Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SULFUR DIOXIDE INSERTION INTO CARBON–LEAD BONDS

CLIFFORD W. FONG AND WILLIAM KITCHING
Department of Chemistry, University of Queensland, St. Lucia, Brisbane (Australia)

(Received September 2nd, 1969)

SUMMARY

The insertion of sulfur dioxide into a variety of carbon–lead systems has been studied, and all products possess *O*-sulfinato structures. Spectroscopic (IR, mass spectra and PMR) and molecular weight data strongly suggest the presence of bridging $-SO_2-$ and essentially planar R_3Pb moieties. Relative rates of insertion into a number of differing R–Pb bonds are completely in line with an electrophilic cleavage description of the insertion process. Differences from (*e.g.* ready poly-insertion) and similarities with the behaviour of analogous organotin systems are rationalised.

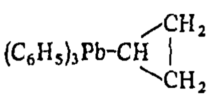
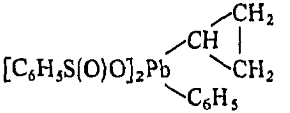
INTRODUCTION

Insertion reactions particularly involving carbon–metal bonds, are of much interest and recently a number of reports have described some aspects of sulfur dioxide insertion into a rather wide variety of carbon–metal systems[1-10]. We have taken the view that sulfur dioxide insertion into bonds between carbon and the heavy, more electropositive, borderline metals such as mercury[5,6], tin[1,2] and lead[9,10] are examples of electrophilic cleavage, producing organometal *O*- or *S*-sulfinates, and mechanisms accommodating these results have been advanced for the tin[1] and mercury[5] cases. A previous report[9] has drawn attention to the reaction between tetraorganolead compounds and sulfur dioxide, and both mono- and di-insertion products were characterised, and *O*-sulfinato structures were suggested. We initiated the present work because of its important place in the general framework of S_E reactions of carbon–metal systems, and to expose possible behavioral differences among the Group IV derived systems.

RESULTS AND DISCUSSION

The aims of this work were (a) to establish rigorously the *O*- or *S*-sulfinato nature of the insertion products and the coordination about lead (b) to provide information on relative rates of insertion and sites of insertion with various organic groups attached to lead and (c) to demonstrate rearrangements accompanying the insertion, as already shown for the related organotin systems[1]. Aims (a) and (b) were achieved but synthetic and stability problems were acute for the crotyllead systems required to test for allylic rearrangements. From a PMR approach, the trimethyllead(IV) derivatives (usually liquids) are eminently suitable but a number of con-

TABLE 1

Starting product	Insertion product	Analysis (%)				Reaction time (h)	M.p. (°C)
		Calcd.		Found			
		C	H	C	H		
$(CH_3)_4Pb$	$(CH_3)_3PbSO_2CH_3$	14.49	3.62	14.72	3.70	0.2	123–124
$(CH_3)_3PbC_6H_4$-*p*-F	$(CH_3)_3PbSO_2C_6H_4$-*p*-F	26.27	3.16	26.25	3.14	1	93–94
$(C_6H_5)_3PbCH_2C_6H_5$	$(C_6H_5)_2Pb(SO_2C_6H_5)CH_2C_6H_4$	50.59	3.70	50.27	3.72	0.5	143–144
$(C_6H_5)_3PbCH_2CH{=}CH_2$	$(C_6H_5)_3PbSO_2CH_2CH{=}CH_2$	46.39	3.68	46.70	3.87	<0.1	109–110
$(C_6H_5)_3PbCH_2C(CH_3){=}CH_2$	$(C_6H_5)_3PbSO_2CH_2C(CH_3){=}CH_2$	47.39	3.94	47.21	3.99	<0.1	216–217
$(C_6H_5)_3PbCH(CH_3)_2$	$[C_6H_5S(O)O]_3PbCH(CH_3)_2$	37.44	2.97	36.82	3.11	100	>300
 $(C_6H_5)_3Pb{-}CH\begin{smallmatrix}CH_2\\ \vert\\ CH_2\end{smallmatrix}$	 $[C_6H_5S(O)O]_2Pb\begin{smallmatrix}CH\begin{smallmatrix}CH_2\\ \vert\\ CH_2\end{smallmatrix}\\ C_6H_5\end{smallmatrix}$	41.51	3.29	42.11	3.52	100	>300
$(CH_3C_6H_4)_4Pb$	$(CH_3C_6H_4)_2Pb[OS(O)C_6H_4{-}CH_3]_2$	48.06	4.00	47.24	4.10	130	>300
$(CH_3)_3PbC_6H_5$	$(CH_3)_3PbSO_2C_6H_5$	27.46	3.56	27.55	3.76	[a]	99–100
$(CH_3)_3PbC_6H_4$-*p*-CH_3	$(CH_3)_3PbSO_2C_6H_4$-*p*-CH_3	29.46	4.17	29.62	3.88	[a]	72–73
$(CH_3)_3PbC_6H_4$-*p*-Cl	$(CH_3)_3PbSO_2C_6H_4$-*p*-Cl	25.25	3.03	25.42	3.11	0.2[a]	119–120
$(C_6H_5)_3PbCH_2C_6H_4$-*p*-F	$(C_6H_5SO_2)_3PbCH_2C_6H_4$-*p*-F	40.58	2.84	40.60	2.99	80	>300
$(C_6H_5)_3PbCH_2C_6H_4$-*m*-F	$(C_6H_5SO_2)_3PbCH_2C_6H_4$-*m*-F	40.58	2.84	41.13	3.01	80	>300

