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DIRECT SYNTHESIS OF MIXED METHYLETHYLLEAD ALKYLS

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Summary

The reactions of lead oxide, sulphide, and chloride with a mixture of dimethyl- and diethyl-aluminium chloride in the presence of Lewis bases have been studied. Mixtures of methylethyllead compounds of the type $Me_{4-n}PbEt_n$ ($0 \leqslant n \leqslant 4$) are formed.

A reaction path is proposed.

Introduction

A physical mixture of tetramethyl- and tetraethyl-lead in the presence of catalysts such as aluminium chloride [1,2], boron trifluoride and organoaluminium compounds containing a halogen atom (complexes of methylaluminium dichloride with trimethyllead chloride, dimethyllead dichloride or lead chloride) [3] undergoes a redistribution reaction (eqn. 1).

$$Me_4Pb + Et_4Pb \xrightarrow{\text{catalyst}} Me_4Pb + Me_3PbEt + Me_2PbEt_2 + MePbEt_3 + PbEt_4 \quad (1)$$

In reaction 1 all the possible mixed methylethyllead alkyls are formed in amounts in agreement with Newton's binomial distribution. A similar distribution of concentrations of mixed methylethyllead alkyls was observed in the simultaneous disproportionation of an equimolar hexamethyl- and hexaethyl-dilead mixture [4] (eqn. 2).

$$Me_6Pb_2 + Et_6Pb_2 \rightarrow Me_4Pb + Me_3PbEt + Me_2PbEt_2 + MePbEt_3 + PbEt_4 + Pb \quad (2)$$

In this paper the possibility of synthesis of methylethyllead compounds in reactions between lead salts and a dimethyl- and diethyl-aluminium chloride mixture has been studied.

Results and discussion

In previous work we showed that lead oxide and sulphide react with trimethylaluminium according to eqn. 3:

$$2\,\mathrm{PbX} + 4\,\mathrm{Me_3Al} \rightarrow \mathrm{Me_4Pb} + \mathrm{Pb} + 2\,\mathrm{Me_2AlXAlMe_2} \quad (\mathrm{X} = \mathrm{O, S}) \qquad (3)$$

Tetramethyllead and tetramethylalumoxane [5] are formed for X = O and bis(dimethylaluminium) sulphide [6] for X = S. Metallic lead is also formed, in an equimolar ratio to tetramethyllead.

In syntheses where trimethylaluminium was used instead of dimethylaluminium chloride, the favourable influence of several Lewis bases on the tetramethyllead yield was observed [7].

It has now been found that in reactions of lead oxide, sulphide, or chloride with a dimethyl- and diethyl-aluminium chloride mixture in the presence of Lewis bases (D) such as potassium chloride, sodium chloride, benzonitrile, or anisole, methylethyllead compounds are formed according to the general reaction (eqn. 4):

$$\mathrm{PbX} + \mathrm{Me_2AlCl} + \mathrm{Et_2AlCl} + \mathrm{D} \rightarrow \mathrm{Me}_{4-n}\mathrm{PbEt}_n + \mathrm{Pb} + \underset{(\mathrm{I})}{\mathrm{Me(Cl)AlXAl(Cl)Me} \cdot \mathrm{KCl}} + \underset{(\mathrm{II})}{\mathrm{Et(Cl)AlXAl(Cl)Et} \cdot \mathrm{KCl}} \qquad (4)$$

$(\mathrm{X} = \mathrm{O, S};\ 0 \leqslant n \leqslant 4)$

As appears from data presented in Table 1, the kind of lead salt used for the synthesis has an influence on the overall yield of organolead compounds. The highest yield of methylethyllead compounds ($\approx$50 mole % with respect to lead introduced in the PbX compound) was obtained when lead oxide was used. Depending on the kind of PbX compound, the yield decreases in the series $\mathrm{PbO} > \mathrm{PbS} > \mathrm{PbCl_2}$. The yield also depends on the kind of Lewis base used (Table 2) and decreases in the series $\mathrm{KCl} > \mathrm{NaCl} > \mathrm{PhCN} > \mathrm{PhOMe}$.

From the summarizations presented in Tables 1 and 2 it appears that the distribution of concentrations of mixed lead alkyls, that is $\mathrm{Me_4Pb}$, $\mathrm{Me_3PbEt}$, $\mathrm{Me_2PbEt_2}$, $\mathrm{MePbEt_3}$ and $\mathrm{Et_4Pb}$, is not in line with Newton's binomial distribution. In mixtures of organolead compounds an excess of Et—Pb linkages is present.

