Group IVB Organometallic Sulphides. Part V.[1] Reactions of Lead Sulphides with Some Electrophilic Species and Mercury Compounds. Comparison of the Reactions of Aryl Triorganolead Sulphides with Those of the Other Group IVB Sulphides

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Reactions of aryl triphenyl-lead sulphides, Ph_3PbSAr, with halogens, sulphur(II) halides, carbon halides, and mercury halides are reported. Unlike the analogous tin and germanium reactions, the reactions of the organolead sulphides do not lead exclusively to cleavage of the metal–sulphur bond. Ease of cleavage of the phenyl–lead bond, decomposition of organolead(IV) compounds to inorganic lead(II) species, and photochemical reaction with solvents, such as carbon tetrachloride, all make the organolead sulphide reactions particularly complex. Similiarities and differences in the reactions of R_3MSAr compounds, where $R \neq H$, M = C, Si, Ge, Sn, and Pb are mentioned. Some bis(arylthio)lead reactions are also reported.

REACTIONS of Group IVB organometallic sulphides have been fairly widely reported,[2] with almost all reactions involving cleavage of the metal–sulphur bonds. Earlier, we reported [3] upon cleavage of the tin–sulphur and germanium–sulphur bonds, mainly in R_3MSAr ($M = Ge$ or Sn) but also in $(R_3Sn)_2S$ and $(R_2SnS)_3$ compounds, by halogens, bivalent sulphur halides, carbon halides, and mercury(II) halides. Other studies with these reagents and related systems have been made including reactions of halogens with organosilicon, organogermanium, and organotin sulphides of differing types.[4] Silicon–sulphur bonds, as are germanium- and tin–sulphur bonds, are cleaved by sulphenyl halides (and esters) [5] and sulphur mono- and di-chlorides.[4a] A diverse array of carbon halides [4d,6] and mercury compounds have also been used. Tin sulphide reactions have been particularly well studied with the latter compounds, which include mercury(II) halides [4f,7a] (also with germanium sulphides),[7b] $Hg(OAc)_2$,[4f] $Hg(CH_2CO_2Me)_2$ (also with silicon and germanium sulphides),[7c] and $Hg(NPhCO_2Me)_2$.[7d] Mercury(II) oxide cleaves specifically silicon sulphides.[7e]

As is apparent from the foregoing, organolead sulphides have not been as well studied as the other Group IVB sulphides. We now wish to report some reactions of aryl triphenyl-lead sulphides. In order to make a more useful comparison of these lead sulphide reactions with those of the other Group IVB sulphides, some tin sulphide reactions are also reported. Furthermore, some related reactions of bis(arylthio)lead compounds are included.

EXPERIMENTAL

Materials.—Solvents were dried when necessary with calcium hydride.

Triphenylmethyl chloride, thiols, sulphur mono- and di-chlorides were all purified commercial samples. Phenylmercuric chloride was a recrystallised sample from a previous study [3] (Found: C, 22·7; H, 1·8; Cl, 11·2. Calc. for C_6H_5ClHg: C, 23·0; H, 1·6; Cl, 11·3%). Diaryl disulphides, $(p\text{-X-}C_6H_4S)_2$; X = H, CH_3, Cl, and Bu^t, were prepared by oxidation of the appropriate thiols, with iodine in alkaline media; [8] all had physical properties in good agreement with literature values. *o*-Nitrobenzenesulphenyl chloride was prepared by chlorinating [10] di-*o*-nitrophenyl disulphide,[9] m.p. 74°, lit.,[10] m.p. 75°. *p*-Toluene- and *p*-chlorobenzene-sulphenyl chlorides were prepared from the chlorination of the appropriate thiol in carbon tetrachloride solution.[11]

Tin Compounds.—Tributyltin and triphenyltin chlorides were commercial samples. Aryl triorganotin sulphides, prepared in yields *ca.* 75% from the reaction of equimolar ratios (16 mmol) of triorganotin halides and thiols in carbon tetrachloride solutions in the presence of triethylamine, were either recrystallised or redistilled before use.