[a] Prepared by alternative method of synthesis, see experimental.

siderations led to the general use of the crystalline triphenyllead(IV) compounds. Firstly distillation (for purification) of $(CH_3)_3PbR$ leads to extensive redistribution giving product mixtures and we feared the toxicity of the liquid alkyllead compounds for the duration of a full program.

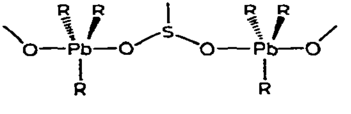
The equation describing monoinsertion may be written

$$R_3PbR' + SO_2 \rightarrow R_3Pb{-}SO_2{-}R'$$

although the site of insertion depends on the nature of R and R′ (*vide infra*). In some cases under certain conditions, di-insertion and tri-insertion may occur depending on reaction time, but monoinsertion products generally can be isolated. The starting compounds and insertion products are located in Table 1 together with analytical data (new compounds), and melting points, although the latter are quite indefinite in some cases, apparently due to agrregation, consistent with generally poor solubility. Most reactions were conducted in a chloroform/SO_2 solvent system for several days, but the allylic derivatives $(C_6H_5)_3PbR$ (R = allyl, 2-methylallyl) reacted rapidly with gaseous SO_2.

Structures of the products

The analytical data confirm the R_4PbSO_2, $R_4Pb(SO_2)_2$ or $R_4Pb(SO_2)_3$ formulations and all show S–O stretching frequencies ν_{as}(S–O) and ν_s(S–O) below 1000 cm^{-1} (nujol mulls), totally consistent with *O*-sulfinato structures in the solid, as previously suggested[1,6,9,10]. Solution spectra ($CHCl_3$) are essentially the same, so that *S*-sulfinato species (linkage isomers) are quite unimportant for lead, as they were for the tin systems. For trimethyllead methanesulfinate molecular weight measurements (CH_2Cl_2) indicate considerable aggregation ($i \sim 3$) and far IR spectra of the insertion products of tetramethyllead and the *para*-substituted phenyltrimethylleads show a single sharp lead–carbon stretching frequency at 495–509 cm^{-1}, assignable to ν_{as}(Pb–C). These agree with observations on organolead carboxylates[11]. The absence of a band assignable to ν_s(Pb–C) suggests that the $(CH_3)_3Pb$ fragment is planar (C_{3v} symmetry), since although ν_s(Pb–C) is not symmetry forbidden a rather weak band is expected due to the small change in dipole moment. A similar situation appears to apply with the triphenyllead sulfinates, and structures of the following types with bridging SO_2 groups and planar sulfur, are strongly indicated for the mono-insertion products. Alkyllead *O*-sulfinates have also been prepared from $(CH_3)_3PbCl$ and the sodium salts of appropriate arylsulfinic acids, and in one case (*p*-Cl) absolute identity has been established. Cyclic varieties, accommodating a five coordinate lead atom may also be written (*cf.* tin systems[1]). The trigonal bipyramidal array about lead is supported by the values of $J(^{207}Pb{-}CH_3)$ (82–84 Hz) in the in-



