10. *Some Physical Properties of the Alkyl Compounds of Mercury, Tin, and Lead.*

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An investigation of the gradation of physical properties in the series of alkyl compounds of mercury, tin, and lead has been made on lines similar to those already carried out in the case of the compounds of phosphorus, arsenic, antimony, and bismuth (J., 1930, 1310;

1931, 2109; 1932, 2284; *Bull. Soc. chim.*, 1931, **49**, 187; *J. Physical Chem.*, 1933, **37**, 583). In the present work it has been necessary to prepare a number of new members of each series, and in order further to characterise these compounds, certain of their derivatives have been prepared also.

In this paper, formulæ for the b. p. and molecular volume of a mercury, tin, or lead alkyl are given. It has been found that the atomic refractivities, for D light, of mercury, tin, and lead, when attached to primary alkyl groups, are 12·84, 13·87, and 18·33, respectively. Optical exaltation is exhibited where *sec.*- and *tert.*-alkyl groups are present. The heats of formation of the mercury and tin compounds rise regularly as the *n*-alkyl series are ascended, but the heats of formation of compounds containing secondary alkyl groups differ considerably from those of the compounds containing the corresponding primary alkyl groups.

EXPERIMENTAL.

Mercury Dialkyls.—*Di*-n-*amylmercury* (Found : C, 35·3; Hg, 58·7. $C_{10}H_{22}Hg$ requires C, 35·0; Hg, 58·5%) was obtained by the interaction of 180 g. (0·5 mol.) of mercuric bromide, gradually added, and a solution of *n*-amylmagnesium bromide (2 mols., 48 g. of magnesium, 258 c.c. of *n*-amyl bromide, and 1500 c.c. of ether) that had been filtered through glass-wool in hydrogen. The mixture was refluxed and mechanically stirred for 15 hours and then 1000 c.c. of water were added. The whole was filtered to remove precipitated *n*-amylmercuric bromide, and the ethereal layer was separated and dried over calcium chloride. The ether was evaporated, and the residue of di-*n*-amylmercury, *n*-decane, and *n*-amylmercuric bromide filtered off. The filtrate was washed with a small quantity of cold absolute alcohol, the heavy layer being then run off and treated with an excess of alcoholic silver nitrate. Ether (400 c.c.) was added, and the mixture was again filtered. In this way all traces of *n*-amylmercuric bromide were removed. The ethereal layer was then separated, dried, and fractionally distilled under low pressure. The residue left after removal of ether gave 24 c.c. of *n*-decane and 36 g. of di-*n*-amylmercury, b. p. 106°/0·5 mm.

When treated with iodine, di-*n*-amylmercury forms n-*amylmercuric iodide* (Found : I, 31·6; Hg, 50·7. $C_5H_{11}IHg$ requires I, 31·9; Hg, 50·3%). n-*Amylmercuric thiocyanate* (Found : Hg, 61·0; CNS, 17·6. $C_6H_{11}NSHg$ requires Hg, 60·8; CNS, 17·6%) was obtained as an insoluble, white powder, m. p. 108°, by treating an alcoholic solution of *n*-amylmercuric hydroxide with ammonium thiocyanate.

Di-dl-*amylmercury* (Found : C, 34·9; Hg, 58·3. $C_{10}H_{22}Hg$ requires C, 35·0; Hg, 58·5%) was prepared by refluxing a solution of *dl*-amylmagnesium bromide (2 mols.) with mercuric bromide (0·5 mol.) for 15 hours. Fractionation of the ethereal extract yielded the dialkylmercury, b. p. 93°/1 mm. Treatment with silver nitrate solution was unnecessary in this preparation, as no *dl*-amylmercuric bromide passed over during the fractionation. dl-*Amylmercuric bromide* (Found : Br, 23·1; Hg, 56·5. $C_5H_{11}BrHg$ requires Br, 22·8; Hg, 57·0%) separated as a by-product in the preparation of di-*dl*-amylmercury; it forms white plates, m. p. 119°, from alcohol. dl-*Amylmercuric iodide* (Found : I, 31·4; Hg, 50·2. $C_5H_{11}IHg$ requires I, 31·9; Hg, 50·3%), obtained by treating di-*dl*-amylmercury first with alcoholic and then with solid iodine, forms white plates from alcohol, m. p. 128°. dl-*Amylmercuric sulphate* (Found : Hg, 62·4; SO_4, 15·1. $C_{10}H_{22}O_4SHg_2$ requires Hg, 62·7; SO_4, 15·3%), from *dl*-amylmercuric hydroxide and dilute sulphuric acid, forms shiny, white plates from water, m. p. 180° (decomp.).

Di-n-*hexylmercury* (Found : Hg, 53·7. $C_{12}H_{26}Hg$ requires Hg, 54·1%) was prepared by refluxing *n*-hexylmagnesium bromide (2 mols.) solution with mercuric bromide (0·5 mol.) for 21 hours. Purification as described for the *n*-amyl compound gave 18 g. of di-*n*-hexylmercury, b. p. 110—112°/0·5 mm., 90 g. of *n*-hexylmercuric bromide, and 42 c.c. of *n*-dodecane, per 48 g. of magnesium used.

Whitmore, Hansen, and Carnahan (*J. Amer. Chem. Soc.*, 1929, **51**, 894) and Beattie and Whitmore (*ibid.*, 1933, **55**, 1571) have shown that, when an alkali alkoxide dissolved in the corresponding alcohol is refluxed with an arylmercuric halide, there is formed the diarylmercury. A similar reaction was observed in the present work on treating *n*-butylmercuric bromide with sodium *n*-propoxide in *n*-propyl alcohol. Sodium (1·5 g.) was dissolved in 100 c.c. of *n*-propyl alcohol, and 15 g. of *n*-butylmercuric bromide were added. The mixture was boiled gently for 5 mins., cooled, and filtered. The excess alcohol was removed by distillation under low pressure. The brown, pasty residue, on being heated under low pressure, yielded a fraction distilling at 80—140°/0·5 mm.; during the distillation some decomposition occurred with separation of metallic mercury. Redistillation of this fraction yielded 6 g. of di-*n*-butylmercury, b. p. 105°/10 mm., which was further identified by its conversion into *n*-butylmercuric iodide, m. p. 116° (from alcohol).