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Lead Compounds.—A sample of tetraphenyl-lead was generously given by Prof. G. J. M. van der Kerk and Dr. L. C. Willemsens on behalf of the International Lead Zinc Research Organisation Inc., New York. Additional material was prepared using van der Kerk and Willemsens' methods.[12,13] Triphenyl-lead iodide was prepared from iodine and tetraphenyl-lead.[15] It was recrystallised from ethanol–chloroform, m.p. 143°, lit.,[14] m.p. 142°. Hexaphenyldilead was prepared according to the basic method of van der Kerk and Willemsens.[13] Bis(*p*-tolylthio)lead was obtained from lead acetate and *p*-toluenethiol in almost quantitative yield,[15] m.p. 203—204°, lit.,[15] m.p. 197—199° (Found: C, 36·7; H, 3·4; S, 14·2. Calc. for $C_{14}H_{14}S_2Pb$: C, 37·0; H, 3·1; S, 14·1%).

Aryl triphenyl-lead sulphides were prepared by two different methods. First, from equimolar quantities of triphenyl-lead iodide and a thiol in tetrahydrofuran solution in the presence of a slight molar excess of triethylamine and secondly by the reaction of equimolar quantities of hexaphenyldilead and diaryl disulphide in refluxing aqueous benzene (1 : 20).[12] The crude products were recrystallised from ethanol. Yields of pure compounds from both methods were greater than 60%.

Organometallic sulphides

No.	Compounds	Method of preparation[a]	M.p. or b.p./mmHg (t/°C) Present work	M.p. or b.p./mmHg (t/°C) Lit. value	Analysis * (%) C	Analysis * (%) H	Analysis * (%) S
(1)	$Ph_3SnSC_6H_4\text{-}Bu^t\text{-}p$	A	112	105[b]	65·6 (65·3)	5·2 (5·4)	6·1 (6·2)
(2)	Ph_3SnSPh	A	102—103	102—103[c]	63·0 (62·8)	4·3 (4·4)	7·0 (7·0)
(3)	$Bu_3SnSC_6H_4\text{-}CH_3\text{-}p$	A	132/0·08		54·9 (55·2)	8·5 (8·2)	8·0 (7·8)
(4)	Ph_3PbSPh	B	109	105[d]	52·7 (52·6)	3·4 (3·7)	5·9 (5·9)
(5)	$Ph_3PbSC_6H_4\text{-}CH_3\text{-}p$	A	121—122		53·4 (53·4)	4·2 (3·9)	
(5)	$Ph_3PbSC_6H_4\text{-}CH_3\text{-}p$	B	119—120		53·4 (53·4)	3·8 (3·9)	5·4 (5·7)
(6)	$Ph_3PbSC_6H_4\text{-}Cl\text{-}p$	B	101·5—102·5	102·5[d]	49·5 (49·5)	3·6 (3·3)	5·2 (5·5)
(7)	$Ph_3PbSC_6H_4\text{-}Bu^t\text{-}p$	B	110·5—112		56·3 (55·7)	5·0 (4·6)	5·4 (5·3)

* Calc. in parentheses.

[a] Method A: triorganometallic halide and thiol in presence of NEt_3; method B: hexaphenyldilead and disulphide. [b] Ref. 3(*a*). [c] Ref. 20. [d] Ref. 12.

Tributyltin p-*Tolyl Sulphide and Triphenylmethyl Chloride.*—A mixture of tributyltin *p*-tolyl sulphide (4·13 g, 10 mmol) and triphenylmethyl chloride (2·79 g, 10 mmol) in tetrahydrofuran was refluxed for 10 min. After cooling, the solvent was removed and a little ether added to the residue in order to precipitate triphenylmethyl *p*-tolyl sulphide, which was recrystallised from acetone (3·05 g, 83%), m.p. 151°, lit.,[16] m.p. 149° (Found: C, 85·2; H, 6·0; S, 8·4. Calc. for $C_{26}H_{22}S$: C, 85·3; H, 6·0; S, 8·8%).

