

## 159. The Ethylmercury Phosphates.

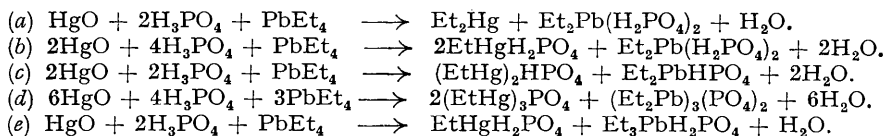
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A study of the reaction between tetraethyl-lead, mercuric oxide, and phosphoric acid has led to the preparation and characterisation of the three ethylmercury phosphates. Bisethylmercury phosphate gives addition compounds with diethyl-lead phosphate and with anthraquinone-1-sulphonic acid.

THE only mention of an ethylmercury phosphate in the literature is by Dünhaupt (*J. pr. Chem.*, 1854, **61**, 399) who, by treatment of an alcoholic solution of ethylmercury chloride with silver phosphate isolated the phosphate as a crystalline mass, very soluble in water. No melting point or analysis was given. As silver phosphate is usually regarded as being  $\text{Ag}_3\text{PO}_4$  (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans & Co., Vol. III, p. 485), it would appear that the product isolated by Dünhaupt was trisethylmercury phosphate  $(\text{C}_2\text{H}_5\text{Hg})_3\text{PO}_4$ .

The three possible ethylmercury phosphates have now been prepared and characterised, and it has been shown that the product prepared by Dünhaupt's method is not pure but consists mainly of the *trisethylmercury phosphate* together with some of the difficulty separable *bis-salt*  $(\text{C}_2\text{H}_5\text{Hg})_2\text{HPO}_4$ .

For the preparation of the three ethylmercury phosphates in pure form use was made of the method of preparation of ethylmercury salts from tetraethyl-lead described in B.P. 331,494. It is well known that the mobility of alkyl or aryl groups in compounds of the type  $\text{PbR}_4$  in reaction with metallic halides, *e.g.*, mercury, bismuth, thallium, arsenic, etc., is a general property of such groups attached to electropositive elements (Calingaert, *Chem. Rev.*, 1925, **2**, 43; Friend, "Text Book of Inorganic Chemistry," Griffin & Co., Vol. XI, Part I, p. 340). By treating tetraethyl-lead with mercuric oxide and the equivalent quantities of phosphoric acid required by the equations (b), (c), and (d) it should be possible to prepare all three ethylmercury phosphates, and this has been done.



It was not possible to isolate *ethylmercury phosphate* by utilisation of only one ethyl group of tetraethyl-lead according to equation (e), the reaction proceeding further with ultimate formation of diethylmercury and diethyl-lead phosphate [equation (a)], thus affording another example of the alkylating action of triethyl-lead salts. In the case of bisethylmercury phosphate the lead compound as formed is already of type  $\text{R}_2\text{PbX}_2$  and would thus not show the tendency to react further with the mercuric oxide and phosphoric acid. No diethylmercury was formed during this reaction and bisethylmercury phosphate is the most readily obtainable and easily characterised of the ethylmercury phosphates. It has been found, however, that when the reaction is carried out in alcohol according to equation (c) only half the product can be isolated by filtration and evaporation of the alcohol, although the mercurial phosphate is readily soluble in alcohol. The remainder is present as an alcohol-insoluble complex compound corresponding approximately to the composition  $(\text{EtHg})_2\text{HPO}_4 \cdot 2\text{Et}_2\text{PbHPO}_4$ . This complex, although stable to boiling alcohol, is decomposed quantitatively by cold water into an insoluble lead compound and bisethylmercury phosphate. No complex-salt formation has been observed in reactions (b) and (d) since trisethylmercury phosphate can be completely extracted by means of alcohol. The reaction (d), however, proceeds much more slowly than (b) and (c).

