630. *Organo-lead Compounds. Part II.* (a) *Novel Types in the Trialkyl-lead Series.* (b) *Further Examples of Sternutators.*

By R. Heap and B. C. Saunders.

New types of trialkyl-lead compounds are represented by *triethyl-lead ethyl sulphide* (a liquid) and *triethyl-lead phthalimide* (a solid). Both show pronounced sternutatory properties. Thirty-three other trialkyl-lead compounds have been prepared and examined. Trimethyl-lead salts are exceedingly feeble sternutators irrespective of the acid radical. The superiority of tri-*n*-propyl-lead salts has been confirmed. Within a series (trimethyl excepted) there are variations of virulence depending upon the nature of the acid radical.

Triethyl-lead chloride reacts rapidly with the sodium salts of certain weak acids (*e.g.*, phenylnitromethane) with the generation of tetraethyl-lead. The mechanism of this reaction is discussed. A convenient method for identifying small quantities of tetraethyl-lead is described.

In Part I (this vol., p. 919) an account was given of the preparation and physiological properties of a variety of trialkyl-lead salts, including triethyl-lead salts (I). All these were solids and were ionic. Two triethyl-lead derivatives, *viz.*, *triethyl-lead ethyl sulphide* and *triethyl-lead phenyl sulphide* (*triethyl-ethylthio-* and *-phenylthio-lead*) are now described. These are unstable liquids, soluble in organic solvents and slowly hydrolysed by water, and it is to be presumed that the link between lead and sulphur atoms is covalent (II).

They are prepared by the action of the thiol on triethyl-lead hydroxide. The composition of the product was readily established by fission of the compound, in dry ether, by hydrogen chloride:

$$Et_3Pb{\cdot}SEt + HCl = PbEt_3Cl + EtSH.$$

The sternutatory action of these non-ionised sulphides, at concentrations of 1 in 10^6 and 1 in 10^7, was of the same type and magnitude as that of the ionic compounds (I), and quite

$[PbEt_3]^+ X^-$ (I.) $\quad Et_3Pb{\cdot}SR$ (II.) $\quad PbEt_4$ (III.) $\quad Et_3Pb{\cdot}N\langle^{CO}_{CO}\rangle C_6H_4$ (IV.)

different from the toxic action exerted by the non-ionic tetraethyl-lead (III). We also showed that the corresponding compounds of inorganic lead [$Pb(SH)_2$ and $Pb(S{\cdot}C_6H_5)_2$] were quite ineffective at concentrations of 1 in 10^7. The sternutatory effects of the organic sulphides on the human system were therefore most probably due to the products of hydrolysis:

$$Et_3Pb{\cdot}SEt + H_2O = PbEt_3^+ + OH^- + EtSH$$

Another new type of organo-lead compound is *triethyl-lead phthalimide* (IV), a crystalline compound, prepared by the direct action of triethyl-lead hydroxide on phthalimide. It possessed sternutatory properties similar to those shown by triethyl-lead chloride (taken as a convenient standard, cf. Part I). *Tri*-n-*propyl-lead phthalimide* was also prepared and, in accordance with expectation, was much more potent than the corresponding triethyl compound; it was intolerable at a concentration of 1 in 10^7 (Grade 3, Part I), and even at 1 in $2{\cdot}5 \times 10^7$ produced a difficultly-respirable atmosphere.

Triethyl-lead monochloroacetate (Grade 1) was prepared, as a stable, highly crystalline compound, by the action of silver chloroacetate on triethyl-lead chloride and also directly from chloroacetic acid and triethyl-lead hydroxide. A third preparation (based on the method of Browne and Reid, *J. Amer. Chem. Soc.*, 1927, **49**, 833) served as a useful way of identifying small quantities of tetraethyl-lead. The procedure is simple and rapid and consists in heating tetraethyl-lead in ethereal solution with chloroacetic acid in the presence of silica gel for a few minutes: the derivative obtained is pure.

Triethyl-lead bromoacetate, trichloroacetate, and propionate were also graded 1, whereas the β-*chloropropionate*, *crotonate*, and *cyanide* were distinctly more virulent and were placed in Grade 2.