The carbon in the organo-mercuric compounds was determined by combustion, the mercury and water being eliminated by condensation in a cooled U-tube, and the carbon dioxide being passed, through a sulphuric acid and pumice U-tube, into a potassium hydroxide absorption vessel for weighing. The mercury in its dialkyls was determined by the methods of Volhard (*Annalen*, 1892, **267**, 172) and Koten and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 2764), in its alkyl bromides by the method of Kharasch and Flenner (*ibid.*, 1932, **54**, 686), but that in its alkyl iodides by the following new method. A mixture of 20 c.c. of fuming sulphuric acid and 10 c.c. of fuming nitric acid was added in the cold to 0·3 g. of the alkylmercuric iodide. Then the dropwise addition of 20 c.c. of water developed sufficient heat to effect complete decomposition of the iodide. An excess of solid sodium carbonate and 50 c.c. of water added to the solution precipitated mercuric iodide, which was then redissolved by adding a dilute solution of potassium iodide. The brown colour that developed was destroyed by rendering the solution neutral or very slightly acid with sulphuric acid and then boiling. On addition of fresh ammonium sulphide solution, mercuric sulphide was quantitatively precipitated.

Tin Tetra-alkyls.—*Tetra-*n*-butyltin* (Found : C, 55·3; H, 10·3; Sn, 34·1. $C_{16}H_{36}Sn$ requires C, 55·3; H, 10·5; Sn, 34·2%) was prepared by the action of a benzene solution of 64 g. of anhydrous stannic chloride upon the cooled Grignard reagent from 48 g. of magnesium, 216 c.c. of *n*-butyl bromide, and 1200 c.c. of ether. To the product were added 200 g. of ammonium chloride in 1000 c.c. of water, and the ethereal layer was separated, filtered, dried, and fractionally distilled under low pressure. There were thus obtained 8 g. of *n*-octane, b. p. 18°/10 mm., and 50 g. of pure tetra-*n*-butyltin, b. p. 145°/10 mm. after repeated fractionation. The tin in the tetra-alkyls was determined by decomposition with fuming nitric acid in a sealed tube, and weighing as stannic oxide. *Tri-*n*-butyltin bromide* (Found : Br, 21·5. $C_{12}H_{27}BrSn$ requires Br, 21·6%), b. p. 163°/12 mm., was obtained in good yield by slowly dropping bromine (2 atoms per atom of tin) on to tetra-*n*-butyltin and distilling the product. *Tri-*n*-butyltin iodide* (Found: I, 30·4. $C_{12}H_{27}ISn$ requires I, 30·4%) was prepared by adding 13 g. of iodine in 100 c.c. of carbon tetrachloride to 18 g. of tetra-*n*-butyltin. After a day, the product was fractionated, giving 18 g. of the iodide, b. p. 172°/10 mm.

The following stannanes and derivatives were prepared and purified as in the case of the *n*-butyl compounds : *tetra-*n*-amyltin* (Found : C, 59·3; H, 10·9; Sn, 29·2. $C_{20}H_{44}Sn$ requires C, 59·5; H, 11·0; Sn, 29·4%), b. p. 181°/10 mm.; *tetra-*dl*-amyltin* (Found : C, 59·2; H, 10·9; Sn, 29·4%), b. p. 174°/10 mm.; *tetra-*n*-hexyltin* (Found : C, 62·7; H, 11·3; Sn, 25·8. $C_{24}H_{52}Sn$ requires C, 62·7; H, 11·4; Sn 25·9%), b. p. 209°/10 mm.; *tetra-*n*-heptyltin* (Found : C, 65·4; H, 11·8; Sn, 22·9. $C_{28}H_{60}Sn$ requires C, 65·3; H, 11·7; Sn, 23·0%), b. p. 239°/10 mm.; *tetra-*n*-octyltin* (Found : C, 67·4; H, 12·0; Sn, 20·7. $C_{32}H_{68}Sn$ requires C, 67·2; H, 12·0; Sn, 20·8%), b. p. 268°/10 mm.; *tetra-β-phenylethyltin* (Found : C, 71·5; H, 6·8. $C_{32}H_{36}Sn$ requires C, 71·2; H, 6·7%), b. p. 288°/12 mm.; *tri-*n*-amyltin bromide* (Found : Br, 19·6. $C_{15}H_{33}BrSn$ requires Br, 19·4%), b. p. 189°/13 mm.; *tri-*n*-amyltin iodide* (Found : I, 27·7. $C_{15}H_{33}ISn$ requires I, 27·7%), b. p. 198°/15 mm. *Di-*n*-propyltin dibromide* (Found : Br, 43·8; Sn 31·9. $C_6H_{14}Br_2Sn$ requires Br, 43·8; Sn, 32·6%) was prepared by dissolving 18 g. of tetra-*n*-propyltin in carbon tetrachloride, cooling in ice, and adding 6·2 c.c. of bromine dissolved in the same solvent. On the next day another solution of 6·2 c.c. of bromine was added. On concentration of the solution, the dibromide separated as a white, crystalline solid, m. p. 53° (recryst.).

Several new mixed alkyltins were prepared by the interaction of trialkyltin bromides with Grignard reagents, and were isolated and purified as described for the tetra-alkyltins. *Methyl-tri-*n*-propyltin* (Found : C, 45·5; H, 9·2. $C_{10}H_{24}Sn$ requires C, 45·6; H, 9·2%), b. p. 93°/10 mm., $d^{20^\circ}_{4^\circ}$ 1·1404; *tri-*n*-propyl-*n*-butyltin* (Found : C, 51·1; H, 9·9. $C_{13}H_{30}Sn$ requires C, 51·2; H, 9·9%), b. p. 121°/10 mm., $d^{20^\circ}_{4^\circ}$ 1·0908; *methyltri-*n*-butyltin* (Found : C, 51·2; H, 9·9. $C_{13}H_{30}Sn$ requires C, 51·2; H, 9·9%), b. p. 121°/10 mm.; *ethyltri-*n*-butyltin* (Found : C, 52·5; H, 10·2. $C_{14}H_{32}Sn$ requires C, 52·7; H, 10·1%), b. p. 129°/10 mm.; *n-propyltri-*n*-amyltin* (Found : C, 57·5; H, 10·7. $C_{18}H_{40}Sn$ requires C, 57·6; H, 10·7%), b. p. 163°/10 mm.