Tributyltin p-*Tolyl Sulphide and Phenylmercury Chloride.*—Tributyltin *p*-tolyl sulphide (4·13 g, 10 mmol) and phenylmercury chloride (3·13 g, 10 mmol) were refluxed in benzene for 15 min. The solvent was removed and light petroleum (b.p. 40—60°) added to the residue and, on cooling in an acetone–CO_2 bath, phenylmercury *p*-tolyl sulphide crystallised out; this was recrystallised from light petroleum (b.p. 60—80°) (3·19 g, 80%), m.p. 103°, lit.,[17] m.p. 104° (Found: C, 39·1; H, 3·0; S, 7·8. Calc. for $C_{13}H_{12}HgS$: C, 38·9; H, 3·0; S, 8·0%).

Triphenyl-lead p-*Chlorophenyl Sulphide and* p-*Chlorobenzenesulphenyl Chloride.*—Solutions of triphenyl-lead *p*-chlorophenyl sulphide (1·19 g, 20 mmol) and *p*-chlorobenzenesulphenyl chloride (0·37 g, 21 mmol) in chloroform were mixed and then refluxed for 1 h. The solvent was removed to leave a solid residue, containing two major components. These were separated by preparative t.l.c. Di-*p*-chlorophenyl disulphide (0·38 g, 66%), m.p. 70°, lit.,[8b] m.p. 71° was obtained (Found: S, 22·3. Calc. for $C_{12}H_8Cl_2S_2$: S, 22·8%).

Triphenyl-lead p-*Tolyl Sulphide and* o-*Nitrobenzenesulphenyl Chloride.*—To a solution of triphenyl-lead *p*-tolyl sulphide (2·55 g, 4·5 mmol) in carbon tetrachloride (25 ml) at 0° was added a solution of *o*-nitrobenzenesulphenyl chloride (0·86 g, 4·5 mmol) also in carbon tetrachloride (10 ml). An immediate white precipitate (Ph_3PbCl) appeared. The reaction mixture was stirred at 0° for 4 h and then filtered. The filtrate was evaporated and the residue chromatographed using an alumina column with benzene as eluant to give *o*-nitrophenyl *p*-tolyl disulphide which was crystallised from ethanol (0·91 g, 62%), m.p. 69—72°, lit.,[8b] m.p. 74° (Found: C, 56·1; H, 3·7; S, 22·8. Calc. for $C_{13}H_{11}NO_2S_2$: C, 56·4; H, 4·0; S, 23·2%).

Triphenyl-lead p-*Tolyl Sulphide and* p-*Toluenesulphenyl Chloride.*—To a solution of triphenyl-lead *p*-tolyl sulphide (2·81 g, 5 mmol) in carbon tetrachloride was added a solution of *p*-toluenesulphenyl chloride (0·79 g, 5 mmol) in carbon tetrachloride. There was an immediate decolouration of the sulphenyl halide solution on mixing and formation of triphenyl-lead chloride. The precipitate was collected and the filtrate evaporated to leave a residue. To the residue was added light petroleum (b.p. 40—60°) to precipitate more triphenyl-lead chloride. The solution was filtered again and on cooling the pale yellow filtrate in an acetone–CO_2 bath, di-*p*-tolyl disulphide crystallised out (0·98 g, 79%), m.p. 44—45°, lit.,[8b] m.p. 46° (Found: C, 68·5; H, 5·4; S, 26·1. Calc. for $C_{13}H_{14}S_2$: C, 68·2; H, 5·7; S, 26·1%). Total triphenyl-lead chloride collected was 2·13 g, 90%.

