

Note

Thin-layer chromatography of compounds of the type $\text{Ar}_n\text{Pb}(\text{OAc})_{4-n}$ ($n = 1-4$)

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Increasing interest in the environmental chemistry of organolead compounds^{1,2} has stimulated many investigations on analysis for such compounds². During our research programme, we needed a rapid method for determining compounds of the type $\text{Ar}_n\text{Pb}(\text{OAc})_{4-n}$ in which $n = 1-4$.

Barbieri *et al.*^{3,4}, and others^{5,6}, have devised several elegant paper-chromatographic methods for the separation of compounds of the type $\text{R}_n\text{PbX}_{4-n}$ ($n = 2-4$), where R is a phenyl, methyl or ethyl substituent and X is Cl or Br. Also, mixed tetra-alkyl-lead compounds of the type $\text{Me}_n\text{Et}_{4-n}\text{Pb}$ ($n = 1-4$) have been analysed⁶. Barbieri *et al.*^{7,8} have studied the chromatography of complexes of Et_3Pb^+ and $\text{Et}_2\text{Pb}^{2+}$ on anion-exchange paper and have also used paper electrophoresis.

In contrast to the extensive research on the paper chromatography of organolead compounds, little has been published on the TLC of these compounds. Willemssen⁹ obtained useful TLC results for the analysis of tri- and di-alkyl-lead acetates, and some data on the TLC of $(\text{C}_6\text{H}_5)_4\text{Pb}$, $(\text{C}_6\text{H}_5)_3\text{PbCl}$ and $(\text{C}_6\text{H}_5)_2\text{PbCl}_2$ have been reported¹⁰.

We had two main objectives: first, the separation of members of series of compounds such as Ar_4Pb , Ar_3PbOAc , $\text{Ar}_2\text{Pb}(\text{OAc})_2$ and $\text{ArPb}(\text{OAc})_3$, wherein Ar denotes an aryl group and OAc an acetate group; secondly (and much more complicated), we required a chromatographic system suitable for separating the compounds Ar_4Pb , $\text{Ar}_4'\text{Pb}$, etc. We thought that TLC could provide us with a fast and selective analytical procedure for use with our organolead compounds.

MATERIALS

The solvents used were obtained from Merck (analytical grade), as were the silica gel 60 F 254 plates (Fertig Platten No. 5729); disposable micropipettes were used for sample application. The several series of aryl-lead compounds were synthesized and characterized as described earlier¹¹.

METHODS

The appropriate solvent system was allowed to equilibrate in a glass vessel

for 2 h. Standard solutions of the organolead compounds in chloroform were prepared: 2- μ l portions, corresponding to 8 μ g of each compound, were applied *ca.* 2 cm from the edge of a TLC plate (pre-activated at 100° for 1 h). The plates were dried by blowing warm air on to the surface and quickly placed in a solvent vessel. Plates were developed for 0.5 h, dried and subsequently examined in UV radiation and sprayed with dithizone¹² and phenothiazine⁹ reagents. Colours and R_F values were noted.

RESULTS AND DISCUSSION

We began by investigating several solvents to establish their usefulness for the separation of the series $(C_6H_5)_nPb(OAc)_{4-n}$ ($n = 1-4$); the results are shown in Table I.

TABLE I

RESULTS FOR $C_6H_5Pb(OAc)_3$ (1), $(C_6H_5)_2Pb(OAc)_2$ (2), $(C_6H_5)_3PbOAc$ (3) and $(C_6H_5)_4Pb$ (4)*

