

**141.** *Organo-lead Compounds. Part IV. (a) A New Method for preparing Diethyl-lead Salts. (b) Derivatives of Mixed Plumbanes.*

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An account is given of methods of obtaining diethyl-lead salts, including a new unambiguous preparation which consists in treating diethyl-lead sulphite,  $\text{PbEt}_2\text{SO}_3$ , with the appropriate acid. The ready disproportionation of some dialkyl-lead salts is described.

Some derivatives of mixed plumbanes are described, and their sternutatory properties recorded.

WHEN a plumbane is treated with an acid and silica gel, the trialkyl-lead salt (cf. I) is usually produced in good yield (Saunders and Stacey, Part I, *J.*, 1949, 919). We have found, however, that sometimes a dialkyl-lead salt of type (II) is formed, and occasionally a mixture of products is obtained:  $\text{PbEt}_4 + \text{Me}\cdot\text{CO}_2\text{H} = \text{PbEt}_3\cdot\text{O}\cdot\text{COMe}$  (I) +  $\text{C}_2\text{H}_6$ ,  $\text{PbEt}_4 + 2\text{Ph}\cdot\text{CO}_2\text{H} = \text{PbEt}_2(\text{O}\cdot\text{COPh})_2$  (II) +  $2\text{C}_2\text{H}_6$ .

It is not very clear what governs this difference in behaviour. Apart from time of heating, temperature, and presence of catalyst, in some cases the nature of the acid seems to be one of the factors concerned. Frequently, the analyses of trialkyl-lead salts and of the corresponding dialkyl-lead salts are close and therefore independent methods of preparation are described.

The constitution of the trialkyl-lead salts is readily established by neutralisation of a trialkyl-lead hydroxide with the appropriate acid (Part I, *ibid.*; Heap and Saunders, Part II, *J.*, 1949, 2983). As a starting point for an independent method for preparing diethyl-lead salts we first selected diethyl-lead dichloride. This was prepared in pure condition by a modification of Gilman and Robinson's method (*J. Amer. Chem. Soc.*, 1930, 52, 1975), and was then free from both triethyl-lead chloride and plumbous chloride. Diethyl-lead dichloride reacted with metallic salts to give the corresponding diethyl-lead salts; *e.g.*, silver chloroacetate gave diethyl-lead bischloroacetate,  $\text{PbEt}_2(\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Cl})_2$ . This type of reaction was not wholly successful because of the difficulty of finding suitable solvents. The reaction was therefore performed heterogeneously in water, and although a pure product could be obtained, care had to be taken to avoid disproportionation (see p. 660).

Although the conversion of triethyl-lead chloride into the hydroxide by aqueous sodium hydroxide is well known (Part I, *loc. cit.*), the corresponding conversion of diethyl-lead dichloride into the dihydroxide has not previously been investigated. The latter reaction did not, however, proceed in a similar manner, because the dihydroxide,  $\text{PbEt}_2(\text{OH})_2$ , was readily soluble in the alkaline layer. Under the correct conditions, however, it could be crystallised from the alkaline layer and purified by recrystallisation from a small volume of water at a low temperature. It was then obtained as the efflorescent hexahydrate,  $\text{PbEt}_2(\text{OH})_2\cdot 6\text{H}_2\text{O}$ , which was readily dehydrated *in vacuo* at room temperature to the corresponding oxide  $\text{PbEt}_2\text{O}$ . The hydrated dihydroxide reacted readily with the appropriate acid, giving the dichloride, the diacetate, and the bischloroacetate. Hence this dihydroxide could be used as a basis for a general method of preparing diethyl-lead salts, were it not for the inconvenience involved in isolating it from alkaline solutions. The action of moist silver oxide in place of sodium hydroxide on the dichloride was investigated, but although excess of silver oxide was used the reaction did not proceed rapidly or completely, and the dihydroxide was difficult to isolate from solution in the presence of unchanged diethyl-lead dichloride.

No evidence was obtained to distinguish between the two possible formulæ  $\text{PbEt}_2\text{O}\cdot 7\text{H}_2\text{O}$  and  $\text{PbEt}_2(\text{OH})_2\cdot 6\text{H}_2\text{O}$ , but the latter was adopted merely to afford a parallel with triethyl-lead hydroxide. In quantitative dehydration experiments, it was not possible to stop precisely at the dihydroxide (anhydrous stage).