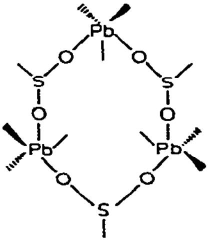


TABLE 2

Starting compound	PMR data[a]	Insertion compound	PMR data[a]
$(CH_3^a)_4Pb$	(a) 9.13, 1, $J'=60.5$	$(CH_3^a)_3Pb(SO_2)CH_3^b$	(a) 8.52, 1, $J'=84$ (b) 7.82, 1, $J'=0$
$(CH_3^a)_3PbC_6H_4^b\text{-}p\text{-}F$	(a) 8.95, 1, $J'=65$ (b) 2.73, complex	$(CH_3^a)_3Pb(SO_2)C_6H_4^b\text{-}p\text{-}F$	(a) 8.60, 1, $J'=82$ (b) 2.73 complex
$(CH_3^a)_3PbC_6H_4^b\text{-}p\text{-}Cl$[b]	(a) 8.96, 1, $J'=65.5$ (b) AA'BB' quartet centre 2.66	$(CH_3^a)_3Pb(SO_2)C_6H_4^b\text{-}p\text{-}Cl$	(a) 8.65, 1, $J'=82.5$ (b) 2.60, 1
$(CH_3^a)_3PbC_6H_5^b$[b]	(a) 8.95, 1, $J'=64$ (b) 2.43, 1	$(CH_3^a)_3Pb(SO_2)C_6H_5^c$	(a) 8.55, 1, $J'=88$ (b) 2.55, 1
$(CH_3^a)_3PbC_6H_4^b\text{-}p\text{-}CH_3^c$[b]	(a) 8.98, 1, $J'=65$ (b) AA'BB' quartet (c) 7.76, 1	$(CH_3^a)_3Pb(SO_2)C_6H_4^b\text{-}p\text{-}CH_3^c$	(a) 8.63, 1, $J'=83$ (b) AA'BB' quartet centre 2.70 (c) 7.65, 1
$(C_6H_5)_3PbCH_2^a\text{-}C_6H_5$	(a) 6.58, 1, $J'=76.5$	$(C_6H_5)_2Pb(CH_2^a\text{-}C_6H_5)(SO_2)C_6H_5$	(a) 6.64, 1, $J'=104$
$(C_6H_5)_3PbCH_2^a\text{-}C(CH_3^b)=CH_2^{c,d}$	(a) 7.03, 1, $J'=85.5$ (b) 8.28, 1, $J'=26$ (c) 5.26, 1, $J'=50$ (d) 5.45, 1, $J'=44$	$(C_6H_5)_3Pb(SO_2)CH_2^a\text{-}C(CH_3^b)=CH_2^c$	(a) 8.27, 1, $J'=0$ (b) 8.27, 1, $J'=0$ (c) 5.27, 1, $J'=0$
$(C_6H_5)_3PbCH_2^a\text{-}CH^b=CH_2^c$	(a) 7.06, 2, $J=8$, $J'=88$ (b) 3.84 complex, $J'=44$ (c) 5.26 complex, $J'=50$	$(C_6H_5)_3Pb(SO_2)CH_2^a\text{-}CH^b=CH_2^c$	(a) 7.63, 1, $J=6.5$, $J'=0$ (b), (c) 5.17 complex
$(C_6H_5)_3PbCH^a(CH_3^b)_2$	(a) 7.15, 7, $J=7.5$ (b) 8.25, 2, $J=7.5$, $J'=173$	$Pb[(SO_2)C_6H_5]_3CH^a(CH_3^b)_2$	insoluble

---

[a] Protons indicated by superscripts are given in the order: τ value (ppm), multiplicity, $J(={}^1H\text{-}{}^1H$ coupling) (Hz), $J'(={}^{207}Pb\text{-}{}^1H$ coupling) (Hz). $(C_6H_5)_3Pb$ resonances arose uniformly in the region τ 2.5, and all spectra integrated satisfactorily. Spectra were run in $CDCl_3$ from internal TMS standard. [b] See ref. 20.

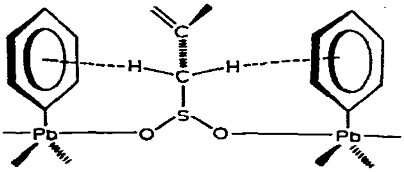
sertion products, such values being appropriate for the suggested planar $(CH_3)_3Pb$ moieties, if the proposal, that the 6*s*-orbital will concentrate in the bonding orbitals towards the least electronegative ligands, is accepted. *J* values of this magnitude[12] have been observed for five coordinate complexes $(CH_3)_3PbCl \cdot L$ (L = DMSO, pyridine-*N*-oxide etc.).