Lead Tetra-alkyls.—An ethereal solution containing tri- and tetra-*n*-butyl-lead was obtained by the interaction of lead chloride with excess of *n*-butyl Grignard reagent, the mixture being refluxed for 3 hours until the colour became greenish-yellow. The mixture, having been cooled, was treated with ice-water, and the ethereal layer was separated, dried over calcium chloride, and then saturated at −10° with chlorine. *Di-*n*-butyl-lead dichloride* (Found : Cl, 18·1; Pb, 52·8. $C_8H_{18}Cl_2Pb$ requires Cl. 18·1; Pb, 52·8%) separated from the solution, and, after being washed, was recrystallised from alcohol. From 380 g. of lead chloride there were obtained 100 g. of the organic dichloride, which formed shiny, pale yellow plates, decomp. 108°. Di-*n*-butyl-lead dibromide (Found : Pb, 42·9. Calc. for $C_8H_{18}Br_2Pb$: Pb, 43·0%) was obtained in 80% yield by treating di-*n*-butyl-lead dichloride, suspended in cold alcohol, with excess of silver oxide, filtering the mixture, and adding excess of dilute hydrobromic acid to the clear filtrate. The bromide forms pale yellow needles from alcohol, which sinter and turn white at 110°. This compound has been previously made by Danzer (*Monatsh.*, 1925, **46**, 241), but no m. p. or decomposition point is recorded.

Treated with alkyl Grignard reagents by the method of Grüttner and Krause (*Ber.*, 1916, **49**, 1546), di-*n*-butyl-lead dichloride yields mixed tetra-alkyl-leads of the type $R_2PbR'_2$. The following compounds were so prepared, the yields given being from 20 g. of di-*n*-butyl-lead dichloride. *Dimethyldi-*n*-butyl-lead* (Found : C, 33·8; H, 6·8; Pb, 58·7. $C_{10}H_{24}Pb$ requires C, 34·2; H, 6·8; Pb, 59·0%), yield 10 g., b. p. 96·5°/5 mm., 108°/10 mm.; *diethyldi-*n*-butyl-lead* (Found : C, 38·0; H, 7·4; Pb, 54·6. $C_{12}H_{28}Pb$ requires C, 38·0; H, 7·4; Pb, 54·6%), yield 14 g., b. p. 90°/1 mm.; *di-*n*-propyldi-*n*-butyl-lead* (Found : C, 41·1; H, 7·9; Pb, 50·9. $C_{14}H_{32}Pb$ requires C, 41·2; H, 7·9; Pb, 50·9%), yield 17 g., b. p. 120°/1 mm.; tetra-*n*-butyl-lead (Found : Pb, 47·2. Calc. for $C_{16}H_{36}Pb$: Pb, 47·6%), prepared previously by Danzer (*loc. cit.*), was obtained in the present work from di-*n*-butyl-lead dichloride and *n*-butylmagnesium bromide, yield 17 g., b. p. 140°/1 mm., 157°/5 mm. (some decomp.) (Danzer gives b. p. 156°/10 mm. in carbon dioxide, which does not accord with our observation); *di-*n*-butyldi*iso*butyl-lead* (Found : C, 44·0; H, 8·2; Pb, 47·1. $C_{16}H_{36}Pb$ requires C, 44·1; H, 8·3; Pb, 47·6%), yield 13 g., b. p. 135°/1 mm.; *di-*n*-butyldi*iso*amyl-lead* (Found : C, 46·4; H, 8·6; Pb, 44·4. $C_{18}H_{40}Pb$ requires C, 46·6; H, 8·7; Pb, 44·7%), yield 20 g., b. p. 135°/0·5 mm.; *di-*n*-butyldi-*dl*-amyl-lead* (Found : C, 46·5; H, 8·5; Pb, 44·6%), yield 20 g., b. p. 135°/0·5 mm.

*Di-*n*-amyl-lead dichloride* (Found : Cl, 16·7; Pb, 48·9. $C_{10}H_{22}Cl_2Pb$ requires Cl, 16·9; Pb, 49·3%), obtained similarly to the corresponding *n*-butyl compound, crystallises from alcohol in thin, glistening, white plates, decomp. 123—125°, turning yellow. The solid decomposes in contact with hot solvents, forming lead chloride. *Di-*n*-amyl-lead dibromide* (Found : Pb, 41·1. $C_{10}H_{22}Br_2Pb$ requires Pb, 40·8%) was prepared similarly to the dichloride by the addition of bromine to an ether–alcohol solution of tri- and tetra-*n*-amyl-leads at –10° until a permanent red colour was developed. The dibromide, which separated out, recrystallised from alcohol as glistening, pale yellow plates, which sintered at 89°. On long standing, and also in contact with hot solvents, the dibromide undergoes partial decomposition to form lead bromide. An alcoholic solution of di-*n*-amyl-lead dibromide gives a yellow precipitate of lead iodide with aqueous potassium iodide. Attempts to prepare di-*n*-amyl-lead di-iodide were unsuccessful, an unstable iodide being obtained that readily decomposed, setting free iodine and lead iodide. *Di-*n*-amyl-lead sulphate* (Found : Pb, 46·1; $C_{10}H_{22}O_4SPb$ requires Pb, 46·6%) was obtained as a fine, white, insoluble powder by neutralising di-*n*-amyl-lead dihydroxide in alcoholic solution with sulphuric acid. The solid sinters at 177°, but remains white.

The following tetra-alkyl-leads were obtained by treating di-*n*-amyl-lead dichloride with alkyl Grignard reagents. *Dimethyldi-*n*-amyl-lead* (Found : C, 38·0; H, 7·5; Pb, 54·2. $C_{12}H_{28}Pb$ requires C, 38·0; H, 7·4; Pb, 54·6%), yield 16 g., b. p. 113°/4 mm., 121°/5 mm., 135°/10 mm.; *diethyldi-*n*-amyl-lead* (Found : C, 41·2; H, 7·9; Pb, 50·7. $C_{14}H_{32}Pb$ requires C, 41·2; H, 7·9; Pb, 50·9%), yield 10 g. from 20 g. of di-*n*-amyl-lead dibromide, b. p. 116—118°/0·5 mm., 157—158°/10 mm. (decomp.); *di-*n*-propyldi-*n*-amyl-lead* (Found : C, 43·9; H, 8·3; Pb, 47·2. $C_{16}H_{36}Pb$ requires C, 44·1; H, 8·3; Pb, 47·6%), yield 17 g., b. p. 150°/1 mm.—when heated towards its b. p. under 10 mm., the liquid decomposes completely with separation of lead; *di-*n*-butyldi-*n*-amyl-lead* (Found : C, 46·6; H, 8·6; Pb, 44·4. $C_{18}H_{40}Pb$ requires C, 46·6; H, 8·7; Pb, 44·7%), yield 12 g., b. p. 170°/1 mm.; *di*iso*butyldi-*n*-amyl-lead* (Found : C, 46·7; H, 8·6; Pb, 44·2%), yield 16 g., b. p. 140°/0·5 mm.; *tetra-*n*-amyl-lead* (Found : C, 48·8; H, 9·0; Pb, 41·7. $C_{20}H_{44}Pb$ requires C, 48·8; H, 9·0; Pb, 42·2%), yield 20 g., b. p. 170°/1 mm.; *di-*n*-amyldi*iso*amyl-lead* (Found : C, 48·8; H, 9·0; Pb, 41·8%), yield 16 g., b. p. 160°/0·5 mm.; *di-*n*-amyldi-*dl*-amyl-lead* (Found : C, 48·9; H, 9·0; Pb, 42·2%), yield 18 g., b. p. 160°/1 mm.; *di-*n*-amyldi-*n*-hexyl-lead* (Found : Pb, 39·6. $C_{22}H_{48}Pb$ requires Pb, 39·9%), yield 10 g., b. p. 180°/0·5 mm., $d_{4°}^{20°}$ 1·153.