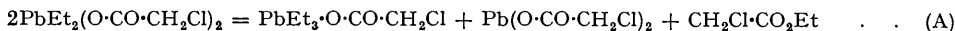
We next investigated the action of sulphur dioxide on tetraethyl-lead in ethereal solution. This reaction is quoted by Goddard (Friend's "Textbook of Inorganic Chemistry," Vol. XI, i, p. 333) as giving diethyl sulphone, but no mention is made of the fate of the lead. Employing the conditions described on p. 662, we found that the hitherto undescribed diethyl-lead sulphite,  $\text{PbEt}_2\text{SO}_3$ , was precipitated quantitatively as an amorphous powder. It dissolved readily in dilute mineral acids and in weak acids with the evolution of sulphur dioxide. In this way diethyl-lead dichloride, dibenzoate, bischloroacetate, bistrichloroacetate, ditoluene-*p*-sulphonate, ditoluene-*o*-sulphonate, and bithioacetate were obtained. These compounds were highly crystalline, and aqueous solutions (where obtainable) gave cream-coloured precipitates with hydrogen sulphide, showing that they were uncontaminated with plumbous compounds (see p. 660).

The diethyl-lead compounds mentioned above, when dispersed at concentrations of 1 part in  $10^6$  in a testing-chamber, did not exert any appreciable sternutatory effects on observers. These compounds were therefore Grade 0 (see Part I, *loc. cit.*, for grading). Incidentally, this physiological test could be used to prove the absence in these compounds of the corresponding triethyl-lead compounds, which possess powerful sternutatory properties at 1 in  $10^7$  and are easily detectable at much greater dilutions.

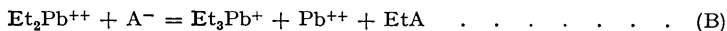
A complete series of salts was obtained from tetraethyl-lead and thioacetic acid under appropriate conditions. Thioacetic acid reacted with tetraethyl-lead in the cold to give triethyl-lead thiolacetate,  $\text{PbEt}_3\text{S}\cdot\text{COMe}$ , identical with the product obtained by the action of thioacetic acid on triethyl-lead hydroxide. At  $100^\circ$ , thioacetic acid and tetraethyl-lead in the absence of silica gel gave a mixture of triethyl-lead thiolacetate, diethyl-lead bithiolacetate (identical with the compound from diethyl-lead sulphite and thioacetic acid), and plumbous thiolacetate, whereas in the presence of silica gel the sole product was plumbous thiolacetate.

In many of the preparations of diethyl-lead salts, difficulty was caused by decomposition, with the production of plumbous compounds, particularly on heating. We therefore

investigated the decomposition of diethyl-lead bischloroacetate in hot water and it seemed that disproportionation took place into plumbous chloroacetate, triethyl-lead chloroacetate, and ethyl chloroacetate :



Such a reaction taking place in a single stage seems unlikely, and a possible mechanism is as follows. From cryoscopic measurements we have shown that many diethyl- and triethyl-lead salts are ionised to a considerable extent in aqueous solution. Equation (A) can then be written as the ionic equation (B) where A = acidic ion. It can be assumed that, in the diethyl-lead



ion, the two ethyl groups are attached by weak bonds which are susceptible to strain such as could be produced by an electric field set up by the other ions present. This ion may be written as  $\overset{\delta^+}{\text{Et}}-\overset{\delta^{++}}{\text{Pb}}-\overset{\delta^-}{\text{Et}}$ . Under sufficient strain the rupture of one of the Pb-Et bonds becomes probable and an unstable stage may be represented thus :



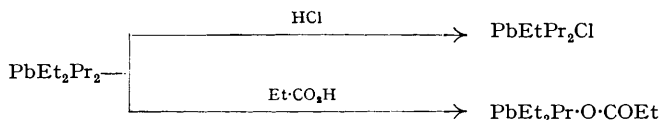
In the highly reactive unstable  $\text{:Pb}^+-\text{Et}$ , the remaining ethyl group would be expelled by the lead atom to restore electron stability, and the final products will be  $\text{AEt} + \text{Pb}^{++} + \text{Et}_3\text{Pb}^+$ .

Diethyl-lead bischloroacetate can be recrystallised from cold (but not hot) water and also from hot absolute ethyl alcohol without disproportionation. A similar disproportionation of di-*n*-propyl-lead diacetate was observed when its aqueous-alcoholic solution was evaporated on a water-bath. At room temperature negligible disproportionation took place. Diethyl-lead dibenzoate does not dissolve in water and was unaffected by boiling water but, when it was heated alone above its melting point, the odour of ethyl benzoate was observed.

The lability of the ethyl radicals in organo-lead compounds is probably the cause of the instability frequently encountered, and in this connexion reference may be made to production of tetraethyl-lead from triethyl-lead chloride and certain sodium compounds (*e.g.*, sodium nitromethane, see Part II, *loc. cit.*).

