The reaction of silver nitrate with some organo-lead compounds and the chemical reactions of alkali metal aromatic compounds

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The Reaction of Silver Nitrate with some Organo-Lead Compounds

and

The Chemical Reactions of Alkali Metal Aromatic Compounds

by

D. KINGSTON

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MEMORANDUM

The work described in this thesis was carried out in the Durham Colleges in the University of Durham, between September 1957 and August 1960. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

The work described in Part IA of this thesis has been the subject of one publication, with F. Glockling; Journal of the Chemical Society, 3001, (1959).

PREFACE

The work on organo-lead compounds is divided into Parts IA and IB; Part IB, entitled "The Low Temperature Reactions of some Organo-Metallic Reagents with Lead Halides", being in the nature of an appendix to Part IA, entitled "The Reaction of Silver Nitrate with some Organo-Lead Compounds". This is followed by Part II, entitled "The Chemical Reactions of Alkali Metal Aromatic Compounds".

The presentation does not represent the chronological order, since Part IB was the last research undertaken.

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PART 1A

THE REACTION OF SILVER NITRATE WITH SOME ORGANO-LEAD COMPOUNDS

SUMMARY

The reaction of silver nitrate in ethanol solution with a number of unsymmetrical organo-lead compounds, Et_3PbR, is described. The lead compounds prepared, were chosen with the object of investigating the factors which influence the stability of the primary product of the reaction, the unstable organo-silver compound AgR, and the reason for the cleavage of the R-Pb bond rather than the Et-Pb bond.

The compounds described are:-

(i)	2-Methylprop-2-enyltriethyllead	$Et_3PbCH_2C(CH_3){:}CH_2$
(ii)	Benzyltriethyllead	Et_3PbCH_2Ph
(iii)	Triethyl-4-trifluoromethylphenyllead	$Et_3PbC_6H_4CF_3\underline{p}$
(iv)	4-Dimethylaminophenyltriethyllead	$Et_3PbC_6H_4NMe_2\underline{p}$
(v)	2-Styryltriethyllead	$Et_3PbCH{:}CHC_6H_5$

Compounds (i), (iii), and (v) have not been previously described, and are all unstable liquids. Compound (iv) has been previously described, but without practical details, and compound (ii) has been previously prepared in poor yield. Both these compounds have been obtained here in good yield.

For each of the above compounds reaction with an equivalent or excess of silver nitrate results in the exclusive cleavage of the unsymmetrical R group. In no case are C_2 or C_4 hydrocarbons formed.

Compound (i), which should give the resonance stabilised _iso_but-2-enyl radicals on decomposition with Ag^+ ions, shows no indication of the formation of an intermediate organo-silver compound. The same is true for compound (ii) _viz_: there is no intermediate formation of benzyl-silver.

Compounds (iii), (iv), and (v) all show the formation of an intermediate red or red-brown colouration, indicative of the formation of an organo-silver compound, with silver nitrate. The deep red precipitate, thought to be styryl silver, obtained from compound (v), is stable for several hours in solution at room temperature.

In general it appears that the greater the stability of the radical R, the lower is the stability of the organo-silver compound. In the extreme cases of methallyl and benzyl, no silver compounds are formed under the conditions of these experiments. The abnormally high thermal stability of styryl-silver is probably connected with the low stability of the styryl radical, and the presence of a double bond adjacent to the silver atom. This is compatible with the comparatively high stability of _iso_but-1-enyl-silver.

INTRODUCTION

The elements germanium, tin, and lead of Group IV B all form stable organo-metal compounds. Tin and lead in particular form large numbers of these compounds, and the number known has been steadily growing since the first compounds were prepared in the middle of the last century.

The tetraalkyls and aryls of germanium, tin, and lead are much more stable than are the fully substituted organic compounds of the Group III B and Group V B metals. Tetraethyllead, tetraphenyltin, and tetramethylgermane, for example, are all stable towards air and water. Tripropylboron, however, reacts instantly with oxygen. Trimethylaluminium reacts explosively with water and takes fire in air, as do the lower trialkylgallium compounds. In Group V both trimethylstibine and trimethylbismuth react readily with oxygen, although the aryl compounds are much more stable.

The lower reactivity of the Group IV B elements may be attributed to the fact that the elements have no tendency to expand their covalency above four, except when bonded to electronegative groups.

Within Group IV B itself, there is a decrease in stability of the organic compounds in the series germanium, tin, and lead, which is most marked in going from tin to lead. This is especially true for compounds containing metal-metal bonds. Hexaphenylditin is quite stable and easily obtained, whereas lead-lead bonds are readily broken, and hexaphenyldilead decomposes at 155°C without melting. Compounds containing metal-metal bonds are not common, and only a few examples outside of Group IV B are known, e.g. hexamethyldiplatinum, the cacodyls and a few corresponding antimony compounds, and compounds having a boron-boron bond.

1. Covalent Compounds of Lead

Lead with atomic number 82 has four electrons in the valence shell. In the ground state it has the configuration, $5d^{10}6s^{2}6p^{2}$, hence a covalence of 2 would be expected, and lead does in fact exhibit this covalence in a highly unstable group of aryl derivatives. In this type of compound the lead atom is only surrounded by six electrons in the valence shell, two in the form of an inert pair.

The energy required for promotion of an electron from the 6s to the 6p orbital, to give the higher energy state of configuration Sp^{3}, is more than compensated for in the stable bond formation found in the 4-covalent lead compounds, in which the central lead atom is surrounded by a complete octet of electrons. In fact almost all organo-lead compounds are those of 4-covalent lead.

2. Symmetrical Organo-Lead Compounds

The symmetrical organo-lead compounds are those of the type R_4Pb, of which the most well known example is tetraethyllead, used on a large scale as an anti-knock additive for petrol. The alkyl compounds are colourless liquids up to tetratetradecyllead, $(C_{14}H_{29})_4Pb$, which has a melting point of 31°C.[1] The straight chain compounds are thermally stable up to about 100°C, but the branch chain compounds are rather less stable. The first member of the series, tetramethyllead, is notoriously unstable, and may explode during distillation. Since even tetramethyllead has a boiling point over 100°C, purification always involves vacuum distillation in the case of the liquids.

The aryl compounds are generally colourless crystalline solids, tetraphenyllead having a melting point of 223°C.

There are three main methods of preparation of these compounds.

(1) The action of a Grignard compound on lead chloride[2], often gives good yields of the tetraalkyl or aryl compounds. This method involves the formation of the

hexaalkyl or aryldilead compound, and its subsequent decomposition on prolonged heating.

$$2RMgX + PbCl_2 \longrightarrow R_2Pb + MgX_2 + MgCl_2 \quad (i)$$

$$3R_2Pb \longrightarrow R_6Pb_2 + Pb \quad (ii)$$

$$2R_6Pb_2 \longrightarrow 3R_4Pb + Pb \quad (iii)$$

The mechanism proposed by Krause and Grosse[2] must seem suspect, since it contains two termolecular stages. The fact that Krause[3] isolates diaryl lead compounds in poor yield from the reaction of a Grignard compound with lead chloride, would seem to confirm that diaryl lead compounds are formed as intermediates in this reaction. However rather than a termolecular first stage, this reaction could proceed via an aryl lead chloride.

$$RMgX + PbX_2 \longrightarrow RPbX + MgX_2$$

$$RPbX + RMgX \longrightarrow R_2Pb + MgX_2$$

Krause[3] reports on the instability of the diaryllead compounds; only yields of about 5% were obtained, and sometimes none at all. Thus to visualise a reaction, in which three such molecules combine together to produce hexaphenyldilead, is extremely difficult.

