

LEAD**ANNUAL SURVEY COVERING THE YEAR 1984**

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I. Books and Reviews

Several reviews have been published: the 1983 annual survey [1], a group IV review [2], a 1982 review [3], a survey of gaschromatography [4] and a review on marine pollution [5]. A book on the biological effects of organolead compounds [6] has already been discussed in ref. [1]. Finally the Medical Research Council (UK) has published a review on lead and neurophysiological effects in children [7].

II. Syntheses

Pb(II)salts reacted with a $\text{Me}_2\text{Co(III)}$ macrocyclic complex to give Me_4Pb [8]. This reaction was studied in relation to natural methylation processes. Et_4Pb has been prepared from Pb and EtBr by cathodic alkylation in a yield of 92% [9,10]. An apparatus has been described to prepare granulated NaPb for the synthesis of Et_4Pb [11].

The synthesis of $\text{Ph}_3\text{Pb-C}\equiv\text{C-C}_6\text{H}_4\text{F-p}$ (55%) and $(\text{p-CH}_3\text{C}_6\text{H}_4)_3\text{Pb-C}\equiv\text{C-C}_6\text{H}_4\text{F-p}$ (60%) has been reported [12]. ^{19}F spectra, recorded in various solvents, showed hydrogen bonding and coordination interaction.

$[\text{Pb}(\text{NMe}_2)_2]_2$ has been obtained from LiNMe_2 and PbCl_2 in Et_2O [13].

Triorganolead derivatives of amino acids have been prepared from R_3PbOH

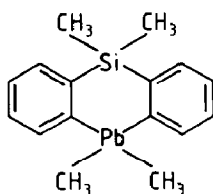
($\text{R} = \text{Me}, \text{Ph}$) and N-acetyl-amino acids. Spectroscopic data of the new compounds were presented, the structure of $\text{Ph}_3\text{PbAcGly}$ having been determined by X-ray [14]. 1,3-Dithiolate organolead complexes have been prepared in yields of 81 - 93.5% [15]. Compounds $(\text{R}_3\text{Pb})_2(\text{C}_6\text{H}_3\text{XS}_2)(\text{C}_6\text{H}_3\text{XS}_2 = 1,3\text{-dithiobenzene for } \text{X} = \text{H or } 1,3\text{-dithio-4-chlorobenzene for } \text{X} = \text{Cl})$ were monomeric in solution, compounds $\text{R}_2\text{Pb}(\text{C}_6\text{H}_3\text{XS}_2)$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5; \text{X} = \text{H}, \text{Cl}$) dimeric.

Vibrational and $^1\text{H-NMR}$ data have been presented: $\nu(\text{Pb-S})$ was in the $280\text{-}380\text{cm}^{-1}$ range, $J^{207}\text{Pb-}^1\text{H}$ values increased with going from CDCl_3 to DMSO-d_6 indicating an increased coordination number. Tri- and diphenylhaloplumbates of the type $[\text{Et}_4\text{N}][\text{Ph}_3\text{PbXY}]$ ($\text{X or Y} = \text{Cl}, \text{Br}, \text{I}$), $[\text{Et}_4\text{N}][\text{Ph}_6\text{Pb}_2\text{X}_2\text{Y}]$ ($\text{X or Y} = \text{Cl}, \text{Br}$), $[\text{Et}_4\text{N}][\text{Ph}_2\text{PbX}_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $[\text{Me}_4\text{N}]_2[\text{Ph}_2\text{PbX}_4]$ ($\text{X} = \text{Cl}, \text{Br}$), $[\text{Me}_4\text{N}][\text{Ph}_3\text{PbX}_2]$ ($\text{X} = \text{Cl}, \text{Br}$), $[\text{Me}_4\text{N}][\text{Ph}_2\text{PbCl}_3]$, Ph_3PbX and Ph_2PbX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been synthesized in yields of 70 - 95% [16].

Raman and IR spectra of these compounds have been studied. The Ph_3Pb systems have 5-coordinate trigonal bipyramidal structures (except Ph_3PbI).

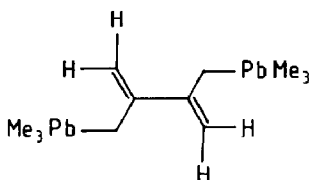
6-Coordinate, octahedral structures have been proposed for Ph_2Pb systems (except Ph_2PbI_2). An unperturbed $\nu_3(\text{Ph}_2\text{Pb})$ of $194 - 198\text{ cm}^{-1}$ and a $\nu_3(\text{Ph}_3\text{Pb})$ of $195 - 200\text{ cm}^{-1}$ have been reported.