Klippel (*Jahresber.*, 1860, 381) claimed to have prepared *triethyl-lead thiocyanate* by the action of triethyl-lead chloride on silver thiocyanate, but he gave neither m. p. nor analysis of his product. We found that no appreciable reaction took place between these reactants. This is not surprising since the solubility product of silver thiocyanate is less than that of silver chloride. When, however, alcoholic solutions of triethyl-lead chloride and potassium thiocyanate were heated under reflux the required thiocyanate was obtained as a low-melting solid in good

yield (Grade 2 with unpleasant after-effects). *Triethyl-lead selenocyanate* was similarly prepared, but it proved to be inferior to the thiocyanate.

Triethyl-lead acrylate was readily prepared in theoretical yield from triethyl-lead hydroxide and acrylic acid. It had very pronounced sternutatory action and in this respect was greatly superior (Grade 2) to triethyl-lead chloride.

The influence of a carbethoxy group was seen in *triethyl-lead ethyl oxalate* which was intolerable at a concentration of 1 in 10^6, the nose, throat, chest, and gums being all quickly affected (Grade 2). It appeared then that the introduction of a free carboxyl group might be even more effective as a subsidiary toxic group. Attempts were therefore made to obtain triethyl-lead hydrogen oxalate from the calculated quantities of oxalic acid and triethyl-lead hydroxide. It was found, however, that only the di(triethyl-lead) oxalate could be obtained, and that this compound was insoluble in water and organic solvents. Its intractability made it difficult to test it physiologically.

In addition to the triethyl-lead salts described above, the following were also prepared and examined for sternutatory properties (for results see below): toluene-*p*-sulphonate, toluene-*o*-sulphonate, *naphthalene*-2-*sulphonate*, propionate, and salicylate. Tri-*n*-propyl-lead acetate, prepared by the action of glacial acetic acid on tetrapropyl-lead, was found to be identical with the compound prepared by neutralising tripropyl-lead hydroxide with dilute acetic acid (Part I). The *toluene*-o-*sulphonate* and *toluene*-p-*sulphonate* were similarly prepared. By the action of *iso*butyl bromide on sodium–lead alloy (containing 20% of sodium) tetra-*iso*butyl-lead was obtained; owing to its tendency to decomposition on distillation, the crude dried product was successfully used for the preparation of the following: tri*iso*butyl-lead chloride, *acetate*, *propionate*, *butyrate* and *toluene*-o- and -p-*sulphonate*. Tetramethyl-lead was also prepared by the action of sodium–lead alloy on methyl iodide, and a pure product was obtained on distillation under reduced pressure. From this, the chloride, *formate*, *acetate*, iso*valerate*, *toluene*-p-*sulphonate*, *monochloroacetate*, and *trichloroacetate* were obtained without difficulty.

In view of the ready reaction between triethyl-lead hydroxide and a very weak acid such as phthalimide, attempts were made to bring about a reaction between the hydroxide and nitromethane, phenylnitromethane, oximes, and alcohols: however, no reaction occurred. On the other hand, a vigorous reaction took place between the sodium derivative of nitromethane and triethyl-lead chloride, either in methyl alcoholic solution or heterogeneously in suspension in dry benzene. From these reactions, however, the desired triethyl-lead *aci*nitromethane, $Et_3Pb{\cdot}O{\cdot}N\langle^{O}_{CH_2}$ was not isolated, but tetraethyl-lead was obtained in good yield and its identity confirmed by conversion into triethyl-lead monochloroacetate as described above. The unexpected formation of tetraethyl-lead may be explained by the formation of the triethyl-lead derivative $PbEt_3R$ in the first instance, thus:

$$PbEt_3Cl + NaR = PbEt_3R + NaCl$$

$$\left(R = \cdot O{\cdot}N\langle^{O}_{CH_2}, \quad \cdot O{\cdot}N\langle^{O}_{CHPh}, \quad \cdot OMe, \quad \cdot O{\cdot}N{:}CMe_2\right).$$

Because of its non-isolation, this derivative is undoubtedly extremely unstable, and dismutation according to the equation, $2PbEt_3R = PbEt_4 + PbEt_2R_2$, would be in accordance with expectation. The diethyl-lead compound can then undergo further dismutation to $PbEt_3R$ and a plumbous salt, PbR_2. The $PbEt_3R$ will then further dismute, and the overall result will be the production of tetraethyl lead on the one hand and the complete degradation of all other possible organo-lead compounds into the inorganic plumbous salt.