Gilman, Summers, and Leeper[4] report on the reaction of phenyl lithium with lead chloride at -10°C in ether, when lead chloride reacts with three equivalents of phenyl lithium to give triphenyllead lithium. Here again, it is possible that an intermediate aryl lead chloride is formed.

$$PhLi + PbCl_2 \longrightarrow PhPbCl + LiCl$$
$$PhPbCl + PhLi \longrightarrow Ph_2Pb + LiCl$$
$$Ph_2Pb + PhLi \longrightarrow Ph_3PbLi$$

It is claimed that the yellow colouration obtained during the addition of phenyl lithium to lead chloride is due to the formation of diphenyl lead, which, according to Krause[3], is deep red. There is no real experimental evidence for this, though such a reaction mechanism is possible. Gilman and co-workers have also postulated that an equilibrium exists between diphenyllead and triphenyllead lithium.

$$Ph_2Pb + PhLi \rightleftharpoons Ph_3PbLi \ (80\%)$$

(2) The action of an organic lithium derivative, in the presence of the organic halide, on lead chloride.[5] This is often a better method than the previous one, since there is no loss of lead.

$$4RLi + 2PbX_2 \longrightarrow R_4Pb + Pb + 4LiX$$
$$2RI + Pb \longrightarrow R_2PbI_2$$
$$2RLi + R_2PbI_2 \longrightarrow R_4Pb + 2LiI$$

(3) The action of a lead-sodium alloy on the organic halide. This method is used for the commercial preparation of tetraethyllead from ethyl chloride.[6]

3. Unsymmetrical Organo—Lead Compounds

These are compounds in which one or all of the organic groups bonded to the lead are different from the others, e.g. $R'R_3Pb$, $R'R''R_2Pb$, $R'R''R'''RPb$. The tetraalkyl- and aryltrialkyllead compounds are usually liquid, the diaaryldialkyllead and triarylalkyllead compounds are liquid or solid, and the tetraaryl compounds are solids. All these compounds tend to be thermally less stable than the symmetrical compounds, and chemically more reactive. This adds to the difficulty of obtaining pure compounds, particularly the liquids, since they often decompose on distillation, many tending to disproportionate to give the more stable symmetrical compound.

The two most useful methods of preparation of these compounds are:-

1. The action of a Grignard compound on a trialkyl- or triarylhalide

$$R_3PbX + R'MgX \longrightarrow R_3PbR' + MgX_2$$

2. The action of organolead-metal compounds on organic halides

$$R_3PbLi \xrightarrow{R'X} R_3PbR'$$
$$R_3PbNa \xrightarrow{R'X} R_3PbR'$$

3. The preparation of compounds, in which the organic groups are all different, is much more difficult, and the step-wise synthesis employed is dependent on the groups concerned.

4. Hexaalkyl- and Hexaaryldilead Compounds

These are compounds containing the weak lead-lead bond, e.g. $R_3Pb \cdot PbR_3$. In all known compounds the R groups are all the same. They are readily decomposed by heat to give the symmetrical tetraorganolead compound, and lead. The thermal stability in the alkyl series increases with molecular weight of the organic group, whilst the aryl compounds decompose before melting.

In dilute solution these compounds are said to exhibit a decrease in molecular weight approaching that of R_3Pb.[7(a)] The supposition that the dilead compounds dissociate into R_3Pb radicals is not borne out by physical evidence. There is no paramagnetism. However decomposition of some kind is indicated.

These compounds are obtained from the Grignard reaction with lead chloride, as already mentioned in the preparation of the symmetrical compounds, and they can be isolated if prolonged heating is avoided. The product generally contains some of the R_4Pb compound, more or less, depending on the stability of the dilead compound.

A more recent method of preparation is the reaction of a solution of sodium in liquid ammonia on the triaryl- or trialkyl halide.7(b)

$$R_3PbI + 2Na \longrightarrow R_3PbNa + NaI$$

$$R_3PbNa + R_3\ PbI \longrightarrow R_3Pb{\cdot}PbR_3 + NaI$$

5. The Compounds of Lead (II)

The R_2Pb compounds are thermally unstable, and are formed as the first products in the preparation of symmetrical tetraorgano-lead compounds from lead chloride and Grignard compounds. The only examples to have been isolated are diphenyllead and di-p-tolyllead.[3]

These two compounds were prepared from lead chloride and the corresponding Grignard reagent at 2°C. Yields were low, about 4%, decomposition occurring even at this low temperature. The products are reported as blood-red solids. Molecular weight determinations in benzene show them to be monomeric, in contrast to the analagous diphenyltin, which, although monomeric when freshly prepared, quickly polymerises.

Attempts to repeat this work have so far been unsuccessful.

The reaction between phenyl lithium and lead chloride to produce diphenyllead has already been discussed, (see section on tetraorgano-lead compounds).

Gilman and Apperson[8] attempted to prepare diaryllead compounds by the reduction of diaryllead dihalide with alkali metal-liquid ammonia solutions. It was found that two equivalents of alkali metal on the dihalide gave hexaphenyldilead and inorganic lead compounds. Using four equivalents of lithium a red solution, containing much inorganic lead, was obtained. Addition of ethyl bromide to this solution gave diethyldiphenyllead, Ph_2Et_2Pb (60%), ethyltriphenyllead, $EtPh_3Pb$ (25%), triethylphenyllead Et_3PhPb (8%), and tetraethyllead. Probably the main reaction is via the compound diphenyldilithiumlead. No diphenyllead was obtained.

Jensen and Kaas[9] viewed the dissociation of hexaaryldilead compounds as giving diaryl and tetraaryl compounds, rather than the triaryllead radical, which is inconsistent with magnetic measurements, (see section on hexaorganodilead compounds).

$$Ph_6Pb_2 \rightleftharpoons Ph_2Pb + Ph_4Pb$$

However they were unable to isolate any diaryllead compounds.

Radical Cleavage Reactions

1. Cleavage of Symmetrical Tetraorgano-lead Compounds

It has been known for some time that pyrolysis of organo-lead compounds results in the formation of free radicals. Paneth[10] first demonstrated this phenomena when he produced methyl radicals by heating tetramethyllead in an inert gas at low pressures. The method he used for showing the presence of free radicals is now well known. It involves the movement of a metallic mirror from the cold to the hot part of a tube. The mechanism being, obviously, the formation of an organo-metal compound at the cold surface, followed by decomposition and deposition of the metal at the hot surface.

In the same way tetraethyllead has been shown to form ethyl radicals, and phenyl radicals have been obtained from tetraphenyllead.

The production of free radicals by the thermal decomposition of organo-lead compounds has been a much investigated topic. As may be expected decomposition of these radicals leads to many different products, e.g. acetylene, isobutylene, propylene, ethylene, hydrogen, methane, and ethane have been identified from the pyrolysis of tetramethyllead.[11]

It has also been shown that free radicals can be produced from symmetrical lead compounds by methods other than pyrolysis. Semerano and Riccoboni,[12] working on the behaviour of free radicals at low temperatures used radicals obtained from the decomposition of the very unstable organo-silver compounds. These organo-silver compounds were prepared from organo-lead compounds by the action of ethanolic silver nitrate at low temperatures (-80°C), and may be considered as intermediates only. It was found that at low temperatures, methyl radicals, obtained from tetramethyllead, via methyl silver, produced ethane,

$$(CH_3)_4Pb \xrightarrow{Ag^+} (CH_3)_3Pb^+ + AgCH_3$$

$$AgCH_3 \longrightarrow Ag + CH_3\cdot$$

$$2CH_3\cdot \longrightarrow C_2H_6$$

A later paper by Costa and Camus[13] reports on the formation of a complex, $2AgCH_3 \cdot AgNO_3$, obtained from the reaction between silver nitrate and tetramethyllead in ethanol. It's composition is independent of the ratio of silver nitrate to tetramethyllead, and the formation of the complex is almost quantitative at 0°C with a silver nitrate/tetramethyllead ratio up to 2. Ethane and silver are exclusively formed by the decomposition of the silver methyl part of the complex.

Bawn and Whitby[14] have shown that tetramethyllead is cleaved by copper nitrate in the same way. However the intermediate copper methyl does not decompose to give methyl radicals, but reacts with the solvent to give methane.

$$\begin{aligned}
&Cu^{++} + Pb(CH_3)_4 \longrightarrow Cu^{+} + Pb(CH_3)_3^{+} + CH_3\cdot \\
&Cu^{+} + Pb(CH_3)_4 \longrightarrow CuCH_3 + Pb(CH_3)_3^{+} \\
&CuCH_3 + C_2H_5OH \longrightarrow Cu + CH_4 + C_2H_5O\cdot \\
&2C_2H_5O\cdot \longrightarrow C_2H_5OH + CH_3CHO
\end{aligned}$$

In the aromatic series, cleavage of tetraphenyllead with silver nitrate[15] gave diphenyl and triphenyllead nitrate, whilst cleavage by copper nitrate gave mainly benzene, in addition to diphenyl and triphenyllead nitrate.

2. Cleavage of Unsymmetrical Organo-lead Compounds

Radical cleavage reactions of these compounds have not been studied to any extent, but they are capable of being cleaved by the same reagents as are the symmetrical compounds. Free radicals are, of course, produced by pyrolysis. However in this series of compounds there is the added problem of which group is more easily cleaved.