Products of tri- and di-insertion, are too insoluble to allow probing of solution properties. This insolubility, indicative of long-chain association, and IR spectra, suggest polymeric structures with linear R_2Pb skeletons and bridging SO_2 group (for di-insertion) so that an octahedral array about lead results. These products however, were only cursorily studied.

Proton magnetic resonance spectra

The PMR data for the sufficiently soluble compounds is located in Table 2.

In most cases the persistence or disappearance of lead–proton coupling confirms the site of insertion, and it is quite clear that the relative order of reactivity of the various lead–carbon bonds is phenyl > methyl; phenyl > benzyl and allyl > phenyl. These sequences will be considered in the section on mechanism. In Fig. 1 is the allyl portion of the spectrum of 2-methylallyltriphenyllead and its insertion product, and it is striking that the $-CH_2-$ resonance moves upfield (*i.e.* to higher τ values) by 73 Hz as a result of insertion. This is contrary to the behaviour of the methanesulfinate resonance in the insertion product of tetramethyllead, which suffers a substantial downfield shift of 78 Hz compared with its precursor. We believe the former observation is due to diamagnetic shielding associated with a certain geometrical proximity of the CH_2- group and the phenyl groups attached to lead. This is extraordinarily feasible for a planar triphenyllead moiety as molecular models and the figure indicate. Similar observations[13] for certain triphenyltin sulfinates have been made also. Such a structure, with an achiral sulfur center accounts also for methylene proton equivalence in the allyl cases, and some details of the arguments have been outlined previously[1,3].



Mass spectra

We suggested, on the basis of far IR and PMR data, that the lead-*O*-sulfinates were aggregated with planar Me_3Pb moieties. Direct evidence for aggregation in the vapor phase was obtained from mass spectral measurements in a number of cases.

The mass spectrum of $(CH_3)_3PbOS(O)CH_3$ (Fig. 2a) shows a small molecular ion (for monomer) (less than 1% base peak) at *m/e* 332, and a fragment of mass 362 identifiable by its lead isotopes. This latter peak could arise only from an aggregated species, hence surviving under conditions of direct sample heating (150°) in the ion

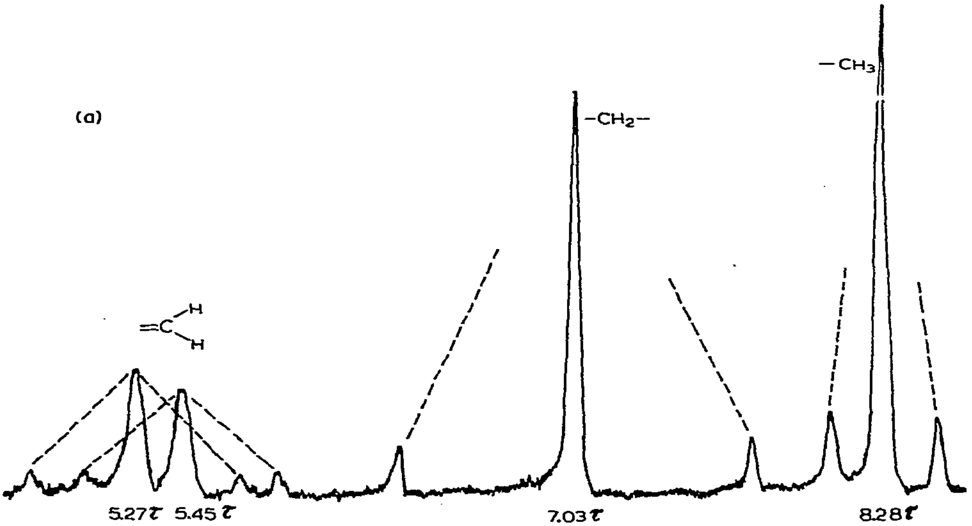


Fig. 1(a). 60 MHz spectrum of 2-methylallyltriphenyllead ($CDCl_3$), with aromatic resonance omitted. Assignments are on the figure and ^{207}Pb–^{1}H coupling is indicated; J values are in Table 2.

