roughly comparable in solvent power at room temperature (24°) according to the curves shown in Fig. 1. Of these four, however, benzene is the only solvent which is immiscible with water, a factor of much importance when the strip solution has to be evaporated to near dryness before its content of DDT can be determined. Furthermore, since DDT may decompose above its melting point,[2] dioxane and pyridine become doubly impracticable because of the proximity of their boiling points to the melting point of DDT. Thus, we may conclude that benzene is an ideal stripping solvent for pure DDT at room temperature.

Summary

The wt. % solubilities of pure DDT in various common organic solvents have been determined for certain temperatures between 0 and 48° and rough solubility curves have been plotted. From the data so obtained, it is concluded that benzene is the most efficient "stripping" solvent for pure DDT at room temperature.

RIVERSIDE, CALIF. RECEIVED SEPTEMBER 8, 1944

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[2] Zeidler, *Ber.*, **7**, 1180 (1874).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE ETHYL CORPORATION]

The Preparation of Alkyllead Salts

BY GEORGE CALINGAERT, F. J. DYKSTRA AND HYMIN SHAPIRO

Alkyllead salts are usually prepared by one of three general methods: (a) reaction of an acid with a tetraalkyllead compound or trialkyllead hydroxide; (b) interaction of an inorganic salt and an alkyllead salt; and (c) for the halides, reaction of a halogen with a lead tetraalkyl.[1] Since each of these general methods is not applicable for the preparation of all alkyllead salts, it is necessary to select the proper method and conditions for each salt in order to obtain a satisfactory yield of pure product. This Laboratory has made a large number of preparations of organolead compounds, and we have found that some of the methods reported in the literature for alkyllead salts are unsatisfactory, since they give impure products. For example, we have found that preparations of trialkyllead bromides and dialkyllead dichlorides by reaction of lead alkyls with hydrogen bromide and hydrogen chloride,[2] respectively, are badly contaminated with lead bromide and lead chloride, respectively.

In the course of our work, improved methods of preparation of several alkyllead salts were developed. This paper presents these methods and also the syntheses of several salts heretofore undescribed.

Trialkyllead Chlorides.—Trialkyllead chlorides containing like alkyl groups may be prepared in good purity and yield by treating a 5–10% solution of lead tetraalkyl in hexane at room temperature with hydrogen chloride. The trialkyllead chlorides precipitate, and successive crops of product may be removed by filtration at intervals, thus precluding their further and slow conversion to dialkyllead dichlorides. This method gave consistently higher yields of purer products than the treatment of lead tetraalkyls with concentrated aqueous hydrochloric acid,[3] or reaction with chlorine in an inert solvent,[4] or treatment with hydrogen chloride in ether.[2,5] The use of hexane as a solvent has two distinct advantages over the use of ether: no special effort need be made to dry the solvent, and excess hydrogen chloride has no adverse effect on the nature or yield of the product, unless the time of reaction is excessive.

Reaction of mixed methylethyllead alkyls with hydrogen chloride usually resulted in oils instead of crystalline products, and both the analyses and the appearance of the R_3PbCl products were indicative of mixtures. Apparently both methyl and ethyl radicals were cleaved because of the small difference in electronegativity[6] of the two groups, or the initial R_3PbCl produced underwent redistribution[7] to yield a mixture of R_3PbCl compounds.

In the reaction of hydrogen chloride with trimethylethyllead in hexane solution, pure dimethylethyllead chloride was isolated from the crude product by careful handling and recrystallization.

Trialkyllead Iodides.—These compounds are readily synthesized by interaction of lead alkyls with iodine in ether at −65°.[8] The trialkyllead iodides are less stable than the other trialkyllead halides but may be isolated in a fair state of purity. Triethyllead iodide, described in the literature[9] as an oil of low stability which cannot be obtained pure, was obtained as a clear liquid, freezing at 19–20°, stable to diffused light, and unchanged for months on storage at about 5°.

Alkyllead Hydroxides and Carbonates.—Many attempts, in this Laboratory and by

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[1] Calingaert, *Chem. Rev.*, **2**, 43 (1925).

