CXIV.—*Organo-derivatives of Tin and Lead. Part I. Application of Lead and Tin Tetraphenyls in the Preparation of Organo-metallic Compounds.*

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It has recently been shown (Goddard and Goddard, this vol., p. 256) that lead and tin tetraphenyls can be used for the preparation of thallium diphenyl chloride, and experiments have now been carried out with the object of ascertaining whether this type of reaction could be utilised in the preparation of organo-metallic compounds which are difficult to isolate by the usual methods.

Lead tetraphenyl and arsenic trichloride react to form diphenylarsenious chloride, according to the equation $Ph_4Pb + AsCl_3 = Ph_2PbCl_2 + Ph_2AsCl$. All previous methods used to obtain this compound yield it only as a by-product (Michaelis and La Coste, *Annalen*, 1880, **201**, 196; Michaelis and Link, *ibid.*, 1881, **207**, 195; Michaelis and Reese, *Ber.*, 1882, **15**, 2873; Roeder and Blasé, *ibid.*, 1914, **47**, 2750).

The tendency shown by arsenic to give mono- or tri-aryl compounds, and not diaryl derivatives, is again in evidence with antimony. The latter type of compound has now been obtained directly by the following reactions: (1) $Ph_4Pb + SbCl_3 = Ph_2PbCl_2 + Ph_2SbCl$, (2) $Ph_4Pb + SbCl_5 = Ph_2PbCl_2 + Ph_2SbCl_3$ (compare Michaelis and Reese, *Annalen*, 1886, **233**, 58; Hasenbäumer, *Ber.*, 1898, **31**, 2911).

A similar reaction takes place with bismuth bromide, lead diphenyl chloride and diphenylbromobismuthine resulting; the latter compound has been previously obtained by Michaelis and Marquardt (*Annalen*, 1889, **251**, 327) by the interaction of bismuth bromide and triphenylbismuthine.

Of the chlorides of Group VI, tellurium tetrachloride was the only one to yield definite products, tellurium diphenyl chloride and lead diphenyl chloride being obtained (compare Krafft and Lyons, *Ber.*, 1894, **27**, 1761; Lederer, *Ber.*, 1911, **44**, 2287; *Annalen*, 1912, **391**, 326).

The interaction of lead tetraphenyl and stannic chloride, and subsequent treatment with water, lead to the production of lead diphenyl chloride, tin diphenyl hydroxychloride and oxide; but stannous chloride reacted as follows: (1) $Ph_4Pb + 2SnCl_2,2H_2O = Ph_2PbCl_2 + Ph_2SnCl_2 + Sn + 2H_2O$, (2) $Ph_2SnCl_2 + H_2O = Ph_2SnCl{\cdot}OH + HCl$, (3) $Sn + 2HCl = SnCl_2 + H_2$. Tin tetraphenyl and stannic chloride, when caused to react as above, gave a theoretical yield of tin diphenyl hydroxychloride (see Aronheim, *Annalen*, 1878, **194**, 145).

The following compounds gave no products with lead tetraphenyl under the same conditions of experiment: phosphorus tri- or penta-chloride, mercuric or lead chloride, thionyl or acetyl chloride, although in the latter case heat was developed, nor were derivatives isolated from tin tetraphenyl and the chlorides of mercury or sulphur.

Polis (*Ber.*, 1887, **20**, 3331) showed that lead tetraphenyl, when boiled for some time with acetic acid in benzene solution, gives rise to lead diphenyl acetate, but the authors have failed to obtain the same result with tin tetraphenyl. By the action of propionic and valeric acids in xylene solution, *acid lead diphenyl propionate* and *lead diphenyl valerate* were isolated. Only unchanged lead tetraphenyl was recovered when *n*-hexoic, *n*-octoic, mono- or di-chloroacetic acid was used, and lead diphenyl oxide did not react with citric or tartaric acid. The following salts were isolated: *acid lead diphenyl trichloroacetate, oxalate, iodate*, and p-*nitrobenzoate.* Other investigations of this type are being carried out in the aliphatic series, and also with mixed tetra-alkyls, tetra-aryls, and alkyl aryls of tin and lead.

EXPERIMENTAL.

All the yields given in the following experiments are based on the weight of metallic chloride used.

Diphenylarsenious Chloride.—Three grams of lead tetraphenyl and 1·13 grams of arsenic trichloride in 30 c.c. of toluene were heated under reflux for one hour, and after standing for twelve hours the solution was again warmed and filtered. The residue (2·34 grams) consisted of lead diphenyl chloride, and evaporation of the filtrate gave 1·5 grams of an oil, identified as diphenylarsenious chloride (yield 91 per cent.). From the latter, by chlorination and twice recrystallising from benzene, crystals of diphenylarsenious trichloride, m. p. 174°, were obtained.

Diphenylstibine Chloride.—Lead tetraphenyl (3·27 grams) and 1·44 grams of antimony trichloride were heated under reflux with 5 c.c. of toluene for half an hour, when a solid mass resulted, which was treated with a further 15 c.c. of toluene and heated again. After cooling and filtering, 2·55 grams of residue, melting above 280°, were obtained (lead diphenyl chloride), whilst the filtrate, after removal of the toluene, gave 1·81 grams of diphenylstibine chloride in the form of an oil (yield 92 per cent.). The latter product was chlorinated in dry ether and the mass recrystallised from hydrochloric acid, when diphenylstibine trichloride, m. p. 176°, was isolated.

Diphenylstibine Trichloride.—A mixture of 2·88 grams of lead tetraphenyl and 1·67 grams of antimony pentachloride in 50 c.c. of carbon tetrachloride was boiled for one hour, then filtered hot. The residue (3·87 grams), which did not melt completely at 180°, was boiled with hydrochloric acid and filtered; lead diphenyl chloride (2·4 grams) remained, and the hydrochloric acid filtrate deposited 1·3 grams of diphenylstibine trichloride, m. p. 176°. The carbon tetrachloride filtrate yielded a further 0·4 gram of the trichloride (total yield 81 per cent.).