Among several 9,10-dihydro-9,10-dihetero-anthracenes, prepared from $(\text{o-XC}_6\text{H}_4)_2\text{SiMeR}$ ($\text{R} = \text{H}, \text{Me}; \text{X} = \text{Cl}, \text{Br}$) and RR'MCl_2 ($\text{R}, \text{R}' = \text{H}, \text{Me}, \text{Ph}; \text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$), also lead derivatives have been mentioned e.g. 9,9,10,10-tetramethyl-9,10-dihydro-10-plumba-9-silaanthracene (I) [17].



(I)

The Me_3Pb substituted butadiene (II) has been obtained in a 30% yield from the dianion of butadiene and Me_3PbCl [18].



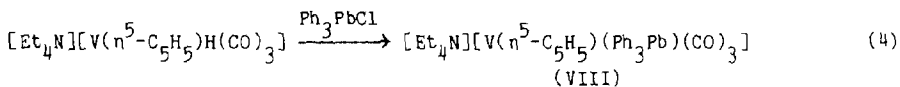
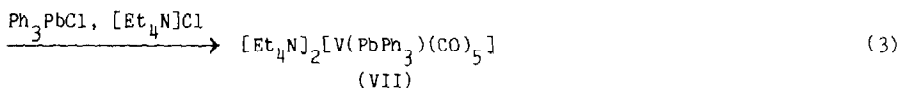
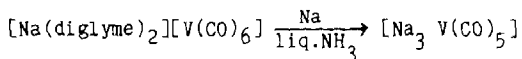
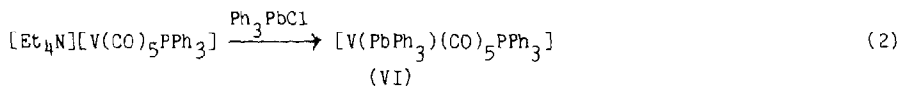
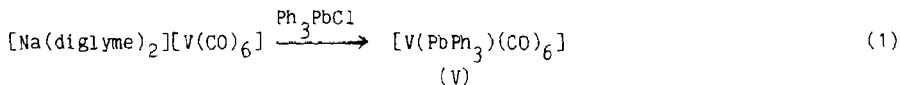
(II)

$\text{Ph}_3\text{PbSnPh}_3$ has been synthesized in a 38% yield from Ph_3SnCl and Ph_3PbLi in THF [19]. $\text{Ph}_3\text{PbGePh}_3$ was obtained in a yield of 37% by reacting Ph_3GeCl and Ph_3PbLi . An attempt to prepare $\text{Ph}_3\text{PbSiPh}_3$ resulted in the formation of a regular 1:1 $\text{Pb}_2\text{Ph}_6 \cdot \text{Si}_2\text{Ph}_6$ phase. The compounds $\text{Ph}_3\text{PbSnPh}_3$ (III) and $\text{Ph}_3\text{PbGePh}_3$ (IV) have been studied spectroscopically. The mass spectrum of (III) showed Pb-Sn bond break, that of (IV) indicated the release of 1 or 2 Ph groups. ^{207}Pb -NMR gave the following δ 's (reference Me_4Pb): Ph_6Pb_2 - 79.8, (III) - 256.5 and (IV) - 271.5 ppm. The Raman spectra showed the Pb-Pb, Pb-Sn and Pb-Ge vibration at 110, 125 and 138 cm^{-1} respectively, the latter spectrum being also IR active.

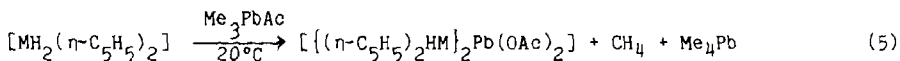
The crystal structures of (III), (IV) and the regular 1:1 phase $\text{Ph}_6\text{Pb}_2 \cdot \text{Si}_2\text{Ph}_6$ have been determined. Bond lengths of Pb-Pb, Pb-Sn and Pb-Ge were 285, 283 and 262 pm respectively.

Red complexes $[\text{Et}_4\text{N}][\text{Nb}(\text{Cp})\text{PbR}_3(\text{CO})_3]$ ($\text{R} = \text{Et}, \text{Ph}$) have been prepared from $\text{Na}[\text{NbCp}(\text{H})(\text{CO})_3]$ and R_3PbCl followed by reaction with $[\text{Et}_4\text{N}]\text{Cl}$. IR and ^{93}Nb NMR data have been studied [20].