For example the ease of cleavage of certain groups by halogens or hydrogen halides is given by Krause and Schlöttig[16] as:-

α-naphthyl, p xylyl, p tolyl, phenyl, methyl, ethyl, n-propyl, isobutyl, isoamyl, cyclohexyl,

α-naphthyl being the easiest group to cleave. This is similar to cleavage of organo-tin[17] and organo-mercury compounds.

Free Radicals in Solution

Reactions of free radicals in solution can, and usually do, involve many steps, resulting in the formation of several different products. The reactivity of free radicals in solution varies enormously from the highly reactive methyl or ethyl radicals to the resonance stabilised radicals, such as triphenylmethyl, which are formed in solution by dissociation of hexaphenylethane.

$$Ph_6C_2 \rightleftharpoons 2Ph_3C\cdot$$

Free radicals are non ionic, and not usually polarised to any extent, hence they are not appreciably affected by the polarisability of the solvent. As may be expected, however, the type of solvent, together with the nature of the free radical itself, will determine the products obtained.

Free radicals in solution commonly undergo the following three types of reaction:-

(i) Dimerisation.

$$2R^{\bullet} \longrightarrow RR$$

(ii) Attack on solvent, which commonly takes the form of hydrogen abstraction.

$$R^{\bullet} + \text{solv.} \longrightarrow RH + \text{solv.}^{\bullet}$$

This leads to further products, due to the formation of another free radical.

$$\text{e.g.} \quad R^{\bullet} + \text{solv}^{\bullet} \longrightarrow R\text{-solv.}$$

$$\text{or} \quad \text{solv}^{\bullet} + \text{solv}^{\bullet} \longrightarrow \text{solv-solv.}$$

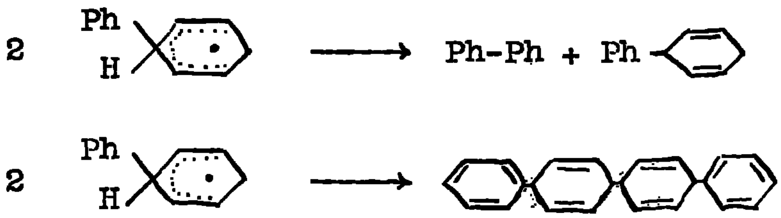
(iii) Disproportionation

$$2R^{\bullet} \longrightarrow \underset{\text{saturated}}{R_{(+H)}} + \underset{\text{unsaturated}}{R_{(-H)}}$$

Hence the products from the formation of free radicals in solution, in general, depends on the reactivity of the radical, and the ease of hydrogen abstraction from the solvent. The highly reactive phenyl radicals in solution have little chance to dimerise, and generally form benzene by hydrogen abstraction from the solvent. This is readily understood since the proportion of solvent molecules to phenyl radicals must be very high, i.e. the chance of two phenyl radicals meeting and combining to give diphenyl is low. It is thought that, when diphenyl is formed, as it is, in very small amounts, it is by attack of the phenyl radical on the benzene already produced by hydrogen abstraction.

Reactions of phenyl radicals in solution, particularly in aromatic solutions, frequently give high yields of polyphenyls and tars[18]. The mechanism recently postulated[19] is based on the phenylation of the aromatic nucleus.

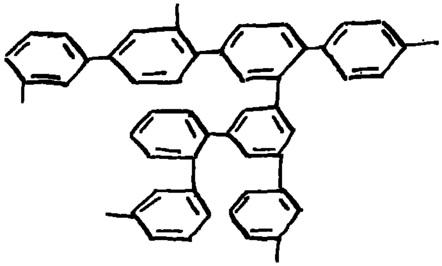
This "Wheland intermediate" can then disproportionate or dimerise.



1'4',1"4" tetrahydroquaterphenyl

Lynch and Pausacker[20] found quantities of terphenyl and quaterphenyl, together with quantities of high boiling products from these reactions. 1'4',1",4", tetrahydro-p-quaterphenyl has been isolated[21] by carrying out phenylation reactions under nitrogen. It is readily understood how tars can be formed, since there are many possibilities for cross linking.

e.g.



Methyl radicals, too, mainly attack the solvent, resulting in the formation of methane, but a small quantity of ethane is formed. If it is considered that the activity of a free radical is a measure of it's reactivity towards other compounds, and the stability is the actual stability of an isolated radical, then it can be understood why ethyl radicals, which are less stable, and less active, than methyl radicals, undergo disproportionation to give ethane and ethylene. Propyl radicals are less active and more stable than ethyl radicals, and they show dimerisation up to 50%, as well as disproportionation. In general the more stable and less active the radical, the greater the extent of dimerisation, e.g. the resonance stabilised benzyl radicals dimerise almost exclusively.

Attack on solvent by free radicals commonly involves hydrogen abstraction resulting in the formation of another free radical.

$$R^{\bullet} + \text{solv} \longrightarrow RH + \text{solv}^{\bullet}$$

Hence it is frequently found that isolation of certain products indicates a free radical mechanism, e.g. products (1) and (2)

$$\text{e.g.}\quad R^{\bullet} + \text{solv}^{\bullet} \longrightarrow R\text{-solv} \qquad (1)$$

$$\text{solv}^{\bullet} + \text{solv}^{\bullet} \longrightarrow \text{solv-solv} \qquad (2)$$

Free radicals normally react with other compounds in two ways:-

(i) Addition, e.g. $Br^{\bullet} + CH_2{=}CH{\cdot}CH_3 \longrightarrow BrCH_2{\cdot}\dot{C}H{\cdot}CH_3$

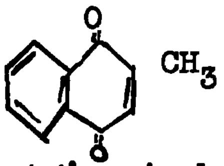
(ii) Displacement, e.g. $R^{\bullet} + CCl_4 \longrightarrow RCl + \dot{C}Cl_3$

Reactions of this type, by a study of products, could be used to indicate a free radical mechanism.

It is now a well established fact that free radicals induce the polymerisation of certain olefines. It is found that introduction of compounds, which give rise to free radicals, increase the rate of polymerisation of a monomer. In general it is dangerous to use the polymerisation of an unsaturated compound as a diagnostic test for free radicals, unless supported by other evidence, e.g. the nature of the reaction products, and the relative independence of reaction rate on the dielectric constant of the solvent.

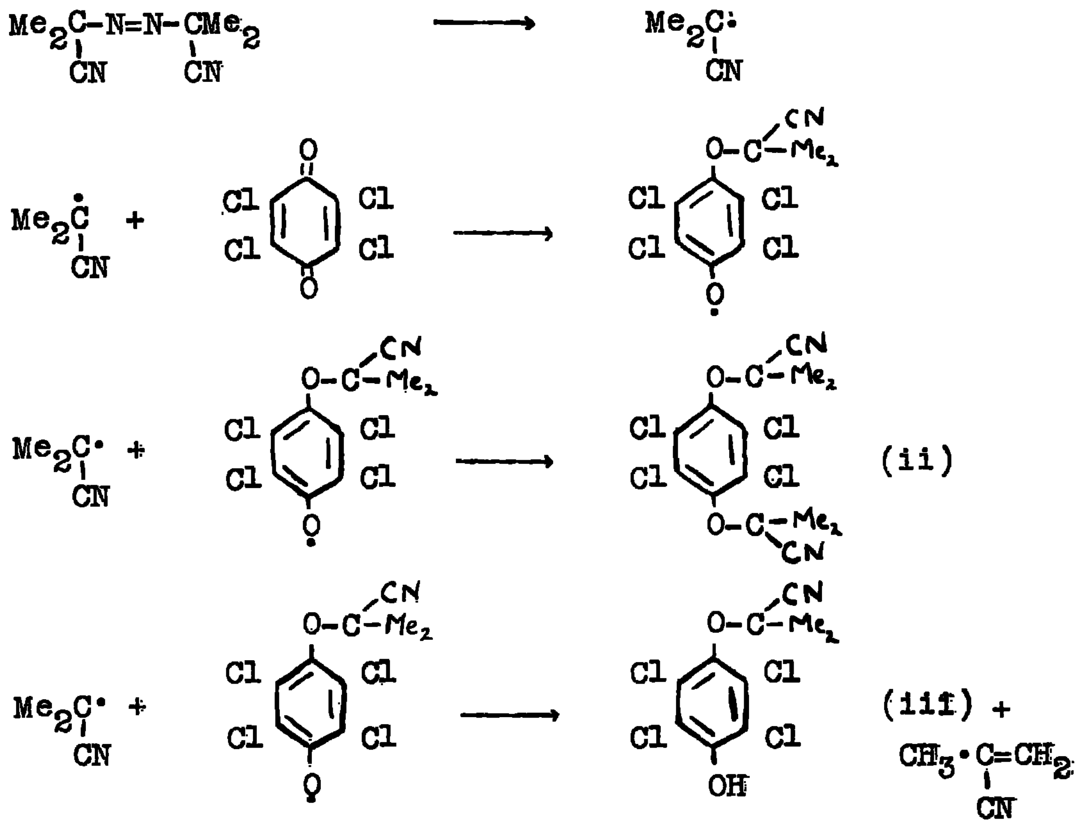
Introduction of quinones or aromatic polynitro compounds are found to inhibit polymerisations initiated by free radicals. These inhibitors, of which there are numerous examples, simply remove the radicals from the system by forming a stable reaction product. Styrene, which is notorious for its ease of polymerisation, is normally stored containing an inhibitor.