Triphenyl-lead p-*Tolyl Sulphide and Sulphur Dichloride.*—To a solution of triphenyl-lead *p*-tolyl sulphide (1·82 g, 3·3 mmol) in tetrahydrofuran was added at −78° a solution of sulphur dichloride (0·17 g, 1·65 mmol) in tetrahydrofuran dropwise with stirring. When addition was complete, the solution was stirred at room temperature for 2 days. The solvent was then removed and light petroleum (b.p. 40—60°) added to the residue to yield a white solid and a yellow solution. The solution was filtered and the filtrate

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[17] M. P. Balfe, J. Kenyon, and R. Wicks, *J. Chem. Soc.*, 1946, 807.

gave on evaporation, a solid, which was recrystallised from ethanol, 0·16 g (Found: S, 32·6. Calc. for $C_{14}H_{14}S_3$: S, 34·6%).

Triphenyl-lead p-*Tolyl Sulphide and Bromine*.—To a solution of triphenyl-lead *p*-tolyl sulphide (1·03 g, 1·9 mmol) in carbon tetrachloride at −78° was added a solution of bromine (0·95 mmol) in the same solvent. Immediate decolouration of the bromine solution occurred with the precipitation of a white solid. T.l.c. of the reaction mixture with benzene indicated the presence of disulphide and both triphenyl-lead(IV) and lead(II) species (on spraying with dithizone).

Triphenyl-lead p-*Tolyl Sulphide and Iodine in the Presence of Potassium Iodide*.—To a solution of triphenyl-lead *p*-tolyl sulphide (2·81 g, 5 mmol) in tetrahydrofuran (25 ml) and water (25 ml) was added dropwise at 5° a solution of iodine (0·64 g, 2·5 mmol) and potassium iodide (2·08 g, 12·5 mmol) in tetrahydrofuran (12·5 ml) and water (2·5 ml). The brown colour of the tri-iodide solution immediately changed on addition. After the addition was complete, the pale yellow reaction mixture was heated at 60° for 2 h. The solvent was then removed and to the residue was added chloroform and water. The chloroform layer was collected, dried, and the solvent evaporated. To the residue was added light petroleum (b.p. 40—60°). A very pale yellow solid, Ph_3PbI, was collected (2·36 g, 83·5%), m.p. 143°, lit.,[14] m.p. 143° (Found: C, 38·2; H, 2·8. Calc. for $C_{18}H_{15}IPb$: C, 38·2; H, 2·7%). The filtrate gave on cooling in acetone–CO_2, di-*p*-tolyl disulphide, which was recrystallised from ethanol (0·16 g, 98·5%), m.p. 44—46°, lit.,[8b] m.p. 46° (Found: C, 68·6; H, 6·0. Calc. for $C_{14}H_{14}S_2$: C, 68·2; H, 5·7%).

Titration of Iodine against Triphenyl-lead p-*Tolyl Sulphide*.—An iodine solution in chloroform was added dropwise with stirring to a solution of triphenyl-lead *p*-tolyl sulphide (0·5613 g, 1 mmol) in chloroform at room temperature until the iodine colour persisted for at least 1 min after addition. The total iodine added was 1·37 mmol.

Triphenyl-lead p-*Tolyl Sulphide and Mercuric Chloride*.—To a solution of mercuric chloride (0·28 g, 1 mmol) in tetrahydrofuran was added a solution of triphenyl-lead *p*-tolyl sulphide (1·16 g, 2·1 mmol) in the same solvent at room temperature. The reaction mixture was refluxed for 2 h. A white precipitate, $PbCl_2$, was collected (0·19 g). The filtrate was shown by t.l.c. (benzene–light petroleum as eluant) to contain at least six products.

Reaction of Triphenyl-lead p-*Tolyl Sulphide and Phenylmercury Chloride*.—To a solution of triphenyl-lead p-tolyl sulphide (1·11 g, 2·98 mmol) in dry tetrahydrofuran was added a solution of phenylmercury chloride (0·62 g, 1·98 mmol) in tetrahydrofuran dropwise with stirring at 0°. Stirring was continued for a further 2 h at 0° after addition. The solvent was removed under reduced pressure and the resulting solid dissolved in chloroform and chromatographed on silica gel (column). Phenylmercury *p*-tolyl sulphide was initially collected with the second fraction containing phenylmercury *p*-tolyl sulphide mixed with some triphenyl-lead chloride. This latter mixture was separated by preparative t.l.c. [silica gel; CCl_4: $CHCl_3$ (1 : 1) as eluant]. Total yield of $PhHgSC_6H_4CH_3$ was 0·41 g, 51%, m.p. 106—107°, lit.,[18] m.p. 104° (Found: C, 38·7; H, 3·1; S, 7·9. Calc. for $C_{13}H_{12}SHg$: C, 39·0; H, 3·0; S, 8·0%).

