 ml). On standing, a yellow coloured solution developed, the colour of which disappeared when the mixture was stirred overnight. The solvent was removed under reduced pressure, chloroform added to the white solid residue and the insoluble inorganic material removed by filtration. The solvent, from the filtrate was removed under reduced pressure and the residue washed with light petroleum. The IR spectrum of the white powder remaining showed a band at 770 cm^{-1}, characteristic of bis(triphenyltin) oxide [25], although by comparison with the IR spectrum of an authentic sample of bis(triphenyltin) oxide, the amount of bis(triphenyltin) oxide was seen to be fairly small. Washing this mixture with ethanol, left a white powder, m.p. 152—154°C, yield ca. 3.5 g; IR:

1078s, 1065(sh), 1025s, 1015(sh), 1000s, 990m, 975w, 891m, 730s(br), 698(br). Analysis: Found: C, 52.8; H, 4.1; I, 7.6; Sn, 29.5. $C_{72}H_{61}IO_6Sn_4$ calcd.: C, 53.1; H, 3.8; I, 7.8; Sn, 29.4%. The solvent from the light petroleum filtrate was removed under reduced pressure yielding crude bis(*p*-t-butylphenyl) disulphide, m.p. 81—85°C (lit. [24] m.p. 89°C), yield 2.7 g, 85%.

Sodium metaperiodate and triphenyltin p-tolyl sulphide. (a) Sodium metaperiodate was treated with triphenyltin *p*-tolyl sulphide using the same conditions detailed above for the reaction of sodium metaperiodate with triphenyltin *p*-t-butylphenyl sulphide. The same tin-containing product was obtained, as well as di-*p*-tolyl disulphide, m.p. 44°C (lit. [26] m.p. 46°C).

(b) A solution of sodium metaperiodate (0.12 g, 0.56 mmol) in water (6 ml) was added to a solution of triphenyltin *p*-tolyl sulphide (0.5 g, 1.06 mmol) in dioxane (6 ml). On standing, no yellow colour was observed. The mixture was stirred overnight, then the solvent removed under reduced pressure. Chloroform was added to the residue and the inorganic material removed by filtration. The filtrate was shown, by thin layer chromatography, to contain di-*p*-tolyl disulphide, but not triphenyl tolyl sulphide. The solvent from the filtrate was removed under reduced pressure, and the IR spectrum taken of the white solid residue. The IR spectrum indicated that the residue contained bis(triphenyltin) oxide.

Sodium metaperiodate and triphenyltin hydroxide. A solution of sodium metaperiodate (0.1 g, 0.47 mmol) in water (10 ml) was added to a solution of triphenyltin hydroxide (0.5 g, 1.4 mmol) in dioxane (10 ml) and the mixture stirred overnight. The solvent was removed under reduced pressure and chloroform added to the residue. The insoluble inorganic material was removed by filtration, then the solvent from the filtrate removed under reduced pressure. The residue was dissolved in a small volume of chloroform and a white powder, m.p. 135—155°C, precipitated by the addition of light petroleum. This white powder was washed thoroughly with hot water and hot light petroleum, m.p. 150—155°C, the IR spectrum was almost identical to that of the product from the reaction of a triphenyltin aryl sulphide and sodium metaperiodate.

Hydrogen peroxide and triphenyltin p-t-butylphenyl sulphide. Hydrogen peroxide (30% v/w, 0.21 ml, 3.9 mmol) dissolved in methanol (10 ml) was added to a solution of triphenyltin *p*-t-butylphenyl sulphide (2.0 g, 3.9 mmol) in refluxing methanol. The resulting solution was heated under reflux overnight. On cooling, bis(triphenyltin) oxide crystallised, m.p. 120—122°C (lit. [27] m.p. 123—124°C), yield 1.42 g. By evaporation of the methanol under reduced pressure and precipitation from the residual oil by the addition of ethanol, bis(*p*-t-butylphenyl) disulphide was obtained. Recrystallisation was from ethanol, m.p. 86—88°C (lit. [24] m.p. 89°C).

Fremy's salt and triphenyltin p-t-butylphenyl sulphide. Triphenyltin *p*-t-butylphenyl sulphide (1.0 g, 2 mmol) in dioxane (20 ml) was added quickly to a solution of Femy's salt (0.5 g, 2 mmol) and buffer (0.5 *N* potassium dihydrogen phosphate, 60 ml) in water (180 ml), and the resulting purple solution shaken overnight. Although the solution was decolourised, triphenyltin *p*-t-butylphenyl sulphide was recovered in 90% yield.

Dimethyl sulphoxide and triphenyltin p-t-butylphenyl sulphide. Triphenyltin *p*-t-butylphenyl sulphide (1.0 g, 2 mmol) dissolved in dimethyl sulphoxide (20 ml) was heated under reflux overnight. The brown solution thus produced was a mixture of many compounds, none of which was isolated.