Solvent	R_F			
	1	2	3	4
Benzene	0	0	0	0.63
Acetone	0.05	0.79	0	0.81
Chloroform	0	0.20	0	0.75
Ethanol	0.43	0.75	0	0
Acetone-water (1:1)	0	0	0	0
Chloroform-ethanol (1:1)	0.43	0.87	0	0.89
Acetone-chloroform (1:1)	0.15	0.66	0	0.75
Acetone-acetic acid (9:1)	0.76	0.96	0.46	0.94
Chloroform-acetic acid (9:1)	0.66	0.86	0.59	0.94
Chloroform-acetic acid-acetone (5:5:1)	0.58	0.77	0.44	0.81
Chloroform-acetic acid-acetone (6:6:1)	0.57	0.74	0.42	0.78
Chloroform-acetic acid-acetone (9:0.5:1)	0.66	0.84	0.54	0.88
Chloroform-acetic acid-benzene (9:1:1)	0.40	0.46	0.73	0.85
Chloroform-acetic acid-acetone-benzene (9:1:1:1)	0.39	0.49	0.75	0.84

* Colours with dithizone: 1, green-yellow; 2, orange-yellow; 3, yellow; 4, yellow. With phenothiazine, 1 gives a green colour.

After detection in UV radiation, dithizone was used to visualize the compounds. Compounds of the type $ArPb(OAc)_3$ are able to oxidize phenothiazine, thus producing a green colour when sprayed with a phenothiazine solution.

The best results for the series $(C_6H_5)_nPb(OAc)_{4-n}$ ($n = 1-4$) were observed with the solvent system chloroform-acetic acid-acetone-benzene (9:1:1:1), and this system was also useful for other series of compounds, *e.g.*, $Ar_nPb(OAc)_{4-n}$ ($n = 1-4$); results obtained for three series are shown in Table II.

The results indicate that good separation of the members of one series depends first on the number of acetate groups and then on the nature of the aryl group on the lead atom.

When separation between two compounds is not satisfactory, as with o - $CH_3OC_6H_4Pb(OAc)_3$ and $(o$ - $CH_3OC_6H_4)_2Pb(OAc)_2$, a second development should be performed with a fresh solvent system chosen from Table I. Some compounds of

TABLE II

RESULTS FOR ArPb(OAc)_3 (1), $\text{Ar}_2\text{Pb(OAc)}_2$ (2), Ar_3PbOAc (3) AND Ar_4Pb (4) WITH THE SOLVENT CHLOROFORM-ACETIC ACID-ACETONE-BENZENE (9:1:1:1)

Ar	R_F			
	1	2	3	4
Phenyl	0.39	0.49	0.75	0.84
<i>p</i> -Tolyl	0.44	0.50	0.54*	0.82
			0.76	
<i>o</i> -Methoxyphenyl	0.59	0.56	0.77	0.87

* With decomposition (see text).

the type Ar_3PbOAc are not stable towards acids and decompose into $\text{Ar}_2\text{Pb(OAc)}_2$ and ArH . For the specific separation of compounds Ar_3PbOAc and $\text{Ar}_2\text{Pb(OAc)}_2$, a solvent system from Table I can be used.

The properties of tetra-aryl-lead compounds are changed less drastically by substitution in the aryl nucleus than by replacing an aryl group by an acetate group. Hence it is difficult to find an adequate solvent for the TLC of Ar_4Pb , $\text{Ar}'_4\text{Pb}$, etc. However, we found benzene-*n*-hexane-diethylamine (50:50:1) to be a suitable system. The R_F values of $(\text{C}_6\text{H}_5)_4\text{Pb}$, $(p\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Pb}$, $(o\text{-CH}_3\text{OC}_6\text{H}_4)_4\text{Pb}$, $(p\text{-CH}_3\text{OC}_6\text{H}_4)_4\text{Pb}$ and $(p\text{-ClC}_6\text{H}_4)_4\text{Pb}$ were 0.53, 0.60, 0.23, 0.10 and 0.66, respectively, in this system.

In conclusion, it may be stated that compounds of the type $\text{Ar}_n\text{Pb(OAc)}_{4-n}$ ($n = 1-4$) can be readily analysed by TLC. Also, compounds of the type Ar_4Pb can be satisfactorily separated by TLC.

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