Reaction of Triphenyl-lead p-*Tolyl Sulphide and Triphenylmethyl Chloride*.—Triphenyl-lead *p*-tolyl sulphide (0·76 g, 1·4 mmol) and triphenylmethyl chloride (0·38 g, 1·4 mmol) in tetrahydrofuran (10 ml) were left at room temperature for 15 h. The solvent was removed and on addition of carbon tetrachloride, triphenyl-lead chloride separated out and was collected (0·487 g, 76%). The filtrate gave, on evaporation, triphenylmethyl *p*-tolyl sulphide, which was crystallised from aqueous acetone (0·29 g, 58%), m.p. 148°, lit.,[17] m.p. 149° (Found: C, 84·9; H, 6·2; S, 9·1. Calc. for $C_{26}H_{22}S$: C, 85·3; H, 6·0; S, 8·8%).

Triphenyl-lead p-*Tolyl Sulphide and Methyl Iodide in Carbon Tetrachloride*.—To a solution of triphenyl-lead *p*-tolyl sulphide (0·75 g, 1·3 mmol) in carbon tetrachloride (50 ml) was added methyl iodide (0·19 g, 1·3 mmol). The reaction mixture was left in a stoppered vessel for 7 days at room temperature in the light; during this time solid Ph_3PbCl separated out, 0·40 g, m.p. 210°, lit.,[12] m.p. 210° (Found: C, 45·4; H, 3·0. Calc. for $C_{18}H_{15}PbCl$: C, 45·6; H, 3·2%).

Triphenyl-lead p-*Tolyl Sulphide and Methyl Iodide*.—A solution of triphenyl *p*-tolyl sulphide (0·65 g, 1·1 mmol) in methyl iodide (5 ml) was left in sunlight for 3 days. Decomposition was evident by the formation of a black deposit on the sides of the flask and a yellow precipitate in solution. This precipitate was collected (0·03 g, m.p. > 350°) and the solvent removed from the filtrate. To the residue was added carbon tetrachloride and a white precipitate, Ph_3PbI, collected, 0·20 g, m.p. 138°. The filtrate was chromatographed on an alumina column and methyl *p*-tolyl sulphide obtained.

Triphenyl-lead p-*Tolyl Sulphide and Carbon Tetrachloride*. (a) *In sunlight*. Triphenyl-lead *p*-tolyl sulphide (0·61 g, 1·1 mmol) in carbon tetrachloride (50 ml) gave after 13 days Ph_3PbCl (0·32 g), m.p. 209°. A little lead(II) material was also obtained.

(b) *In the dark*. No reaction occurred with the same concentration of triphenyl-lead *p*-tolyl sulphide, which was recovered.

(c) *In the presence of benzoyl peroxide*. To a warm solution of triphenyl-lead *p*-tolyl sulphide (0·82 g, 1·5 mmol) in carbon tetrachloride (5 ml), was added a little benzoyl peroxide (0·02 g). Immediate effervescence occurred and a little white precipitate appeared. The stoppered solution was left 2 days in the sunlight and then filtered; triphenyl-lead chloride, Ph_3PbCl (0·45 g), m.p. 208°, was collected. The filtrate was evaporated and carbon tetrachloride added; more precipitate appeared (0·08 g). The filtrate contained at least five components, including di-*p*-tolyl disulphide.