In general, the three classes of lead salt are readily distinguished in aqueous solution. The plumbous ion gives a heavy black precipitate with hydrogen sulphide, insoluble in organic acids and dilute mineral acids. Diethyl-lead salts of weak acids, when soluble in water, give a flocculent cream-coloured precipitate with hydrogen sulphide or ammonium sulphide; this precipitate dissolves immediately in dilute mineral acids. Under similar conditions triethyl-lead salts of weak acids give a milky-white precipitate also soluble in dilute mineral acid. Thus the hydroxide or acetate will give precipitates with hydrogen sulphide, whereas the chloride does not unless the solution is buffered with sodium acetate or rendered faintly alkaline with ammonia.

*Derivatives of Mixed Plumbanes.*—In our search for trialkyl-lead salts of high sternutatory power, we investigated compounds in which the alkyl groups attached to the lead atom were not all the same. A convenient starting point was the mixed plumbane, diethyldi-*n*-propyl-lead, which on treatment with a strong acid appeared to lose one ethyl group, whereas a weaker acid appeared to eliminate one propyl group. It should be emphasised, however, that the analytical figures of the likely products lie very close together, thus rendering identification difficult :



The action of hydrogen chloride falls into line with Grüttner and Krause's observation (*Ber.*, 1917, 50, 202) that halogens displace first the lightest group.

From ethyldipropyl-lead chloride and the sodium derivative of toluene-*p*-sulphonamide we obtained *N*-(ethyldipropylplumbi)toluene-*p*-sulphonamide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{PbEtPr}_2$ , as a highly crystalline compound, soluble in non-polar solvents. It was also prepared by first converting the chloride into the hydroxide and then treating the latter with toluene-*p*-sulphonamide (*cf.* Saunders, *J.*, 1950, 684). An ethereal solution of di-*n*-butyldiethyl-lead when treated with dry hydrogen chloride at 0° gave what appeared to be a mixture of products. It is noteworthy that Calingaert, Soroos, and Shapiro (*J. Amer. Chem. Soc.*, 1940, 62, 1104) showed

that ethyldimethyl-lead chloride, when heated in acetone, undergoes a redistribution reaction, yielding a random mixture containing all four possible trialkyl-lead chlorides. Such a redistribution may occur slowly in the cold.

With chloroacetic acid, however, some success was obtained. When this was warmed with dibutyldiethyl-lead in ethereal solution, a colourless crystalline compound was formed which appeared to be impure *n*-butyldiethyl-lead chloroacetate, *i.e.*, a heavier group had been replaced by the acid.

The sternutatory action of ethyldipropyl-lead chloride, ethyldipropylplumbitoluene-*p*-sulphonamide, diethylpropyl-lead propionate, diethylpropyl-lead chloroacetate, and *n*-butyldiethyl-lead chloroacetate was powerful, and these compounds were probably slightly superior to tri-*n*-propyl- and tri-*n*-butyl-lead salts, in this respect. Hence they are placed in sternutatory grade 3<sup>+</sup>.

#### EXPERIMENTAL.

*Diethyl-lead Dibenzoate*.—Benzoic acid (5 g.) was heated with tetraethyl-lead (8 c.c.) and a small piece of silica gel on a water-bath for  $\frac{1}{2}$  hour. The mass liquefied, then effervesced and finally solidified. The *dibenzoate* recrystallised from benzene as long colourless needles, m. p. 168° (Found: Pb, 40.8.  $C_{18}H_{20}O_4Pb$  requires Pb, 40.8%). The same product was obtained without the gel, but longer heating was required (1 hour). The compound was insoluble in water, but soluble in hot alcohol and benzene. When heated slowly it gave the odour of ethyl benzoate and, when heated rapidly, it decomposed with a mild explosion.

A weighed quantity of the dibenzoate (*ca.* 1 g.) was dissolved in dry benzene, and dry hydrogen chloride passed into the solution for a few minutes. The precipitated diethyl-lead dichloride was filtered off, washed with benzene, and dried *in vacuo* (Found: Cl, 21.2. Calc. for  $C_4H_{10}Cl_2Pb$ : Cl, 21.1%).

*Tripropyl-lead Chloroacetate*.—Tetrapropyl-lead (3 c.c.), chloroacetic acid (1 g.), and silica gel were heated on a water-bath for  $\frac{1}{2}$  hour. The chloroacetate, recrystallised from light petroleum (b. p. 40–60°), had m. p. 109–110° (Found: Pb, 48.3. Calc. for  $C_{11}H_{23}O_2ClPb$ : Pb, 48.2%), and was identical with the compound obtained by the action of chloroacetic acid on tripropyl-lead hydroxide (Part I, *loc. cit.*).

