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# CLEAVAGE REACTIONS OF THE LEAD–CARBON BOND

## III*. THE REACTION OF TETRAORGANOLEAD AND HEXAORGANODILEAD COMPOUNDS WITH AMMONIUM HEXACHLOROPLUMBATE

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## SUMMARY

Triorganolead chlorides have been prepared in excellent yields by the reaction between tetraorganolead compounds and ammonium hexachloroplumbate in benzene or tetrahydrofuran at ambient temperature. The reaction was extended to cleavage of the metal–metal bond of hexaorganodi-Group IV element derivatives. A tentative mechanism is proposed.

## INTRODUCTION

The cleavage of lead–carbon bond by halogens and halogen acids has been investigated in detail[1–3]. Apart from providing a suitable route for synthesizing various organolead salts, such reactions also afforded an insight to the strength of the lead–carbon bond and the relative rates of elimination of various organic groups from tetraorganolead compounds. Other workers have investigated the cleavage of lead–carbon bonds by organic reagents[4,5]. In this paper we describe the cleavage of the lead–carbon bond in tetraorganolead compounds and of the lead–lead bond in hexaorganodilead compounds by ammonium and alkali metal (K, Cs and Rb) hexachloroplumbates.

## RESULTS AND DISCUSSION

In an earlier publication[6] we reported that under appropriate reaction conditions potassium hexachloroplumbate reacts with lithium derivatives of various acetylenic compounds to give tetraacetylenic derivatives of lead in good yields:

$$K_2PbCl_6 + 4\,R{-}C{\equiv}CLi \xrightarrow[-78^\circ]{THF} (R{-}C{\equiv}C)_4Pb + 4\,LiCl + 2\,KCl$$

$$R = C_6H_5,\ CH_3,\ CH_3(CH_2)_n,\ (CH_3)_3C \text{ etc.}$$

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* For Parts I and II see ref. 9.

An extension of that work revealed that ammonium, rubidium and cesium hexachloroplumbates reacted analogously, but best yields were obtained with potassium hexachloroplumbate. The reaction of various alkyl and aryllithium reagents with potassium hexachloroplumbate was also studied[7]. The results led us to study the reactions of hexachloroplumbates in more detail under various conditions and with a variety of organic and organometallic compounds. We have now found that hexachloroplumbates also act as chlorinating agents when allowed to react with tetraorganolead or hexaorganodilead derivatives in benzene or tetrahydrofuran at room temperature:

$$(NH_4)_2PbCl_6 + R_4Pb \rightarrow R_3PbCl + 2\,NH_4Cl + PbCl_2 + RCl$$

$R = CH_3, C_6H_5, C_4H_3S$ etc.

$$(NH_4)_2PbCl + R_3PbPbR_3 \rightarrow 2\,R_3PbCl + 2\,NH_4Cl + PbCl_2$$

$R = p\text{-}CH_3OC_6H_4, C_6H_5, C_{12}H_{25}$

As ammonium hexachloroplumbate was found to be the most suitable reagent (although analogous reactions were found to occur with K, Cs and Rb hexachloroplumbates also) most of our study was carried out with this reagent. The noteworthy features of the reaction are:

1. Among the hexachloroplumbates the ammonium derivative is the cheapest and easiest to synthesize, and can be stored for several years without any significant decomposition.

2. The completion of the reaction is easily detected by the disappearance of the distinct yellow color of ammonium hexachloroplumbate.

3. The yields of the organolead chlorides are excellent, and their isolation presents no problem because of their solubility in the solvent used for the reaction, whereas the inorganic chlorides ($PbCl_2$ and $NH_4Cl$) precipitate out.

4. The lead dichloride obtained as a by-product has been found to be very suitable for preparing tetraorganolead derivatives via its reaction with Grignard or lithium reagents:

$$\begin{tikzcd} R_4Pb\ (\text{or } R_3PbPbR_3) + (NH_4)_2\,PbCl_6 \arrow[d] \\ PbCl_2 + 2\,NH_4Cl + R_3PbCl + RCl \arrow[u, bend left=60, "\text{RLi or}"', "\text{RMgX}"] \end{tikzcd}$$

The various reactions are summarized in Table 1.