The reaction of free radicals with quinones is not yet fully understood. A variety of products have been isolated from various reactions, and authors claim either attack on the carbon-carbon double bond[22] or the oxygen double bond,[23] e.g. methyl radicals with naphthaquinone give as a first product (i)

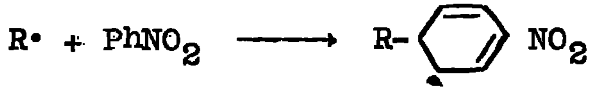


(i)

whereas with radicals from α,α'azo*iso*butyronitrile or α,α'azo*iso*butyrate products (ii) and (iii) are obtained pointing to attack on the oxygen double bond.[23]



When nitrobenzene is attacked by methyl or phenyl radicals, ring substituted compounds are obtained, and it has been proposed[24] that the initial step in the inhibition process is the radical addition to the aromatic nucleus.



The increased possibility for resonance stabilisation of this intermediate would seem to offer some explanation of its action as an inhibitor, and this is substantiated by the fact that an increase in the number of nitro groups increases the retarding influence.

It has also been suggested that attack on the nitro group may occur.[25]

In conclusion it can be said that the reactions of free radicals in solution is a highly complex topic, and much work remains to be done. Only a few of the more important aspects, insofar as the present work is concerned, have been mentioned.

PREVIOUS WORK ON THE CLEAVAGE OF LEAD COMPOUNDS WITH SILVER NITRATE

Semmerano and Riccoboni[12] investigated the decomposition of lead tetraalkyls with silver nitrate at low temperatures. They found that the tetramethyl, ethyl, and npropyl compounds react, by a single electron transfer process, to give coloured, unstable, silver alkyls and triethyllead nitrate.

$$R_4Pb + AgNO_3 \longrightarrow R_3PbNO_3 + AgR$$

Methyl and ethyl silver decompose above -70°C to give silver and hydrocarbons resulting from reactions of methyl and ethyl radicals in solution. At these low temperatures (-40°C) the methyl radicals were found to give ethane only, whilst ethane, ethylene, and n butane were obtained from ethyl radicals.

Bawn and Whitby[14] confirmed these results and showed that the kinetics of the decomposition of silver ethyl were compatible with the following reaction mechanism:-

$$Et_4Pb + AgNO_3 \longrightarrow Et_3PbNO_3 + AgC_2H_5 \text{ (fast)}$$

$$AgC_2H_5 \longrightarrow Ag + C_2H_5\cdot \text{ (slow)}$$

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6$$

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_4H_{10}$$

Again for tetramethyllead the kinetics were in agreement with the scheme:-

$$\begin{aligned} Me_4Pb + AgNO_3 &\longrightarrow Me_3PbNO_3 + AgCH_3 \text{ (fast)} \\ AgCH_3 &\longrightarrow Ag + CH_3\cdot \quad \text{(slow)} \\ 2CH_3\cdot &\longrightarrow C_2H_6 \end{aligned}$$

It is rather remarkable that methyl radicals, even if produced at low temperatures, should exclusively dimerise, rather than give rise to the formation of at least some methane by hydrogen abstraction from the solvent. This rather suggests that the methyl radicals may never be 'free', and that ethane results from a bimolecular reaction, in which the two methyl groups always remain

$$2AgMe \longrightarrow 2Ag + C_2H_6$$

in close proximity. Probably no final answer can be given to this problem until the structure of silver methyl is known. There is at present no evidence as to whether organo-silver compounds are associated or not. The low thermal stability of these compounds renders physical investigations extremely difficult.

More recent work[13] on the reaction between silver nitrate and tetramethyllead would seem to cast some doubt on the formation of free silver methyl. Costa and Camus[13] obtained a compound of composition $2AgCH_3.AgNO_3$ when silver nitrate was added to tetramethyllead. Furthermore this compound was formed irrespective of the ratio of silver nitrate to tetramethyllead. The reaction was found to be quantitative at 0°C with a silver nitrate/lead compound ratio up to 2, but not quantitative at -78°C. The products of decomposition are exclusively ethane and silver.

Gilman and Woods[15] have shown that tetraphenyllead reacts in a like manner with silver nitrate, producing phenyl silver and triphenyllead nitrate. The subsequent decomposition of phenyl silver gives silver and diphenyl.

The only work so far published on the cleavage of unsymmetrical and unsaturated lead compounds was by Glockling,[26] who found that isobut-1-enyltriethyllead, $Et_3PbCH{:}CMe_2$ gave the unstable, orange, isobut-1-enylsilver with silver nitrate in ethanol solution at -78°C. This decomposes above -20°C with the formation of isobut-1-enyl radicals, 10% of which dimerise, but the main reaction product is isobutene. Triethyllead nitrate was also isolated in high yield. There is no cleavage of any of the ethyl groups.

It is also reported[26] that with the lead alkyl in excess, more isobutene is produced than is compatible with the equations,

$$Et_3PbCH{:}CMe_2 + AgNO_3 \longrightarrow Et_3PbNO_3 + Me_2C{:}CHAg$$
$$Me_2C{:}CHAg \longrightarrow Ag + Me_2C{:}CH\cdot$$
$$2Me_2C{:}CH\cdot \longrightarrow Me_2C{:}CH\cdot CH{:}CMe_2$$

hence in addition a chain reaction was postulated,

$$Me_2C{:}CH\cdot + EtOH \longrightarrow Me_2C{:}CH_2 + EtO\cdot$$
$$Et_3Pb\cdot CH{:}CMe_2 + EtO\cdot \longrightarrow Et_3PbOEt + Me_2C{:}CH\cdot$$
$$2EtO\cdot \longrightarrow EtOH + CH_3CHO$$

This mechanism was supported by the fact that the ethanol solution gave strong positive tests for aldehydes, and that use of ethyl deuteroxide instead of ethanol resulted in the formation of 1-deutero*iso*butene.

$$C_2H_5OD + (CH_3)_2C{:}CH^{\cdot} \longrightarrow C_2H_5O^{\cdot} + (CH_3)_2C{:}CHD$$

DISCUSSION

The present work began with the idea of preparing isobut-2-enyl silver, $Ag\cdot CH_2\cdot C(CH_3):CH_2$, and studying its stability and decomposition in solution. Interest in this compound centred around its expected decomposition to give, initially, the resonance stabilised methallyl radical, $\cdot CH_2C(CH_3):CH_2$, which is isomeric with the already known isobut-1-enyl radical, formed by the decomposition of isobut-1-enyl silver[26]. Thus a comparison of these two isomeric silver derivatives was expected to produce information on the relative stabilities of the two organo-silver compounds and also on the behaviour of the two isomeric free radicals, in solution.

It had previously been shown[26] that the unsymmetrical lead compound, isobut-1-enyltriethyllead reacts with silver ions to produce isobut-1-enylsilver.

$$Me_2C:CH\cdot Pb\cdot Et_3 + Ag^+ \longrightarrow Ag\cdot CH:CMe_2 + Et_3Pb^+$$

This was at the time the only clearly investigated example of the cleavage of an unsymmetrical lead alkyl or aryl by silver ions, and there seemed to be no clear reason why the unsymmetrical, isobut-1-enyl group should be exclusively cleaved, rather than one of the ethyl groups.