*Di-*dl*-amyl-lead dichloride* (Found : Cl, 17·0; Pb, 49·5. $C_{10}H_{22}Cl_2Pb$ requires Cl, 16·9; Pb, 49·3%) was prepared similarly to the corresponding *n*-butyl compound; from alcohol it separates as pale yellow plates, which partly melt at 67° and decompose very readily, giving lead chloride.

*Tetra-*dl*-amyl-lead* (Found : Pb, 42·0. $C_{20}H_{44}Pb$ requires Pb, 42·2%), b. p. 150°/0·5 mm., was obtained in poor yield by the distillation of a mixture of tetra- and tri-*dl*-amyl-leads prepared by the method of Grüttner and Krause (*loc. cit.*).

When dimethyldi-*n*-amyl lead is stirred with concentrated hydrochloric acid at 35°, very little reaction occurs, but the addition of a small quantity of finely powdered silica gel initiates action, and after 3 hours the whole of the lead alkyl has dissolved, the solid product floating on the excess of acid. Treatment of the product with alcohol effects separation of its constituents, lead chloride, di-*n*-amyl-lead dichloride, and *methyldi*-n-*amyl-lead chloride* (Found : Pb, 51·3. $C_{11}H_{25}ClPb$ requires Pb, 51·8%), short, fine, white needles which sinter at 121—122°, and turn yellow (decomp.).

Calingaërt (*Chem. Rev.*, 1926, **2**, 50) states that when a simple tetra-alkyl-lead is boiled with concentrated nitric acid, lead nitrate is formed. On the other hand, according to Polis (*Ber.*, 1887, **20**, 716, 3331), tetra-aryl-leads when treated with nitric acid give rise to aryl-lead nitrates, $Ar_2Pb(NO_3)_2,xH_2O$. This reaction has been examined in the present work, with a view to ascertain the nature of the primary products. It has been found that when cold concentrated nitric acid is added to a tetra-alkyl-lead, the reaction that follows takes place very slowly with the formation, in the case of compounds containing alkyl groups higher than ethyl, of a dialkyl-lead dinitrate, $2HNO_3 + PbR_4 = R_2Pb(NO_3)_2 + 2RH$. The product floats on the excess of acid, and, after separation, can be recrystallised from alcohol–ether. The addition of a small amount of finely powdered silica gel to the mixture of nitric acid and tetra-alkyl lead increases the rate of interaction, and then bubbles of paraffin rise at a visible speed, but the reaction is still slow. However, a violent reaction ensues on the addition of 1—2 c.c. of ether, and dense fumes of nitrogen oxides are evolved; with most of the alkyl compounds there is also an immediate precipitation of a solid, and in all cases, on cooling, the dinitrate separates.

The reaction was carried out as follows : 2—3 g. of the tetra-alkyl-lead were weighed into a 100-c.c. round-bottomed, long-necked flask fixed in an inclined position, 2 c.c. of ether were then added, and the mixture was well shaken. An excess of nitric acid (*d* 1·42, 10—15 c.c.) was next added, and, after the initial violent reaction had subsided, the mixture was cooled by means of running water. The white solid was filtered off, washed with ether to remove any mononitrate that might have been formed, and then recrystallised from alcohol–ether. An alternative procedure, adopted in certain cases, consisted in evaporating the mixture of nitric acid and organo-lead nitrate in a vacuum desiccator, washing the residue with ether, and recrystallising from alcohol–ether. *Di*-n-*butyl-lead dinitrate* crystallises with 2 mols. of water [Found : Pb, 43·0; H_2O, 7·9. $(C_4H_9)_2Pb(NO_3)_2,2H_2O$ requires Pb, 43·0; H_2O, 7·5%], yield 1·9 g. from 2 g. of tetra-*n*-butyl-lead. The salt separates from alcohol–ether as transparent, hexagonal prisms, which sinter at 116—117°. On standing over phosphoric oxide in a desiccator, the hydrated solid slowly loses water, and forms a white powder of the dehydrated salt, which melts to a milky liquid at 123·5°. Dehydration is quantitative at 40° after 12 hrs. in a vacuum with phosphoric oxide. *Di*-n-*amyl-lead dinitrate dihydrate* [Found : Pb, 40·7; H_2O, 7·1. $(C_5H_{11})_2Pb(NO_3)_2,2H_2O$ requires Pb, 40·7; H_2O, 7·1%] forms hexagonal plates from alcohol–ether, which sinter at 96—98°; yield 0·75 g. from 1·5 g. of tetra-*n*-amyl-lead. Dehydration gives *di*-n-*amyl-lead dinitrate* (Found : Pb, 43·8. $C_{10}H_{22}O_6N_2Pb$ requires Pb, 43·8%). These two alkyl-lead nitrates were also prepared in quantitative yield by treating the corresponding dialkyl-lead dihydroxide in alcohol with nitric acid, and evaporating to the point of crystallisation. *Di*-n-*propyl-lead dinitrate dihydrate* [Found : Pb, 45·8; H_2O, 7·9. $(C_3H_7)_2Pb(NO_3)_2,2H_2O$ requires Pb, 45·7; H_2O, 7·9%] also was obtained in this way; it forms thin plates, m. p. 87—89°.