[2] Gilman and Robinson, THIS JOURNAL, **52**, 1975 (1930).

[3] (a) Browne and Reid, *ibid.*, **49**, 830 (1927); (b) Cahours, *Ann.*, **122**, 48 (1862).

[4] Grüttner and Krause, *Ber.*, **49**, 1415 (1916).

[5] (a) Pfeiffer, Truskier and Disselkampf, *ibid.*, **49**, 2445 (1916); (b) Buckton, *Ann.*, **112**, 220 (1859).

[6] Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926).

[7] (a) Calingaert, Beatty and Hess, *ibid.*, **61**, 3300 (1939); (b) Calingaert, Soroos and Shapiro, *ibid.*, **62**, 1104 (1940).

[8] Calingaert and Soroos, *J. Org. Chem.*, **2**, 537 (1938).

[9] (a) Löwig, *Ann.*, **88**, 318 (1853); (b) Klippel, *Jahresber.*, 380 (1860); (c) Klippel, *J. prakt. Chem.*, **81**, 286 (1860).

others,[5b,9a,9b,10] have shown that pure triethyllead hydroxide cannot be obtained by the reaction of aqueous alkali with triethyllead halides dissolved in ether, since the product cannot be freed of halide by recrystallization. However, the compound can be obtained in pure state by either of two methods: a modification of the reaction mentioned above, using benzene in place of ether, or by treatment of triethyllead chloride in aqueous solution with silver oxide.[9a] This latter method has also been used successfully to prepare diethyllead dihydroxide, heretofore unreported.

Both ethyllead hydroxides form weakly alkaline aqueous solutions, approximately equal in basicity to ammonium hydroxide. These solutions may be titrated with strong acids to give salts, and yield the corresponding carbonates on treatment with carbon dioxide. Indeed, treatment with carbon dioxide provides a good method for the preparation of the carbonates, one of which, diethyllead carbonate, has not been hitherto reported. Excess carbon dioxide converts triethyllead carbonate to triethyllead bicarbonate, also unreported previously; the reaction is reversible and the product is reconverted to triethyllead carbonate by storage over activated alumina *in vacuo*.

Miscellaneous Alkyllead Salts.—Triethyllead cyanide was readily prepared from potassium cyanide and triethyllead chloride by a modification of Klippel's method[9c] using water as the solvent in place of ethyl alcohol.

Triethyllead sulfide, first prepared by Klippel,[9c] was found to be slowly oxidized by air to yield triethyllead sulfate. This furnishes a more convenient method of preparation of the sulfate than that based on the reaction of triethyllead hydroxide with sulfuric acid.[9a,9c]

Trimethyllead acetate was readily prepared by refluxing tetramethyllead with acetic acid; no silica gel[3a] was necessary to speed the reaction.

Experimental Part

Triethyllead Chloride and Other Trialkyllead Chlorides.—Commercial hydrogen chloride was bubbled for fifteen minutes through a solution of 20.6 g. (0.06 mole) of tetraethyllead in 190 ml. of hexane at room temperature. Triethyllead chloride precipitated as white needles which were filtered on a Büchner funnel. The filtrate was retreated with hydrogen chloride for three additional periods of about five minutes each, separating the product each time. The combined product was washed with hexane and dried *in vacuo*; yield, 86%.

Anal. Calcd. for $(C_2H_5)_3PbCl$: Pb, 62.8; Cl, 10.7. Found: Pb, 62.9; Cl, 11.1.

Trimethyllead chloride was prepared in the same manner from tetramethyllead in 60% yield.

Anal. Calcd. for $(CH_3)_3PbCl$: Pb, 72.0; Cl, 12.3. Found: Pb, 71.7; Cl, 12.2.

Similar treatment of dimethyldiethyllead gave an oil.

Anal. Calcd. for $CH_3(C_2H_5)_2PbCl$: Pb, 65.6; Cl, 11.2. Calcd. for $(CH_3)_2C_2H_5PbCl$: Pb, 68.7; Cl, 11.7. Found: Pb, 66.4; Cl, 12.0.