Dimethyl sulphoxide and tri-n-butyltin p-tolyl sulphide. Tri-n-butyltin *p*-tolyl sulphide (8.26 g, 2 mmol) dissolved in dimethyl sulphoxide (2.3 g, 0.3 mol) was heated at ca. 170°C for three days. The mixture turned brown, and dimethyl sulphide was evolved. The brown mixture was distilled under reduced pressure, yielding only the starting material, tri-n-butyltin *p*-tolyl sulphide.

2,4,4,6-Tetrabromocyclohexa-2,5-dienone and triphenyltin p-t-butylphenyl sulphide. 2,4,4,6-Tetrabromocyclohexa-2,5-dienone (0.8 g, 2 mmol) dissolved in dioxane (8 ml) was added to a suspension of triphenyltin *p*-t-butylphenyl sulphide (1.0 g, 2 mmol) in dioxane/water, (8 : 2, v/v). The suspension was stirred overnight at room temperature, filtered and the solvent from the filtrate evaporated under reduced pressure. Methanol was added to the resulting oil to precipitate bis(*p*-t-butylphenyl) disulphide, which was crystallised from ethanol, m.p. 87—88°C (lit. [24] m.p. 89°C), yield 0.28 g, 80%.

Other reactions

o-Nitrobenzenesulphenyl chloride and triphenylgermanium p-toluenesulphinate. To a solution of triphenylgermanium *p*-toluenesulphinate (0.2 g, 0.44 mmol) in dry carbon tetrachloride (20 ml) was added a solution of *o*-nitrobenzenesulphenyl chloride (0.082 g, 0.44 mmol) in dry carbon tetrachloride (10 ml) and the resulting mixture stirred at room temperature for thirty minutes. The solvent was evaporated under reduced pressure and the products separated by thin layer chromatography, using chloroform as eluant. *o*-Nitrophenyl *p*-tolyl sulphide sulphone was obtained and recrystallised from chloroform/light petroleum (b.p. 60—80°C), m.p. 94—96°C (lit. [28] m.p. 97°C), yield 0.08 g, 79%. Analysis: Found: C, 50.6; H, 3.6; S, 20.9. $C_{13}H_{11}NO_4S_2$ calcd.: C, 50.5; H, 3.6; S, 20.7%.

o-Nitrobenzenesulphenyl chloride and triphenylgermanium p-toluenesulphonate. After heating overnight under reflux a solution of triphenylgermanium *p*-toluene sulphonate (0.05 g, 0.12 mmol) and *o*-nitrobenzenesulphenyl chloride (0.021 g, 0.12 mmol) in dry carbon tetrachloride, with the exclusion of light, thin layer chromatography showed that there was no reaction.

o-Nitrobenzenesulphenyl chloride and tri-n-butyltin p-toluenesulphinate. A solution of *o*-nitrobenzenesulphenyl chloride (0.87 g, 4.6 mmol) in anhydrous carbon tetrachloride (20 ml) was added dropwise to tri-n-butyltin *p*-toluene sulphinate (2.0 g, 4.6 mmol) dissolved in dry carbon tetrachloride (35 ml). The resulting solution was stirred at room temperature for one hour, then the solvent was removed under reduced pressure and light petroleum added to the residual oil, precipitating yellow *o*-nitrophenyl *p*-tolyl sulphide sulphone. Recrystallisation was from chloroform/light petroleum, m.p. 95—96°C (lit. [28] m.p. 97°C), yield 0.92 g, 65%.

o-Nitrobenzenesulphenyl chloride amd triphenyltin p-toluenesulphinate. *o*-Nitrobenzenesulphenyl chloride (0.19 g, 0.1 mmol) dissolved in dry carbon tetrachloride (10 ml) was added to a suspension of triphenyltin *p*-toluenesulphinate (0.5 g, 0.1 mmol) in refluxing carbon tetrachloride (75 ml), with the exclusion of light. The mixture was heated under reflux for twenty minutes to give a clear, pale-yellow, solution. The solvent was evaporated under reduced pressure and the products in the residual yellow oil separated by thin layer chromatography using chloroform as eluant. *o*-Nitrophenyl *p*-tolyl sulphide sulphone was obtained from the plate, m.p. 96—98°C (lit. [28] m.p. 97°C), yield 0.14 g, 46%.