Bis(p-*tolylthio*)*lead and* o-*Nitrobenzenesulphenyl Chloride*.—To a suspension of bis-(*p*-tolylthio)lead (1·45 g, 3·2 mmol) in benzene was added a solution of *o*-nitrobenzenesulphenyl chloride (1·21 g, 6·4 mmol) in benzene. The mixture was stirred at room temperature for 4 h and centrifuged. The solvent was removed from the supernatant liquid and the resultant oil chromatographed (on silica gel column using benzene as eluant), to give *o*-nitrophenyl *p*-tolyl disulphide, which was crystallised from ethanol (1·35 g, 76%), m.p. 69—71°, lit.,[8b] m.p. 74° (Found: C, 56·4; H, 4·2; S, 23·3; N, 4·8. Calc. for $C_{13}H_{11}NO_2S_2$: C, 56·4; H, 4·0; S, 23·2; N, 5·1%).

Bis(p-*tolylthio*)*lead and Triphenylmethyl Chloride*.—To a suspension of bis(*p*-tolylthio)lead (3·1 g, 6·8 mmol) in benzene was added a solution of triphenylmethyl chloride (3·8 g, 13·7 mmol) in benzene. On addition of the triphenyl-

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[18] S. Takagi, H. Tsukatani, and H. Tanaka, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1951, **27**, 71.

methyl chloride, there was an immediate decolouration of the yellow lead thiolate. The reaction mixture was refluxed for 2 h, cooled, centrifuged, and decanted. The filtrate on evaporation gave an oil, from which triphenylmethyl *p*-tolyl sulphide separated on addition of hexane; recrystallisation was from acetone (3·3 g, 66%), m.p. 151°, lit.,[17] m.p. 149° (Found: C, 85·0; H, 6·0; S, 8·9. Calc. for $C_{26}H_{22}S$: C, 85·3; H, 6·0; S, 8·8%).

Bis-(p*-tolylthio)lead and Methyl Iodide*.—A suspension of bis(*p*-tolylthio)lead (0·76 g, 1·7 mmol) in methyl iodide (10 ml) was gently heated for 30 min. The orange solid (PbI_2) was collected and the filtrate evaporated to leave a colourless oil (0·35 g). This was chromatographed on alumina (carbon tetrachloride eluant) to give methyl *p*-tolyl sulphide (0·29 g, 63%) identical with an authentic sample.

RESULTS AND DISCUSSION

Preparation of Organolead Sulphides.—The major route to the triphenyl-lead aryl sulphides used in this study was the reaction of hexaphenyldilead with diaryl disulphides.[12] An analogous reaction has been used for the preparation of organotin sulphides,[19] but with less application. The other method of preparing the lead sulphides was from the reaction of triphenyl-lead iodide and the appropriate thiol in the presence of triethylamine.[20] Because Ph_3PbI had to be prepared from either tetraphenyl-lead or hexaphenyldilead, the method involving direct cleavage of $Ph_3Pb{\cdot}PbPh_3$ by disulphide was preferred.

Reactions.—Previously reported reactions of organotin, -germanium, and -silicon sulphides with some carbon halides, halogens, bivalent sulphur halides, and mercury halides are summarised in equations (1—6). As clearly found in this study the analogous reactions (equations 1—6, M = Pb) of the organolead sulphides, Ph_3PbSAr, are neither as selective or simple, especially with the more reactive electrophiles. However, the products indicated in these reactions could be obtained as the major, if not the sole ones, when attempts were made to control the reaction conditions. Among the extra compounds were products of lead–carbon bond cleavage, in particular lead(II) material. This additional material could be generally limited by the use of lower reaction temperatures and carefully controlled rates of mixing the reagents.

