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## On Preparation of Lead Tetraethyl.

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### Abstract.

Lead tetraethyl, known as a powerful antiknock material, may be prepared by the reaction of ethyl magnesium iodide or bromide (Grignard's reagent) with lead chloride. In this method, it is known that ethyl iodide or ethyl bromide is a good starting material, whereas ethyl chloride can not be used for the sake of very weak activity.

The present authors have found that an ethereal solution containing ethyl iodide (or bromide) and iodine was a suitable catalyser for the reaction between ethyl chloride and magnesium. When this solution was added to magnesium, ethyl magnesium iodide  $C_2H_5MgI$  was instantaneously formed and the latter accelerates catalytically the reaction between ethyl chloride and magnesium. After the reaction once started between ethyl chloride and magnesium, the subsequent reaction is accelerated by ethyl magnesium chloride  $C_2H_5MgCl$  formed. Then the crude lead tetraethyl may be readily prepared by the reaction of ethyl magnesium chloride and lead chloride.

The crude lead tetraethyl containing a considerable proportion of unsaturated lead triethyl was treated with air or oxygen in presence of dilute hydrochloric acid, by which lead tetraethyl remained unchanged, and lead triethyl was converted into crystalline mass of triethyl lead chloride  $(C_2H_5)_3PbCl$ . The latter was then transformed into lead tetraethyl by the action of ethyl magnesium chloride, with the yield of 95% of the theory. The total yield of lead tetraethyl to the amount of ethyl chloride used was approximately 74% of the theory.

The pure lead tetraethyl had a specific gravity ( $d_{40}^{180}$  vac.) of 1.6600, refractive index ( $n_D^{180}$ ) of 1.5206, and boiling point of 81.6–82.0°C. at 11mm. or 85.4–85.7°C at 13mm. It decomposes at about 400°C., separating metallic lead. Other properties were also investigated.

### Introduction.

It was early in 1854 that lead tetraethyl was first prepared in very impure state by Löwig by the interaction of sodium-lead amalgam and ethyl iodide. Hitherto it has been investigated only with scientific interest as an organic compound of lead. But some years ago, by the investigation performed by T. Midgley, lead tetraethyl was found to be the most powerful antiknock material of motor fuel and so this found a practical usage in considerable quantity for this purpose.

The principal preparative methods hitherto known are, (1) the earliest method used by Löwig<sup>(1)</sup> and recently by T. Midgley<sup>(2)</sup> that sodium-lead amalgam are treated with ethyl iodide or bromide, (2) Buckton's method<sup>(3)</sup> that zinc ethyl are treated with lead chloride, and Pfeiffer's method<sup>(4)</sup> that Grignard's reagent as ethyl magnesium iodide or bromide are reacted with lead chloride.

It is generally agreed that in the Pfeiffer's method ethyl bromide or ethyl iodide is a good starting material and ethyl chloride can not be used for the sake of very weak activity.

In the present paper, a study of the preparation of lead tetraethyl by Grignard's reaction using ethyl chloride as the starting material, and the reasonable method on the purification of lead

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(1) Löwing, Ann., 88, 318.

(2) General Motors Research Corp., Assees. of T. Midgley, E. P. 216, 083, 14.8.23.

(3) G. B. Buckton, Ann., 109, 222; 112; 226.

(4) P. Pfeiffer und P. Truskier, Ber., 37, 1125, (1904); Grüttner und Krause, Ber., 49, 415 (1916).

tetraethyl was investigated and the yield of it was increased up to 74% of the theory. Chemically pure lead tetraethyl was isolated and some physical constants and chemical properties were also observed.

## Experimental.

### I. Preparation of Ethyl Magnesium Chloride and Crude Lead Tetraethyl.

Magnesium compounds of ethyl halides known as Grignard's reagent have been used in organic synthesis not only in laboratory but also in manufacturing scale. But the ethyl halides ever used were confined to iodide and bromide, as aliphatic iodides and bromides readily attack magnesium, whereas aliphatic chlorides react with difficulty or not at all.

The present authors have found a suitable catalyser for the reaction between ethyl chloride and magnesium, and ethyl magnesium chloride has been prepared with very high yield.

#### (1) *Catalyser to Expedite the Formation of Ethyl Magnesium Chloride.*

It is already known that the catalysers to expedite the formation of Grignard's reagent are iodine,<sup>(1)</sup> mercuric chloride,<sup>(2)</sup> ethyl bromide, ethyl iodide,<sup>(3)</sup> ethyl (or methyl) magnesium iodide or bromide,<sup>(4)</sup> and others. On the mechanism of the catalytic action of iodine, Wohl<sup>(5)</sup> proposed the following scheme.