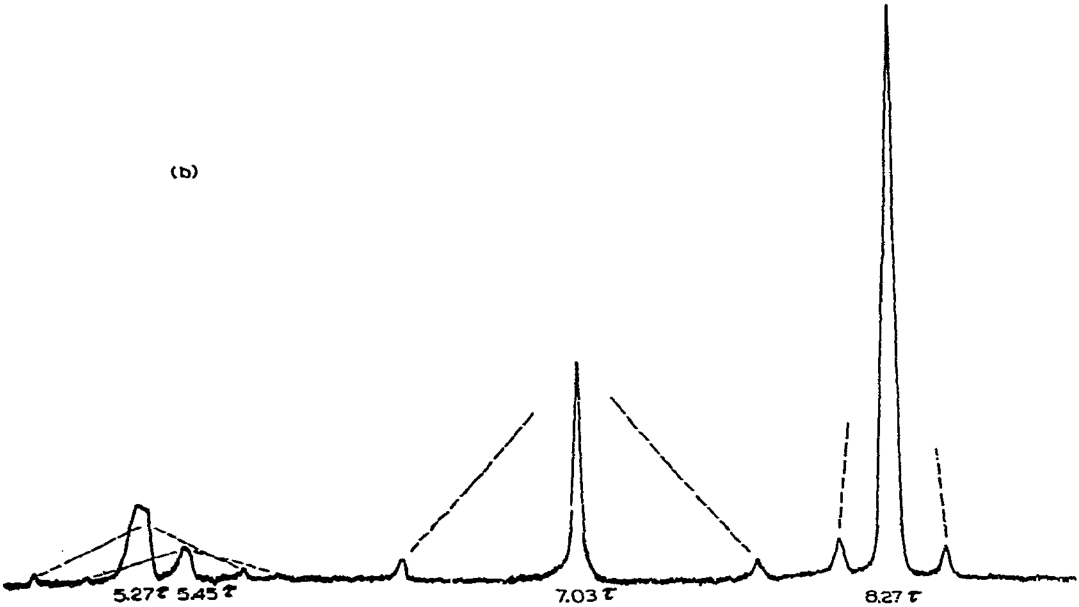


Fig. 1(b). 60 MHz spectrum after partial reaction. In the insertion compound, the broad vinyl resonance overlaps the lower vinyl resonance in the starting compound, and the CH_2 and CH_3 resonances in the insertion product essentially coincide with the CH_3 resonance in the starting compound.

source. The base peak is $(CH_3)_3Pb^+$ (*m/e* 253) while a peak at *m/e* 79 (61.1% of base peak) is assignable to $CH_3SO_2^+$. Other peaks at *m/e* 208 (Pb^+), 223 (CH_3Pb^+) and 238 [$(CH_3)_2Pb^+$] are observed, while *m/e* 94 is tentatively assigned to $(CH_3)_2SO_2^+$. There is no peak assignable to SO_2^+ (*m/e* 64). A major fragmentation pattern would appear to involve fission of the Pb–O bonds.

Fig. 1(c). 60 MHz spectrum at completion of reaction, showing the absence of ^{207}Pb–^{1}H coupling.

These results contrast with our data[13] on $(CH_3)_3SnOS(O)CH_3$ ($M^{\cdot+}$ 244), which show no evidence of Sn–O bond cleavage as a major fragmentation pattern, and seems to be in line with the greater strength of Sn–O bonds[14]. However, peaks corresponding to fragments greater than $M^{\cdot+}$ were observed, again being consistent with aggregation (established for solution).

The spectrum of $(C_6H_5)_3Pb{-}O{-}S(O){-}CH_2{-}CH{=}CH_2$ [Fig. (2b)] shows a weak $M^{\cdot+}$ at 544, but experimental conditions prevented observation of higher mass

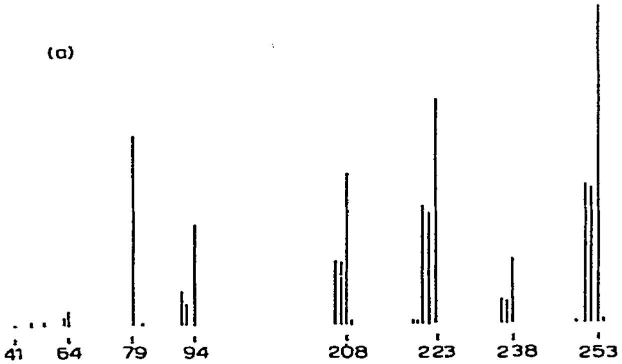


Fig. 2(a). Mass spectrum of trimethyllead methanesulfinate.