We have not been able to establish the exact mechanism of the reaction, but two possible routes can be considered, as follows:

1. On the basis of an analogous mechanism proposed for the reaction of potassium hexachloroplumbate with organoaluminium compounds[8], the reaction may proceed via an exchange reaction followed by the decomposition of the unstable intermediate formed:

$$R_4Pb + (NH_4)_2PbCl_6 \rightarrow R_3PbCl + [RPbCl_3] + 2\,NH_4Cl$$

$$[RPbCl_3] \rightarrow RCl + PbCl_2$$

TABLE 1

REACTION OF TETRAORGANOLEAD AND HEXAORGANODILEAD COMPOUNDS WITH AMMONIUM HEXACHLOROPLUMBATE

| *Reactants* | *Solvent* | *Organolead halide obtained* | *M.p. (°C) found (lit. value)* | *Yield (%)* | *Cl(%) found (calcd.)* |
|---|---|---|---|---|---|
| $(CH_3)_4Pb+(NH_4)_2PbCl_6$ | $C_6H_6$ | $(CH_3)_3PbCl$ | 190<br>(190) | 95 | 12.4<br>(12.3) |
| $(C_6H_5)_4Pb+(NH_4)_2PbCl_6$ | $C_6H_6$ | $(C_6H_5)_3PbCl$ | 208<br>(210) | 96 | 7.6<br>(7.5) |
| $(C_6H_5)_4Pb+(NH_4)_2PbCl_6$ | THF | $(C_6H_5)_3PbCl$ | 208<br>(210) | 96 | 7.5<br>(7.5) |
| $(2\text{-}C_4H_3S)_4+(NH_4)_2PbCl_6$ | $C_6H_6$ | $(2\text{-}C_4H_3S)_2PbCl_2$ | 200<br>(202) | | 15.1<br>(15.9) |
| $(C_6H_5)_3PbCH_2CH{=}CH_2+(NH_4)_2PbCl_6$ | $C_6H_6$ | $(C_6H_6)_3PbCl$ | 209<br>(210) | 97 | 7.5<br>(7.5) |
| $(C_6H_5)_3PbC{\equiv}CC(CH_3)_3+(NH_4)_2PbCl_6$ | $C_6H_6$ | $(C_6H_5)_3PbCl$ | 208<br>(210) | 95 | 7.6<br>(7.5) |
| $(C_6H_5)_3PbPb(C_6H_5)_3+(NH_4)_2PbCl_6$ | $C_6H_6$ | $(C_6H_5)_3PbCl$ | 208<br>(210) | 96 | 7.5<br>(7.5) |
| $(C_6H_5)_3PbPb(C_6H_5)_3+(NH_4)_2PbCl_6$ | THF | $(C_6H_5)_3PbCl$ | 208<br>(210) | 95 | 7.5<br>(7.5) |
| $(p\text{-}CH_3OC_6H_4)_3PbPb(p\text{-}CH_3OC_6H_4)_3$<br>$+(NH_4)_2PbCl_6$ | THF | $(p\text{-}CH_3OC_6H_4)_3PbCl$<br>+<br>$(p\text{-}CH_3OC_6H_4)_2PbCl_2$ | | | (6.3)<br>11.9<br>(14.4) |
| $(p\text{-}OCH_3C_6H_4)_3PbPb(p\text{-}CH_3OC_6H_4)_3$<br>$+(NH_4)_2PbCl_6$ | $C_6H_6$ | $(p\text{-}CH_3OC_6H_4)_3PbCl$ | 154<br>(152–153) | 90 | 6.3<br>(6.3) |
| $(C_{12}H_{25})_3PbPb(C_{12}H_{25})_3+(NH_4)_2PbCl_6$ | $C_6H_6$ | $(C_{12}H_{25})_3PbCl$ | 64–65 | 95 | 4.6<br>(4.8) |
| $(C_{12}H_{25})_3PbPb(C_{12}H_{25})_3+(NH_4)_2PbCl_6$ | THF | $(C_{12}H_{25})_3PbCl$<br>+<br>$(C_{12}H_{25})_2PbCl_2$ | | | (4.8)<br>6.7<br>(11.5) |

2. Decomposion of ammonium hexachloroplumbate cannot be totally excluded:

$$(NH_4)_2PbCl_6 \rightleftarrows 2\,NH_4Cl+[PbCl_4]$$

$$[PbCl_4] \rightarrow PbCl_2+Cl_2$$

$$R_4Pb+Cl_2 \rightarrow R_3PbCl+RCl$$

$$R_3PbPbR_3+Cl_2 \rightarrow 2\,R_3PbCl$$

However, no such decomposition was observed on refluxing a benzene suspension of ammonium hexachloroplumbate for 6 h.

The rate of cleavage was observed to be faster in tetrahydrofuran than in benzene or toluene.

The order of reactivity for various Group IV metal containing tetraorgano or hexaorganodi derivatives was found to be as follows: $Pb > Sn > Ge > Si$ (Table 2).

The total time taken for the completion of reaction was least with ammonium hexachloroplumbate (Table 3).