In the case of sodium phenylnitromethane, the yield of tetraethyl-lead was exactly in accordance with this scheme. With sodium methoxide we isolated also pure tetraethyl-lead. Browne and Reid (*loc. cit.*) obtained an oil from this reaction, but did not identify it.

For much of the work described in this paper pure triethyl-lead chloride was required. The standard method (Part I) consisted in passing hydrogen chloride through an ethereal solution of tetraethyl-lead. The first crop of crystals obtained during the first half-hour was reasonably pure, but in order to obtain a good yield, the passage of gas must be continued longer than this. We found that the later crops contain very little triethyl-lead chloride and consist largely of diethyl-lead dichloride. The cause of this was probably the high local concentration of hydrogen chloride, and also the heat of solution of the gas. These difficulties were overcome by the improved method described in the Experimental (p. 2987). The effects

of the heat of solution of hydrogen chloride were avoided by using a previously saturated ethereal solution of the gas. In this way the concentration was fixed within narrow limits. The cooled acid solution was then run into the tetraethyl-lead, and a 96% yield of pure crystalline triethyl-lead chloride was obtained.

General Inferences.—All the trimethyl-lead salts are almost devoid of sternutatory properties, irrespective of the acid radical, and at a concentration of 1 : 10^7 were of grade 0. Tri-*n*-propyl-lead salts are superior to triethyl-lead salts. Tri*iso*butyl-lead salts are also superior to triethyl-lead salts, but not as potent as the tri-*n*-propyl-lead salts. Within a particular series (trimethyl excepted) there are variations of virulence depending on the nature of the acid radical. Salts of organic acids are more virulent than salts of inorganic acids (*e.g.*, the chloride). Of the organic acids, the acrylates, crotonates, β-chloropropionates, and sulphonates are the most potent.

Experimental.

Triethyl-lead Ethyl Sulphide.—Triethyl-lead hydroxide (4·9 g.) was shaken with ether (50 c.c.), ethanethiol (0·97 g.) was added, and the whole thoroughly shaken. The aqueous layer was run off and solid calcium chloride added immediately. During the drying (1½ hours) more of the aqueous layer was formed and was run off. After 2 hours (when a small quantity of yellow precipitate had appeared) the ethereal solution was filtered and the ether distilled off. The accumulated yield (19 g.) of several preparations was distilled in an atmosphere of nitrogen at 0·075 mm. and had b. p. 76—78°. The *sulphide* is a colourless liquid which decomposes slowly in light but not in the dark (Found: Pb, 57·95. $C_8H_{20}SPb$ requires Pb, 58·3%). The odour resembles that of horseradish.

Triethyl-lead Phenyl Sulphide.—Triethyl-lead hydroxide (13·5 g., 35% excess) was shaken with ether (20 c.c.) in a separating funnel, and a solution of thiophenol (3·5 g.) in ether (30 c.c.) was added. There was a slight evolution of heat, and the aqueous layer was run off as it was formed during the reaction (½ hour). The ether was then separated and dried ($CaCl_2$). The ether was distilled off, the last traces being removed at 100°/18 mm. The residue was not further distilled as decomposition took place. After the removal of the ether, the residue was a pale yellow oil which was proved to be the almost pure *sulphide* (Found: Pb, 51·1. $C_{12}H_{20}SPb$ requires Pb, 51·4%). Distillation of the sulphide at above 125°/0·3 mm. caused rapid decomposition and the production of a yellow solid in the flask. This solid, which contained lead and sulphur, was insoluble in organic solvents. Hydrochloric acid decomposed it, giving lead chloride, and analysis for lead showed it to be $(PhS)_2Pb$.

Cleavage of Triethyl-lead Phenyl Sulphide by Hydrogen Chloride.—The sulphide (1 g.) was dissolved in dry ether, and a stream of dry hydrogen chloride passed through until, after a few seconds, precipitation ceased. The white crystals were filtered off immediately and washed with dry ether. The ethereal filtrate contained thiophenol. A weighed quantity of the dried crystals was dissolved in hot dilute nitric acid, and the chloride determined (Found: Cl, 10·75. Calc. for triethyl-lead chloride, $C_6H_{15}ClPb$: Cl, 10·8%).