Red vanadiumcarbonyl complexes containing a V-Pb bond have been synthesized [21]. IR data of the carbonyl groups and δ (^{51}V) data relative to VOCl_3 were studied: (V) - 1750, (VI) - 1565, (VII) - 1967 and (VIII) - 1789 ppm.



Violet Mo and W complexes have been prepared according to (5) in a 70% yield [22]. Other reaction products were CH_4 and Me_4Pb together with unidentified products.



M = Mo, W

The Mo compound reacted with $\text{HC}\equiv\text{CCN}$ to form $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{HC}\equiv\text{CHCN})_2$.

The crystal structure of The Mo compound consisted of discrete molecules with a Pb atom bridging two $(\eta\text{-C}_5\text{H}_5)_2\text{HMo}$ moieties; the Mo-Pb bond was 2.808 Å.

The reaction of $(\text{Me}_2\text{N})_3\text{P}=\text{CH}_2$ with R_3PbCl ($\text{R}=\text{Ph}$) yielded the white compound $[(\text{Me}_2\text{N})_3\text{PCH}_2\text{-PbR}_3]\text{Cl}$ (45%) [23]. PbCl_2 was also reacted with $(\text{Me}_2\text{N})_3\text{P}=\text{CH}_2$ resulting in the white compound $[(\text{Me}_2\text{N})_3\text{PCH}_2]_2\text{PbCl}_2$ in 75% yield.

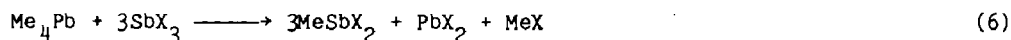
III. Reactions

High purity Pb has been prepared by the thermal decomposition of Et_4Pb [24]. Rate constants and activation energy have been determined for the ozonolysis of Me_4Pb under varying conditions [25].

Pulse radiolysis of H_2 , H_2S and H_2O vapor has been studied including reactions of radiolytically produced OH with tetraalkyllead compounds and hydrocarbons [26].

An EPR study of the reaction between the Cu (II) dithiocarbamate complex, $\text{Cu}(\text{dte})_2$, and Et_4Pb showed the formation of an intermediate product [27].

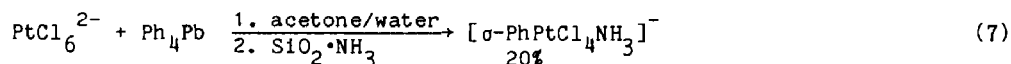
Me_4Pb has been reacted with SbX_3 in boiling benzene for 12 hours to give methylhalogenostibanes [28].



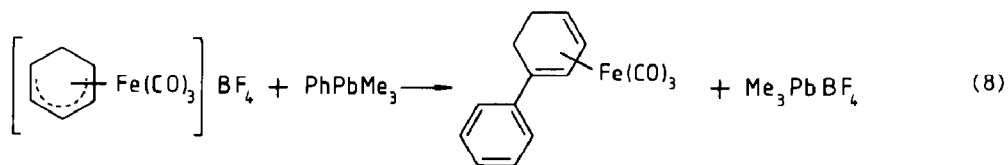
X = Cl 63% yield

X = Br 55% yield

The reaction of PtCl_6^{2-} and Ph_4Pb afforded a σ -phenyl complex of platinum (IV). This complex gave diaryls on reaction with arenes and phenyl substituted olefins resulted from the reaction with olefins [29].



The reaction rate of (8) has been reported in a broader study on comparable reactions of organometallic compounds [30].

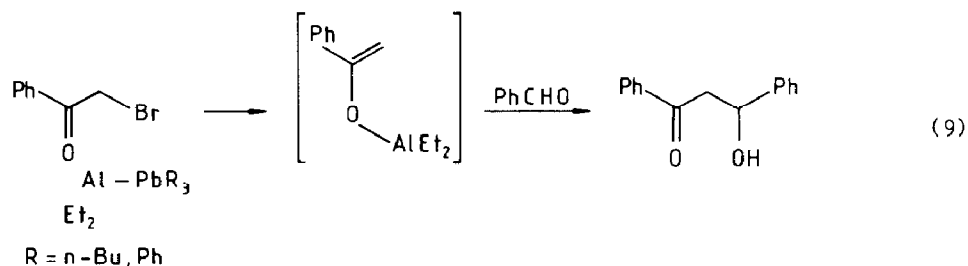


From the complexes $[(\eta^5\text{-C}_5\text{H}_5)_n\text{M}(\text{CO})_n\text{PbPh}_3]$ (M = Fe, Cr, Mo, W) only the Fe complex rearranged thermally via a 1,2-phenyl migration to the corresponding aryl complex $[(\eta^5\text{-C}_5\text{H}_5)_n\text{Fe}(\text{CO})_n\text{Ph}]$ in a 24% yield. During the reaction metallic lead precipitated and Ph_4Pb was formed [31]. The same reaction took place photochemically (yield 60%). The W complex gave photochemically but not