$$R_3MSR^1 + R^2X \longrightarrow R_3MX + R^2SR^1 \qquad (1)$$

e.g. $M = Si, Ge, Sn;\ R^1,R = \text{alkyl};\ R^2X = MeI$

$M = Ge, Sn;\ R^1,R = \text{alkyl or aryl};\ R^2X = Ph_3CCl$

$$2R_3MSR^1 + X_2 \longrightarrow 2R_3MX + R^1SSR^1 \qquad (2)$$

$X = Br, I$

$$R_3MSR^1 + R^2SCl \longrightarrow R_3MCl + R^2SSR^1 \qquad (3)$$

$$2R_3MSR^1 + S_mCl_2 \longrightarrow 2R_3MCl + R^1{}_2S_{m+2} \qquad (4)$$

$m = 1;\ M = Si, Ge, Sn \quad m = 2;\ M = Ge, Sn$

$$2R_3MSR^1 + HgX_2 \longrightarrow 2R_3MX + Hg(SR^1)_2 \qquad (5)$$

$$R_3MSR^1 + PhHgCl \longrightarrow R_3MCl + PhHgSR^1 \qquad (6)$$

Reactions with Halogens.—Specifically for the iodine reaction (equation 2, X = I, M = Pb) the addition of iodide ion and the use of partially aqueous solvent medium led to significant product selectivity with only a very little lead(II) iodide contaminating the two major products, triphenyl-lead iodide and diaryl disulphide. A greater selectivity of I_2/I^- mixtures compared to I_2 alone has also been shown by van der Kerk and Willemsens in reactions with hexaphenyldilead.[12] (Use of I_2/I^- in aqueous tetrahydrofuran there led to triphenyl-lead iodide and only a little PbI_2, while the iodine reaction in chloroform gave significant amounts of PbI_2 and tetraphenyl-lead as well as Ph_3PbI.) Van der Kerk and Willemsens implied that the change in selectivity was due to a nucleophilic I_3^- taking over from the electrophilic I_2. This need not be the case. Because I_3^- is involved in the equilibrium: $I_2 + I^- \rightleftharpoons I_3^-$, some free iodine, albeit in low concentration, must always be present and so the reaction could still be an electrophilic one involving iodine. Furthermore, a trihalide ion, Br_3^-, has been shown to act as an electrophile, *e.g.* in the halogenations of activated aromatic hydrocarbons.[21]

When iodine was titrated in this study against triphenyl-lead *p*-tolyl sulphide at room temperature in chloroform solution, 1·37 mole equivalents of the halogen were required, using the arbitary end point of the decolouration of the iodine within 1 min of its addition. More iodine would no doubt have reacted if a longer reaction time had been adopted. This behaviour should be contrasted with the suggested usage of iodine to quantitatively determine tin–sulphur compounds.[4e]

The free bromine reaction with triphenyl-lead *p*-tolyl sulphide was complex. No attempt was made to estimate the relative amounts of the products formed in the instantaneous reaction at −78°. Despite using a 2 : 1 mole ratio [as demanded by equation (2)], some starting material was present at the end of the reaction along with $PbBr_2$ and the other expected products.

Reactions with Sulphur Electrophiles.—Another reaction of particular complexity was that with disulphur dichloride; this was much more complex than the reactions with aromatic sulphenyl halides, ArSX. This is rationalised by the reduced reactivity of the latter compounds. The sulphenyl halide reactions gave fairly good yields of disulphide products. With $Ph_3PbSC_6H_4\text{-}CH_3\text{-}p$, sulphur dichloride gave a sulphide product which had a sulphur content intermediate between that expected for di-*p*-tolyl di- and tri-sulphides and should thus be considered as a mixture of the two. This reaction was thus of no synthetic value.

Reactions with Mercury Halides.—In line with the general findings, phenylmercury chloride gave a much

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clearer reaction than did the more reactive mercury(II) chloride. Good yields of aryl phenylmercury sulphides were produced in the reactions of the former.

Reactions with Carbon Halides.—Successful reactions with two carbon halides were obtained; these carbon halides were triphenylmethyl chloride and methyl iodide (for more details of the latters' reaction see below).

Photochemical Reactions.—Further complications with these organolead sulphide reactions were photochemical reactions with solvents such as carbon tetrachloride and chloroform leading to triphenyl-lead chloride. That these reactions were photochemical was suggested by the reactions occurring in sunlight but not in the dark. Several other products, including symmetric diaryl disulphides and lead(II) material, were formed. When a catalytic amount of benzoyl peroxide was added to a hot solution of triphenyl-lead *p*-tolyl sulphide in carbon tetrachloride, only a little solid Ph_3PbCl was evident immediately after the addition. Considering how poorly soluble Ph_3PbCl is in carbon tetrachloride (the primary reason for choosing this solvent for the reactions producing triphenyl-lead halides), little reaction could have occurred at this stage. On leaving this solution exposed to sunlight, a considerable amount of Ph_3PbCl precipitated (70% within 2 days).