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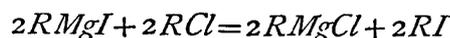
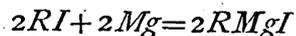
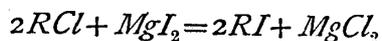
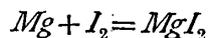
(1) Bayer, Ber., **38**, 2759 (1905); Wohl, Ber., **39**, 1952 (1906).

(2) Sommelet, Centralbl., 872, **1**, (1907).

(3) Sachs und Ehrlich, Ber., **36**, 4296 (1903).

(4) Hesse, Ber., **39**, 1132 (1906); N. Zelinsky, Centralbl., 277, **11**, (1903); H. Schmalfluss, J. prak. Chem., **108**, 88 (1924).

(5) Wohl, Loc. Cit.



N. Zelinsky<sup>(1)</sup> described that on the reaction between naphthen chloride and magnesium, the heat of formation of organo-magnesium compound was the cause of starting the reaction. Reycheler<sup>(2)</sup> indicated that the highly probable catalyser which expedites the reaction might be the organo-magnesium compound, that formed by the reaction of ethyl iodide or bromide and magnesium.

The present authors have found that not only ethyl magnesium bromide or iodide but also ethyl magnesium chloride has a powerful action to expedite the reaction between ethyl chloride and magnesium. From this fact, Reycheler's consideration was proved to be highly reasonable.

In practice, however, it is inconvenient to stock these ethyl magnesium halides for the use as catalyser, as they are rather unstable. The present authors found that an ethereal solution containing ethyl iodide (or bromide) and iodine was the convenient and strong catalyser for the technical purpose. When this solution was added to magnesium,  $C_2H_5MgI$  was instantaneously formed and  $C_2H_5MgI$  formed accelerates catalytically the reaction between  $C_2H_5Cl$  and  $Mg$ . After reaction once started between  $C_2H_5Cl$  and  $Mg$ , the subsequent reaction is accelerated by  $C_2H_5MgCl$  formed.

### (2) Preparation of Ethyl Magnesium Chloride.

Ethyl chloride was prepared from ethyl alcohol, zinc chloride and dry hydrochloric acid gas.<sup>(3)</sup> Metallic magnesium was used in

(1) N. Zelinsky, Loc. Cit.

(2) Reycheler, Centralbl., 455, 1, (1907).

(3) Vanino, Präparative Chemie, Bd. II, p. 18.

powdered form. Ether was purified by washing with a small quantity of water, dried over calcium chloride and metallic sodium, and finally distilled.

Apparatus used in this experiment was nearly analogous to that used by Gilman and Meyers.<sup>(1)</sup> A reaction flask of 100 c.c. capacity to the line marked in midway of long neck was used. The flask was provided with a glass stirrer having mercury seal, a reflux condenser and a dropping funnel, through which a mixture of ether and ethyl chloride was introduced. Beside these, the flask had a side tube, from which the sample was pipetted at intervals for the determination of ethyl magnesium chloride.

A few drops of ethereal solution of ethyl iodide and iodine was poured on magnesium in the flask. The reaction took place instantaneously and considerable heat was evolved. The mixture of ether and ethyl chloride was then added drop by drop from the dropping funnel, vigorous stirring and cooling at the temperatures lower than 5°C being necessary.

Ethyl magnesium chloride produced was determined according to the method of Gilman, Wilkinson, Fishel and Meyers,<sup>(2)</sup> viz., after the reaction was completed dry ether was added to the flask up to the mark and a measured volume of sample was taken from a side tube of the flask by means of a dry pipette. The sample was poured into the large quantity of water and ethyl magnesium chloride was decomposed to basic magnesium chloride, which was titrated with standard acid solution using methyl orange as indicator.

The yield of ethyl magnesium chloride was 99.2% of the theory.

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(1) H. Gilman and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 159 (1923).

(2) H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

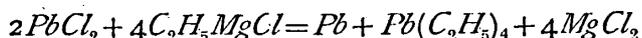
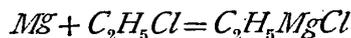
(3) *Preparation of Crude Lead Tetraethyl.*

Ethyl magnesium chloride reacts readily with lead chloride, separating metallic lead in a spongy condition and lead tetraethyl is produced in an impure state.

To prepare lead tetraethyl, a grayish solution of ethyl magnesium chloride obtained, was diluted with absolute ether and dry lead chloride was added slowly under vigorous stirring.