*Diethyl-lead Dichloride*.—Tetraethyl-lead (12 c.c.) was dissolved in anhydrous toluene (100 c.c.) in a conical three-necked flask fitted with a reflux condenser (closed by a calcium chloride tube), an inlet tube for hydrogen chloride, and a thermometer dipping into the liquid, and heated to 90°. Dry hydrogen chloride was passed in, and after about 20 minutes a white precipitate began to form. After passage of the gas for a further hour, the solid was filtered off from the hot solution, and washed with boiling toluene (in which the triethyl-lead chloride is soluble). It was dried *in vacuo* over wax and was then pure (16 g., 80%), having m. p. 220° (decomp. leaving an infusible residue). If desired, it could be recrystallised in small quantity from hot water (Found: Cl, 21.1; Pb, 61.9. Calc. for  $C_4H_{10}Cl_2Pb$ : Cl, 21.1; Pb, 61.6%). Solubility: 2% in water at 15°, 0.1% in boiling alcohol. The aqueous solution of the pure dichloride gave a cream-coloured precipitate with ammonium sulphide. If traces of plumbous chloride were present, the precipitate was black.

*Reaction between Diethyl-lead Dichloride and Silver Chloroacetate*.—(a) Diethyl-lead dichloride (3.36 g.) suspended in ethyl alcohol (40 c.c.), was mixed with silver chloroacetate (4 g.) dissolved in hot water (40 c.c.). The mixture was heated and silver chloride (92% yield) was filtered off. On cooling, the filtrate deposited colourless crystals with a silvery lustre, m. p. *ca.* 179°, and were proved to be lead chloroacetate. The filtrate, on slow evaporation, gave long needles, m. p. and mixed m. p. with authentic specimen of triethyl-lead chloroacetate, 147° (Found: Pb, 53.8. Calc. for  $C_8H_{17}O_2ClPb$ : Pb, 53.5%).

(b) *In the cold*. Silver chloroacetate (5 g.) was ground in a mortar with diethyl-lead dichloride (4 g.) and sufficient water to make a paste, and set aside for an hour. The mixture was filtered, and hydrogen sulphide was passed through the solution to remove traces of lead; the black sulphide was filtered off, and a small portion of the filtrate then gave with hydrogen sulphide a cream-coloured precipitate of  $PbEt_2S$ . The remainder of the filtrate was evaporated below 25°. Colourless crystals of *diethyl-lead bischloroacetate* were obtained and, recrystallised from absolute alcohol, had m. p. 180° (efferv.) (Found: Pb, 45.8.  $C_8H_{14}O_4Cl_2Pb$  requires Pb, 45.8%). An aqueous solution gave a cream-coloured precipitate with hydrogen sulphide, thus showing that no  $Pb^{++}$  had been produced during the recrystallisation from alcohol.

*Diethyl-lead Dihydroxide and Oxide*.—Diethyl-lead dichloride (15 g.) was shaken with ether (75 c.c.) in a separating-funnel together with aqueous sodium hydroxide solution (30%, 50 c.c.). The solid dissolved, and after for 24 hours dense crystals were produced and sank to the bottom of the aqueous layer. These crystals were run off together with the minimum amount of aqueous sodium hydroxide, and were collected in a sintered funnel, washed with a small volume of aqueous acetone (1 : 1 by vol.), and dried on a porous tile. They were purified by dissolving them in the minimum quantity of warm water (40°) and placing the solution in a desiccator over concentrated sulphuric acid. After several days *diethyl-lead dihydroxide hexahydrate* crystallised and was filtered off and dried on a porous tile (Found: Pb, 51.2.  $C_4H_{12}O_8Pb \cdot 6H_2O$  requires Pb, 50.9%). The hexahydrate formed white transparent needles, readily soluble in cold water, less soluble in alcohol, insoluble in ether, acetone, benzene, and light petroleum. When heated in a capillary tube, it lost water at *ca.* 120°, a brown colour developed at

135°, and above 210° the solid blackened. When it was heated strongly in bulk in a crucible, a mild explosion took place.

*Loss of weight determinations.* A weighed quantity of the hexahydrate (*ca.* 0.25 g.) was placed in a vacuum-desiccator over concentrated sulphuric acid until no further loss in weight took place (16 hours) [Found: loss, 30.4.  $\text{PbEt}_2(\text{OH})_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{PbEt}_2\text{O}$  requires loss, 31.0%]. The residue of *diethyl-lead oxide* contained Pb, 73.7% ( $\text{C}_4\text{H}_{10}\text{OPb}$  requires Pb, 73.7%). The oxide was insoluble in water, but dissolved in dilute acetic acid. The loss in weight after long heating at 100° showed that the composition of the residue approximated to  $\text{PbO}$ .