Sulphur dichloride and tri-n-butyltin p-toluenesulphinate. To a solution of tri-n-butyltin *p*-toluenesulphinate (2.0 g, 4.5 mmol) in dry carbon tetrachloride (75 ml) was added a solution of sulphur dichloride (0.24 g, 23 mmol) in dry carbon tetrachloride. There was an immediate colour change from red to yellow, and the solution was stirred overnight at room temperature. The solvent was evaporated under reduced pressure, and bis(*p*-toluenesulphonyl) sulphide precipitated by addition of light petroleum to the residue. The product was collected by filtration and recrystallised from chloroform/light petroleum, m.p. 138—140°C (lit. [29] m.p. 138°C), yield 0.45 g, 56%. Analysis: Found: C, 49.8; H, 4.4; S, 27.8; $C_{14}H_{14}O_4S_3$ calcd.: C, 49.2; H, 4.1; S, 28.0%.

Results and discussion

The oxidants successfully used were sodium metaperiodate, 2,4,4,6-tetrabromocyclohexa-2,5-dienone (I) * and hydrogen peroxide, while no oxidations occurred with Fremy's salt and dimethyl sulphoxide.

Using the oxidants in a 1 : 1 molar ratio, $(Ph_3Sn)_2O$ was obtained from reaction of $Ph_3SnSC_6H_4$-t-Bu with both H_2O_2 and I as well as $(Ph_3Ge)_2O$ from reaction of $Ph_3GeSC_6H_4$-t-Bu with sodium metaperiodate. In all three reactions, the disulphide $(p\text{-t-BuC}_6H_4S)_2$, was produced in at least 70% yield.

In contrast to the $Ph_3GeSC_6H_4$-t-Bu/$NaIO_4$ reaction, the $Ph_3SnSC_6H_4$-t-Bu reaction did not lead to the simple $(Ph_3M)_2O$ compound, but rather to a complex species II, analysing as C, 52.8; H, 4.1; I, 7.6; Sn, 29.5%. Basically, the same tin-containing compound was achieved from the analogous oxidation of $Ph_3SnSC_6H_4Me$-*p*, but not however from oxidations of R_3SnSAr, where R = Ph. In all these cases, the appropriate disulphides were always obtained in good yield, i.e. >80%.

Different preparations of this white, solid complex did give some slight differences in melting points (but always in the region 150—157°C) with also a little $(Ph_3Sn)_2O$ sometimes occurring. X-ray powder diffraction patterns were essentially the same. Crystallisation did not result in a really sharp melting point. The infrared spectrum indicated the absence of water of crystallisation (no absorptions at 3500 and 1650 cm^{-1}) and that neither Ph_3SnOH (e.g. no strong absorption at ca. 912 and 895 cm^{-1}) nor $(Ph_3Sn)_2O$ (no strong absorption at 770 cm^{-1}) were present in a free state in the complex or complex mixture. The Mössbauer parameters at 80 K were isomer shift +1.18 mm cm^{-1} (relative to $BaSnO_3$) and quadrupole splitting 2.12 mm sec^{-1}. This confirms the absence of free $(Ph_2SnO)_n$ as well as of Ph_3SnOH and $(Ph_3Sn)_2O$ but is indicative of a Ph_3SnO species [31]. The average line width at half height of the absorption peaks was 0.93. In the mass spectrum, the highest *m/e* value at 70 eV was at 716 indicating $[Ph_3SnOSnPh_3]^+$, with all the features of the fragmentations of an authentic sample of $(Ph_3Sn)_2O$. The complex II gave a weak postive test for periodate [32].

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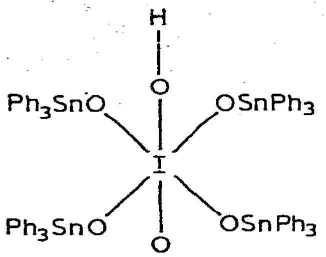
* This compound has been shown to oxidise organic sulphides to sulphoxides [30].

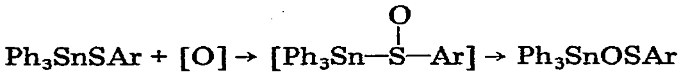
II was also obtained from reactions of Ph_3SnOH with sodium metaperiodate but not however from Ph_3SnSAr with sodium iodate, nor from Ph_3SnOH and HIO_3 (4 : 1 ratio).

All these data put together suggests, that II is of the type $(Ph_3Sn)_4IO_6H$. [$C_{72}H_{21}SnIO_6$ calcd.: C, 53.1; H, 3.8; I, 7.8; Sn, 29.4%]. The molecular weight (av. 830 ± 40) determinations indicated considerable dissociation in benzene solution.