It was observed that the reaction time has an influence on the distribution of concentrations of mixed methylethyllead alkyls (Fig. 1). On carrying out the

TABLE 1

COMPOSITION OF METHYLETHYLLEAD ALKYLS IN THE REACTION MIXTURE DEPENDING ON KIND OF LEAD SALT USED

Temperature, 135°C; reaction time, 1 h; $\mathrm{Me_2AlCl/Et_2AlCl/PbX/KCl} = 1/1/1/1$

Lead salt	Products (mole %)					Yield (mole %)
	$\mathrm{Me_4Pb}$	$\mathrm{Me_3PbEt}$	$\mathrm{Me_2PbEt_2}$	$\mathrm{MePbEt_3}$	$\mathrm{PbEt_4}$	
PbO	0.1	1.4	14.4	46.0	38.1	50
PbS	0.4	0.7	3.7	27.6	67.7	21
$\mathrm{PbCl_2}$	0.0	1.0	7.5	87.5	4.0	11

TABLE 2

COMPOSITION OF METHYLETHYLLEAD ALKYLS IN THE REACTION PRODUCTS DEPENDING ON THE LEWIS BASE

Temperature, 135°C; reaction time, 1 h; $Me_2AlCl/Et_2AlCl/Pb/D$ = 1/1/1/1

Donor D	Products (mole %)					Yield (mole %)
	Me_4Pb	Me_3PbEt	Me_2PbEt_2	$MePbEt_3$	$PbEt_4$	
KCl	0.1	1.4	14.4	46.0	38.1	50
NaCl	0.0	1.8	16.9	50.7	30.6	33
PhCN	0.0	1.5	23.4	51.4	23.7	23
$PhOCH_3$	0.0	0.0	12.8	27.6	59.6	5

reactions at times of up to 30 min, practically no tetramethyl- and trimethylethyllead were found in the mixture, but high concentrations of methyltriethyl- and tetraethyl-lead were present.

The alkylation of lead salts by the studied mixture of organoaluminium compounds proceeds even at room temperature. In the 20—135°C range of temperatures (Fig. 2) an excess of Et—Pb linkages occurs. Simultaneously it was observed that at 20°C the reaction of lead oxide with diethylaluminium chloride proceeds immediately after the organoaluminium compound is introduced, but for dimethylaluminium chloride only after a delay.

The influence of the Me_2AlCl/Et_2AlCl molar ratios on the distribution of concentrations of methyllead compounds has been determined (Fig. 3) and it was found that for the Me_2AlCl/Et_2AlCl molar ratio of 8/3 an equal number of Me—Pb and Et—Pb linkages occur. Above this molar ratio an excess of methyllead derivatives are formed. A change of the Al/Pb molar ratio while preserving a constant molar ratio of Me_2AlCl/Et_2AlCl = 1 (Table 3) does not influence the

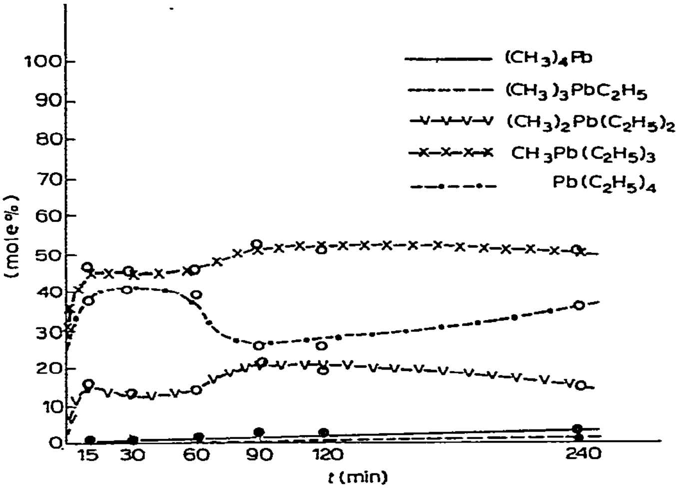


Fig. 1. Composition of lead alkyls in the reaction products depending on reaction time. Temperature, 135°C; $Me_2AlCl/Et_2AlCl/PbO/KCl$ = 1/1/1/1