*Conversion of Diethyl-lead Dihydroxide Hexahydrate into the Dichloride.*—The hexahydrate (10.5 g.) was dissolved in water and neutralised with dilute hydrochloric acid. The solution was rapidly evaporated to dryness in a vacuum-desiccator and the residue weighed [Found: ratio  $\text{PbEt}_2\text{Cl}_2$  :  $\text{PbEt}_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , 0.806. Calc.: 0.825]. The chloride content of the residue was determined gravimetrically (Found: Cl, 20.7. Calc. for  $\text{PbEt}_2\text{Cl}_2$  : Cl, 21.1. Calc. for  $\text{PbEt}_2\text{Cl}$  : Cl, 10.8%).

*Diethyl-lead Sulphite.*—Tetraethyl-lead (10 c.c., 0.05 mol.) was dissolved in ether (100 c.c.), and water (2 c.c., *ca.* 0.1 mol.) added. Sulphur dioxide was passed in for about 5 hours and a white amorphous powder was precipitated. This was filtered off, and the filtrate returned to the apparatus and again treated with sulphur dioxide until no further precipitation occurred. A further small yield (*ca.* 0.3 g.) of solid could be obtained by keeping the reaction mixture for a further 15 hours. The product was washed with ether and dried *in vacuo* over concentrated sulphuric acid; yield 17 g. (99%). *Diethyl-lead sulphite* was then obtained as an amorphous white powder which did not melt (Found: Pb, 59.8, 60.15.  $\text{C}_4\text{H}_{10}\text{O}_3\text{SPb}$  requires Pb, 60.0%). The sulphite is insoluble in water, alcohol, and ether, and soluble in dilute acids with evolution of sulphur dioxide. When treated with dilute hydrochloric acid in the cold and kept, it afforded pure crystals of diethyl-lead dichloride.

The above preparation was carried out in a tall cylindrical vessel in order (*a*) to ensure maximum absorption of sulphur dioxide, and (*b*) to avoid loss of tetraethyl-lead by creeping over the sides.

*Diethyl-lead Dibenzoate.*—Diethyl-lead sulphite (3 g., 50% excess) was heated under reflux for 1½ hours with benzoic acid (1.5 g.) dissolved in alcohol, sulphur dioxide being evolved. The unchanged sulphite was then filtered off, and the filtrate evaporated to dryness. The solid thus obtained was extracted with successive quantities of boiling water (20 c.c.) to remove benzoic acid, and the extract filtered hot each time. The insoluble residue from this treatment had *m. p.* 168°, and was further purified, if necessary, by recrystallisation from benzene; the yield was nearly theoretical, and the *m. p.* and mixed *m. p.* with the product obtained from tetraethyl-lead and benzoic acid, 168°.

*Note.* In order to show that the hot water extraction used to remove traces of benzoic acid did not promote disproportionation, the product from tetraethyl-lead was subjected to prolonged boiling with water without change of *m. p.* When it was heated gently in the open, an odour of ethyl benzoate was noted, but on strong heating a mild explosion took place.

*Action of Benzoic Acid on Triethyl-lead Hydroxide.*—To an aqueous-alcoholic solution of triethyl-lead hydroxide (see Part I, *J.*, 1949, 919) was added a concentrated alcoholic solution of benzoic acid (*ca.* 1.5 g.) until the mixture was acid to litmus; the whole was then made just alkaline by more triethyl-lead hydroxide. The product was poured into cold water, and the precipitate filtered off. The filtrate gave more of the product on evaporation. The crude *triethyl-lead benzoate* recrystallised from light petroleum (*b. p.* 100—120°) as colourless crystals, *m. p.* 126° (3.5 g., 80%) (Found: Pb, 49.6.  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Pb}$  requires Pb, 49.9%). The compound is very soluble in cold alcohol, acetone, and benzene.

*Diethyl-lead Bischloroacetate.*—Diethyl-lead sulphite (3.5 g., 0.01 mol.) was treated with a concentrated solution of chloroacetic acid (3.5 g., 0.04 mol., in 5 c.c. of water) and, when effervescence had subsided, the mixture was gently warmed to complete the reaction. It was then filtered, and the filtrate cooled and concentrated in a desiccator containing solid potassium hydroxide. The crystals thus obtained, when filtered off and washed with ether, were pure, having *m. p.* and mixed *m. p.* with product from diethyl-lead chloride and silver chloroacetate, 180° (efferv.). A solution of this first crop of crystals in water gave a yellow precipitate with hydrogen sulphide, thus proving the absence of lead chloroacetate.

Later crops of crystals which separated from the concentrated filtrate were less pure and were contaminated with plumbous ions. Purification of these could be effected by recrystallisation from absolute alcohol or by partial precipitation with hydrogen sulphide.