(II)

The common initial step in all the oxidations in the mixed aqueous/organic solvent media could be oxygen-transfer to give a sulphoxide and followed by a rapid transformation to an organometallic sulphenate (III). To discuss the fate



$$Ph_3SnSAr + [O] \rightarrow [Ph_3Sn{-}\overset{O}{\overset{|}{S}}{-}Ar] \rightarrow Ph_3SnOSAr$$

(III)

of III, it is helpful to consider reactions of ArSOH or $ArSO^-$ generally. From Hogg and Vipond's paper [33] it appears that a variety of sulphur-containing products can be obtained from $ArSO^-$ under basic conditions; the basicity of the media and the reaction time are two of the factors having some influence on the products. The sulphoxide, PhS(O)-t-Bu, has been shown [34] to be hydrolysed under acidic conditions initially to PhSOH, which then produced $PhS(O_2)SPh$ and PhSSPh. Furthermore in water, the product from the hydrolyses of *o*-nitrobenzebesulphenyl chloride [which should involve an ArSOH intermediate] has been considered either as a thiolsulphinate [35] ArSOSAr, or a mixture of the disulphide ArSSAr, thiolsulphonate $ArS(O_2)SAr$, and thiolsulphinate [36]. What can be extracted from this complexity is that hydrolysis of a sulphenic acid or its salt should not give a disulphide in a yield greater than 50%. Our yields of disulphide being at least 70% thus eliminate hydrolyses of $Ph_3SnOSAr$ as a significant step *. Thus, we propose the following reaction:

$$Ph_3SnOSAr + Ph_3SnSAr \rightarrow (Ph_3Sn)_2O + ArSSAr$$

In the presence of more $NaIO_4$, reaction occurs to give the complex periodate. If this sequence is correct, then 2 mol of Ph_3SnSAr would be oxidised per mole of metaperiodate. This was indeed found to be true. Furthermore $(Ph_3Sn)_2O$ was clearly detected as a major product in this reaction, unlike in the 1 : 1 reaction. The oxidations of the germanium sulphides must follow a similar course.

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* None of the infrared absorptions of $ArSO_2SAr$ were observed in the spectrum of the total product mixture.

Thus direct formation of organo-germanium and -tin *O*-sulphinates via oxidation of the corresponding aryl sulphides does not occur.

As well as looking at these oxidations, other potential routes to sulphinates and sulphenates were also investigated. These included reactions of disulphones, $ArS(O_2)(O_2)SAr$, with hexaorgano-ditins and -dileads. While the reactions of disulphides, ArSSAr, with R_6M_2 (M = Sn, Pb) to lead [37] to R_3MSAr, no reaction at all occurred with the disulphones. Another reaction attempted was of Ph_3SnLi with p-$MeC_6H_4S(O)Cl$; instead of obtaining the sulphenate, the product isolated was p-$MeC_6H_4SS(O_2)C_6H_4Me$-p. Disulphoxides, ArS(O)S(O)Ar, are unstable and would appear to undergo rapid isomerisation to thiolsulphinates, $ArS{-}S(O_2)Ar$ [38]. In attempts to account for the formation of the latter in the $ArSOCl/Ph_3SnLi$ reaction it is tempting to involve the following reactions:

$$Ph_3SnLi + ArSOCl \rightarrow Ph_3SnOSAr + LiCl$$

$$Ph_3SnOSAr + ArSOCl \rightarrow Ph_3SnCl + [ArS(O)S(O)Ar]$$

$$[ArS(O)S(O)Ar] \rightarrow ArS{-}SO_2Ar$$

$$(Ar = p\text{-}MeC_6H_4)$$

Reactions of organometal O-sulphinates

We have reported some reactions of Group IVB organometallic sulphides with electrophilic reagents, including sulphur halides. The *O*-sulphinate group is a potential ambient nucleophile and it was thought of interest to look at reactions of $R_3MOS(O)Ar$ (M = Ge, Sn) with sulphur halides. The products of these reactions are shown and clearly show the ambient nature of the sulphinate group:

$$R_3MOS(O)C_6H_4Me\text{-}p + o\text{-}NO_2X_6H_4SCl \rightarrow R_3MCl + o\text{-}NO_2C_6H_4S{-}S(O_2)C_6H_4Me\text{-}p$$

$$(M = Ge, R = Ph; M = Sn, R = Ph, Bu)$$

$$2BuSnOS(O)C_6H_4Me\text{-}p + SCl_2 \rightarrow 2Bu_3MCl + p\text{-}MeC_6H_4S{-}S(O_2)SC_6H_4Me\text{-}p$$

The sulphonate derivative, $Ph_3GeOS(O_2)C_6H_4Me$-p (IV) on the other hand, did not react with o-$NO_2C_6H_4SCl$. IV was found to be very easily obtained by oxidation of $Ph_3GeOS(O)C_6H_4Me$-p, e.g. on recrystallisation in air from light petroleum solutions. $Ph_3GeOS(O)C_6H_4Me$-p was also easily hydrolysed unlike the tin analogue.

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