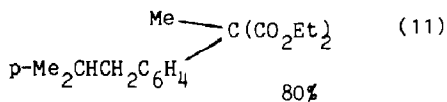
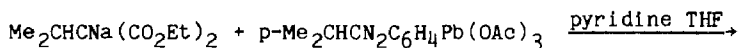
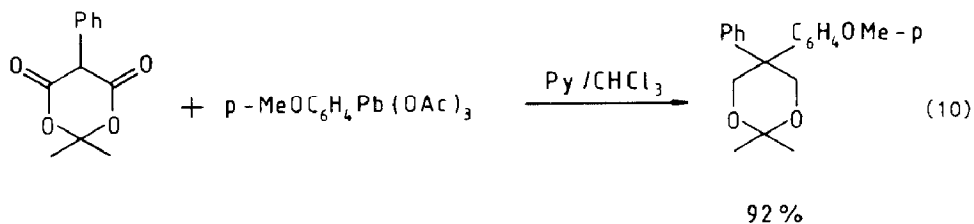
thermally $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Ph}]$ in a yield of 45%. Reaction of all these complexes with SO_2 gave complexes of the type $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n\text{SO}_2\text{Ph}]$ in yields of 73 - 82%.

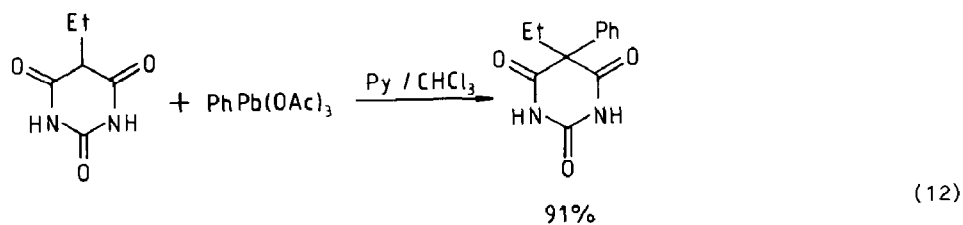
$\text{Me}_2\text{Si}(\text{Nt-Bu})_2\text{Pb}(\text{I})$ reacted with PCl_3 under formation of $\text{Me}_2\text{Si}(\text{Nt-Bu})_2\text{PCl}$ and PbCl_2 [32]. No reaction was observed between I and 2,3-dimethyl-1,3-butadiene.

A Reformatsky type reaction of α -bromocarbonyl derivatives, aldehydes or ketones and $\text{R}_3\text{PbAlEt}_2$ ($\text{R} = \text{n-Bu, Ph}$) gave β -hydroxy esters under mild conditions in yields of 74 - 86% [33].

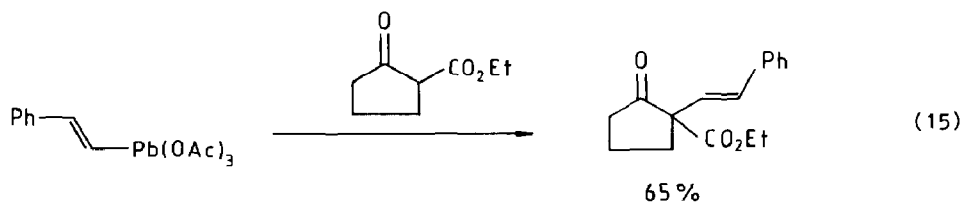
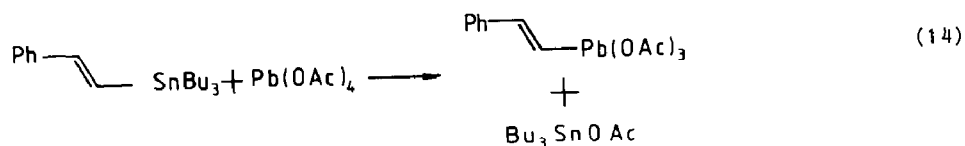
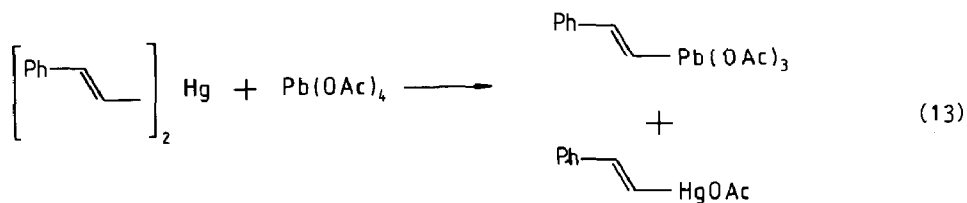