The only product that could be isolated after tetra-ethyl-lead had been treated with nitric acid was lead nitrate, indicating the relative instability of diethyl-lead dinitrate.

The action of concentrated nitric acid on mixed tetra-alkyl-leads of the type $R_2PbR'_2$ yielded dialkyl-lead dinitrates, together with, in some cases, a small quantity of lead nitrate. A yield of 1·2 g. of di-*n*-amyl-lead dinitrate was obtained from 1·6 g. of dimethyldi-*n*-amyl-lead on treatment with excess of concentrated nitric acid in presence of ether. This reaction is similar to that of hydrochloric acid on tetra-aryl-leads (Gilman, *Rec. trav. chim.*, 1932, **51**, 1054; *J. Amer. Chem. Soc.*, 1933, **55**, 4689), the methyl groups being split off in preference to the *n*-amyl radicals; this is in accordance with the order of electronegativity of radicals given by Kharasch (*J. Amer. Chem. Soc.*, 1932, **54**, 686). Dimethyldi-*n*-butyl-lead (0·9 g.) when treated with nitric acid gave di-*n*-butyl-lead dinitrate (0·8 g.). Diethyldi-*n*-butyl-lead on similar treatment gave di-*n*-butyl-lead dinitrate, which was isolated and identified, together with some lead nitrate and an organo-lead nitrate that could not be identified. All the other di-*n*-butyldialkyl-leads described in the present communication gave, with nitric acid, mixtures that could not be resolved.

In the analysis of the tetra-alkyl-leads and of their bromo-derivatives here described, the lead was determined by dissolving or suspending the compound in carbon tetrachloride, adding a large excess of a 10% solution of bromine in the same solvent, evaporating the resulting mixture nearly to dryness, then adding a small quantity of absolute alcohol, boiling, cooling in ice, and collecting and weighing the lead bromide. In the organo-lead chlorides, nitrates, and sulphates, the percentage of lead was found by first heating the compound with a mixture of concentrated sulphuric and fuming nitric acids, then heating the mixture more strongly until colourless to expel nitric acid, cooling, diluting with water, and precipitating lead sulphate by the addition of alcohol.

Cadmium Dialkyls.—Some of the higher alkyl compounds of cadmium were examined in this work, but they were not obtained sufficiently pure to justify the carrying out of physicochemical measurements on them. These substances appreciably decomposed with separation of metallic cadmium on being kept for only an hour in sealed tubes filled with nitrogen. For the determination of cadmium, such a tube of known tare was immediately weighed and broken under alcohol, excess of 2% sulphuric acid was added, the alcohol was removed by boiling, and the solution was saturated with hydrogen sulphide, the cadmium being precipitated as sulphide, which was collected and weighed.

Di-n-*amylcadmium* (Found : C, 47·1; H, 8·6; Cd, 44·3. $C_{10}H_{22}Cd$ requires C, 47·1; H, 8·7; Cd, 44·1%) was prepared by refluxing a mixture of 124 g. of anhydrous cadmium chloride with the ethereal solution of *n*-amylmagnesium bromide obtained from 48 g. of magnesium, and then fractionating the product under low pressure. Yield, 16 g., b. p. 105°/2 mm., $d_{4^\circ}^{20^\circ}$ 1·190. *Di*-dl-*amylcadmium* (Found : C, 47·3; H, 8·6; Cd, 44·2%) was similarly obtained in 8 g. yield, b. p. 94°/2 mm., $d_{4^\circ}^{20^\circ}$ 1·176.

Purification and Measurements.—In addition to the new organo-metallic compounds here described, several others obtained by previous workers have been prepared for the determination of their constants. In every case the substance was finally purified by redistillation under low pressure immediately before the measurements were made on it. Where necessary, due precautions were taken to keep the substance out of contact with the air. The compounds of mercury, tin, and lead used in the measurements were clear, colourless, stable liquids.

Temperature readings were corrected for thermometric errors, and weighings for errors of weights and for buoyancy. Pressures were read by means of standard manometers and barometers. Refractive indices were measured with a Pulfrich refractometer, by Zeiss of Jena, and an Abbé refractometer, by Hilger of London. These instruments were checked at every measurement by the use of water. The measurements of heats of combustion were made with a Berthelot–Mahler bomb calorimeter of the Krocker type, the water equivalent of which had been determined by the combustion of pure benzoic acid, and the thermometer employed had been standardised to 0·01° at the National Physical Laboratory.

Results.—The values of the densities and refractive indices found in the present work are summarised in Table I.

Table II contains the values of the b. p./10 mm., the molecular volumes at 20° (V_{20°), the Lorenz–Lorentz molecular refractivity, $[R_L]$, and the corresponding atomic refractivities $[r_L]$ for the F, D, and C lines. The calculated values of the b. p./10 mm., $t_{10\,\text{mm.}}$, are those given by the following equations, which apply to the organo-metallic compounds containing straight carbon chains only (M = molecular weight) :

$$\text{for mercury compounds, } t_{10\,\text{mm.}} + 273{\cdot}1 = 3{\cdot}378M^{0{\cdot}8200};$$
$$\text{for tin compounds, } t_{10\,\text{mm.}} + 273{\cdot}1 = 22{\cdot}566M^{0{\cdot}5000};$$
$$\text{for lead compounds, } t_{10\,\text{mm.}} + 273{\cdot}1 = 0{\cdot}867M^{1{\cdot}037}.$$

It will be noticed that the calculated does not agree with the found value in the case of the methyls. The calculated values of V_{20° are those given by the following equations, which hold for both *n*- and *iso*-alkyl compounds, C denoting the number of carbon atoms in the molecule :

$$\text{for the mercury dialkyls, } V_{20^\circ} = 41{\cdot}10 + 16{\cdot}66C;$$
$$\text{for the tin tetra-alkyls, } V_{20^\circ} = 64{\cdot}35 + 16{\cdot}55C;$$
$$\text{for the trialkylbromostannanes, } V_{20^\circ} = 75{\cdot}87 + 16{\cdot}55C;$$
$$\text{for the lead tetra-alkyls, } V_{20^\circ} = 66{\cdot}10 + 16{\cdot}55C.$$

The values of $[r_L]$ have been calculated by deducting the values for carbon, hydrogen, and bromine, given by Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 585). For the purpose of comparisons there have been included some of the results of previous workers (Grüttner, Krause, and Wiernik, *Ber.*, 1917, **50**, 1549; Grüttner and Krause, *ibid.*, p. 1802; *Annalen*, 1918, **415**, 338; Marvel and

TABLE I.