The three ethylmercury phosphates are crystalline compounds of characteristic m. p.'s which are depressed on admixture. Bisethylmercury phosphate reacts with phosphoric acid to give the mono-salt  $\text{EtHgH}_2\text{PO}_4$ . This is evidently a balanced reaction, for recrystallisation of the latter from alcohol always gave small quantities of the bisethylmercury salt.

In preparing a number of ethylmercury salts for fungicidal evaluation we had occasion to study the reaction between the bis-salt and sodium anthraquinone-1-sulphonate. This gave rise to a crystalline compound containing an amount of mercury corresponding to the composition  $\text{C}_{14}\text{H}_7\text{O}_2\text{SO}_3\text{HgEt} \cdot 2(\text{EtHg})_2\text{HPO}_4$ . A complete investigation of the constitution of this compound has not been made, but the presence of phosphate was detected qualitatively and it was ascertained by rough titration with aqueous sodium chloride that only part of the ethylmercury was immediately precipitable as the insoluble chloride, the remainder being more firmly bound. Attempts to prepare an addition compound of bisethylmercury phosphate with anthraquinone itself were unsuccessful.

## EXPERIMENTAL.

*Ethylmercury Phosphate*,  $\text{EtHgH}_2\text{PO}_4$ .—Bisethylmercury phosphate (5 g.) was dissolved in hot alcohol containing 90% phosphoric acid (2 g.), and the solution allowed to cool; crystals of *ethylmercury phosphate* separated, m. p. after recrystallisation from alcohol  $115^\circ$  (Found: Hg, 61.2.  $\text{C}_2\text{H}_5\text{O}_4\text{PHg}$  requires Hg, 61.1%).

With the proportions of reagents required by equation (a), under the conditions used for making bisethylmercury phosphate (see below), the insoluble organic lead compound contained no mercury and it was not possible to isolate a pure ethylmercury phosphate from the reaction mixture. The alcohol was removed by distillation, and addition of water precipitated a heavy oil. That this contained diethylmercury was demonstrated by its conversion by means of warm concentrated hydrochloric acid into ethylmercury chloride, identified by mixed m. p. with authentic material.

Mercuric oxide (21.6 g.) was suspended in absolute ethyl alcohol (100 c.c.) and a mixture of 90% phosphoric acid (22 g.) and absolute ethyl alcohol (50 c.c.) added to the stirred suspension. After 5 minutes' stirring, tetraethyl-lead (16.2 g.) was added dropwise during 20 minutes to the stirred mixture and the stirring was continued for 30 minutes, during which the greater part of the mercuric oxide disappeared with simultaneous formation of a heavy white solid. The temperature of the reaction mixture rose to 40° during the addition and the reaction was completed by heating under reflux for 30 minutes, *i.e.*, until the last traces of mercuric oxide had disappeared. The hot reaction mixture was filtered, the white insoluble residue washed with hot alcohol and the combined filtrate and washings evaporated to small bulk. Crystallisation of the product (24.2 g.) from a small volume of ethyl alcohol gave ethylmercury phosphate as small, colourless prisms, m. p. and mixed m. p. with material prepared as above 115°. Crystallisation of a pure sample of ethylmercury phosphate from ethyl alcohol gave initially a small amount of large shining plates of bisethylmercury hydrogen phosphate, m. p. and mixed m. p. with an authentic specimen (prepared as below) 175—176°, followed by the main crop of the monoethylmercury derivative.