Acryllead triacetates in pyridine have been used as arylating agents of derivatives of 2,2-dimethyl-1,3-dioxan-4,6-diones, malonic acid and barbituric acid [34].





α -Alkenylation of β -dicarbonyl compounds has been achieved in yields of 52-80% with alk-1-enyllead triacetates, prepared in situ from alk-1-enylmercury or tin precursors [35]. The alk-1-enyllead triacetates were too unstable to be isolated.



IV. Physical Chemistry

The crystal and molecular structures of compounds MeSMPb_3 ($\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) have been studied [36]. M-S bond lengths were 1.852, 2.138, 2.224, 2.391 and 2.489 Å for $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn},$ and Pb respectively. Pb showed distorted tetrahedral coordination.

^{13}C -NMR data have been reported for compounds $(\text{C}_6\text{H}_5)_3\text{MCH}_2\text{CH}=\text{CH}-\text{CH}_3$ (E) ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ and Pb) [37]. Also the Z isomers of the Pb compounds and $(\text{C}_6\text{H}_5)_3\text{PbCH}(\text{CH}_3)\text{CH}=\text{CH}_2$ were studied. A mesomeric electron donating effect and the mean electronic excitation energy were considered to dominate the chemical shifts and coupling constants in case of ^{207}Pb .

Among a range of carbon-proton coupling constants in alkenes also those of Ph_3Pb vinyl have been discussed: electronegativity, substituent and hybridization effects were of importance [38]. The relation between group IV NMR chemical shifts has also been a subject of discussion [39].

An interpretation of the IR spectrum of $(\text{Ph}_2\text{PbO})_2\text{CrO}_2$ was given: three-dimensional polymers were present [40].

Phase transitions in $\text{Ph}_3\text{Pb}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{PbPh}_3$ (IX) ($\cdot\text{CH}_2\text{Cl}_2$ or $\cdot\text{CHCl}_3$) have been investigated by differential scanning calorimetry and Raman spectroscopy [41].

(IX) $\cdot\text{CH}_2\text{Cl}_2$ showed transitions at 14.4 and 17.7 K, (IX) $\cdot\text{CHCl}_3$ displayed only one phase transition at 145 K. Enthalpy, entropy values and Raman low lying vibrations at 295 K have been presented: 150 (w), 202 (vs) and 225 (w) cm^{-1} . Low temperature Raman data have also been given. Transitions were thought to be related to partial or complex ordering of the CH_2Cl_2 or CHCl_3 molecules.

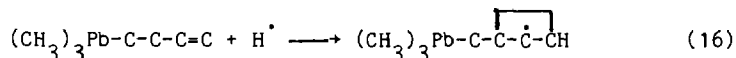
The relationship between the values of the σ_{R}^+ constants of the $\text{p-NO}_2\text{C}_6\text{N}_4\text{XMR}_n$ compounds ($\text{X} = \text{S}, \text{O}, \text{R} = \text{Ph}, \text{M} = \text{Hg}, \text{Sn}, \text{Pb}, \text{Sb}$) and XH groups and the dissociation capacity $\log K_{\text{d}}$ have been investigated in DMSO [42]. S-Pb bonds showed an unusual stability. This was explained by the Pearson principle: the soft Ph_3Pb^+ cation has great affinity to the soft sulfur atom.

The kinetics of the ozon oxidation of Me_4Pb have been studied in different solvents [43]. Surface and gas processes in photodecomposition in small zones have been investigated in relation to organoleads [44].

Details have been presented about the temperature dependence of the lead spin orbit relaxation by atomic hydrogen [45]. Methyl tunneling and reorientation has been investigated for Me_4Pb . From the proton spin-lattice relaxation rate the

barrier to Me rotation. The tunneling splitting does not accommodate the NMR data of Me₄Pb.

He (Iα) and He (IIα) photoelectronspectra of Ph₄Pb have been measured. Band maxima have been assigned and ionization energies presented. The spectra can be interpreted in terms of a perturbed system of four weakly interacting benzene molecules [47].