Substance.	$d_{4^\circ}^{20^\circ}$.	$n_F^{20^\circ}$.	$n_D^{20^\circ}$.	$n_C^{20^\circ}$.
Mercury dialkyls.				
Di-*n*-propyl	2·0208	1·5271	1·5170	1·5128
Di*iso*propyl	2·0024	1·5373	1·5263	1·5218
Di-*n*-butyl	1·7779	1·5152	1·5057	1·5018
Di*iso*butyl	1·7678	1·5057	1·4965	1·4927
Di-*n*-amyl	1·6369	1·5087	1·4998	1·4962
Di*iso*amyl	1·6397	1·5074	1·4989	1·4954
Di-*dl*-amyl	1·6700	1·5103	1·5014	1·4977
Di-*n*-hexyl	1·5361	1·5054	1·4973	1·4939
Tin tetra-alkyls.				
Tetra-*n*-butyl	1·0572	1·4802	1·4730	1·4700
Tetra-*n*-amyl	1·0206	1·4796	1·4720	1·4688
Tetra-*dl*-amyl	1·0222	1·4796	1·4730	1·4703
Tetra-*n*-hexyl	0·9959	1·4776	1·4706	1·4677
Tetra-*n*-heptyl	0·9748	1·4765	1·4698	1·4670
Tetra-*n*-octyl	0·9605	1·4756	1·4691	1·4664
Methyltri-*n*-butyl	1·0898	1·4810	1·4735	1·4704
Ethyltri-*n*-butyl	1·0783	1·4806	1·4732	1·4699
n-Propyltri-*n*-amyl	1·0368	1·4806	1·4732	1·4702
Tin bromides.				
Tri-*n*-butyl bromide	1·3365	1·5089	1·5000	1·4964
Tri-*n*-amyl bromide	1·2678	1·5049	1·4963	1·4927
Lead tetra-alkyls.				
Tetraethyl	1·6524	1·5318	1·5195	1·5144
Tetra-*n*-butyl	1·3233	1·5121	1·5119	1·4977
Tetra-*n*-amyl	1·2457	1·5058	1·4966	1·4928
Tetra-*dl*-amyl	1·2346	1·5048	1·4957	1·4919
Dimethyldi-*n*-butyl	1·5210	1·5157	1·5049	1·5004
Dimethyldi-*n*-amyl	1·4398	1·5109	1·5009	1·4969
Diethyldi-*n*-butyl	1·4580	1·5203	1·5093	1·5048
Diethyldi-*n*-amyl	1·3856	1·5140	1·5038	1·4996
Di-*n*-propyldi-*n*-butyl	1·3842	1·5166	1·5062	1·5019
Di-*n*-butyldi*iso*butyl	1·3258	1·5123	1·5021	1·4979
Di-*n*-propyldi-*n*-amyl	1·3238	1·5119	1·5019	1·4979
Di-*n*-butyldi-*n*-amyl	1·2825	1·5080	1·4984	1·4945
Di-*n*-butyldi*iso*amyl	1·2798	1·5088	1·4982	1·4953
Di-*n*-butyldi-*dl*-amyl	1·2779	1·5088	1·4993	1·4953
Di*iso*butyldi-*n*-amyl	1·2860	1·5092	1·4994	1·4954
Di-*n*-amyldi*iso*amyl	1·2438	1·5052	1·4959	1·4921
Di-*n*-amyldi-*dl*-amyl	1·2421	1·5015	1·4923	1·4885

Calvery, *J. Amer. Chem. Soc.*, 1923, **45**, 820; Hager and Marvel, *ibid.*, 1926, **48**, 2696; Krause, *Ber.*, 1926, **59**, 935). In cases where these workers have not calculated the values of molecular and atomic refractivities, these quantities are marked with an asterisk in Table II, but where values are given by these investigators they are indicated with a dagger.

It is found that, within the limits of the pressures usual in the distillation of these compounds, the reciprocal of the absolute b. p. is a linear function of the logarithm of the pressure; *e.g.*, for tetraethyl-lead, the equation $t + 273{\cdot}1 = 2960{\cdot}0/(9{\cdot}4262 - \log_{10}p)$ gives for the b. p. t°C., under the pressure p mm. of mercury, the following values: 78°/10 mm., 83°/13 mm., 90°/19 mm., 152°/290·5 mm., whilst the respective found values are 77°, 83°, 91—92°, and 152°. For tetra-*n*-propyltin, the corresponding equation is $t + 273{\cdot}1 = 3167{\cdot}8/(9{\cdot}2463 - \log_{10}p)$, and that for diethylmercury is $t + 273{\cdot}1 = 2344{\cdot}7/(8{\cdot}3071 - \log_{10}p)$.

By combining the equations of the last paragraph, and by assuming that the ratio of the abs. b. p.'s of two different alkyls of a metal under one pressure is equal to the ratio of the b. p.'s of the two compounds under another pressure, it is possible to calculate the approximate value of the b. p. of any *n*-alkyl-mercury, -lead, or -tin under any pressure. This is a great help to those engaged in the preparation of new compounds of these types. For instance, if the b. p. of dimethyldiethyl-lead under 18 mm. were required, the equation $t_{10\text{ mm.}} + 273{\cdot}1 = 0{\cdot}867M^{1{\cdot}037}$ gives its b. p. as 43°/10 mm., whilst the equation $t + 273{\cdot}1 = 2960{\cdot}0/(9{\cdot}4262 - \log_{10}p)$ gives for the b. p.'s of tetraethyl-lead 78°/10 mm. and 89°/18 mm., whence the required value of the b. p. $= -273{\cdot}1 + (43 + 273{\cdot}1)\,(89 + 273{\cdot}1)/(78 + 273{\cdot}1) = 53°$ C. (Grüttner and Krause, *Ber.*, 1916, **49**, 1546, found 54°).

The approximate equality of the coefficients of C in the four given equations for the molecular volume indicates the constancy of the volume of the CH_2 in these liquids. These equations

TABLE II.