It was decided, therefore, to attempt an analagous reaction which should lead to the formation of methallyl silver. This required the preparation of triethylmethallyllead, $Et_3Pb \cdot CH_2 \cdot C(CH_3):CH_2$, which was prepared and characterised successfully. Like the isomeric iso-but-1-enyl compound, this reacted with silver ions, with exclusive cleavage of the unsymmetrical, methallyl group. However in striking contrast to the case of the isobut-1-enyl compound no sign of an intermediate organo-silver compound was observed, for at all temperatures above -100°C silver was formed rapidly and quantitatively.

$$Et_3Pb \cdot CH_2 \cdot C(CH_3):CH_2 + Ag^+ \longrightarrow Ag + Et_3Pb^+ + \cdot CH_2 \cdot C(CH_3):CH_2$$

These preliminary observations defined the scope of the present work in the following way. It was proposed to study a series of organo-lead compounds of the type, Et_3PbR, in which the structure of the R group was varied with a view to determining

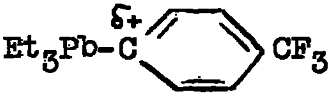
(i) the factors influencing the cleavage of the R group rather than an ethyl group,

and (ii) the factors influencing the stability of any organo-silver primary product.

With these factors in mind, the following compounds were prepared:-

$Et_3Pb\cdot CH_2\cdot C(CH_3){:}CH_2$,	Triethyl-2-methylprop-2-enyllead	I
$Et_3Pb\cdot CH_2C_6H_5$,	Benzyltriethyllead	II
$Et_3Pb\cdot C_6H_4CF_3(p)$,	Triethyl-p-trifluoromethylphenyllead	III
$Et_3Pb\cdot C_6H_4NMe_2(p)$,	p-Dimethylaminophenyltriethyllead	IV
$Et_3Pb\cdot CH{:}CHC_6H_5$,	Triethyl-α-styryllead	V

It was thought that cleavage of the group R from these compounds would be due to the Ag^+ ion, particularly in a fairly polar solvent, such as ethanol. It was for this reason that compounds III and IV were prepared, for in compound III the strongly electronegative trifluoromethyl group should attract electrons, leaving the carbon atom at the lead-carbon bond with a partial positive charge.



Attack by Ag^+ ion would then take place at a more electropositive centre. Thus it was anticipated that an ethyl group would be cleaved. Likewise the methiodide of compound IV, $Et_3Pb\cdot C_6H_4\overset{+}{N}Me_3I$, was expected to produce the same effect.

With the exception of compound II, these unsymmetrical lead compounds were prepared by the action of the appropriate organic halide on triethyllead-sodium in a liquid ammonia-ether solution. Compound II was prepared by the action of benzyl magnesium bromide on triethyllead chloride.

All these compounds are unstable liquids. Only compounds II and IV show reasonable thermal stability, although compound IV decomposes slowly in air at room temperature. In order to avoid undue decomposition, all compounds were stored at -78°C. Even so it was found necessary to redistil them immediately before use. Triethyl-α-styryllead (compound V) proved to be particularly unstable, decomposing slowly even at -78°C. Distillation of this compound was always accompanied by some decomposition to lead.

Reactions with Silver Nitrate

For each of the lead compounds studied, reaction with an equivalent of ethanolic silver nitrate, at low temperature, resulted in exclusive cleavage of the unsymmetrical group R. Although a small quantity of C_2 and C_4 hydrocarbons was sometimes obtained, it was found that further purification of the lead compound either removed this completely or reduced it to a negligible amount. This small quantity of volatile hydrocarbons is obviously produced by the action of silver nitrate on tetraethyllead, present as an impurity. Although tetraethyllead is the starting material in the preparation of all these compounds, it is more likely that its presence is due to decomposition of the unsymmetrical compound on distillation, rather than to it being unchanged starting material. It is well known, unsymmetrical lead compounds exhibit a strong tendency to disproportionate on heating.

This problem was most pronounced in the reaction of the unstable triethyl-α-styryllead with silver nitrate. Gaseous products, varying from 4 to 15% were obtained. The fact that the percentage of hydrocarbons formed was so variable, points to their formation being due to the presence of impurities.

Deliberate addition of small amounts of tetraethyllead to these compounds, gave volatile hydrocarbons on addition of ethanolic silver nitrate.

These results are quite conclusive, since the cleavage of an ethyl group would give ethyl-silver as a primary product. Subsequent decomposition of silver-ethyl would result in the formation of ethyl radicals giving mainly ethane, ethylene, and butane.

The fact that even triethyl-p-trifluoromethylphenyllead

(III) and the methiodide of p-dimethylaminophenyltriethyllead (VI), produce no volatile hydrocarbons on cleavage requires careful consideration. Both the CF_3 and $\overset{+}{N}Me_3$ groups are strongly electron attracting, and this should result in the induction of a partial positive charge on the carbon atom furthest from these groups, i.e. the carbon atom bonded to the lead atom, 

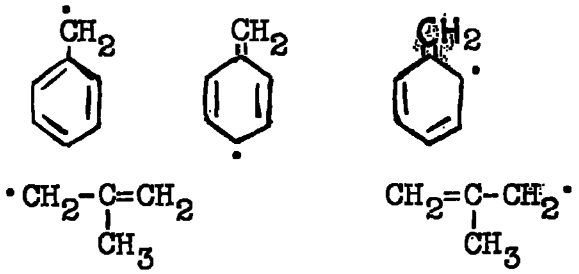
This leads directly to the possibility that attack is not by Ag^+ ions, as previously suggested. However, this explanation hardly seems probable, since it is difficult to postulate a reaction mechanism, which does not involve the Ag^+ ion, in an ionising solvent such as ethanol. The more reasonable answer to this problem would be that there is no residual positive charge induced on the carbon atom of the R-Pb bond. The high polarisability of the lead atom probably accounts for this.

However, this argument offers no explanation as to why the unsymmetrical group R should be cleaved in each of the compounds studied. It is possible that the cleavage is governed by steric factors, that is the greater size of the group R, and the greater stability of the symmetrical triethyllead nitrate, Et_3PbNO_3, over that of the unsymmetrical nitrate, Et_2RPbNO_3. For this reason it may be interesting to study the cleavage of methyltriethyllead, Et_3PbCH_3. Here it might be expected that a compound of the type $AgCH_3.nAgNO_3$ would be formed, since it has beeen already observed[13] that the compound $2AgCH_3.AgNO_3$ has been formed from the reaction of tetramethyllead and silver nitrate.

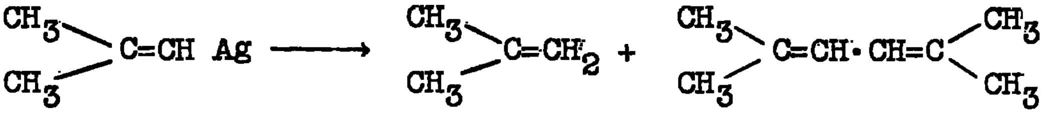
Some idea of the influence of the organic radical R on the stability of the organo-silver compound, AgR, has emerged from the behaviour of these five compounds. It is known that the simple alkyls of silver decompose rapidly above -50°C,[12,14] whilst *iso*but-1-enyl silver[26] is stable for several days below -30°. Triethyl-2-methylprop-2-enyllead should give the isomeric *iso*but-2-enyl silver with silver nitrate at low temperature. However at all temperatures above -100°C it was found that precipitation of silver was immediate. In addition 2,5-dimethylhexa-1,5-diene was isolated in 96% yield, and triethyllead nitrate was obtained as previously described.[26]

Benzyltriethyllead (II) behaves in a like manner. There is no indication of any organo-silver compound at -78°C, but silver is deposited instantly and recovered together with dibenzyl in high yield.

The behaviour of compounds I and II is consistent with the immediate formation of the organic radical R. High yields of the dimer would be expected from these resonance stabilised radicals.



The isobut-2-enyl radical is not resonance stabilised, and would therefore not be expected to form high yields of the dimer. In fact, it is found[26] that isobutene is formed in some 60-80% yield, together with only 10% of the dimer, 2,5-dimethylhexa-2:4-diene, from the decomposition of isobut-2-enyl silver.



These results are consistent with the following mechanisms for the cleavage of compounds I and II by silver nitrate.

