[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

PREPARATION, PROPERTIES AND REACTIONS OF LEAD MERCAPTIDES[1]

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Lead mercaptides have been known for a long time and have been used primarily for the removal of mercaptans from solution or in synthetic work for the introduction of the mercapto group. In the last few years the petroleum industry has also become interested in the properties of the lead mercaptides in connection with the "sweetening" of petroleum by the use of sodium plumbite.[5] In studying the properties of these mercaptides, there is a lack of information on the purity and solubility. In this paper certain lead mercaptides will be discussed as to methods of preparation, their analyses, solubility and some reactions.

TABLE I

PREPARATION AND ANALYSES OF LEAD MERCAPTIDES

Mercaptan	Percentage of lead Calculated	Percentage of lead Found	Preparation
Ethyl	62.92	62.84, 62.89	Recrystd. from EtOH
n-Propyl	58.02	57.66, 58.41	Washed thoroughly, vacuum dried
*Iso*propyl	58.02	57.99, 57.98	Washed thoroughly, vacuum dried
n-Butyl	53.79	53.41, 53.35, 53.36	Recrystd. from *n*-BuOH or EtOH
*Iso*butyl	53.79	54.03, 54.26	Recrystd. from EtOH
Iso-amyl	50.10	50.13, 50.42	Recrystd. from MeOH
Benzyl	45.72	45.55, 45.55	Washed and vacuum dried
Thiophenol	48.70	48.72, 48.96	Washed and vacuum dried
γ-Hydroxypropyl	53.21	53.13, 53.15	Recrystd. from 50% EtOH

Experimental

Preparation of Lead Mercaptides.—The desired mercaptan dissolved in 6 to 10 parts of ethyl alcohol was added to a warm 50% alcoholic solution of *M*/4 lead acetate until a cloudiness appeared. It was then heated to boiling (more alcohol added if necessary to obtain a clear solution), allowed to cool and crystallize. The crystals were washed several times by decantation, then thoroughly on the filter and finally dried in a vacuum desiccator. Whether it is desirable to recrystallize is questionable, for the analyses given in Table I of different mercaptides show no improvement in purity for the recrystallized samples. Recrystallization may even be detrimental, for unrecrys-

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[5] W. A. Gruse, "Petroleum and Its Products," McGraw-Hill Book Co., New York,

tallized *n*-propyl, *iso*propyl and thiophenol mercaptides were more stable than *iso*-amyl, benzyl and γ-hydroxypropyl which were recrystallized. If, in preparation of the mercaptides, the concentration of lead acetate and mercaptan was too great, the lead mercaptide often separated as an oil which solidified on cooling. This occurred with *n*-butyl and *iso*-amyl. *n*-Butyl mercaptide can be recrystallized from *n*-butyl alcohol as well as ethyl alcohol, but if the oil or crystals became slightly superheated, immediate darkening occurred and decomposition began. This happened with the *n*-butyl readily. *Iso*-amyl mercaptan in oily form was slightly soluble in acetone, *n*-butyl alcohol, ethyl alcohol and methyl alcohol. It was finally recrystallized from methyl alcohol, which was a slow process due to low solubilities. The lower mercaptides, that is, ethyl, *n*-propyl and *iso*propyl separated very readily in the crystalline form when prepared and therefore were analyzed as prepared.

To obtain lead mercaptides that have a constant melting point on recrystallization was impossible. On recrystallizing there probably is a slight decomposition due to reaction with the alcohol and this slight impurity may be the cause of the indefinite values found. For instance, one sample of ethyl lead mercaptide recrystallized from 95% ethyl alcohol coalesced at 119° and blackened at 124° and on an attempted second recrystallization had undergone decomposition and did not melt up to 170°. A second sample of this coalesced at 104°, and pronounced change occurred at 110° turning deep red. Another sample dried *in vacuo* for twenty-four hours darkened at 110–112°.[6] With *n*-propyl lead mercaptide the usual temperature at which a first change appeared was 89–90° when softening occurred; it melted at about 94–96°; but even this was not at all satisfactory. *Iso*butyl mercaptide changed to a wax-like substance at 66° and melted at 71°. On recrystallization it became wax-like at 60–61° and was not completely molten at 130°. Benzyl mercaptide began to coalesce at 98° and decomposed without melting at 100–101°.