	B. p./10 mm.		V_{20°.							
Substance.	Found.	Calc.	Found.	Calc.	$[R_L]_{\mathrm{F}}$.	$[R_L]_{\mathrm{D}}$.	$[R_L]_{\mathrm{C}}$.	$[r_L]_{\mathrm{F}}$.	$[r_L]_{\mathrm{D}}$.	$[r_L]_{\mathrm{C}}$.
Mercury dialkyls.										
Dimethyl	0°	19°	74·8	74·4	—	23·72†	23·53†	—	12·28†	12·15†
Diethyl	48	48	104·9	107·7	—	33·26†	33·02†	—	12·59†	12·45†
Di-*n*-propyl	73	77	141·9	141·1	43·63	42·93	42·64	13·39	13·02	12·87
Di*iso*propyl	63	—	143·2	141·1	44·74	43·98	43·66	14·50	14·07	13·90
Di-*n*-butyl	105	105	177·0	174·4	53·41	52·57	52·23	13·83	13·43	13·27
Di*iso*butyl	86	—	178·1	174·4	52·87	52·06	51·72	13·30	12·91	12·76
Di-*sec*.-butyl	—	—	178·5	174·4	—	53·48*	—	—	14·34*	—
Di-*tert*.-butyl	—	—	180·0	174·4	—	54·80*	—	—	15·65*	—
Di-*n*-amyl	133	132	209·4	207·7	62·49	61·57	61·19	13·58	13·19	13·04
Di*iso*amyl	125	—	209·1	207·7	62·25	61·37	61·00	13·34	12·99	12·85
Di-*dl*-amyl	—	—	205·4	207·7	61·42	60·51	60·13	12·51	12·13	11·98
Di-*tert*.-amyl	—	—	207·9	207·7	—	—	—	—	—	—
Di-*n*-hexyl	158	159	241·4	241·0	71·65	70·67	70·26	13·40	13·06	12·91
Tin tetra-alkyls.										
Tetraethyl	73	73	195·9	196·8	55·75*	54·90*	54·56*	13·95*	13·56*	13·42*
Tetra-*n*-propyl	112	112	262·9	263·0	75·03*	73·95*	73·52*	14·56*	14·13*	13·99*
Tetra-*n*-butyl	145	147	328·2	329·2	93·27	92·07	91·57	14·12	13·78	13·65
Tetra-*n*-amyl	181	180	394·9	395·5	112·10	110·64	109·99	14·28	13·88	13·63
Tetra-*dl*-amyl	174	—	394·3	395·5	111·93	110·60	110·00	14·11	13·84	13·69
Tetra-*n*-hexyl	209	210	461·1	461·6	130·40	128·78	128·10	13·91	13·55	13·40
Tetra-*n*-heptyl	239	239	528·5	527·8	149·20	147·40	146·74	14·04	13·70	13·66
Tetra-*n*-octyl	268	266	594·8	594·1	167·62	165·66	164·84	13·78	13·48	13·37
Triethyl-*n*-propyl	77	83	213·8	213·3	60·86*	59·95*	59·58*	14·39*	13·99*	13·85*
Triethyl*iso*butyl	86	—	230·8	229·9	65·72*	64·76*	64·37*	14·58*	14·18*	14·03*
Methyltri-*n*-propyl	93	93	230·5	229·9	—	—	—	—	—	—
Triethyl*iso*amyl	—	—	247·5	246·4	70·28*	69·27*	68·86*	14·47*	14·07*	13·92*
Ethyltri-*n*-propyl	101	102	246·1	246·4	70·33*	69·30*	68·89*	14·52*	14·10*	13·95*
Triethyl-*n*-amyl	102	102	246·0	246·4	70·15*	69·13*	68·72*	14·34*	13·93*	13·78*
Methyltri-*n*-butyl	121	121	279·8	279·5	79·66	78·61	78·15	14·52	14·17	14·02
Tri-*n*-propyl-*n*-butyl	121	121	279·6	279·5	—	—	—	—	—	—
Ethyltri*iso*butyl	115	—	295·9	296·1	84·31*	83·12*	82·64*	14·50*	14·06*	13·91*
Ethyltri-*n*-butyl	129	130	295·8	296·1	84·11	82·97	82·50	14·30	13·91	13·77
n-Propyltri-*n*-amyl	163	164	361·7	362·3	102·87	101·51	100·95	14·39	13·99	13·84
Tin bromides.										
Tri-*n*-butyl	—	—	276·7	274·5	82·62	81·39	80·90	14·26	13·81	13·66
Tri-*n*-amyl	—	—	324·9	324·1	96·37	94·98	94·39	14·00	13·54	13·36
Diethyl*iso*butyl	—	—	207·7	208·3	63·76*	62·72*	62·32*	14·07*	13·61*	13·47*
Diethyl dibromide	—	—	—	—	53·36*	52·30*	51·91*	14·46*	13·90*	13·73*
Tin tetrabromide	—	—	130·4	—	49·91*	48·60*	48·10*	13·91*	13·14*	12·89*
Lead tetra-alkyls.										
Tetramethyl	6	12	134·0	132·3	—	40·18†	39·83†	—	17·31†	17·07†
Tetraethyl	78	74	195·7	198·5	60·62	59·45	58·96	18·82	18·10	17·81
Tetra-*n*-propyl	—	—	260·0*	264·7	—	78·60†	78·03†	—	18·78†	18·49†
Tetra*iso*propyl	—	—	258·6*	264·7	—	79·87†	79·24†	—	20·05†	19·70†
Tetra-*n*-butyl	—	—	329·9	330·9	98·77	97·11	96·42	19·63	18·82	18·50
Tetra-*n*-amyl	—	—	394·6	397·1	117·20	115·39	114·64	19·38	18·63	18·34
Tetra-*dl*-amyl	—	—	398·2	397·1	118·05	116·25	115·49	20·23	19·49	19·19
Tetra*iso*amyl	—	—	398·4	397·1	—	116·13†	115·37†	—	19·37†	19·05†
Trimethylethyl	27	27	149·5	148·9	—	45·07†	44·68†	—	17·58†	17·33†
Trimethyl-*n*-propyl	39	43	167·2	165·4	—	49·95†	49·53†	—	17·84†	17·57†
Methyltriethyl	60	59	180·7	182·0	—	54·70†	54·25†	—	17·97†	17·70†
Trimethyl-*n*-butyl	58	59	184·4	182·0	—	54·63†	54·20†	—	17·90†	17·65†
Dimethylethyl-*n*-propyl	56	59	182·4	182·0	—	54·66†	54·26†	—	17·93†	17·71†
Dimethyldi-*n*-propyl	72	74	198·8	198·5	—	59·28†	58·81†	—	17·94†	17·66†
Methyldiethyl-*n*-propyl	72	74	197·0	198·5	—	59·34†	58·87†	—	18·00†	17·72†
Triethyl-*n*-propyl	93	90	212·4	215·1	—	64·19†	63·69†	—	18·23†	17·94†
Methyltri-*n*-propyl	100	105	230·6	231·6	—	68·93†	68·41†	—	18·35†	18·06†
Dimethyldi-*n*-butyl	108	105	231·0	231·6	69·75	68·52	68·00	18·61	17·94	17·66
Diethyldi-*n*-propyl	99	105	229·3	231·6	—	69·04†	68·52†	—	18·46†	18·19†
Ethyltri-*n*-propyl	111	121	246·0	248·2	—	73·77†	73·23†	—	18·57†	18·29†
Dimethyldi-*n*-amyl	135	137	263·5	264·7	78·94	77·63	77·10	18·46	17·82	17·57
Diethyldi-*n*-butyl	—	—	260·3	264·7	79·16	77·75	77·16	18·68	17·93	17·63
Diethyldi-*n*-amyl	—	—	294·1	297·8	88·53	87·05	86·43	18·73	18·00	17·71
Di-*n*-propyldi-*n*-butyl	—	—	294·4	297·8	89·00	87·49	86·86	19·19	18·43	18·13
Di-*n*-butyldi*iso*butyl	—	—	328·5	330·9	98·62	96·96	96·27	19·47	18·67	18·35
Di-*n*-propyldi-*n*-amyl	—	—	329·0	330·9	98·70	97·07	96·41	19·56	18·78	18·49
Di*iso*butyldi-*n*-amyl	—	—	360·0	364·0	107·66	105·91	105·18	19·18	18·38	18·07
Di-*n*-butyldi-*n*-amyl	—	—	361·4	364·0	107·74	106·01	105·31	19·27	18·49	18·20
Di-*n*-butyldi*iso*amyl	—	—	362·0	364·0	108·11	106·20	105·68	19·64	18·68	18·56
Di-*n*-butyldi-*dl*-amyl	—	—	362·7	364·0	108·27	106·56	105·83	19·79	19·03	18·72
Di-*n*-amyldi-*dl*-amyl	—	—	395·8	397·1	116·69	114·88	114·12	18·87	18·12	17·81
Di-*n*-amyldi*iso*amyl	—	—	395·2	397·1	117·26	115·43	114·68	19·44	18·67	18·38