(I) $Et_3Pb{\cdot}CH_2{\cdot}C(CH_3){:}CH_2 + AgNO_3 \longrightarrow Et_3PbNO_3 + Ag + {\cdot}CH_2{\cdot}C(CH_3){:}CH_2$

$2\ {\cdot}CH_2{\cdot}C(CH_3){:}CH_2 \longrightarrow CH_2{:}C(CH_3)CH_2CH_2C(CH_3){:}CH_2$

(II) $Et_3Pb{\cdot}CH_2C_6H_5 + AgNO_3 \longrightarrow Ag + Et_3PbNO_3 + {\cdot}CH_2C_6H_5$

$$2\ {\cdot}CH_2C_6H_5 \longrightarrow C_6H_5CH_2{\cdot}CH_2C_6H_5$$

Triethyl-4-trifluoromethylphenyllead (III) shows no sign of reaction with silver nitrate at -78°C, but on allowing to warm slowly to room temperature there is the formation of a transitory red colouration, before black silver is precipitated. The silver was recovered in high yield, but only a small amount of organic material, in some tarry form, was isolated. The formation of the highly unstable 4-trifluoromethylphenylradicals would probably result in hydrogen abstraction from the solvent, giving mainly the volatile benzotrifluoride (B.pt. 102·4°C) as well as a small amount of tarry material. The isolation of a small quantity of benzotrifluoride from the comparatively large volume of ethanol, which is necessary to dissolve the silver nitrate and lead compound, would prove to be extremely difficult. Since the reason for the preparation of this compound was to try to obtain an unsymmetrical lead compound, Et_3PbR, in which an ethyl group was cleaved rather than the group R, it was not thought essential to isolate any benzotrifluoride that may have been formed. The formation of a red colouration is indicative of the formation of an organo-silver compound.

$$Et_3PbC_6H_4CF_3\ (p) + AgNO_3 \longrightarrow \left[Ag\cdot C_6H_4CF_3(p)\right] + Et_3PbNO_3$$

$$\left[Ag\cdot C_6H_4CF_3(p)\right] \longrightarrow Ag + \cdot C_6H_4CF3(p)$$

If dimerisation had occurred to any great extent the dimer would have been isolated by the method used.

The addition of ethanolic silver nitrate to 4-Dimethylaminophenyltriethyllead at -78°C, resulted in the formation of a brown solid, which slowly decomposes at room temperature with the deposition of silver. The amount of silver deposited from solution, when the silver nitrate is in excess, is 110%, based on the lead compound, Whether this significant observation is consistent with the formation of a silver-organo, silver nitrate complex, $AgR.AgNO_3$, or with the reduction of some excess silver nitrate by ethoxy radicals or acetaldehyde ($2EtO\cdot \longrightarrow EtOH + CH_3CHO$)[26], is not known. Dimethylaniline was isolated as a reaction product together with tarry material. It is a known fact that the formation of appreciable amounts of tarry material is observed in reactions involving phenyl or substituted phenyl radicals.[18] Hence these results are compatible with the formation and subsequent decomposition of 4-dimethylaminophenyl silver, or its silver nitrate complex.

$$Et_3PbC_6H_4NMe_2(p) + AgNO_3 \longrightarrow Et_3PbNO_3 + AgC_6H_4NMe_2$$

$$\text{or} \longrightarrow Et_3PbNO_3 + AgC_6H_4NMe2\cdot AgNO_3$$

$$Ag\cdot C_6H_4NMe_2 \longrightarrow Ag + \cdot C_6H_4NMe_2(p)$$

$$\text{and possibly}\quad EtOH + \cdot C_6H_4NMe_2 \longrightarrow C_6H_5NMe_2 + EtO\cdot$$

$$\text{and} \;—\; 2EtO\cdot \longrightarrow EtOH + CH_3CHO$$

The methiodide of compound (IV), $[Et_3PbC_6H_4\overset{+}{N}Me_3]\,I^-$, behaved in a similar way with silver nitrate, that is, no volatile hydrocarbons were formed. At -78°C there is an initial yellow-white precipitate , presumably of silver iodide, followed slowly by a pink precipitate,gradually turning brown. On allowing to warm to room temperature this precipitate quickly showed signs of decomposition, and decomposition of silver was complete after standing overnight. The following mechanism is tentatively suggested.

$$[Et_3PbC_6H_4\overset{+}{N}Me_3]\,I^- + AgNO_3 \longrightarrow [Et_3PbC_6H_4\overset{+}{N}Me_3]\,NO_3^- + AgI$$

$$[Et_3PbC_6H_4\overset{+}{N}Me_3]\,NO_3^- + AgNO_3 \longrightarrow Et_3PbNO_3 + [AgC_6H_4\overset{+}{N}Me_3]\,NO_3^-$$

$$[Ag\cdot C_6H_4\overset{+}{N}Me_3]\,NO_3^- \longrightarrow Ag + [\cdot C_6H_4\overset{+}{N}Me_3]\,NO_3^-$$

Perhaps the most interesting reaction is that between triethyl-α-styryllead (V) and silver nitrate at low temperature. On mixing,an immediate, intense, deep red precipitate forms, which is stable in solution for several days at room temperature. Analysis of this precipitate indicates that it is styryl silver and not the silver nitrate complex of styryl silver. On refluxing for several hours to effect decomposition, m.gm. quantities of styrene were found, and a large amount of some highly insoluble and evidently polymeric compound was formed. The nature of this insoluble material was not discovered. However it is almost certainly due to the production of styryl radicals from the decomposition of styryl silver. It is not normal polystyrene since it is insoluble in boiling benzene.

$$\mathrm{Et_3Pb{\cdot}CH{:}CHC_6H_5 + AgNO_3 \longrightarrow Et_3PbNO_3 + Ag{\cdot}CH{:}CHC_6H_5}$$

$$\mathrm{AgCH{:}CHC_6H_5 \longrightarrow Ag + {\cdot}CH{:}CHC_6H_5}$$

$$\mathrm{{\cdot}CH{:}CHC_6H_5 \longrightarrow} \text{ insoluble products.}$$

In general it appears that the greater the stability of the radical R, the less stable is the organo-silver compound AgR. In the case of compounds I and II the stability of the *iso*but-1-enyl and benzyl radicals are such that an intermediate silver compound is not formed, at least under the conditions used in these experiments. There are good indications that compounds III and IV form intermediate organo-silver compounds, and the radicals formed, being substituted phenyl radicals, are very unstable. The remarkable stability of styryl silver may well be reflected in the instability of the styryl radical. The fact that there is a double bond adjacent to the silver atom may also be significant, since this is true in the case of isobut-2-enyl silver, and this compound is stable up to -30°C.

Examination for Free Radicals

Since this work involves the postulation of the formation of organic free radicals, either directly or via an unstable organo-silver intermediate, it was thought that the formation of free radicals should be more directly demonstrated.

Although initiation of the polymerisation of some olefines cannot, in itself, be taken as evidence for the existence of free radicals, if free radicals are formed, it might be expected that polymerisation will occur. It was found that reaction of alcoholic silver nitrate, in the presence of styrene with compounds I, II, and IV produced polystyrene. Under the same reaction conditions tetraethyllead produced 15, 13.5, and 12 times as much polystyrene as did compounds I, II, and IV. No polystyrene was obtained from a blank experiment carried out under the same conditions, but without the presence of a lead compound.

A small amount of polyacrylonitrile was obtained in a similar experiment with compound I and silver nitrate, in the presence of acrylonitrile.

Reactions were carried out between compound I and silver nitrate in the presence of n-butyl mercaptan. In this case it was hoped that the methallyl radicals produced would abstract hydrogen from the thiol to produce <u>iso</u>-butene. This could well be so, since S-H bond dissociation energies appear to be about 10 K.cal. less than corresponding C-H values,[27] and the bond dissociation energies of S-H bonds are also considerably less than O-H values,

(CH_3O-H, 100 K.cals/mole ; CH_3S-H, 88.8 K.cals/mole).

However, it was found that reaction took place between the lead compound and the mercaptan <u>without</u> the addition of silver nitrate. Some yellow plate crystals were obtained from the reaction products. These crystals proved to be insoluble in most organic solvents, but could be recrystallised from NN-dimethylformamide. Volatile hydrocarbons were also formed, and were found to analyse to the formula, C_2. If this had been a free radical reaction involving ethyl radicals then a mixture of C_2 and C_4 hydrocarbons would have been expected.

$$2C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6$$

$$C_2H_5\cdot \longrightarrow C_2H_6 \text{ by H abstraction}$$

$$2C_2H_5\cdot \longrightarrow C_4H_{10}$$

The analagous reaction with tetraethyllead proved to be very photosensitive. Disulphides, likewise, could not be used, since they too reacted with the lead compound without the addition of silver nitrate. Since these reactions did not serve the purpose of showing the presence of free radicals in the cleavage reaction, the topic was not pursued.