Triethyl-lead Phthalimide.—Triethyl-lead hydroxide (1·55 g.), dissolved in alcohol, was heated under reflux with phthalimide (0·73 g.), also dissolved in alcohol, for 10 minutes. The solution was then filtered from traces of triethyl-lead carbonate, and water added to the filtrate until crystallisation started. The m. p. of crude *triethyl-lead phthalimide* was 131°. The compound was crystallised by dissolving it in a very small volume of benzene and adding light petroleum (b. p. 40—60°) and then had m. p. 131° (Found: Pb, 46·9. $C_{14}H_{19}O_2NPb$ requires Pb, 47·1%). The compound responded to the fluorescein reaction. When it was dissolved in ether and dry hydrogen chloride passed through the solution, phthalimide was precipitated immediately.

*Tri-*n*-propyl-lead Phthalimide.*—An alcoholic solution of tri-*n*-propyl-lead hydroxide was obtained by shaking moist silver oxide (2·3 g.) with an alcoholic solution of tripropyl-lead chloride (3 g.), and filtering the mixture. The filtrate was added to an alcoholic solution of an approx. equivalent quantity (1·2 g.) of phthalimide, and the mixture was heated on a water-bath for 10 minutes. It was then cooled and filtered, and to the filtrate water was added; a precipitate separated after some minutes. *Tri-propyl-lead phthalimide* was recrystallised from light petroleum (b. p. 40—60°) (Found: Pb, 42·7. $C_{17}H_{25}O_2NPb$ requires Pb, 43·0%). The compound responded to the fluorescein reaction.

Triethyl-lead Monochloroacetate.—(*a*) Silver chloroacetate (2 g.) was suspended in water (20 c.c.) and poured into a solution of triethyl-lead chloride (3·3 g.) in alcohol (20 c.c.). The mixture was thoroughly stirred and the silver chloride filtered off. The filtrate was concentrated and long, colourless, needles separated, which were recrystallised from benzene and then had m. p. 147° (Found: C, 24·5; H, 4·6; Pb, 53·3. Calc. for $C_8H_{17}O_2ClPb$: C, 24·7; H, 4·4; Pb, 53·4%).

(*b*) An aqueous solution of chloroacetic acid was run into an aqueous solution of triethyl-lead hydroxide until no more precipitate was formed. The solid was filtered off and washed with water; it had m. p. 147°.

Identification of Small Quantities of Tetraethyl-lead.—Tetraethyl-lead (0·1 g.) dissolved in dry ether (0·5 c.c.), and dry chloroacetic acid (0·027 g.), together with a minute piece of silica gel, were warmed for 10 minutes and set aside for ¼ hour, and then dry ether (5 c.c.) was added. The crystals were filtered off and washed with ether, and were then pure, having m. p. 146·7° (mixed m. p. with authentic triethyl-lead monochloroacetate prepared as in (*a*) and (*b*) above, 146·5°). Recrystallisation was usually not necessary.

Triethyl-lead Bromoacetate.—To a solution of triethyl-lead hydroxide in water was added a solution of bromoacetic acid until no more precipitate was formed. The solid was filtered off, washed with water, and crystallised from benzene in long, colourless, needles, m. p. 120° (Found: Pb, 48·4. Calc. for $C_8H_{17}O_2BrPb$: Pb, 47·95%). This compound had previously been prepared from tetraethyl-lead (Browne and Reid, *J. Amer. Chem. Soc.*, 1927, **49**, 833).

Triethyl-lead Trichloroacetate.—(*a*) Prepared from the hydroxide, and recrystallised from alcohol, this melted at 140° (Found: Pb, 45·2. Calc. for $C_8H_{15}O_2Cl_3Pb$: Pb, 45·4%).

(*b*) Trichloroacetic acid (5 g.) was dissolved in the minimum amount of ether and then tetraethyl-lead (2 c.c.) was added. A piece of porous tile was added, and the mixture gently heated for a few seconds. When no more crystals were precipitated, the solid was filtered and washed with a small quantity of ether; it had m. p. 141° (Found: Pb, 45·2%). Browne and Reid (*loc. cit.*) gave m. p. 135·5—138·5°.

Triethyl-lead Propionate.—Propionic acid (0·74 c.c.) and tetraethyl-lead (2 c.c.) were heated under reflux for 1 hour with silica gel. The solid which separated was recrystallised from benzene and had m. p. 141° (decomp.) (Found: Pb, 56·3. Calc. for $C_9H_{20}O_2Pb$: Pb, 56·4%).