TABLE 2

REACTIVITY OF TETRAPHENYL- AND HEXAPHENYLDIORGANOMETALLIC COMPOUNDS OF GROUP IV ELEMENTS TOWARDS AMMONIUM HEXACHLOROPLUMBATE

| *Compound* | *Amount of triphenylmetal chloride obtained (%)* | *Reaction period (h)* |
|---|---|---|
| $(C_6H_5)_4$ Ge | 10 | 20 |
| $(C_6H_5)_4$ Sn | 40 | 10 |
| $(C_6H_5)_4$ Pb | 96 | 10 |
| $(C_6H_5)_3$ SiSi$(C_6H_5)_3$ | | 20 |
| $(C_6H_5)_3$ GeGe$(C_6H_5)_3$ | 5 | 20 |
| $(C_6H_5)_3$ SnSn$(C_6H_5)_3$ | 30 | 20 |
| $(C_6H_5)_3$ PbPb$(C_6H_5)_3$ | 95 | 4 |

TABLE 3

EFFECT OF THE NATURE OF THE RADICAL OR ALKALI METAL ATTACHED TO HEXACHLOROPLUMBATE

| *Hexachloroplumbate taken* | *Organolead compound taken* | *Total time required for completion of reaction (h)* |
|---|---|---|
| $(NH_4)_2PbCl_6$ | $(CH_3)_4Pb$ | 8 |
| $K_2PbCl_6$ | $(CH_3)_4Pb$ | 25 |
| $Rb_2PbCl_6$ | $(CH_3)_4Pb$ | 30 |
| $Cs_2PbCl_6$ | $(CH_3)_4Pb$ | 40 |

## EXPERIMENTAL

Tetramethyllead was used as an 80% solution in toluene. Samples of tetraorganolead and hexaorganodilead derivatives were obtained from the Institute of Organic Chemistry, TNO, Utrecht, The Netherlands, and were used without further purification. The products were characterized by mixed melting point and thin layer chromatography with authentic samples.

### *Preparation of ammonium hexachloroplumbate*

Lead dioxide (459 g) was added in small portions to stirred concentrated hydrochloric acid (3 l, analytical grade) at 0°. The dioxide dissolved slowly in hydrochloric acid forming a lemon yellow solution. The color of the solution darkened with each addition. The solution, however, stayed clear until approximately 85% of the lead dioxide had been added. It was essential not to allow the temperature of the solution to rise above 5° nor fali below 0°, since hexachloroplumbic acid ($H_2PbCl_6$) tends to decompose above 5°; and below 0° the reaction proceeds very slowly. During the addition of the last 15% of the dioxide, the solution became turbid and a dirty gray precipitate was formed. After adding the last portion of lead dioxide, the mixture was stirred for a further 30 min at 0°. A cold solution of ammonium chloride (216 g) in water (700 ml) was then added during 30 min with vigorous stirring. Ammonium hexachloroplumbate was formed as a bright yellow precipitate which was filtered off, washed with ether, and air-dried. A golden yellow, free-flowing powder was obtained (775 g, 88% yield).

### *Reaction between tetramethyllead and ammonium hexachloroplumbate*

Ammonium hexachloroplumbate (4.5 g, 0.01 mole) was added to a stirred solution of tetramethyllead (3.3 g of 80% solution in toluene, 0.01 mole) in benzene (50 ml) at room temperature until the golden yellow color of the complex disappeared. The white precipitate of inorganic salts was filtered off, and the solvent was removed under vacuum. Subsequent extraction of the residue and the precipitate with hot chloroform gave a total of 2.7 g (95% yield) of trimethyllead chloride.

### *Reaction between tetraphenyllead and ammonium hexachloroplumbate*

Tetraphenyllead (10.3 g, 0.02 mole) and ammonium hexachloroplumbate (9.2 g, 0.02 mole) were stirred in tetrahydrofuran (100 ml) until the yellow color of the complex disappeared. The filtrate on evaporation gave triphenyllead chloride (9.1 g, 96% yield).

### *Reaction between hexaphenyldilead and ammonium hexachloroplumbate*

Ammonium hexachloroplumbate (13.7 g, 0.03 mole) was added to a stirred solution of hexaphenyldilead (26.3 g, 0.03 mole) in tetrahydrofuran (250 ml). The temperature of the mixture started to rise after approximately 10 min. The initial bright yellow color of ammonium hexachloroplumbate changed to creamish white within an hour. The transformation of hexaphenyldilead into triphenyllead chloride was followed by thin layer chromatography. After the completion of the reaction the precipitate of inorganic halides was filtered and washed twice with tetrahydrofuran. Evaporation of the solvent gave triphenyllead chloride (27 g, 95%).

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