Likewise the use of quinones for detecting the presence of free radicals, in the silver nitrate cleavage reaction, was discarded, since it was found that these compounds reacted with *iso*but-1-enyltriethyllead, without the addition of silver nitrate, to produce deep red solutions. Addition of silver nitrate to these coloured solutions produces no precipitation of silver.

In conclusion, although these further experiments proved to be of no value in showing the presence of free radicals, it may well be profitable to investigate the reactions of lead compounds with quinones and mercaptans. It is also suggested that the products of the cleavage reactions, themselves, are compatible with a free radical mechanism, as is the case in the cleavage of other lead compounds.[12,26] The production of polystyrene and polyacrylonitrile can then be recognised as confirmatory evidence.

EXPERIMENTAL

1. Handling Techniques

The toxicity of lead compounds is well known and care must be exercised in handling them. Volatile liquids are both readily absorbed through the skin, and inhaled. Since most of the lead compounds used in this work were liquids, rubber gloves were always worn, when there was any chance of the lead compound coming into contact with the skin. All the work was carried out in a good fumes cupboard.

The stability of the compounds towards oxygen and water is such that no special precautions were taken to exclude air or atmospheric moisture, except in the initial stages of preparations from the reactive triethyllead-sodium or Grignard compounds. However the thermal stability is low, and the prepared compounds were stored at -78°C to prevent decomposition. Precautions were also taken against subjecting them to sunlight, which causes deposition of lead.

In order to obtain pure samples of the lead compounds, it was necessary to keep the distillation temperature as low as possible. Standard high vacuum techniques were employed. The use of normal fractionating columns was discarded, since at very low pressures they served only to raise the temperature to which the compound had to be heated for distillation. Pure samples were obtained by taking the middle fraction only and redistilling.

Unwanted lead compounds were destroyed by addition of a 4% solution of bromine in carbon tetrachloride.

Lead analyses were carried out by the method of Saunders.[28]

2. Preparation of the Unsymmetrical Organo-Lead Compounds

(1) Triethyl-2-methylprop-2-enyllead $Et_3Pb \cdot CH_2 \cdot C(CH_3):CH_2$

3-Chloro-2-methyl propene was purified by refluxing with a small quantity of sodium, followed by distillation through a good column. The sharp fraction boiling between 71-71.5°C was taken.

A solution of sodium (9.5 g.; 0.413 mole) in liquid ammonia (600 c.c.) was added quickly to a solution of tetraethyllead (44 c.c.; 0.266 mole) in dry ether (250 c.c.), at -80°C to -100°C, contained in a 5 litre silvered vacuum flask. There was immediate evolution of ethane and discharge of the blue colour, leaving a yellow solution containing triethyllead-sodium.[29] After 1 minute, 3-chloro-2-methyl propene (30 c.c.; 0.2 mole) in ether

(100 c.c.) was added, with vigorous stirring, over a period of 1-3 minutes. The residue after evaporation of ammonia was extracted with water and ether. Distillation of the dried ether extract gave triethyl-2-methylprop-2-enyllead (30 g.; 43% yield) as a colourless liquid, boiling at 45-50°C/0.1 mm. Two further vacuum distillations were necessary to remove tetraethyllead.

Found C 33.6, H 6.5, Pb 58.6%

$C_{10}H_{22}Pb$ requires C 34.4, H 6.3, Pb 59.3%

This lead compound is fairly stable towards air at room temperature, but reacts violently at elevated temperatures (e.g. 70°C) with the deposition of large pieces of lead. Strong sunlight causes lead to be rapidly deposited, hence the compound was stored in solid carbon dioxide, in the dark.

A solution of the alkyl (10 c.c. in 100 c.c. carbon tetrachloride) was brominated by addition of an excess of a 10% solution of bromine in carbon tetrachloride at room temperature, stirring being maintained during the addition. The precipitated lead bromide was filtered off, and the filtrate washed with sodium carbonate solution to remove the excess bromine. After washing with water, drying over anhydrous magnesium sulphate, and distilling, this solution gave 1,2,3-tribromo-2-methylpropane as a colourless liquid, boiling at 95°/6 mm.

Found	C 15.8	H 2.4	Br 81.4 %
Calculated for $C_4H_7Br_3$	C 16.3	H 2.4	Br 81.3 %

$$Et_4Pb + 2Na/Liq\ NH_3 \longrightarrow Et_3PbNa + C_2H_6 + NaNH_2$$

$$Et_3PbNa + Cl\cdot CH_2\cdot C(CH_3){:}CH_2 \longrightarrow Et_3Pb\cdot CH_2\cdot C(CH_3){:}CH_2 + NaCl$$

$$Et_3Pb\cdot CH_2\cdot C(CH_3){:}CH_2 \xrightarrow{Br_2} 3EtBr + PbBr_2 + BrCH_2\cdot C(CH_3)Br\cdot CH_2Br$$

(II) <u>Benzyltriethyllead</u> $Et_3Pb\cdot CH_2C_6H_5$

Previous preparations of this compound[30] have resulted in very poor yield. The following procedure gave a 67% yield of pure product.

Triethyllead chloride (83 g.; 0.25 mole), prepared by the method of Saunders,[31] was added to a filtered solution of benzylmagnesium chloride, prepared, from benzyl chloride (56 g.; 0.4 mole) and magnesium (10.5 g; 0.43 mole) in 200 c.c.s ether, at room temperature. There was an initial evolution of heat, after which the mixture was refluxed for 1 hour and left stirring at room temperature overnight (nitrogen atmosphere). The products were poured into ice-water and extracted with ether. Distillation of the dried ether extract gave benzyltriethyllead as a pale yellow liquid, boiling point 82°C/.05 mm, (quoted B.pt. 149-150°C/13 mm).[30] On cooling to -30°C there was no separation of dibenzyl. The product was redistilled.

Found	C	40.6	H	5.8	%
Calculated for $C_{13}H_{22}Pb$	C	40.5	H	5.75	%

It is possible that previous preparations have resulted in low yields, due to the higher temperature of distillation, since this compound was found to be unstable at elevated temperatures.

$$Et_3PbCl + PhCH_2MgCl \longrightarrow Et_3PbCH_2Ph + MgCl_2$$

(III) <u>Triethyl-p-trifluoromethylphenyllead</u> $Et_3Pb \cdot C_6H_4 \cdot CF_3$(p)

(i) p-Bromobenzotrifluoride[32] was prepared from p-bromotoluene, which was converted to p-bromobenzotribromide by the action of bromine and ultra-violet light. p-Bromobenzotribromide was ground intimately with ~~(p)~~ antimony trifluoride and dry-distilled, when p-bromobenzotrifluoride, B.pt. 153-155°C, was obtained.

$$p\text{-}CH_3C_6H_4Br \xrightarrow[U.V.]{Br_2} p\text{-}Br\ C_6H_4CBr_3 \xrightarrow{SbF_3} p\text{-}BrC_6H_4 \cdot CF_3$$

(ii) The lead compound was prepared from p-bromobenzotrifluoride (22.5 g; 0.1 mole), tetraethyllead (39 g; 0.12

mole), and sodium (5.5 g; 0.24 mole) in liquid ammonia, in a similar manner to the preparation of triethyl-2-methylprop-2-enyllead (I). After addition of the halide to triethyllead-sodium a blood red colouration was observed, which persisted in the ether extract. Distillation of the dried ether extract yielded 14 g. (32% yield) of product, B.pt. 80°C/0.06 mm. Distillation was always accompanied by slight decomposition to lead.

Found C, 34.5; H, 4.6; F, 12.0; Pb, 47.8%

$C_{13}H_{19}F_3Pb$ requires C, 35.5; H, 4.4; F, 13.0; Pb, 47.1%

This lead compound is a pale yellow liquid, decomposing slowly at room temperature.

p-Chlorobenzotrifluoride did not react with triethyllead-sodium under these conditions.

$$pBrC_6H_4CF_3 + Et_3PbNa \longrightarrow Et_3PbC_6H_4CF_3(p) + NaBr$$

(IV) p-Dimethylaminophenyltriethyllead $Et_3Pb{\cdot}C_6H_4{\cdot}NMe_2(p)$

This was prepared by the liquid ammonia method from p-bromo-NN-dimethyl aniline (40 g; 0.2 mole), tetraethyllead (71 g; 0.22 mole), and sodium (10.5 g; 0.46 mole). After addition of the halide to triethyllead-sodium the reaction mixture was dark green in colour, and the ether extract deep red. Distillation of the dried ether extract gave the lead compound as a fairly viscous, yellow liquid, boiling point 150°C/0.6 mm. The yield was 43 g. (52%).