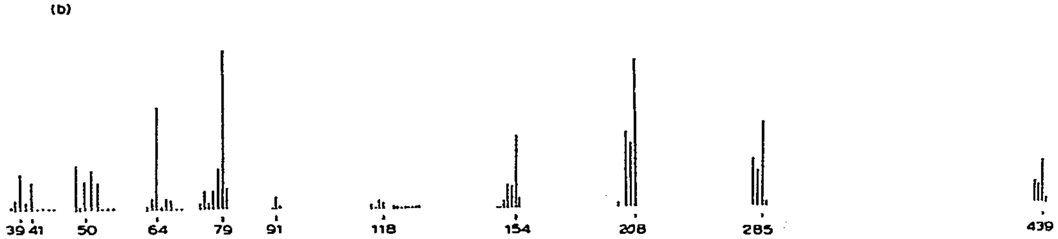


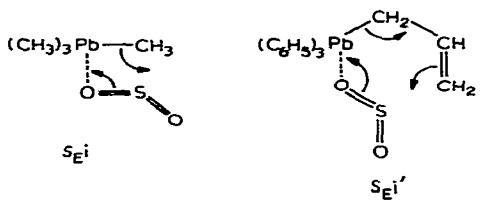
Fig. 2(b). Mass spectrum of triphenyllead allylsulfinate.

peaks. The base peak (m/e 78) is due to $C_6H_6^+$ while m/e 208, 285 and 439 are attributed to Pb^+, $C_6H_5Pb^+$ and $(C_6H_5)_3Pb^+$. The low abundance of $(C_6H_5)_2Pb^+$ is in line with results on the fragmentation behaviour of $(C_6H_5)_4Pb$[15]. The peak at m/e 154 is assigned to $(C_6H_5{-}C_6H_5)^+$, while no fragment due to $(CH_2{=}CH{-}CH_2{-}SO_2)^+$ was observed, but ready fragmentation into $CH_2{=}CH{-}CH_2^+$ and SO_2^+ (m/e 64; 64.7% of base peak) would be anticipated. A peak at m/e 41 is assigned to $(CH_2{=}CH{-}CH_2)^+$.

Mechanism of insertion

Recently we suggested that electrophilic cleavage mechanisms seemed most in accord with the data for organotin[1] and certain organomercury systems[16]. Since then, stereochemical and kinetic studies have supported this contention for the tin systems[17], and radical mechanisms seem definitely unlikely as a general phenomenon. However, we would be disinclined to dismiss completely, radical mechanisms for certain other carbon–metal systems.

There is a close well-established relation between electrophilic cleavage of carbon–tin and carbon–lead bonds, the latter being more reactive. It seems a safe exercise to propose similar mechanisms for SO_2 insertion below *i.e.* either S_Ei or S_Ei':



The data available are definitely in accord with this view. The rate sequence allyl > phenyl > benzyl, well authenticated for bimolecular electrophilic cleavage, is followed, while alkyl groups lag behind.

We have no proof of the allylic rearrangement mechanism (S_Ei') written above, since the 2-butenyllead systems are approaching the lower limits of stability. However, the very rapid reaction of the allyl compounds compared with phenyl, and the established rearrangement for 2-butenyl- and cinnamyltin systems, makes any other pathway unlikely. Although bimolecular mechanisms have been written above, the true order is probably higher than one in SO_2, since additional molecules are probably carried into the transition state by donor–acceptor interaction with the phenyl groups. This is indicated from kinetic studies with aryltrimethylstannane[17].

In the tin systems di-insertion of SO_2 occurred only with groups quite susceptible to electrophilic cleavage[1], *e.g.* allenyl:

$$(CH_3)_2Sn(CH{=}C{=}CH_2)_2 \xrightarrow{2\,SO_2} (CH_3)_2Sn(SO_2{-}CH_2{-}C{\equiv}CH)_2$$

whereas monoinsertion only, occurred with $(CH_3)_4Sn$:

$$(CH_3)_4Sn \xrightarrow{SO_2} (CH_3)_3SnSO_2CH_3$$

Although elementary considerations account for the lessened reactivity of $(CH_3)_3SnSO_2CH_3$ compared with $(CH_3)_4Sn$, such considerations require an electrophilic description of the cleavage process. Thus the electronegative sulfinate group reduces the electron density at the carbon centre attached to tin.