Methyltriethyllead also yielded an oil.

Anal. Calcd. for $CH_3(C_2H_5)_2PbCl$: Pb, 65.6; Cl, 11.2. Calcd. for $(C_2H_5)_3PbCl$: Pb, 62.8; Cl, 10.7. Found: Pb, 64.8; Cl, 11.3.

Trimethylethyllead yielded a solid product, mainly dimethylethyllead chloride.

Anal. Calcd. for $(CH_3)_2C_2H_5PbCl$: Pb, 68.7; Cl, 11.7. Calcd. for $(CH_3)_3PbCl$: Pb, 72.0; Cl, 12.3. Found (on crude product): Pb, 69.4; Cl, 11.8. Found (on product recrystallized from benzene immediately after preparation): Pb, 68.6; Cl, 11.8.

Triethyllead Iodide.—A solution of 25.4 g. (0.20 g. atom) of iodine in 160 ml. of ether was added dropwise with stirring to a solution of 32.3 g. (0.10 mole) of tetraethyllead in 50 ml. of ether at −65°. The ether and ethyl iodide were removed at room temperature *in vacuo*, leaving a yellow residue. This was purified by solution in ether, and filtration and evaporation of the solvent *in vacuo*, repeating the process three times. The product, obtained in 73% yield, was a clear yellow liquid freezing at 19–20° to a crystalline solid.

Anal. Calcd. for $(C_2H_5)_3PbI$: Pb, 49.2; I, 30.1. Found: Pb, 48.8; I, 29.6.

Triethyllead Hydroxide.—Following the procedure of Löwig,[9a] 25.0 g. (0.08 mole) of triethyllead chloride was shaken with wet silver oxide and 170 ml. of water. The silver oxide had been freshly prepared from 15.0 g. (0.09 mole) of silver nitrate and a solution of 7.1 g. (0.13 mole) of potassium hydroxide in 19 ml. of water. After shaking for twenty minutes, the mixture was filtered, and the triethyllead hydroxide was recovered from the filtrate by evaporation of the water *in vacuo*. The filtrate was free of silver and chloride ions; yield, 93%.

Anal. Calcd. for $(C_2H_5)_3PbOH$: Pb, 66.5. Found: Pb, 66.2; [Pb]/[OH] ratio, 0.98 (OH^- determined by titration with hydrochloric acid using methyl orange indicator).

Halide-free triethyllead hydroxide was also prepared as follows. A solution of 10.0 g. (0.03 mole) of triethyllead chloride in 150 ml. of thiophene-free benzene was shaken vigorously in a separatory funnel for twenty minutes with a solution of 56.0 g. (1.40 moles) of sodium hydroxide in 84 ml. of water. After separating the aqueous layer from the benzene suspension of triethyllead hydroxide, 150 ml. of benzene heated to about 70° was added to the suspension, and the mixture was shaken vigorously for about thirty seconds. The benzene was then decanted and filtered quickly through a Büchner funnel into a filter flask cooled in ice; triethyllead hydroxide precipitated as a white crystalline solid. The supernatant benzene was decanted, reheated and used to make a second extraction. This procedure was repeated until all the solid material was dissolved. The combined product was washed with hexane. The washings and mother liquor were combined, evaporated *in vacuo* at 50–60° to a volume of about 100 ml., and cooled in ice-water. This produced another crop of product, which was washed with hexane and combined with the main product. The combined material was dried *in vacuo*; yield, 78%.

Anal. Calcd. for $(C_2H_5)_3PbOH$: Pb, 66.5. Found: Pb, 66.6; [Pb]/[OH] ratio, 1.000.

Diethyllead Dihydroxide.—Wet silver oxide prepared from 21.0 g. (0.12 mole) of silver nitrate was shaken for twenty minutes with 19.0 g. (0.06 mole) of diethyllead dichloride and 400 ml. of water. The solid hydroxide was recovered chlorine-free from the filtered solution by evaporation of the water *in vacuo*; yield, 84%.