*Bisethylmercury Phosphate*,  $(\text{EtHg})_2\text{HPO}_4$ .—90% Phosphoric acid (8.5 g.) was dissolved in alcohol (100 c.c.), and mercuric oxide (16.5 g.) added. Tetraethyl-lead (12.4 g.) was added dropwise during 10 minutes to the stirred mixture, after which the reaction was completed by boiling until the yellow colour of mercuric oxide disappeared ( $\frac{1}{2}$  hr.). The hot reaction mixture was filtered and the insoluble material washed with hot alcohol. Evaporation of the filtrate and washings afforded crystals of *bisethylmercury phosphate*, m. p. after recrystallisation from alcohol 176° (Found: Hg, 72.4.  $\text{C}_4\text{H}_{11}\text{O}_4\text{PHg}_2$  requires Hg, 72.2%). [Since our work was carried out, Rumpf (*A.*, 1945, II, 379) has given m. p. 176° for this compound prepared from the hydroxide and phosphoric acid.] The residue insoluble in alcohol could not be purified by crystallisation and the mean analyses of the product from several experiments gave Hg, 32; Pb, 30% approx. The double compound formulated above requires Hg, 31.5; Pb, 32.5%. Extraction of the residue with water removed all the mercury, which was recovered from the aqueous extract by evaporation in the form of bisethylmercury phosphate, m. p. 174—176° undepressed on admixture with the original material obtained from alcohol.

*Trisethylmercury Phosphate*,  $(\text{EtHg})_3\text{PO}_4$ .—Mercuric oxide (43.3 g.), 90% phosphoric acid (14.5 g.), and tetraethyl-lead (20 c.c.) in hot alcohol (150 c.c.) were boiled as described in the preceding paragraph, 4 hours' boiling being necessary to ensure disappearance of the yellow oxide. The residue after filtration contained no mercury, and the filtrate was evaporated to dryness, yielding *trisethylmercury phosphate*. Purified by repeated crystallisation from alcohol-ethyl acetate, it formed colourless prisms which softened at 110° and melted at 145° (Found: Hg, 76.1.  $\text{C}_6\text{H}_{15}\text{O}_4\text{PHg}_3$  requires Hg, 76.7%).

*Reaction of Silver Phosphate and Ethylmercury Bromide*.—To an aqueous solution of silver nitrate (25 g.) was added a saturated solution of disodium hydrogen phosphate until there was no further precipitate of silver phosphate. The precipitate was washed with alcohol, suspended in alcohol, and an equivalent quantity of ethylmercury bromide added. After digestion with occasional shaking and warming for 2 days, the reaction mixture was filtered and the filtrate evaporated to dryness. The product resisted purification by crystallisation from alcohol or benzene and its m. p. was indefinite. A small quantity of bisethylmercury phosphate (0.5 g.) was eventually obtained by careful manipulation, but the main bulk of material melted over the range 115—135° (cf. *trisethylmercury phosphate*, m. p. 145° with previous softening).

*Ethylmercury Anthraquinone-1-sulphonate*.—Sodium anthraquinone-1-sulphonate (6.2 g.) in hot water (140 c.c.) was added to a solution of bisethylmercury phosphate (11 g.) in water (70 c.c.). A small amount of flocculent precipitate was removed, and the solution allowed to cool. The crystals which separated were removed and the filtrate evaporated to dryness. Recrystallisation from water or alcohol gave clusters of pale yellow needles, m. p. 213—214° (decomp.) (Found: Hg, 62.3.  $\text{C}_{24}\text{H}_{34}\text{O}_{13}\text{SP}_2\text{Hg}_5$  requires Hg, 61.6%). The molybdate test was positive for phosphate, and the compound gave no precipitate with sodium hydroxide.

The above compound (5 g.) was dissolved in warm water (200 c.c.) and 10% sodium chloride gradually added. After the addition of 5 c.c. (corresponding to three-fifths of the ethylmercury present) there was no further immediate precipitate of ethylmercury chloride. The amount separated by filtration (2.18 g.) was approximately equivalent to three ethylmercury radicals as ethylmercury chloride (theory, 2.4 g.). Addition of hydrochloric acid to the filtrate gave an immediate precipitate of ethylmercury chloride.

*Bisethylmercury Phosphate and Anthraquinone*.—Reaction between these two substances was attempted in boiling alcohol for 20 hours, and in  $\beta$ -ethoxyethyl alcohol or anisole overnight on the steam-bath. No compound formation was observed.

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