Di or tri-insertion for R_4Pb is not greatly disfavoured [as it is for $(CH_3)_4Sn$] and this is probably due to the greater ability of lead to support a positve charge, with lessened drainage of electron density from the attached carbon sites, as well as the reduced carbon–lead bond strength compared to carbon–tin.

The sequence of reactivity in the group IV compounds towards SO_2 is thus C–Pb > C–Sn ≫ either C–Ge or C–Si, an order in complete harmony with an electrophilic description of the process.

Actual details of the transition state for SO_2 insertion into C–metal bonds follow only from kinetic and substituent effect studies which are currently being conducted on the organotin systems. Since organoledad compounds appropriate for stereochemical studies appear accessible only with considerable difficulty, we have not pursued this line. However, our findings for the less unruly tin systems would be strongly implicated for the lead systems.

EXPERIMENTAL

General procedure for preparation of $(C_6H_5)_3PbR$ *compounds*

(2-Methylallyl)triphenyllead. The preparation of (2-methylallyl)triphenyllead is illustrative of the experimental procedures used. In a 200 ml flask equipped with a stirrer, reflux condenser and addition funnel was placed 1.3 g (0.054 g-atom) of magnesium. The magnesium was covered with 50 ml of ether and a crystal of iodine added as initiator. A solution of 4.8 g (0.05 mole) of 2-methylallyl chloride in 50 ml of ether was added dropwise over a half hour period. The mixture was stirred for a half hour after addition was complete, then a slurry of 14.2 g (0.03 mole) of triphenyllead chloride in 50 ml of ether was added with stirring. The reaction mixture was stirred overnight then hydrolysed with saturated ammonium chloride. The salts were washed with an additional 50 ml of ether; the combined ether layers filtered, dried over anhydrous calcium chloride and the ether removed under vacuum. The crude solid was recrystallized from absolute ethanol and melted at 75.5–76.0°. Yield 25%. (Found: C, 53.70; H, 4.49. $C_{22}H_{22}Pb$ calcd.: C, 53.52; H, 4.46%.)

Allyltriphenyllead[18]. Prepared in 30% yield and recrystallized from absolute ethanol m.p. 76° (reported[18] m.p. 76–77°). (Found: C, 52.69; H, 4.28. $C_{21}H_{20}Pb$ calcd.: C, 52.58; H, 4.17%.)

Benzyltriphenyllead[19]. Prepared in 50% yield and recrystallized from absolute ethanol m.p. 92–93° (reported[19] m.p. 93°).

*(p-Fluorobenzyl)triphenyllead**. Prepared in 45% yield; recrystallized from ethanol m.p. 93°. (Found: C, 54.75; H, 3.93. $C_{25}H_{21}FPb$ valcd.: C, 54.54; H, 3.56%.)

*(m-Fluorobenzyl)triphenyllead**. Prepared in 40% yield; recrystallized from ethanol m.p. 98°. (Found: C, 54.69, H, 3.91. $C_{25}H_{21}FPb$ calcd.: C, 54.54; H, 3.56%.)

Cyclopropyltriphenyllead. Prepared in 50% yield; recrystallized from ethanol, m.p. 63–63.5°. (Found: C, 52.71; H, 4.09. $C_{21}H_{20}Pb$ calcd.: C, 52.58; H, 4.17%.)

Isopropyltriphenyllead. Prepared in 65% yield; recrystallized from absolute ethanol, m.p. 93–94°. (Found: C, 52.79; H, 4.06. $C_{21}H_{22}Pb$ calcd.: C, 52.36; H, 4.57%.)

p-Fluorophenyltrimethyllead. This compound was isolated in *ca.* 70% purity owing to redistribution of the product. However, the solid insertion compound was obtained pure by recrystallization from ethanol.

---

* Prepared in this laboratory by Mr. A. Smith.

2-Butenyltriphenyllead. Attempted preparation of 2-butenyltriphenyllead via crotylmagnesium bromide and triphenyllead chloride was tried several times; the required compound was obtained once in impure form but could not be characterised fully.

Insertion of sulphur dioxide

Gaseous sulphur dioxide was bubbled into an ether solution of tetramethyllead for *ca.* 5–10 min. A white crystalline solid precipitated; recrystallized from absolute ethanol.