Anal. Calcd. for $(C_2H_5)_2Pb(OH)_2$: Pb, 69.2. Found: Pb, 69.1; [Pb]/[OH] ratio, 0.505.

Diethyllead Carbonate.—Carbon dioxide was bubbled through an aqueous solution of diethyllead dihydroxide for several periods of ten to fifteen minutes each. The product which formed on each successive treatment was separated by filtration, and the combined product was dried *in vacuo*, washed with ether, and redried.

Anal. Calcd. for $(C_2H_5)_2PbCO_3$: Pb, 63.7; CO_2, 18.4.

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[10] Krause and Pohland, *Ber.*, 55, 1282 (1922).

Found: Pb, 63.8; CO_3, 18.4 (carbonate analysis by decomposition of the compound with acid and absorption of CO_2 on ascarite).

Triethyllead Carbonate and Bicarbonate.—Triethyllead carbonate could not be prepared from triethyllead hydroxide by simple treatment with carbon dioxide; the product consisted mainly of triethyllead bicarbonate.

Anal. Calcd. for $(C_2H_5)_3PbHCO_3$: Pb, 58.3; CO_3, 16.9. Found: Pb, 59.7; CO_3, 14.6 (corresponding to about 82% $(C_2H_5)_3PbHCO_3$ and 18% $((C_2H_5)_3Pb)_2CO_3$).

After storage for seventy-two hours in a vacuum desiccator over activated alumina, the material was largely converted to triethyllead carbonate.

Anal. Calcd. for $((C_2H_5)_3Pb)_2CO_3$: Pb, 63.9; CO_3, 9.2. Found: Pb, 63.2; CO_3, 9.6 (corresponding to 91% $((C_2H_5)_3Pb)_2CO_3$ and 9% $(C_2H_5)_3PbHCO_3$).

Triethyllead Cyanide.—A solution of 19.5 g. (0.30 mole) of potassium cyanide in 35 ml. of water was added to a solution of 66.0 g. (0.20 mole) of triethyllead chloride in 3500 ml. of water. The white precipitate was separated by filtration and dried *in vacuo;* yield, 77%.

Anal. Calcd. for $(C_2H_5)_3PbCN$: Pb, 64.7; CN, 8.1. Found: Pb, 64.5; CN, 7.4.

Triethyllead Sulfide.—A cold solution of 10.6 g. (0.04 mole) of sodium sulfide nonahydrate in 350 ml. of water was added dropwise to a solution of 13.9 (0.04 mole) of triethyllead chloride in 700 ml. of water, stirred and cooled in an ice-bath. The product, a yellow oil, was dissolved with ether and filtered, and the ether was evaporated *in vacuo;* this procedure was repeated. The residue was a photosensitive, yellow-green liquid; f. p. −45.1° (uncor.), $n^{20}{}_D$ 1.6249, and $d^{20}{}_4$ 2.05; yield, 86%.

Anal. Calcd. for $((C_2H_5)_3Pb)_2S$: Pb, 66.8; S, 5.2. Found: Pb, 66.8; S, 5.0.

Triethyllead Sulfate.[11]—Air was bubbled for forty hours through a solution of 68.3 g. (0.11 mole) of triethyllead sulfide in 1000 ml. of dry ether in a darkroom. Evaporation losses were made up by the addition of ether from time to time. Triethyllead sulfate precipitated as a white solid and was separated by filtration through a sintered-glass Büchner funnel. After being washed several times with ether, the product was dried *in vacuo;* yield, 55%. After recrystallization from water, the product was chloride-free. Contrary to a statement by Klippel,[9b,9c] the material was found to be soluble to the extent of 5.5% in water at room temperature.

Anal. Calcd. for $((C_2H_5)_3Pb)_2SO_4$: Pb, 60.5; SO_4, 14.0. Found: Pb, 60.4; SO_4, 14.2.