In this case, strong cooling at the temperatures below  $5^{\circ}\text{C}$  is preferable to obtain good yield of lead tetraethyl. When the reaction was completed, the whole product was treated with water, resulting a greenish yellow ethereal solution of impure lead tetraethyl.

These reactions may roughly be expressed as follows.



In this experiment, the percentage of ethyl chloride transformed into lead compounds was 75% of the theory.

(4) *Properties of Crude Lead Tetraethyl.*

The crude lead tetraethyl had a greenish yellow colour and when exposed to air, it gave pale yellow amorphous precipitates. It could be distilled under reduced pressure producing a liquid distillate together with gas and metallic lead. The liquid distillate had also a pale yellow colour and becomes turbid after a short time. By the repeated distillations a colourless liquid was obtained, which had  $n_{\text{D}}^{20} = 1.5214$  and was shown to be lead tetraethyl. The pale yellow precipitates produced when the crude lead tetraethyl was allowed to stand in air, contained 80% of lead and when ignited, they burnt with long flame. When the precipitates were treated with hydrochloric acid, a mixture of  $(\text{C}_2\text{H}_5)_3\text{PbCl}$  and  $\text{PbCl}_2$

was obtained. From these facts, the precipitates appear to be a mixture of  $(C_2H_5)_6Pb_2O$  and  $PbO$ .

## II. Purification of Crude Lead Tetraethyl.

It was already indicated by Grüttner and Krause<sup>(1)</sup> that the distillation method was not suitable for the purpose of refining crude lead tetraethyl. The method proposed by those was that crude lead tetraethyl was cooled lower than  $-75^\circ C$  with solid carbon dioxide and treated with chlorine gas. By this treatment, the unsaturated lead compound was added with chlorine and one ethyl group of lead tetraethyl was replaced with chlorine. Thus all lead compounds were converted into triethyl lead chloride  $(C_2H_5)_3PbCl$ , which could readily be converted into lead tetraethyl by the action of the Grignard's reagent.

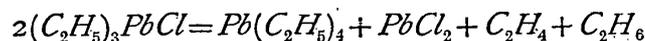
The great drawbacks of this process were that the strong cooling was necessary and that one ethyl group of lead tetraethyl was wasted.

The present authors have found a more reasonable purification method. An ethereal solution of the crude lead tetraethyl was treated with air or oxygen in presence of dilute hydrochloric acid solution until the yellow colour was disappeared. On evaporating the ethereal solution, a liquid containing a white crystalline mass was obtained. The liquid portion was pure lead tetraethyl which was colourless and could be distilled without decomposition under reduced pressure. The crystalline mass was found to be triethyl lead chloride  $(C_2H_5)_3PbCl$ . The chlorine content of this compound showed 10.73% by Volhard's method, being exactly same to the value of 10.75% calculated from the formula of  $(C_2H_5)_3PbCl$ . The triethyl lead chloride obtained melted at  $170^\circ C$  under decomposition,

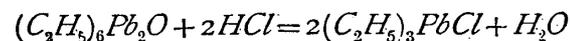
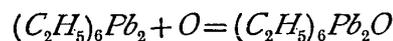
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(1) G. Grüttner und E. Krause, Ber., 49, 1420 (1916).

giving lead tetraethyl, lead chloride and hydrocarbons, as probably shown by the following equation.



Triethyl lead chloride could easily be converted into lead tetraethyl by  $C_2H_5MgCl$  with the good yield of 95% of the theory. Thus, when the crude lead tetraethyl containing a considerable proportion of unsaturated lead triethyl is treated with air or oxygen in presence of dilute  $HCl$ , lead tetraethyl remains unaffected, and lead triethyl is readily attacked by oxygen, producing a basic lead ethyl compound which is converted into crystalline mass of triethyl lead chloride. Triethyl lead chloride is transformed into lead tetraethyl by the action of  $C_2H_5MgCl$ . These reactions may be represented by the following equations.



By the above treatment, all lead triethyl which formed main part of the impurities of the crude lead tetraethyl could be converted into lead tetraethyl. The yield of lead tetraethyl to the amount of ethyl chloride used was approximately 74% of the theory.

### III. Properties of Lead Tetraethyl.

A very few mention was made of the properties of lead tetraethyl and some of the published characteristics are also incorrect.

Pure lead tetraethyl obtained in the present research was a colourless liquid with somewhat peculiar unpleasant odour, and when ignited, it burnt with long flame giving white fumes of lead oxide.

It had a specific gravity ( $d_{40}^{18}$  *vac.*) of 1.6600 and a refractive index ( $n_D^{18}$ ) of 1.5206. The boiling point of lead tetraethyl was 81.6–82.0°C at 11mm. or 85.4–85.7°C at 13mm. These boiling points exactly agreed with that calculated from the formula of Clausius-Clapeyron and Trauton's rule, assuming lead tetraethyl as an unassociated liquid.