Prolonged boiling during the preparation or during recrystallisation must be avoided as the compound decomposes in these circumstances.

*Diethyl-lead Bistrichloroacetate.*—Diethyl-lead sulphite (3 g.) was added to a solution of trichloroacetic acid (5 g., *i.e.* *ca.* 80% excess) in warm water (5 c.c.). A reaction took place with vigorous evolution of sulphur dioxide. On cooling, the mixture solidified and sufficient hot water was therefore added to dissolve the mass, and the resulting solution was filtered. Crystals were deposited on cooling and were filtered off. Further crops were obtained by concentration of the filtrate *in vacuo* at room temperature, over concentrated sulphuric acid. The combined crops were recrystallised as quickly as possible from hot water, and *diethyl-lead bistrichloroacetate* was obtained in clusters of colourless needles, *m. p.* 151° (efferv.) (Found: Pb, 34.5.  $\text{C}_8\text{H}_{10}\text{O}_4\text{Cl}_6\text{Pb}$  requires Pb, 35.0%). A freshly prepared aqueous solution gave a clean cream-coloured precipitate with hydrogen sulphide. The aqueous solution, however, after long storage contained plumbous ions, but this decomposition was less rapid than that of the corresponding chloroacetate.

The following two new compounds were prepared similarly to the bischloroacetate. *Diethyl-lead ditoluene-p-sulphonate.* From sulphite (5 g.) and toluene-*p*-sulphonic acid (5 g.) in water (10 c.c.); recrystallised *in vacuo* at room temperature or quickly from warm water; yield 5 g. (60%); highly

crystalline long needles without m. p., but giving a black, then finally white residue (lead sulphate) on heating (Found : Pb, 33.5.  $C_{18}H_{24}O_6S_2Pb$  requires Pb, 34.1%); soluble in hot water, slightly soluble in alcohol and benzene. *Diethyl-lead ditoluene-o-sulphonate*; yield 60%; perfect colourless oblique rhombohedra; when heated, it contracted at 165°, and then decomposed to lead sulphide and finally lead sulphate (Found : Pb, 33.3%), slightly soluble in cold water, readily soluble in hot water, much less soluble in alcohol, benzene, and other organic solvents.

*Diethyl-lead Bisthiolacetate*.—This was prepared in the cold from sulphite (4 g.) and thioacetic acid (2 g., 13% excess). The cold reaction mixture went almost solid, and after filtration was dried *in vacuo*, giving an almost pure product. The *bisthiolacetate* recrystallised from hot benzene or ethyl alcohol in pale yellow rectangular tablets, m. p. 84.5–85° to a pale yellow liquid which then darkened slowly and finally decomposed at 160° (Found : Pb, 49.5.  $C_8H_{16}O_2S_2Pb$  requires Pb, 49.9%). The compound decomposed after storage in a sealed tube for some months.

*Conversion of the Bisthiolacetate into the Dichloride*.—The thiolacetate (1 g.) was dissolved in alcohol, and concentrated hydrochloric acid (5 c.c.) added. The dichloride crystallised, was filtered off, and recrystallised rapidly from hot water (Found : Cl, 21.3. Calc. for  $C_4H_{10}Cl_2Pb$  : Cl, 21.1%). The chloride when dissolved in water gave a cream-coloured precipitate with ammonium sulphide.

*Triethyl-lead Thiolacetate*.—Thioacetic acid (1 g.) was dissolved in aqueous alcohol, and an aqueous solution of triethyl-lead hydroxide added until the mixture was alkaline to litmus. An oil separated, but, on addition of more water and vigorous shaking, it solidified. The *thiolacetate* recrystallised from aqueous dioxan as almost white needles, m. p. 45° (Found : Pb, 56.1.  $C_6H_{18}OSPb$  requires Pb, 56.1%); it decomposed on storage.

*Action of Thioacetic Acid on Tetraethyl-lead*.—(i) *In the cold*. Tetraethyl-lead (4 c.c., 0.02 mol.) was mixed with thioacetic acid (1.5 g.), and the solution kept for *ca.* 20 hours at room temperature. A mass of long white needles was deposited; these were filtered off and washed with ether and were then pure. If necessary they could be recrystallised from benzene and had m. p., and mixed m. p. with product from the foregoing preparation, 45°.

(ii) *At 100°*. Tetraethyl-lead (8 c.c., 0.04 mol.) and thioacetic acid (6 g., 0.08 mol.) were heated under reflux on a water-bath for 3 hours, the mixture filtered while hot, and the filtrate kept overnight; a large mass of pale yellow crystals (A) was deposited, as well as other crystals (B) in the form of orange-coloured nodules. These were filtered off, and the filtrate deposited fine yellow needles (C) when kept for 24 hours.