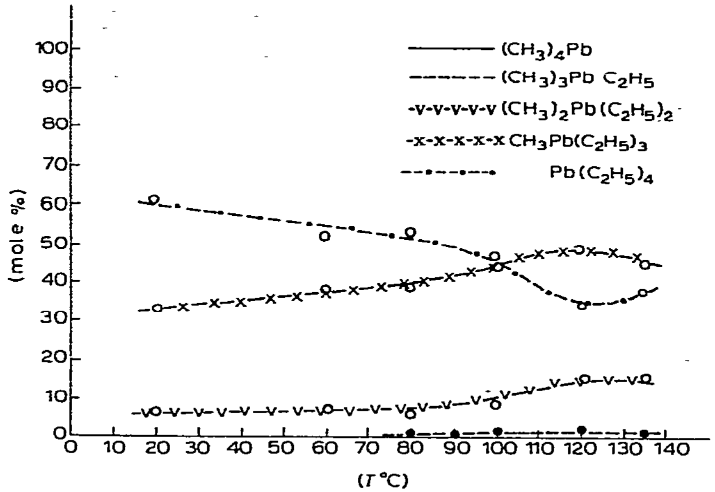


Fig. 2. Composition of lead alkyls in the reaction products depending on reaction temperature. Reaction time, 1 h; $Me_2AlCl/Et_2AlCl/PbO/KCl = 1/1/1/1$

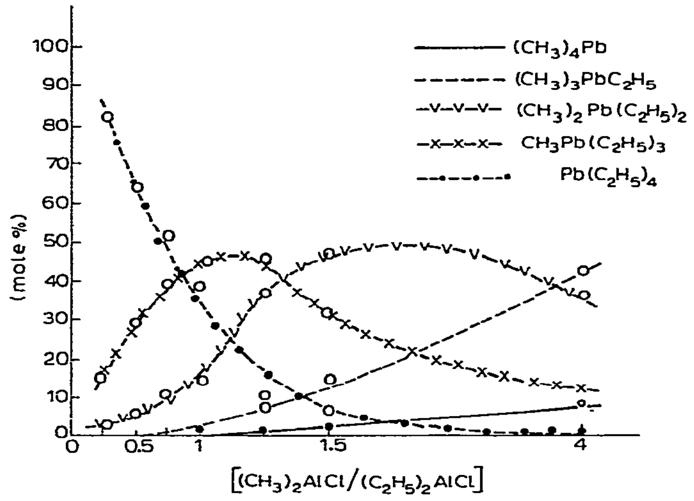


Fig. 3. Composition of lead alkyls in the reaction products depending on the molar ratio of dimethylaluminium chloride to diethylaluminium chloride. Temperature, 135°C; reaction time, 1 h; $Al/PbO/KCl = 2/1/1$.

TABLE 3

COMPOSITION OF METHYLETHYLLEAD ALKYLS IN THE REACTION PRODUCTS DEPENDING ON THE Al/Pb MOLAR RATIO

Temperature, 135°C; reaction time, 1 h; $Me_2AlCl/Et_2AlCl = 1/1$; $PbO/KCl = 1/1$

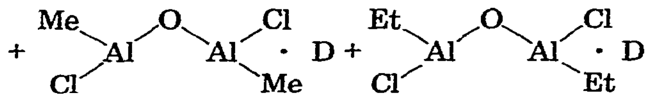
Molar ratio	Products (mole %)				
Al/Pb	Me_4Pb	Me_3PbEt	Me_2PbEt_2	$MePbEt_3$	$PbEt_4$
2/1	0.1	1.4	14.4	46.0	38.1
1.5/1	0.0	1.8	18.4	46.1	33.7
1/1	0.0	0.7	13.7	49.4	36.2
1/1.5	0.3	1.7	15.2	49.4	33.4
1/2	0.7	3.3	16.1	46.3	33.6

distribution of concentrations of mixed methylethyllead alkyls; analogously as in the former syntheses, a considerable excess of ethyl derivatives was observed.

The reaction between the bis(chloroethyl)alumoxane (II) and Lewis base (D) complex with tetramethyllead was studied. Exchange reactions of ethyl groups of the alumoxane (II) for methyl groups of tetramethyllead were found to occur and all the possible mixed methylethyllead alkyls are formed.

The reaction of lead oxide with a dimethyl- and diethyl-aluminium chloride mixture can be represented by eqn. 5.