The chemical activation of 4-(Me₃Pb)-2-butyl radicals has been studied (Eqn 16). Pb did not block internal energy transfer, since energy randomization was found to occur on a subpicosecond time scale in all the radicals studied [48].

Correlations between boiling point and size, polarizability and dipolarity have been used to calculate the boiling points of Me₄Pb and Et₄Pb [49].

Relativistic quantum calculations of low-lying states of PbH have been performed and compared with data from experimental spectra [50]. LCAO calculations have been reported for Cp₂Pb, which possesses a polymeric structure [51]. The interaction of two orbitals, σ on CpPb and π₂ on the bridging Cp (perpendicular to the vector joining adjacent Pb centers), determined the structure of the polymeric chain. In (Cp₂Pb)_n the bonding and antibonding combinations of these orbitals formed occupied bands. As the destabilization coming from the antibonding combination was larger than the stabilization coming from the bonding combination, the chain adopted a geometry that minimizes the overlap between these two orbitals. The well-known ideas about the inert 6s electrons did not apply in case of Cp₂Pb. The PbCp lone-pair fragment orbital possessed appreciable s character. If the 6s orbital was really inert no geometrical preference would be expected.

V. Applications

Lead hydride has been applied as a constituent of a film for data recording using an Ar laser [52]. Me₄Pb has been applied in a low temperature process for depositing epitaxial layers [53]. During the preparation of an electrophotographic photoreceptor gaseous Me₄Pb has been used [54].

The poison-resistance of catalytic flammable-gas sensing elements against Pb poisoning has been investigated [55].

Organolead compounds have been applied as catalysts [56]: olefin metathesis by a Re₂O₇/Al₂O₃ catalyst and a R₄Pb co-catalyst [57], and by a Re aluminate - R₄Pb

mixture [58], aminolysis of 2,4-R(O₂N)C₆H₃OAc (R = H, O₂N) by PhCH₂NH₂, (PhCH₂)₂NH and (Me₂CH)₂NH in C₆H₆ by Et₂Pb(OBz)₂ [59], and the reaction of isocyanate with EtOH by a mixture of KOAc with Et₃N and Bu₂Pb butyrate caprylate [60].

By using triphenyl-p-styryllead the octadecyl metacrylate-triphenyl-p-styryllead copolymer has been synthesized [61].

Et₄Pb did not effect the dewpoint or corrosion rate of exhaust gases from cars [62].

The effect of organic Pb containing fuel on the durability of palladium automotive catalysts has been studied [63].

The anti-detonating activity of Et₄Pb is the result of its thermal dissociation to Pb and Et•.



When the fuel has a higher stability than Et₄Pb, Pb can be oxidized to PbO₂, which may act as an oxidation catalyst [64]. Et₄Pb has been added also to hydrorefined gasoline to increase the octane number [65]. An update has been presented of the octane improvement by Pb alkyls [66]. The effect of different antiknocks, mixtures of Me₄Pb and Et₄Pb, on the antiknock properties of gasoline has been investigated [67].

VI. Analysis

Pb has been determined in blood by AA; the detection limit was 0.01 µg/ml.

Blood samples from tank cleaners and gasoline pump servicemen showed detectable amounts of Me₄Pb [68]. Et₄Pb and Me₄Pb have been analyzed by AA after extraction from different matrices into CCl₄ and re-extraction into aqueous HNO₃ [69]. After electrostatic capture from artificially polluted air, compounds of the type R₄Pb have been determined by electrothermal AA [70].

Organic as well as inorganic lead compounds have been analyzed in urban air by AA [71]. For a 6 hr sampling period the detection limits were 10 ng/m³ for inorganic and 8 ng/m³ for organic lead compounds.

Several GLC methods to analyze alkyllead compounds have been reported. AA and atomic fluorescence atomization systems have been used as detector systems [72]. Ionic alkyllead compounds in water have been detected at the ng/l level in 500 ml of water by GLC followed by AA [73]. Pb²⁺ and various alkyllead species have been isolated by chelation extraction with Na diethyldithiocarbamate, followed

by n-butylation and determination by GLC on a 10% OV-1 on chromosorb W column and AA detection. Detection limits were 7.5 ng/g and 12.5 ng/g for biological and sediment samples of 2 g respectively [74]. In the GLC analysis detection of Et_4Pb occurred by ionization quenching of a hydrogen atmosphere flame [75]. A GLC procedure to determine Et_4Pb in gasoline or aviation fuel has been published [76]. A GLC method to analyze PbEt_4 and PbMe_4 on carbowax 20 M had detection limits of 10^{-5} and $2.5 \times 10^{-6}\%$ respectively [77].