* See p. 45. † See p. 45.

permit the calculation of densities; *e.g.*, for ethyltri-*n*-propyltin, $d_{4^\circ}^{20^\circ}$, calc., 1·124 (found, 1·123); for diethyldi-*n*-propyl-lead, $d_{4^\circ}^{20^\circ}$, calc., 1·517 (found, 1·532).

It will be seen from Table II that, in general, the atomic refractivity in the *n*-alkyl derivatives of mercury and of lead increases slightly with increase of molecular weight up to the butyl member. However, the increment falls off as the series is further ascended (cf. Tiffeneau and Sommaire, *Bull. Soc. chim.*, **1923**, **33**, 293), as will be seen from the following table.

Increments, Δ, in atomic refractivity, $[r_L]$.

Metal	Mercury.		Lead.	
	$[r_L]_D$.	Δ.	$[r_L]_D$.	Δ.
Methyl	12·28		17·31	
		0·31		0·79
Ethyl	12·59		18·10	
		0·43		0·68
n-Propyl	13·02		18·78	
		0·41		0·04
n-Butyl	13·43		18·82	
		−0·24		−0·19
n-Amyl	13·19		18·63	
		−0·13		
n-Hexyl	13·06		—	

The atomic refractivity of mercury is usually the same when the compound contains primary *iso*alkyl groups as it is when corresponding *n*-alkyl groups are present, and this applies also for the atomic refractivities of lead in the corresponding compounds, but there is a definite exaltation when *sec.*-alkyl groups are present, *e.g.*, di-*n*-propylmercury, $[r_L]_D$, 13·02; di*iso*propylmercury, $[r_L]_D$, 14·07; di-*n*-butylmercury, $[r_L]_D$, 13·43; di-*sec.*-butylmercury, $[r_L]_D$, 14·34; tetra-*n*-propyl-lead, $[r_L]_D$, 18·78; tetra*iso*propyl-lead, $[r_L]_D$, 20·05. The effect is still more marked with *tert.*-alkyl groups, *e.g.*, di-*tert.*-butylmercury, $[r_L]_D$, 15·65.

The mean values of the atomic refractivities of mercury, tin, and lead, when attached to primary alkyl groups, calculated from the data of Table II, are given below :

Atomic refractivities.

	F.	D.	C.
Mercury	13·34	12·84	12·70
Tin	14·26	13·87	13·72
Lead	19·24	18·33	18·05

Table III summarises the results obtained in the thermal measurements, and also includes the values given by Berthelot (*Compt. rend.*, 1899, **129**, 918), which are asterisked. On combustion in the bomb calorimeter, the alkyl derivatives of mercury left the metal, and those of tin, stannic oxide. The values of the heats of combustion assumed in calculating the heats of formation are as follows : diamond, 94 kg.-cals.; hydrogen, 34·5; tin, 138.

TABLE III.

	Heat of combustion, kg.-cals. per g.-mol.	Heat of formation, kg.-cals. per g.-mol.		Heat of combustion, kg.-cals. per g.-mol.	Heat of formation, kg.-cals. per g.-mol.
Dimethylmercury	431 *	−36	Di*iso*amylmercury	1653	+ 46
Diethylmercury	734 *	−13	Tetraethyltin	1521	+ 59
Di-*n*-propylmercury	1036	+11	Tetra-*n*-propyltin	2163	+ 69
Di*iso*propylmercury	1050	− 3	Tetra-*n*-butyltin	2773	+111
Di-*n*-butylmercury	1342	+31	Tetra-*n*-amyltin	3384	+152
Di*iso*butylmercury	1341	+32			

It will be observed that in both *n*-alkyl series the heat of formation shows a regular trend with increasing molecular weight.

The considerable difference between the heats of formation of *iso*- and *n*-propylmercury, *i.e.*, between those of a secondary and a primary alkyl compound, is reminiscent of the difference between the molecular refractivities of these compounds, which has already been discussed, whilst the equality of the heats in the cases of the mercury compounds of *iso*- and *n*-butyl, both primary groups, is paralleled by the general closeness of the refractivities of *n*- and corresponding primary *iso*-alkyl compounds.

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