$\mathrm{PbO + Me_2AlCl + Et_2AlCl + D \rightarrow Me_4Pb + Et_4Pb + Pb}$

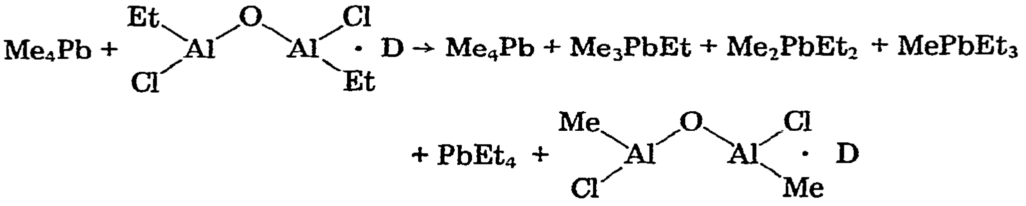


$$\mathrm{+\ Me(Cl)Al{-}O{-}Al(Cl)(Me) \cdot D + Et(Cl)Al{-}O{-}Al(Cl)(Et) \cdot D} \qquad (5)$$

From the results obtained (Tables 1-3 and Figs. 1-3) it can be seen that in the reaction products there is a predominance of ethyllead compounds.

In the presence of organoaluminium compounds ($\mathrm{Me_2AlCl}$, $\mathrm{Et_2AlCl}$), redistribution reactions of methyl and ethyl groups take place [3]. Due to a considerable excess of tetraethyllead, mainly ethyl derivatives are formed, according to eqn. 1.

Besides the greater tendency of the organoaluminium ethyl groups to alkylate, the exchange reactions proceeding between tetramethyllead and organoaluminium products contaning ethyl groups (eqn. 6) have a considerable influence on the higher number of Et—Pb linkages.



$$\mathrm{Me_4Pb + Et(Cl)Al{-}O{-}Al(Cl)(Et) \cdot D \rightarrow Me_4Pb + Me_3PbEt + Me_2PbEt_2 + MePbEt_3 + PbEt_4 + Me(Cl)Al{-}O{-}Al(Cl)(Me) \cdot D} \qquad (6)$$

From the above investigations it appears that diethylaluminium chloride shows a higher ability to alkylate lead salts.

We are continuing investigations on reaction mechanisms and the different possibilities of synthesis of mixed methylethyllead compounds.

Experimental

To a three-necked reaction vessel equipped with a stirrer and cold trap, and flushed out with dry deoxidized argon, potassium chloride and lead oxide were introduced under argon. The vessel was cooled and required amounts (50% wt.) of dimethyl- and diethyl-aluminium solutions in *p*-xylene were injected. The reactor was then placed in an oil ultrathermostat at the required temperature. After completing the synthesis, the contents were cooled and then hydrolyzed with aqueous hydrochloric acid. The organic layer, after drying, was chromatographically analyzed for methylethyllead compounds using a Willy Gide G CH F 18.3 apparatus at 80°C, with a 4 m column filled with 10% glycol 1500 on Diatomite Q as a carrier. A typical chromatogram of the post-reaction mixture is shown in Fig. 4.

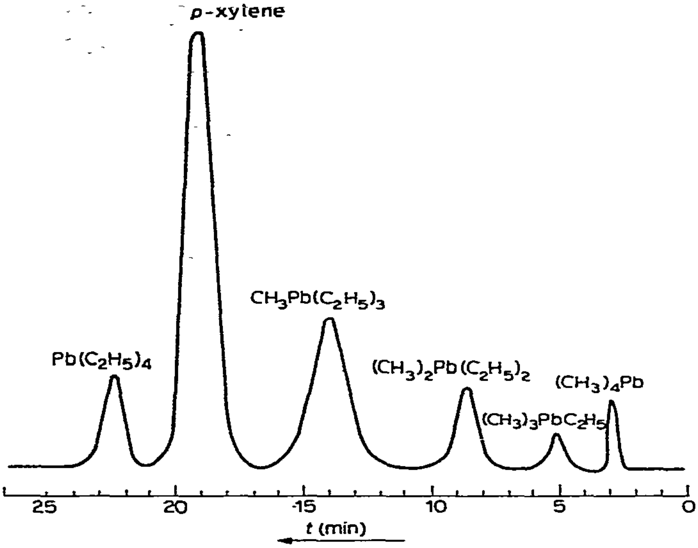


Fig. 4. Example of a chromatogram.

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