Triethyl-lead β-Chloropropionate.—Prepared from the hydroxide and an aqueous solution of β-chloro-propionic acid, the crystalline *triethyl-lead β-chloropropionate* which separated recrystallised from light petroleum (b. p. 60—80°) in short colourless prisms, m. p. 106° (Found: Pb, 51·9. $C_9H_{19}O_2ClPb$ requires Pb, 51·7%).

Triethyl-lead Crotonate.—Similarly prepared, the *crotonate* recrystallised from benzene in short needles, m. p. 135—136°, very soluble in alcohol and subliming when heated (Found: Pb, 54·6. $C_{10}H_{20}O_2Pb$ requires Pb, 54·4%).

Triethyl-lead Cyanide.—Triethyl-lead chloride (6·6 g.), dissolved in alcohol (80 c.c.), was heated under reflux with potassium cyanide (3·0 g.) for 1¼ hours (the potassium cyanide did not completely dissolve). The mixture was filtered while hot and water added to the filtrate until cloudy. The whole was then heated until clear, and allowed to cool; long needles then separated. The *cyanide*, recrystallised from aqueous alcohol, had m. p. 189° (decomp.; becomes yellow at 135°) (Found: CN, 8·1; Pb, 64·7. $C_7H_{15}NPb$ requires CN, 8·1; Pb, 64·7%).

Triethyl-lead Thiocyanate.—Triethyl-lead chloride (3·3 g.), dissolved in alcohol (20 c.c.), was heated under reflux with potassium thiocyanate (1·2 g.), dissolved in alcohol (30 c.c.), for 1½ hours. Potassium chloride was filtered off, the filtrate cooled to −10°, and cold water (30 c.c.) added to start crystallisation. More water was then added and the product well mixed and set aside at −10° for 1 hour. The *thiocyanate* was filtered off and washed with cold dilute aqueous alcohol; it had m. p. 35° (yield: 2·1 g., 60%) (Found: Pb, 58·55; CNS, 16·5. $C_7H_{15}NSPb$ requires Pb, 58·8; CNS, 16·5%). The compound, a white granular crystalline solid, is exceedingly soluble in all the usual organic solvents, but insoluble in water. The aqueous-alcoholic solution gave a red colour with ferric chloride.

Triethyl-lead Selenocyanate.—Potassium selenocyanate (1·5 g.) in alcohol (30 c.c.) was mixed with triethyl-lead chloride (3·3 g.) in alcohol (20 c.c.). A precipitate of potassium chloride was formed almost immediately and was filtered off. The filtrate was heated under reflux for ¼ hour and then cooled to −10°, and water added. The cold solution was set aside, and on scratching the *selenocyanate*, m. p. 26—29° (2·51 g.), separated. Recrystallisation was attempted at −10°, but only a granular solid was obtained, having m. p. 29·5—30·5° (Found: CNSe, 26·2. $C_7H_{15}NSePb$ requires CNSe, 26·3%). When heated in air, the compound burned with evolution of clouds of soot and gave a "lead flame." It was immediately decomposed by dilute or concentrated sulphuric acid depositing selenium.

Triethyl-lead Cyanate.—To potassium cyanate (2 g.) in aqueous alcohol (100 c.c. of 50% v/v) was added a solution of triethyl-lead chloride (6·6 g.) in alcohol (40 c.c.). The mixture was set aside for 36 hours, and a precipitate (probably the dicyanate) was filtered off. The filtrate was concentrated under reduced pressure over calcium chloride, and *triethyl-lead cyanate* separated as colourless crystals. These were filtered off and washed with 30% aqueous alcohol (Found: CNO, 12·2; Pb, 61·2. $C_7H_{15}ONPb$ requires CNO, 12·5; Pb, 61·6%). The filtrate gave a further crop on evaporation. When heated, the compound did not melt, but became yellow at 23° and contracted markedly at 183·5°, with blackening.

Triethyl-lead Acrylate.—Triethyl-lead hydroxide (4·5 g.) was dissolved in alcohol (25 c.c.), and acrylic acid added until the mixture was neutral to litmus. The solution so obtained was evaporated to a small bulk and filtered hot. On cooling, crystals were deposited and were filtered off and washed with light petroleum (b. p. 40—60°). Further crops of crystals were obtained from the mother-liquor by further evaporation and crystallisation (total yield, 5·2 g., 98·5%). The product so obtained was purified by recrystallisation from hot benzene, with animal charcoal to remove polymers. A second recrystallisation from benzene gave *triethyl-lead acrylate* as colourless needles (1·6 g., 30%) which were completely soluble in benzene and alcohol, but only very slightly soluble in water. The pure substance sintered sharply at 120° and when heated in the open exploded feebly (Found: Pb, 56·2. $C_9H_{18}O_2Pb$ requires Pb, 56·7%). For the lead analysis, it was first necessary to heat the compound in a sealed tube with concentrated nitric acid.