The crystals (A) and (B) were separated mechanically, and (A) was recrystallised from benzene and washed with ether, well-defined, pale yellow, flat tablets being obtained. These were identified as diethyl-lead bisthiolacetate by m. p. and mixed m. p. with authentic specimen obtained from diethyl-lead sulphite. The crystals (B) were identified as plumbous thiolacetate (see below). The needles (C) had m. p. 44.5° and were found to be triethyl-lead thiolacetate, identical with the compound obtained from triethyl-lead hydroxide and thioacetic acid.

(iii) *At 100° with silica gel*. Tetraethyl-lead (3.2 g., 0.01 mol.) was heated under reflux on a water-bath with thioacetic acid (1.5 g., 0.02 mol.) and silica gel for 20 minutes. Darkening took place, and the product recrystallised from benzene as dark orange needles (Found : Pb, 58.0.  $C_4H_8O_2S_2Pb$  requires Pb, 58.0%). When heated slowly the *plumbous thiolacetate* darkened at 140–165° and then decomposed. On strong heating in air, lead sulphide and lead sulphate were produced. An aqueous solution was converted into lead sulphide by hydrogen sulphide and into lead chloride by hydrochloric acid. The product was further identified as plumbous thiolacetate by comparison with a specimen prepared from lead carbonate and thioacetic acid, followed by recrystallisation from benzene. Recrystallisation from water gave white instead of pale yellow needles.

*Disproportionation of Diethyl-lead Bischloroacetate*.—It was essential to use absolutely pure diethyl salt, free from plumbous ions, for this investigation. Diethyl-lead dichloride (4 g.) was heated under reflux with water (25 c.c.) for 30 minutes. The reaction mixture was then cooled in ice, and the crystals (A) so obtained were filtered off and washed with cold water. The aqueous filtrate was distilled until about 5 c.c. of liquid remained. This residual liquid on cooling deposited a further crop of (A). Dispersed in the aqueous distillate was an insoluble oil which possessed a powerful odour of ethyl chloroacetate. The aqueous suspension on treatment with potassium iodide and sodium hypochlorite solution, did not give iodoform, showing that ethyl alcohol was not a product of the reaction. The suspension was made alkaline with sodium hydroxide solution and heated under reflux for 15 minutes and distilled, the distillate now giving the iodoform reaction. The alkaline residue was proved to contain sodium chloroacetate.

The solid (A) was dried and extracted with boiling benzene. On cooling, the extract deposited long needles, m. p. 145.5°, proved to be triethyl-lead chloroacetate. The residue, insoluble in benzene, recrystallised from hot water as characteristic pearly leaflets which decomposed gradually on heating with blackening at *ca.* 176°. Its aqueous solution gave a heavy black precipitate with hydrogen sulphide without trace of a cream-coloured precipitate. These properties are characteristic of plumbous chloroacetate.

*Disproportionation of Di-n-propyl-lead Diacetate*.—Moist silver oxide (5.3 g., containing *ca.* 50% of water) was shaken with an alcoholic suspension of di-n-propyl-lead dichloride (3.3 g.). The mixture was filtered, and to the filtrate of the dihydroxide was added dilute acetic acid. No precipitate separated, and the solution was evaporated at 100°. The white residue obtained was dried and extracted with light petroleum (b. p. 40–60°), which on cooling gave white needles (B). The residue after the extraction was recrystallised from alcohol (C).

The substance (B) was twice recrystallised from light petroleum and then had m. p. 126—127° alone and with the *tripropyl-lead acetate* made from acetic acid and tripropyl-lead hydroxide (Found : Pb, 51.9.  $C_{11}H_{22}O_2Pb$  requires Pb, 52.4%). The substance (C) had m. p. 195° and was proved to be lead acetate (Found : Pb, 63.2. Calc. for  $C_4H_8O_4Pb$  : Pb, 63.7%). During the evaporation of the original aqueous-alcoholic solution, an ester was obtained and identified as propyl acetate.

In the above reaction, it was probable that dipropyl-lead diacetate was first produced and then disproportionated to tripropyl-lead acetate and lead acetate. To confirm this, the aqueous-alcoholic solution was allowed to evaporate in a desiccator at room temperature and a solid residue was obtained which was now completely soluble in hot light petroleum (b. p. 40—60°); white needles separated on cooling (Found : Pb, 49.7. Calc. for dipropyl-lead diacetate,  $C_{10}H_{20}O_4Pb$  : Pb, 50.4%), m. p. 120° (decomp.), mixed m. p. with tripropyl-lead acetate 104—114° (cf. Part I, *loc. cit.*). When the solid diacetate was heated a marked ester-like odour was produced. An aqueous-alcoholic solution of the diacetate was evaporated at 100° and worked up as above. The quantities of tripropyl-lead acetate and lead acetate obtained were in accordance with equation (B) (p. 660), and an odour of ester was also produced.