The photochemical reactions of triphenyl-lead sulphides with these solvents were clearly slower than, for example, their reactions with sulphenyl chlorides and triphenylmethyl chloride and so these reactions could be performed without the exclusion of light in carbon tetrachloride solution. On the other hand, from equimolar quantities of the weaker electrophile, methyl iodide, and $Ph_3PbSC_6H_4Me$-*p* (1·3 mmol) in CCl_4 (*ca.* 0·3 mol), the only products after 13 days were from reaction of the organolead sulphide with carbon tetrachloride. Triphenyl-lead aryl sulphides did react with methyl iodide, however, when the latter was used in excess as the solvent especially on exposure to sunlight, suggesting another photochemical reaction.

Reactivity Comparisons of Organotin and Organolead Sulphides.—From previous studies,[6] trimethyl-tin and -lead alkyl sulphides, Me_3MSR, M = Sn, Pb, and from this study, aryl trimethyltin sulphides, Me_3SnSAr, and aryl triphenyl-lead sulphides, Ph_3PbSAr, all were found to react with an excess of methyl iodide to give the appropriate organometallic iodide. On the other hand, we also found that aryl triphenyltin sulphides, Ph_3SnSAr, did not react within an equivalent time, nor did these sulphides react with other methylating agents, such as dimethyl sulphate and methyl *p*-toluenesulphonate. Thus, these methyl iodide reactions clearly distinguish between the reactivities of Ph_3PbSAr and Ph_3SnSAr (but not however those of Me_3PbSMe and Me_3SnSMe).

The difference in reactivity between Me_3SnSAr and Ph_3SnSAr, Ar = *p*-MeC_6H_4, parallels the enhanced reactivity of Me_3SnAr over Ph_3SnAr, Ar = *p*-$MeOC_6H_4$, (by a factor greater than 10^2) towards perchloric acid.[22]

No other electrophile used in this study, including triphenylmethyl chloride and phenylmercury chloride, separated the reactivity of organotin and organolead sulphides. These two electrophilic species have however shown that Ph_3GeSAr was less reactive[3c] than Ph_3SnSAr.

Comparisons with Carbon Sulphides.—The general similarity of reactions, equations (1)—(3), (5), of Group IVB sulphides, R_3MSAr, M = Si, Ge, Sn, Pb extends also to M = C, when $R \neq H$. Thus, sulphenyl halides,[23] halogens,[24] and mercury compounds[25] can cause cleavage of R_3CSAr, especially when R_3C^+ is a particularly stable carbonium ion. When R = H, other reactions occur, *e.g.* bromination of H_3CSPh in acetic acid solution produces *p*- (mainly) and *o*-bromophenyl methyl sulphides.[24c] Although compounds, H_3MSPh, M = Si and Ge, are known,[26] it is extremely unlikely that any useful reactivity comparison could be made between these and H_3CSPh.

Lead Thiolate Reactions.—Considering the complexities of the organolead sulphide reactions and the toxicity of organolead compounds in general, the organolead reactions have very much less synthetic application than have the other organo–Group IVB reactions, especially those of the tin compounds. In contrast, the bis(arylthio)lead reactions with electrophiles could have utility. In this study, aromatic sulphenyl halides, triphenylmethyl chloride, and methyl iodide all gave high yielding reactions with $Pb(SC_6H_4$-Me-*p*$)_2$ to produce unsymmetric disulphides, triphenylmethyl *p*-tolyl sulphide and methyl *p*-tolyl sulphide respectively; in these reactions the insolubility of the lead(II) halides is a distinct advantage. Previous reports of bis(arylthio)lead reactions include those with sulphur dichloride[27] and sulphur.[15]

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