Similarly the 2-methylallyl- and allyllead compounds were inserted in chloroform solution for *ca.* 1–2 min and recrystallized from absolute ethanol.

When longer reaction periods were required a chloroform or carbon tetrachloride solution was mixed with liquid sulphur dioxide and stored at −20°.

Benzyltriphenyllead only gave the mono-insertion compound when stored for *ca.* 2–3 h in neat liquid sulphur dioxide. However, (*p*-fluorobenzyl)triphenyllead and (*m*-fluorobenzyl)triphenyllead reacted with liquid sulphur dioxide over 2–3 days gave the di-insertion products.

Tetratolyllead in carbon tetrachloride reacted over 5 days to give the di-insertion compound.

Similarly carbon tetrachloride solutions of cyclopropyltriphenyllead and isopropyltriphenyllead reacted over 5–6 days to give the di-insertion and tri-insertion product respectively.

Generally the mono-insertion products have reasonable solubility in deuteriochloroform, whilst the di-insertion compound show limited solubility; the tri-insertion product from isopropyltriphenyllead is completely insoluble in a large variety of solvents.

Alternative preparative route of O-sulfinato trimethyllead compounds

Aqueous solutions of trimethyllead chloride were mixed with aqueous solutions of the appropriate sodium arylsulphinate (1/1.5 mole ratio); upon standing crystals of the lead sulphinates separated; removal of some solvent resulted in further yields of product. Recrystallizations were effected from ethanol. Generally yields varied from 60–70%, NMR spectra were recorded on a Varian-A-60 machine, and mass spectra were obtained with an Atlas CH_4 instrument with TO4 ion source.

ACKNOWLEDGEMENTS

We are grateful to Dr. D. Doddrell of Department of Chemistry, Indiana University for obtaining some NMR spectra, and to the Australian Research Grants Committee (Grant No. A.R.G.C.-23) for supporting some of this work. Dr. I. Lauder of University of Queensland and Dr. J. Bowie of University of Adelaide kindly conducted some mass spectral measurements.

REFERENCES

1 W. Kitching, C. W. Fong and A. J. Smith, *J. Amer. Chem. Soc.*, 91 (1967) 767.
2 R. C. Edmondson and M. J. Newlands, *Chem. Commun.*, (1968) 1219.

3 M. GRAZIANI, J. P. BIBLER, R. M. MONTESANO AND A. WOJCICKI, *J. Organometal. Chem.*, 16 (1969) 507 and references therein.
4 F. A. HARTMAN AND A. WOJCICKI, *Inorg. Chim. Acta*, 2 (1968) 351 and references therein.
5 W. KITCHING AND B. F. HEGARTY, *Abstract of Papers, Symposium on Organometallic Chemistry*, Melbourne, May 1968.
6 G. B. DEACON AND P. W. FELDER, *Aust. J. Chem.*, 22 (1969) 549 and references therein.
7 A. G. LEE, *Chem. Commun.*, (1968) 1614.
8 K. S. MURRAY, R. J. COZENS, C. B. DEACON, P. W. FELDER AND B. O. WEST, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 705.
9 F. HUBER AND F. J. PADBERG, *Z. Anorg. Allg. Chem.*, 351 (1967) 1.
10 R. GELIUS, *Z. Anorg. Allg. Chem.*, 349 (1966) 22.
11 R. OKAWARA AND H. SATO, *J. Inorg. Nucl. Chem.*, 11 (1961) 204.
12 V. G. KUMAR DAS, Ph. D. Thesis University of Queensland, 1969.
13 C. W. FONG AND W. KITCHING, to be published.
14 W. P. NEWMANN AND K. KÜHLEIN, *Adv. Organometal. Chem.*, 7 (1968) 241.
15 D. B. CHAMBERS, F. GLOCKLING AND M. WESTON, *J. Chem. Soc. A*, (1967) 1759.
16 W. KITCHING, B. F. HEGARTY, S. WINSTEIN AND W. G. YOUNG, *J. Organometal. Chem.*, 20 (1969) 253.
17. C. W. FONG AND W. KITCHING, unpublished results.
18 P. R. AUSTIN, *J. Amer. Chem. Soc.*, 53 (1931) 3517.
19 H. GILMAN, L. SUMMERS AND R. W. LEEPER, *J. Org. Chem.*, 17 (1952) 630.
20 T. CONDON, personal communication.