An HPLC method with a spectrophotometric chemical reaction detector has been used to analyze Pb^{2+} , Me_3Pb^+ , Et_3Pb^+ , Me_4Pb and Et_4Pb . The detection range was 0.3 - 1.5 nmol. Pb^{2+} and R_2Pb^{2+} salts formed red water soluble complexes at pH 9-10 with 4-(2-pyridylazo) resorcinol, the other compounds did not [78]. Et_4Pb and Me_4Pb have been separated by HPLC and detected by inductively coupled plasma emission spectrometry. Detection limits were 212 ppb and 42 ppb of Pb respectively [79].

A number of other analytical methods have been used to determine organolead compounds, such as inductively coupled plasma emission spectrometry and inductively coupled plasma mass spectrometry [80]. Three assays for the determination of dealkylation products of R_4Pb have been reported: colorimetry using dithizone, polarography and AA [81]. Spectrophotometry using 4-(2-pyridylazo) resorcinol as the reagent was the detection method after HPLC separation of compounds R_4Pb , R_3PbX , R_2PbX_2 in the concentration range 0.1 - 1.6 $\mu\text{g/ml}$ [82]. Emission spectrometry has been mentioned as a method to detect impurities in alkyllead compounds of high purity e.g. Me_4Pb and Et_4Pb [83, 84].

Pb has been determined in gasoline containing Et_4Pb by ionometric titration using F-sensitive electrodes [85]. Ion selective electrodes could also be applied in the determination of F in organolead compounds on titration with $\text{La}(\text{NO}_3)_3$ [86].

Polarography and ^{199}Hg - and ^{207}Pb -FT-NMR have been described to study interferences in the stripping voltametric determination of trimethyllead in seawater. Hg can react with Me_3Pb^+ to give MeHg^{2+} , Pb^{2+} and Me radicals. This reaction may invalidate the method [87]. An analytical procedure has been reported based on selective organic phase extraction coupled with differential pulse electrochemical techniques for the assay of Me_4Pb , Et_4Pb , Me_3Pb^+ , Et_3Pb^+ , $\text{Me}_2\text{Pb}^{2+}$, $\text{Et}_2\text{Pb}^{2+}$ and inorganic Pb in water samples [88]. Me_4Pb has been detected with an improved quadrupole mass spectrometer [89].

VII. Wastes, Pollution and Industrial Hygiene

Analysis of seven different rainwater samples showed trialkyllead pollution of the hydrosphere by wash-out processes. In the city center of Antwerp 330 ng Pb/l was found. While in surface waters the concentration was always below the detection limit of 20 ng/l [90].

Research into blood levels of lead in relation to the traffic intensity levels has been continued. The contribution of lead in petrol has been discussed [91]. The factor water softness has also to be taken into account [92].

Mutagenicity analysis of combustion samples of fuel in waste oil heaters has been performed. Automobile waste oil contained more mutagenic material than truck waste oil [93]. Waste oil heaters have also been examined on possible air discharge of lead compounds [94].

Computerized air and water dispersion modelling systems for chemical spills i.a. Et_4Pb have been studied [95]. The results of a degradation study of Et_4Pb in natural environment have been presented [96].

The amount of Et_4Pb and aromatic hydrocarbons in gasoline affects the polycyclic aromatic hydrocarbon content of exhaust gases [97]. A patent application on the removal of alkylleads from liquid hydrocarbons has been reported [98]. Soil polluted with Et_4Pb can be reclaimed by using selected nitrogen compounds [99]. Also a treatment of sludge from leaded gasoline storage tanks has been described [100]. Methods to identify and evaluate risks of organolead compounds in sewage sludge [101] or sludge-amended soils [102] have been presented.

VIII. Toxicology

The behaviour of Me_4Pb and Et_4Pb in soil and their uptake by spring wheat has been investigated [103]. In soil compounds of the type R_4Pb were converted to water-soluble Pb compounds, which showed a high plant toxicity. Enrichment occurred in particular in the vegetative and generative parts. Higher concentrations of these Pb compounds resulted in a yield depression of spring wheat. Comparable amounts of $\text{Pb}(\text{NO}_3)_2$ did not result in Pb accumulation. In three months the soluble Pb compounds leached out.