An attempt was made to determine qualitatively the solubility of the lead mercaptides after they had been once recrystallized, washed and thoroughly dried in a vacuum desiccator. Ethyl mercaptide recrystallized from ethyl alcohol and *n*-butyl mercaptides recrystallized from *n*-butyl alcohol were used as samples with carbon tetrachloride; both turned dark within twenty-four hours. With acetone (C. P.) the mercaptide became white. With ethyl alcohol there was a change similar to that with acetone but not as marked. With *n*-butyl alcohol there was some solubility, for when the solutions were heated to 50° and then cooled again crystals of the yellow mercaptide separated. This was especially true for *n*-butyl lead mercaptide. With a carefully purified low-boiling hydrocarbon there was practically no solubility, as the naphtha was colorless and on evaporating 25 cc. no stain was found in the beaker. There was no visible decomposition in the same time in which decomposition appeared with carbon tetrachloride. Using C. P. benzene freshly distilled from sodium there was no visible decomposition.

Reactions.—To C. P. benzene freshly distilled from metallic sodium, and the recrystallized mercaptides, in 50-cc. sample bottles, small amounts of C. P. sulfur (powdered) were added. With ethyl mercaptide there was an immediate darkening, sometimes first brown and then to black. With benzyl and *n*-amyl there was the same darkening. With *n*-butyl it became red first and then dark. The reaction was very rapid. Using the same benzene and mercaptides and adding some of this same benzene saturated with dry hydrogen sulfide there appeared immediately a brown to black color with ethyl, *n*-amyl and benzyl. With *n*-butyl a reddish color first appeared at first, which then changed to brown and finally black. This color play has been noted with the "doctor"

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[6] R. Otto, *Ber.*, 13, 1290 (1880), gives the melting point for lead ethyl mercaptide as 150°.

solution and naphthas using sodium plumbite and sulfur.[7] Whether the color play in both cases is due to the same original compound is not proved by these experiments.

An attempt was made to use the titration with iodine in benzene represented by the equation $Pb(SR)_2 + I_2 \longrightarrow PbI_2 + (SR)_2$ as an analytical method, but this was not very successful. The reaction was rapid at first, slow after half of the iodine had been absorbed, and toward the end very slow. The benzene used was freshly distilled from sodium. The lead iodide formed was filtered into a Gooch crucible, washed, dried and weighed. The results are given in Table II.

Table II

Results of Analyses

$Pb(SR)_2$	G.	Mg. of iodine Calcd.	Abs.	%	PbI_2 Calcd.	G.	%
Ethyl	0.3664	282.4	272.2	96.39	0.5129	0.5058	98.61
n-Amyl	.2558	157.1	154.5	98.34	.2854	.2750	96.36
Benzyl	.3788	212.1	178.5	84.16	.3853	.3500	90.83

Summary

Lead mercaptides have been prepared and analyzed and some of their properties noted.

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[Contribution from the Chemical Laboratory of the University of Washington]

THE REACTION OF PHTHALYL CHLORIDE WITH AMIDES

By Theodore W. Evans and William M. Dehn

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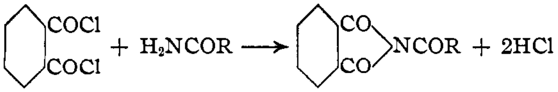
Acetylphthalimide[1] and benzoylphthalimide[2] are the only examples of substitution of the imino hydrogen of phthalimide by acid radicals. The acetyl derivative was prepared by the action of acetic anhydride on phthalimide, also by dehydration of acetylphthalamic acid; the benzoyl derivative was prepared by the action of benzoyl chloride on phthalimide in pyridine solution, also by dehydration of benzoylphthalamic acid.

Because compounds of this type were required in another study, we have investigated different methods for their preparation, and have found that phthalyl chloride reacts normally with amides



giving good yields[3] which were free from other products, especially such as

[7] G. L. Wendt and S. H. Diggs, *Ind. Eng. Chem.*, **16**, 1113 (1924); A. E. Wood, A. Lowy and W. F. Faragher, *ibid.*, **16**, 1116 (1924).

[1] Aschan, *Ber.*, **19**, 1400 (1885).

[2] Titherley and Hicks, *J. Chem. Soc.*, **89**, 708 (1906). For a general discussion of methods of acylation of amides, see Titherley, *ibid.*, **85**, 1679 (1904).

[3] Titherly concluded that the action of an acyl chloride on amides is "a poor method, applicable only to the primary amides of the aliphatic series."