Triethyl-lead Monoethyl Oxalate.—Triethyl-lead hydroxide (3 g., *i.e.*, 14% excess) was dissolved in absolute alcohol (15 c.c.), and monoethyl oxalate (1 g.) added. After a few hours a faint precipitate $[(CO_2 \cdot PbEt_3)_2]$ developed and was filtered off. The filtrate deposited crystals on slow evaporation. These were recrystallised from a concentrated alcoholic solution by slow evaporation, and the product was washed with light petroleum (b. p. 40—60°) and dried on porous plate in a vacuum-desiccator over calcium chloride. No satisfactory solvent was found for recrystallisation in the normal manner. *Triethyl-lead monoethyl oxalate* was obtained as long colourless needles which were soluble in alcohol, benzene, and cold water, but insoluble in light petroleum (b. p. 40—60°) (Found: Pb, 50·1. $C_9H_{20}O_4Pb$ requires Pb, 50·4%). When heated in a capillary tube the substance melted at 55°, decomposed with effervescence at 140°, and finally solidified to a while solid which did not alter further below 210°. Stronger heating of this white residue caused it to char and, when heated in the open, finally to leave a residue of lead oxide. When the original substance was heated more rapidly in the open it decomposed explosively. The aqueous solution of the substance was neutral to litmus, and reduced potassium permanganate acidified with dilute sulphuric acid.

Triethyl-lead Toluene-p-sulphonate.—Toluene-*p*-sulphonic acid (4 g.) and tetraethyl-lead (5 c.c.) were heated under reflux with silica gel for ½ hour. The product was dissolved in benzene and filtered. When light petroleum (b. p. 40—60°) was added, the sulphonate crystallised, having m. p. 170° (decomp.) (Gilman and Robinson, *Rec. Trav. chim.*, 1930, 767, give m. p. 167—168°). It was also found that if

toluene-*p*-sulphonyl chloride (2 g.) and tetraethyl-lead (2 c.c.) were heated under reflux in ether for 6 hours in the presence of gel, the sulphonate, m. p. 170°, separated. In this reaction the sulphonyl chloride may first be hydrolysed to the sulphonic acid, but there is no direct evidence for this at present.

Triethyl-lead Toluene-o-sulphonate.—Prepared similarly to the *p*-sulphonate, the *toluene-o-sulphonate* was recrystallised from benzene and had m. p. 189° (Found: Pb, 44·1. $C_{13}H_{22}O_3Pb$ requires Pb, 44·5%). It was also prepared by heating ethereal solutions of tetraethyl-lead (2 c.c.) and toluene-*o*-sulphonyl chloride (2 c.c.) with silica gel for 4½ hours; the solid which separated was recrystallised from alcohol and had m. p. 189° (Found: Pb, 44·8%).

Triethyl-lead Naphthalene-2-sulphonate.—Naphthalene-2-sulphonic acid (2·08 g.) was heated under reflux with tetraethyl-lead (3·5 c.c.) and silica gel for ½ hour. The *sulphonate* which separated was washed with ether and recrystallised from benzene; it had m. p. 152° (Found: Pb, 40·5. $C_{16}H_{22}O_3SPb$ requires Pb, 41·35%).

Triethyl-lead propionate, m. p. 141° (Found: Pb, 56·3. Calc. for $C_9H_{20}O_2Pb$: Pb, 56·4%), and salicylate, m. p. 93° (Found: Pb, 47·9. Calc. for $C_{13}H_{20}O_3Pb$: Pb, 47·1%), were prepared in a similar manner.