Diphenylbromobismuthine.—Three grams of lead tetraphenyl and 2·61 grams of bismuth bromide were heated under reflux with 30 c.c. of chloroform for half an hour, and the mixture was filtered hot. The residue (1·28 grams) consisted of lead diphenyl bromide, and evaporation of the filtrate gave a residue, from which a further 1·4 grams was extracted, together with 1·95 grams of diphenylbromobismuthine, m. p. 157—158° (yield 75·4 per cent.).

Tellurium Diphenyl Chloride.—Tellurium tetrachloride (2·7 grams) and 5·2 grams of lead tetraphenyl in a mixture of 40 c.c. of toluene and 10 c.c. of xylene were boiled for one hour. After filtration, the residue was extracted with methyl alcohol, when 0·3 gram of tellurium diphenyl chloride was obtained. The solid left after this extraction (3·5 grams) was lead diphenyl chloride. The original filtrate on evaporation yielded 2·9 grams of solid, which were almost completely soluble in methyl alcohol, the solution depositing 1·47 grams of pure tellurium diphenyl chloride, m. p. 160—161°. The small quantity of substance insoluble in methyl alcohol appeared to be metallic tellurium. The above tellurium compound, on boiling with water, gave tellurium diphenyl hydroxychloride, m. p. 233—234° (yield 50 per cent.).

Action of Stannic Chloride on (a) *Lead Tetraphenyl,* (b) *Tin Tetraphenyl.*—(*a*) A mixture of 3·5 grams of lead tetraphenyl and 1·72 grams of stannic chloride in 30 c.c. of toluene was boiled for forty minutes. After filtering, a residue of 2·9 grams of lead diphenyl chloride was obtained, and the filtrate, on evaporation and addition of boiling water, gave a small quantity of tin diphenyl hydroxychloride, m. p. 185°. On evaporation to dryness, 1·49 grams of tin diphenyl oxide remained.

(*b*) Tin tetraphenyl (1·5 grams) and 0·91 gram of stannic chloride were heated under reflux in xylene for three-quarters of an hour. The residue (0·11 gram) was inorganic, and the filtrate, after evaporation and treatment with water, yielded 0·93 gram of tin diphenyl hydroxide, m. p. 188°. The production of the latter being due to the added water, tin diphenyl chloride was evidently formed in the reaction.

Action of Stannous Chloride on Lead Tetraphenyl.—Three grams of lead tetraphenyl and 2·42 grams of stannous chloride ($+ 2H_2O$) in 30 c.c. of xylene were boiled for two and a half hours. The residue obtained after filtering was heated under reflux with absolute alcohol, and subsequent filtration gave 1·5 grams of a mixture of lead diphenyl chloride and stannous chloride, and the alcoholic filtrate gave a further 1·02 grams of the former compound. The xylene filtrate quickly deposited 0·46 gram of tin diphenyl hydroxychloride, m. p. 185°, and, when evaporated, 0·47 gram of tin diphenyl chloride, m. p. 42°.

Acid Lead Diphenyl Propionate.—One gram of lead tetrapheny and 0·58 gram of propionic acid were heated under reflux in xylene for one hour, and the mixture was filtered. Evaporation of the filtrate gave fine needles (0·65 gram), which melted to a clear liquid at 168—169°, this decomposing at 230—235° (Found: C = 42·30; H = 3·87; Pb = 36·13. $C_{18}H_{20}O_4Pb,C_3H_6O_2$ requires C = 43·34; H = 4·51; Pb = 35·64 per cent.). The salt is completely soluble in alcohol, ether, chloroform, carbon tetrachloride, acetone, toluene, or pyridine, moderately soluble in ethyl acetate, and insoluble in light petroleum.

Lead diphenyl valerate forms white needles, m. p. 168—170° (Found: Pb = 36·73. $C_{22}H_{28}O_4Pb$ requires Pb = 36·78 per cent.). With the exception of its solubility in light petroleum, this salt has the same solubilities as the propionate.

Acid lead diphenyl trichloroacetate is a crystalline powder, which softens at 170—175° and decomposes rapidly at 210° without melting (Found: Pb = 26·99, 26·89. $2C_{16}H_{10}O_4Cl_6Pb,C_2HO_2Cl_3$ requires Pb = 26·99 per cent.). The salt is completely soluble in most organic solvents except carbon tetrachloride and light petroleum.

Lead diphenyl oxalate is a white, crystalline powder, which darkens at 280°, and decomposes rapidly at 293—295° (Found: Pb = 43·26; H_2O = 5·64. $2C_{14}H_{10}O_4Pb,3H_2O$ requires Pb = 43·49; H_2O = 5·67 per cent.). The salt is slightly soluble in acetone, pyridine, or dilute sulphuric acid, and insoluble in other organic solvents.

Lead diphenyl iodate is a crystalline, buff-coloured powder (Found: Pb = 29·95, 29·54. $C_{12}H_{10}O_6I_2Pb$ requires Pb = 29·14 per cent.). The salt does not melt at 300°, and explodes when treated with concentrated sulphuric acid, iodine being liberated. It is slightly soluble in pyridine and insoluble in other organic solvents.

Lead diphenyl p-*nitrobenzoate* forms small, pale yellow needles, darkening and melting at 256° (Found: Pb = 29·39; N = 4·08. $C_{26}H_{18}O_8N_2Pb$ requires Pb = 29·88; N = 4·04 per cent.). The salt is moderately soluble in all organic solvents except ether and light petroleum.

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