*Diethyldi-n-propyl-lead*.—Magnesium (14.4 g.), dry ether (150 c.c.), a crystal of iodine, and a small amount of *n*-propyl bromide were mechanically stirred, and the remainder of the alkyl halide (total amount, 73.8 g.) in ether (150 c.c.) added. At the end of the reaction, diethyl-lead dichloride (50 g., 0.25 mol.) was added in small portions. After the vigorous action had subsided, the mixture was heated on a water-bath for 3 hours, cooled, decomposed with water, extracted with ether, and dried. After distillation of the ether, the residue distilled at 70—72°/4 mm.

*Diethylpropyl-lead Chloroacetate*.—Diethyldi-*n*-propyl-lead (2.4 g.), dissolved in a small quantity of ether, chloroacetic acid (0.63 g.), and silica gel were heated on a boiling-water bath for 1½ hours. The *chloroacetate* which separated on cooling was recrystallised from a mixture of benzene and light petroleum (b. p. 60—80°) and had m. p. 112° (Found : Pb, 51.4.  $C_9H_{18}O_2ClPb$  requires Pb, 51.9%).

*Diethylpropyl-lead Propionate*.—This was prepared by heating diethyldipropyl-lead (3.5 g.), propionic acid (0.74 g.), and silica gel on a water-bath for 1½ hours. The *propionate* was recrystallised from ethyl acetate, m. p. 86° (Found : Pb, 54.0.  $C_{10}H_{22}O_2Pb$  requires Pb, 54.4%).

*N-(Ethyldipropylplumbi)toluene-p-sulphonamide*.—Ethyldipropyl-lead chloride was first prepared by passing dry hydrogen chloride through a solution of diethyldipropyl-lead (5 c.c.) in dry light petroleum (b. p. 40—60°; 50 c.c.) until saturated. The product was then filtered, and the filtrate concentrated until solid separated. This was partly purified by extracting the solid with alcohol, filtering, and evaporating the filtrate to dryness. The sodio-derivative of toluene-*p*-sulphonamide (1.28 g.) was suspended in alcohol, and the above chloride (2.1 g.) dissolved in alcohol was added and the mixture heated under reflux for 20 minutes, filtered, and water added to the filtrate. The *N-(ethyldipropylplumbi)toluene-p-sulphonamide*, separated and recrystallised from benzene-light petroleum (b. p. 40—60°), had m. p. 94.5° (Found : C, 36.6; H, 5.7; Pb, 41.7.  $C_8H_4Me\cdot SO_2\cdot NH\cdot PbEtPr_2$  requires C, 36.6; H, 5.5; Pb, 42.1.  $C_8H_4Me\cdot SO_2\cdot NH\cdot PbEt_2Pr$  requires C, 35.1; H, 5.2; Pb, 43.3%).

*Alternative preparation*. The chloride (2.4 g.), dissolved in alcohol, was shaken for 10 minutes with moist silver oxide (2.8 g.), and the silver chloride filtered off. To the filtrate an alcoholic solution of toluene-*p*-sulphonamide was added, and after 10 minutes, water was added. The plumbisulphonamide thus obtained and recrystallised as above had m. p. 94.5° (Found : Pb, 42.1%).

*n-Butyldiethyl-lead Chloroacetate* (impure).—Dibutyldiethyl-lead was prepared according to Jones, Evans, Gulwell, and Griffiths (*J.*, 1935, 41). The plumbane (1.9 g., 0.005 mol.) was added to chloroacetic acid (0.6 g., 0.006 mol.) dissolved in absolute ether (5 c.c.), and the solution heated, with a few pieces of porous pot as catalyst, under reflux for 15 minutes on the water-bath. On addition of excess of water, a white precipitate was formed; this was filtered off, and the chloroacetate recrystallised from a small volume of light petroleum (b. p. 60—80°); m. p. 82—83° (Found : C, 29.9; H, 5.1; Pb, 48.6.  $C_{10}H_{21}O_2ClPb$  requires C, 28.9; H, 5.1; Pb, 49.8%) [other possibilities are :  $PbEt_2(O\cdot CO\cdot CH_2Cl)_2$  requires C, 21.2; H, 3.1; Pb, 45.9%.  $PbEtBu_2(O\cdot CO\cdot CH_2Cl)$  requires C, 32.5; H, 5.7; Pb, 46.7%.  $PbBu_2(O\cdot CO\cdot CH_2Cl)_2$  requires C, 28.3; H, 4.35; Pb, 40.8%].

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