Reaction between Triethyl-lead Chloride and Sodiophenylnitromethane.—Triethyl-lead chloride (4 g.) was dissolved in dry toluene (20 ml.), and the solution was treated with sodiophenylnitromethane (4 g., 100% excess) and shaken thoroughly. The whole was boiled for *ca.* 1 hour under reflux and then filtered. The filtrate was distilled *in vacuo* to remove toluene, whereupon a heavy colourless oily residue remained in the flask together with traces of solid. The oil was filtered and fractionated; the entire liquid distilled at 92°/2 mm. and was nitrogen-free (yield 3 g.) (Found: C, 30·6; H, 6·2. Calc. for $C_8H_{20}Pb$: C, 29·7; H, 6·2%). The liquid was identified conclusively as tetraethyl-lead by conversion into triethyl-lead monochloroacetate.

Sodium nitromethane, sodium methoxide, and sodium acetoxime behaved similarly.

Triethyl-lead Chloride (Modified Method).—Dry ether (250 c.c.) was saturated with hydrogen chloride, and tetraethyl-lead (64·8 g.) was slowly added, with shaking and cooling. The mixture was then set aside in ice-water until the effervescence ceased (usually about 20 minutes) and then for 30 minutes at room temperature. The white needles which had been deposited were filtered off, washed free from hydrochloric acid with dry ether, and dried. The product was usually sufficiently pure for most purposes without recrystallisation (yield: 65 g., 96%) (Found: Cl, 10·9. Calc. for $C_6H_{15}ClPb$: Cl, 10·75%). Crystals deposited later were discarded as they contained diethyl-lead dichloride and lead chloride.

Tri-n-*propyl-lead Acetate.*—Tetrapropyl-lead (3·5 c.c.) and glacial acetic acid (1·5 c.c.) were heated with silica gel on a water-bath for 2 hours. The solid which separated was extracted with light petroleum, and the residue with alcohol. The light petroleum extract deposited white needles of tri-*n*-propyl-lead acetate on cooling; recrystallised from the same solvent, these had m. p. 128° [mixed m. p. with tripropyl-lead acetate made from tripropyl-lead hydroxide (Part I, *loc. cit.*) 127°] (Found: Pb, 52·4. Calc. for $C_{11}H_{24}O_2Pb$: Pb, 52·4%). The alcoholic extract deposited plates, m. p. 195—196° [Found: 63·2. Calc. for $C_4H_6O_4Pb$ (lead acetate): Pb, 63·7%].

Tri-n-*propyl-lead Toluene-o-sulphonate.*—Tetrapropyl-lead (2·6 c.c.) was heated on a water-bath with toluene-*o*-sulphonic acid (3·44 g.) for a few minutes. The solid product was extracted with ether, the ethereal extract evaporated to dryness and dissolved in benzene, and a large excess of light petroleum (b. p. 40—60°) added. The cloudy solution was cooled in ice and on scratching the *toluene-o-sulphonate* separated, having m. p. 87° (Found: Pb, 40·9. $C_{16}H_{28}O_3Pb$ requires Pb, 40·85%).

Tri-n-*propyl-lead Toluene*-p-*sulphonate.*—Prepared as for the *o*-compound, this *salt* melted at 73—74·5° (Found: Pb, 41·0. $C_{16}H_{28}O_3Pb$ requires Pb, 40·85%).

*Tetra*iso*butyl-lead.*—A mixture of *iso*butyl bromide (214 c.c.), pyridine (16 c.c.), and sodium–lead alloy (200 g.; 20% of Na) was heated under reflux on a water-bath with constant stirring during 8 hours. Water (a few c.c. at a time) was added at half-hourly intervals during the stirring. The mixture was then steam-distilled and the residue extracted with ether and dried ($CaCl_2$), the ether removed, and a portion of the product distilled at the Hyvac pump; decomposition took place and so the crude product (60 c.c.) was used in the following reactions.

*Tri*iso*butyl-lead Chloride.*—Tetra*iso*butyl-lead (2 c.c.) in dry light petroleum (b. p. 40—60°; 20 c.c.) was cooled in ice, and a slow stream of hydrogen chloride was passed into the solution for ½ hour. After a further hour at 0°, the solid which had separated was removed by filtration, and extraction with alcohol yielded the chloride. Tri*iso*butyl-lead chloride on being heated darkened at about 145°, became very dark brown at 155°, sintered and decomposed at 164° (Found: Cl, 8·85; Pb, 50·2. Calc. for $C_{12}H_{27}ClPb$: Cl, 8·6; Pb, 50·1%).