Lead tetraethyl decomposes at about 400°C., separating metallic lead. Even at ordinary temperatures this compound becomes turbid by submitting to prolonged exposure in air, especially being accelerated by sunlight. The decomposed liquid exhibits a distinctly alkaline reaction and by neutralizing it with *HCl*, triethyl lead chloride was always obtained.

#### **Summary.**

(1) The method of the preparation of lead tetraethyl by Grignard's reaction using ethyl chloride as starting material has been investigated.

(2) An ethereal solution containing ethyl iodide (or bromide) and iodine has been found to be the convenient and strong catalyser to expedite the reaction of ethyl chloride and magnesium.

(3) The reasonable method of refining crude lead tetraethyl has been investigated.

(4) The properties of chemically pure lead tetraethyl have also been studied.

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昭和二年十二月發行

### 抄 錄

#### 四エチル鉛の調製

所員 工學博士 田 中 芳 雄

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四エチル鉛は夙に1854年に發見された有機性鉛化合物で、近年に到る迄は單に化學的興味の一化合物に過ぎなかつたのである。然るに輒近に此の物質を極微量にガソリン又は燈油に加へて内燃機關燃料として使用する時は、此等燃料の内燃機關内におけるKnockingを防止することが判り、其の需要が増加するに到つた。然るに其の工業的製法は未だ充分に明かでないが、一般に其の原料としては臭化エチル又は沃化エチルを使用する。四エチル鉛の一製法としてグリニアル反應を應用する方法に就ても、其の原料としては臭化エチル又は沃化エチルを使用する。從て臭素又は沃素の資源が豊富でなければならぬ。然るに若し夫等の代りに鹽化エチルを原料として使用し得れば、其の安價にして又其の資源の豊富なるが爲めに、四エチル鉛の工業的生産に甚だ便利である。然るに從來夫れが用ひられなかつたのはグリニアル反應を開始することが困難なる爲めであつた。本研究は鹽化エチルを原料としグリニアル反應に依り四エチル鉛を調製する方法、四エチル鉛の精製法及び純四エチル鉛の性状に關する研究である。

先づグリニアル反應に依り、鹽化エチルから鹽化エチルマグネシウムを生成するに當り、其の反應の開始が困難である。著者は其の反應の促進劑又は開始劑として略當量の沃素を溶解せる沃化エチル又は臭化エチルを乾燥エーテルに溶解したものが實際に甚だ便利であることを認めた。即ち此のものを極微量にマグネシウムに加へ、次に鹽化エチルを加へ、以て良好に鹽化エチルマグネシウム  $C_2H_5MgCl$  の生成を行ひ得た。次に之れに鹽化鉛を作用せしめて粗製四エチル鉛を調製した。

以上の粗製四エチル鉛は四エチル鉛の外に複雑なる鉛化合物を夾雑するから、之れを經濟的方法で精製しなければならぬ。著者は粗製四エチル鉛の性狀を研究し、進で其の精製法を攻究し、終に粗製四エチル鉛を稀鹽酸の存在に於て、空氣又は酸素にて處理し、四エチル鉛の精製を行ひ、同時に不純物は三エチル一鹽化鉛  $(C_2H_5)_3PbCl$  の結晶として分離し、是れは再び鹽化エチルマグネシウムを作用せしめて四エチル鉛とする方法を見出した。此の精製法は比較的簡單で又損失も極めて尠いので經濟的方法と考へられる。斯くして鹽化エチルに對し理論數の約74%の四エチル鉛を得た。

著者は更らに純四エチル鉛の性狀を精査した。即ち純四エチル鉛は特異の微臭を有する無色の液體で、之れに點火すれば長い火焰を以て燃え酸化鉛の白烟を放つ。比重 ( $d_{40}^{18}$ ) は 1.6600、屈折率 ( $n_D^{18}$ ) 1.5206 である。沸點は 11mm. に於て  $81.6-82.0^{\circ}C$  で、13mm. に於ては  $85.4-85.7^{\circ}C$  である。是等の沸點は Clausius-Capeyron の式及び Trauton の法則から計算したものに能く一致する。四エチル鉛は約  $400^{\circ}C$  に於て分解し金屬鉛を分離する。常溫に於ても空氣中に長く放置すれば潤濁を生じ、殊に直射日光は其の作用を促進する。而して分解した液はアルカリ性を呈し之れを鹽酸で中和すれば常に三エチル一鹽化鉛を生ずる。