Et_3PbCl reacted with 2 out of the 18 SH groups in tubulin dimers. The other 16 SH groups were not affected. Other proteins with SH groups as actin did not react with Et_3Pb^+ . Tubulin had lost its capacity for microtubule assembly after complexation of the two SH groups. Polymerized tubulin disassembled on addition of Et_3PbCl [104, 105].

Me_3Pb^+ inhibited the growth and cytokinesis of fresh water algae *E. gracilis* and *P. malhamensis*. The latter was more sensitive to the toxic effect of Me_3Pb^+ than the first: enlarged algae and polydiploidization [106]. *P. malhamensis* was also treated with $\text{Pb}(\text{NO}_3)_2$, Et_3PbCl and Et_4Pb . the organic lead compounds were more toxic than $\text{Pb}(\text{NO}_3)_2$. Ultrastructural changes were complex and involved all cell organelles [107].

NADPH and oxygen are essential in the degradation of Et_4Pb to Et_3Pb^+ by rat liver microsomes. Inhibition by CO and reactivation by a combined action of O_2 and UV light took place. The substrate binding to cytochrome P450 was of type 1. The highest degradation activity was found in methylcholanthrene pre-treated rats. Phenobarbital pre-treatment gave the same results as in control animals [108]. The affinity constants of Et_3PbOAc to rat and cat Hb were $4 \times 10^5 \text{ mol}^{-1}$ and $4.5 \times 10^5 \text{ mol}^{-1}$ respectively. 2 Mol of Et_3PbOAc combined with 1 mol Hb [109].

Groups of male rats were given i.p. Et_4Pb 10 - 80 ng/kg. More than 80% of the rats given doses of $\geq 20 \text{ mg/kg}$ died. Mean survival times were 149.4 - 38.5 hrs for the 20 - 80 mg/kg doses respectively. Tremor, circling behaviour, jumping, hyperexcitation, running fits and tetanic convulsions were seen. No significant change in spontaneous motor activity was observed in the survivors of the 10 and 20 mg/kg groups. Significantly increased motor activity was recorded in the dying rats of the 20 and 40 mg/kg group [110].

Et_3PbCl and Me_3PbCl administered s.c. to male rats produced time and dose related increases in hot plate latencies [111]. 15 I.p. injections of 1 mg of Et_3PbCl to rabbits on alternate days caused more severe liver and kidney degeneration than $\text{Pb}(\text{OAc})_2$. Granular substance was observed in the cytoplasm of epithelial cells in the proximal tubule of the kidneys [112]. The toxicity of Me_3PbCl has also been studied in the Mallard duck [113]. The LD_{50} was 29.9 mg/kg.

The concentrations of Me_3PbCl were found to be highest in kidney and liver in order followed by brain, muscle and body fat. Et_4Pb administered on the 5th day of incubation resulted in 100% mortality on day 11 in chick embryos [114]. Administration on day 8 gave 47% mortality on day 11. All embryos died on day 20 after opening of the egg due to inability to breath by atrophy of the neuromuscular system. Me_4Pb has been administered i.p. to pregnant rats and to the newborns. Birth weight was unaffected. The body/brain weight ratio was increased, but brain myelination and other parameters showed no deficits. So the

body/brain weight ratio is a very sensitive parameter: Me_4Pb is neurotoxic at high concentrations and stimulates body growth at low concentrations [115].

The incorporation of the ^{14}C label of glucose into glutamic acid, glutamine and gaba remained unaltered by $\text{Pb}(\text{OAc})_2$ but was changed by Et_4Pb in a different way in different brain regions. Glucose uptake was not affected, while pyridoxal phosphate reversed the Et_4Pb effect in cerebellum and brain stem but not in the cerebral cortex [116]. Et_4Pb caused a decrease in pyruvate dehydrogenase activity in the brain of young rats by inhibition of the lipoyl dehydrogenase component [117]. Weekly injections of Me_4Pb had no effect on light-histological parameters of neuronal development in rat brains [118].

Lever pressing for food decreased and the behavioral pattern was disordered after administration of 20 and 40 mg/kg Et_4Pb to rats [119]. The daily frequency of discriminative avoidance of electrical shock response increased at a dose of 20 mg/kg.

14 Days after the s.c. administration of 8.0 or 17.0 mg/kg trimethyllead or saline rats were given 3.5 g/kg alcohol i.p. The highest dose of trimethyllead caused a shorter duration of sleep than in the control animals [120].

The treatment of lead poisoning in children has been discussed [121]. There is no indication that exposure to lead at concentrations commonly encountered in British male population is responsible for impaired renal function or increased blood pressure [122].

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IX. References

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