*Tri*iso*butyl-lead Acetate.*—Tetra*iso*butyl-lead (4 g.) and glacial acetic acid (0·6 g.) were heated in contact with silica gel on a water-bath. After 2 hours the solid which had separated was extracted with boiling light petroleum (b. p. 60—80°); on cooling *tri*iso*butyl-lead acetate* was obtained. Recrystallised from light petroleum, this had m. p. 117° (Found: Pb, 47·7. $C_{14}H_{30}O_2Pb$ requires Pb, 47·4%).

*Tri*iso*butyl-lead propionate*, darkens at 117°, m. p. 118° (Found: Pb, 45·9. $C_{15}H_{32}O_2Pb$ requires Pb, 45·9%), and *butyrate*, m. p. 119° (Found: Pb, 45·4. $C_{16}H_{34}O_2Pb$ requires Pb, 44·5%), were similarly obtained as short colourless needles.

*Tri*iso*butyl-lead Toluenesulphonates.*—A mixture of tetra*iso*butyl-lead (4 g.), toluene-*p*-sulphonic acid (1·7 g.), and ether (25 c.c.) was warmed on a water-bath for 5 minutes. After 1 hour the solid was filtered off, the ether removed at room temperature, and the *tri*iso*butyl-lead toluene*-p-*sulphonate*, which remained, crystallised from light petroleum (b. p. 80—100°) (Found: Pb, 37·8. $C_{19}H_{34}O_3Pb$ requires Pb, 37·7%). The m. p. depended on the rate of heating: the salt darkened about 176—180°, and at 190—195° became paler and sintered. The *toluene-o-sulphonate*, obtained in a similar manner, darkened at 166° and slowly sublimed and decomposed at 172° (Found: Pb, 37·3%.)

Tetramethyl-lead.—Prepared according to the details given for tetraethyl-lead (Part I, *loc. cit.*) from

sodium–lead alloy (300 g.), methyl iodide (190 c.c.), and pyridine (24 c.c.) (yield: 115 g., 50%), this had b. p. 101°/760 mm.

Trimethyl-lead Chloride.—This was prepared similarly to triethyl-lead chloride. The colourless needle-like crystals were pure without recrystallisation, having m. p. 190° (decomp.) (Found: Cl, 12·2; Pb, 72·4. Calc. for C_3H_9ClPb: Cl, 12·3; Pb, 72·0%).

Trimethyl-lead formate, m. p. 113° (Found: Pb, 69·3. $C_4H_{10}O_2Pb$ requires Pb, 69·7%), *acetate*, m. p. 194° (Found: Pb, 66·6. $C_5H_{12}O_2Pb$ requires Pb, 67·0%): iso*valerate*, m. p. 160° (from benzene) (Found: Pb, 58·6. $C_8H_{18}O_2Pb$ requires Pb, 58·6%), and *toluene*-p-*sulphonate*, long needles, m. p. < 220° (Found: Pb, 49·0. $C_{10}H_{16}O_3SPb$ requires Pb, 49·0%), were prepared from tetramethyl-lead and the appropriate acid with silica gel as catalyst.

Trimethyl-lead Monochloroacetate.—(*a*) To a suspension of silver chloroacetate (4 g.) in water was added a solution of trimethyl-lead chloride (5·8 g.) also in water. The mixture was stirred and filtered. On concentration of the filtrate, long flat plates, m. p. 169°, separated. The *monochloroacetate* recrystallised from benzene in small white needles without change of m. p.

(*b*) Monochloroacetic acid (4 g.) was dissolved in the minimum quantity of ether, and 5 c.c. of tetramethyl-lead were added. A piece of porous tile was added and the mixture heated on a water-bath for ½ hour. The product was cooled in ice, filtered, and washed with ether; it had m. p. 167° (Found: Pb, 60·1. $C_5H_{11}O_2ClPb$ requires: Pb, 60·0%).

Trimethyl-lead Trichloroacetate.—Trichloroacetic acid (3·5 g.) was dissolved in ether, and lead tetramethyl (3 c.c.) was added. The mixture was warmed gently until crystallisation started and then set aside for about 1 hour. After filtration, the *trichloroacetate* was washed with ether. It darkened when heated to 180°, but did not melt at 220° (Found: Pb, 49·8. $C_8H_9O_2Cl_3Pb$ requires Pb, 50·0%).

We are grateful to the Chief Scientist, Ministry of Supply, for permission to publish this work. Our thanks are due to Dr. F. Wild who prepared some of the tri*iso*butyl-lead salts.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August 3rd*, 1949].