Trimethyllead Acetate.—A mixture of 29.4 g. (0.11 mole) of tetramethyllead with excess glacial acetic acid was refluxed for about five minutes under nitrogen, during which time the reaction mixture set to a solid mass. The excess acetic acid was removed *in vacuo*, leaving glistening white crystals which were recrystallized from water; m. p. 183–184°; yield, 84%.

Anal. Calcd. for $(CH_3)_3PbCO_2CH_3$: Pb, 66.6. Found: Pb, 66.9.

Summary

Improved methods of preparation of some alkyllead salts have been developed, and the following new alkyllead salts have been prepared: diethyllead dihydroxide, diethyllead carbonate, triethyllead bicarbonate and trimethyllead acetate.

[11] This method of preparing triethyllead sulfate was discovered by Mr. J. V. Capinjola, to whom the authors are indebted.

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[CONTRIBUTION FROM THE LABORATORIES OF WALLACE & TIERNAN CO.]

Diethylstilbestrol and Related Compounds

BY MARTIN RUBIN, A. KOZLOWSKI AND M. R. SALMON

Since the original preparation of diethylstilbestrol by Dodds, *et al.*,[1] several alternative procedures[2] of which the simplest is that described by Kharasch and Kleiman,[3] have been reported. The method described in this communication, although lengthy, is characterized by good yields and several points of particular interest.

The alcoholysis of anisaldehyde cyanhydrin by aliphatic alcohols and hydrogen chloride has been found to form the ethers of the expected α-hydroxy esters.[4] The reaction of these alkyl-α-alkoxy-*p*-methoxyphenylacetic esters with the ethyl Grignard reagent proceeded normally.

Pinacol rearrangement of the 4-anisyl-4-alkoxyhexanol-3 formed gave anisyl-4-hexanone-3 as in the case of the non-etherified glycol.[5] The condensation of *p*-halogen anisole with anisyl-4-hexanone-3 by means of sodium in petroleum ether to give 3,4-dianisyl-hexanol-3 offered some advantages in yield and ease of manipulation over the Grignard reagent for this same reaction.[6] This carbinol was dehydrated by heating with potassium acid sulfate to a mixture of crystalline *trans* and other liquid isomers[2c] of diethylstilbestrol dimethyl ether. By use of a combination of iodine and certain metallic halides, notably ferric chloride, the liquid isomers of diethylstilbestrol dimethyl ether could be rearranged in good yield to the desired crystalline *trans* isomer.

Demethylation of the *trans*-diethylstilbestrol dimethyl ether by sodium or sodium hydroxide in boiling carbitol resulted in a mixture in which the monomethyl ether of diethylstilbestrol[7] predominated. This is in contrast to the reaction carried out in ethanol or diethylene glycol and

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(1) Dodds. Golberg. Lawson and Robinson. *Proc. Roy. Soc.* (London). **B127**. 152 (1939).

(2) (a) Kerschbaum. Kleedorfer. Prillinger. Wessely and Zajic. *Naturwissenschaften*. **27**, 131 (1939); (b) Wessely and Kleedorfer. *ibid.*, **27**, 567 (1939); (c) Wessely. Kerschbaum. Kleedorfer. Prillinger and Zajic. *Monatsh.*, **73**. 127 (1940); (d) Kuwada. Sasagawa. *J. Pharm. Soc.*, Japan. **60**, 27 (1940); (e) Kuwada. Sasagawa and Nisikawa. *ibid.*, **60**, 553 (1940); (f) Peteri. *J. Chem. Soc.*, 833 (1940).

(3) Kharasch and Kleiman. THIS JOURNAL. **65**, 11 (1943).

(4) The analogous conversion under similar conditions of anisyl alcohol to anisyl ether has been ascribed to the influence of the *p*-methoxyl group: Quelet and Allard. *Bull. soc. chim.*, [5] **4**, 1468 (1937).

(5) Tiffeneau. Levy and Weill. *ibid.*, [4] **49**, 1709 (1931).

(6) Fieser and Christiansen. U. S. Patent 2,248,019 (1941).

(7) Reid and Wilson. THIS JOURNAL. **64**. 1625 (1942).