Found C, 40.7; H, 6.4; Pb, 50.4 %

$C_{14}H_{25}NPb$ requires C, 40.7; H, 6.1; Pb, 50.0 %

$$pBr\cdot C_6H_4NMe_2 + Et_3PbNa \longrightarrow Et_3Pb\cdot C_6H_4NMe_2(p) + NaBr.$$

p-Dimethylaminophenyltriethyllead proved to be, thermally, the most stable of the lead compounds studied. However the compound slowly decomposes in air at room temperature.

The methiodide of this compound was precipitated from an ether solution by addition of an excess of methyl iodide. The white solid melts at 131-132°C.

Found C, 31.3; H, 4.8 %

$C_{15}H_{28}NIPb$ requires C, 32.4; H, 5.1 %

(V) Triethyl-α-styryllead $Et_3Pb\cdot CH{:}CHPh$

This compound was prepared in 40% yield from 2-bromostyrene (37 g; 0.2 mole), tetraethyllead (87 g; 0.27 mole), and sodium (13 g; 0.56 mole) in liquid ammonia. Distillation gave triethyl-α-styryllead as a yellow liquid, B.pt. 94°C/10^{-2} mm.

Found C, 41.4; H, 5.6; Pb 51.2 %

$C_{14}H_{22}Pb$ requires C, 42.3; H, 5.6; Pb 52.1 %

$$Et_3PbNa + BrCH{:}CH\cdot C_6H_5 \longrightarrow Et_3PbCH{:}CH\cdot C_6H_5 + NaBr.$$

Triethyl-α-styryllead is thermally unstable and, in fact, decomposes slowly in air, even if stored at -78°C. The only satisfactory method for distillation of this compound, was found to be in using a molecular still, in which the temperature of distillation is much lower than in a normal distillation apparatus. Even distillation in a molecular still produces some lead, and great difficulty was experienced in obtaining a reasonably pure sample.

A large excess of sodium and tetraethyllead were used in this preparation, since it was found better for purification purposes to have an excess of tetraethyllead rather than 2-bromostyrene.

Bromination was effected in the same way as for compound I, and 1,2,2-tribromo-1-phenylethane was obtained as a colourless oil, B.pt. 106-110°C/0.1 mm.

Found	C, 28.4;	H, 2.2;	Br, 69.3 %
Calculated for $C_8H_7Br_3$	C, 28.2;	H, 2.1;	Br, 69.7 %

$$Et_3Pb.CH{:}CHC_6H_5 \xrightarrow{Br_2} 3EtBr + PbBr_2 + BrCHBrCHBrC_6H_5$$

3. Reaction with Silver Nitrate

(1) Triethyl-2-methylprop-2-enyllead

(a) Isolation of Dimethallyl $CH_2{:}C(CH_3)\vdots CH_2.CH_2.C(CH_3){:}CH_2$

Silver nitrate (4.0 g; 0.0235 mole) in dry ethanol (150 c.c.) was added dropwise to a stirred solution of the lead alkyl (5.3 g; .0152 mole) at room temperature. Silver was instantly precipitated. The mixture was stirred overnight, and the silver filtered off. The solution was extracted with water (300 c.c.) and ether (3 x 100 c.c. portions), and the ether extracts washed with more water to remove as much ethanol as possible. Distillation of the dried ether extract through a good packed column (1 metre long) yielded approximately 50 c.c. of a concentrated ether solution. This was transferred to a vacuum apparatus and the ether removed by condensation through a trap cooled to -70°C. The residual contents of the trap were then condensed onto an excess of 1-napthyl isocyanate to remove last traces of ethanol, and finally gave 2,5-dimethylhexa-1,5 diene, b.pt. 112°C/760 mm. Yield 0.80 g; 96%.

Found	C, 86.9;	H, 12.8 %
Calculated for C_8H_{14}	C, 87.2;	H, 12.8 %

(b) Estimation of Silver

In a small scale experiment 0.4057 g. lead alkyl were reacted with a slight excess of ethanolic silver nitrate. The precipitated silver was filtered off, washed with water, and dissolved in concentrated nitric acid.

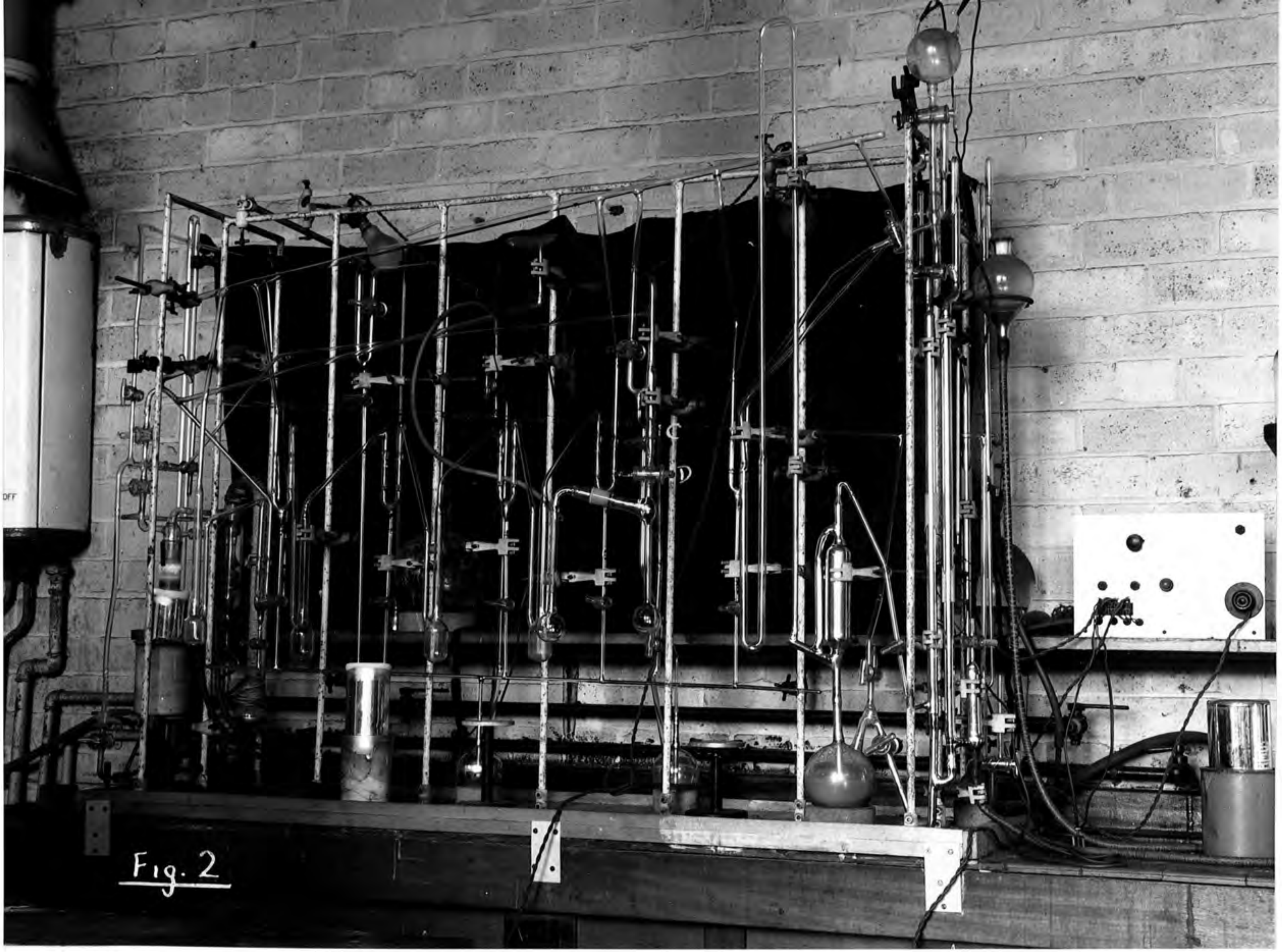
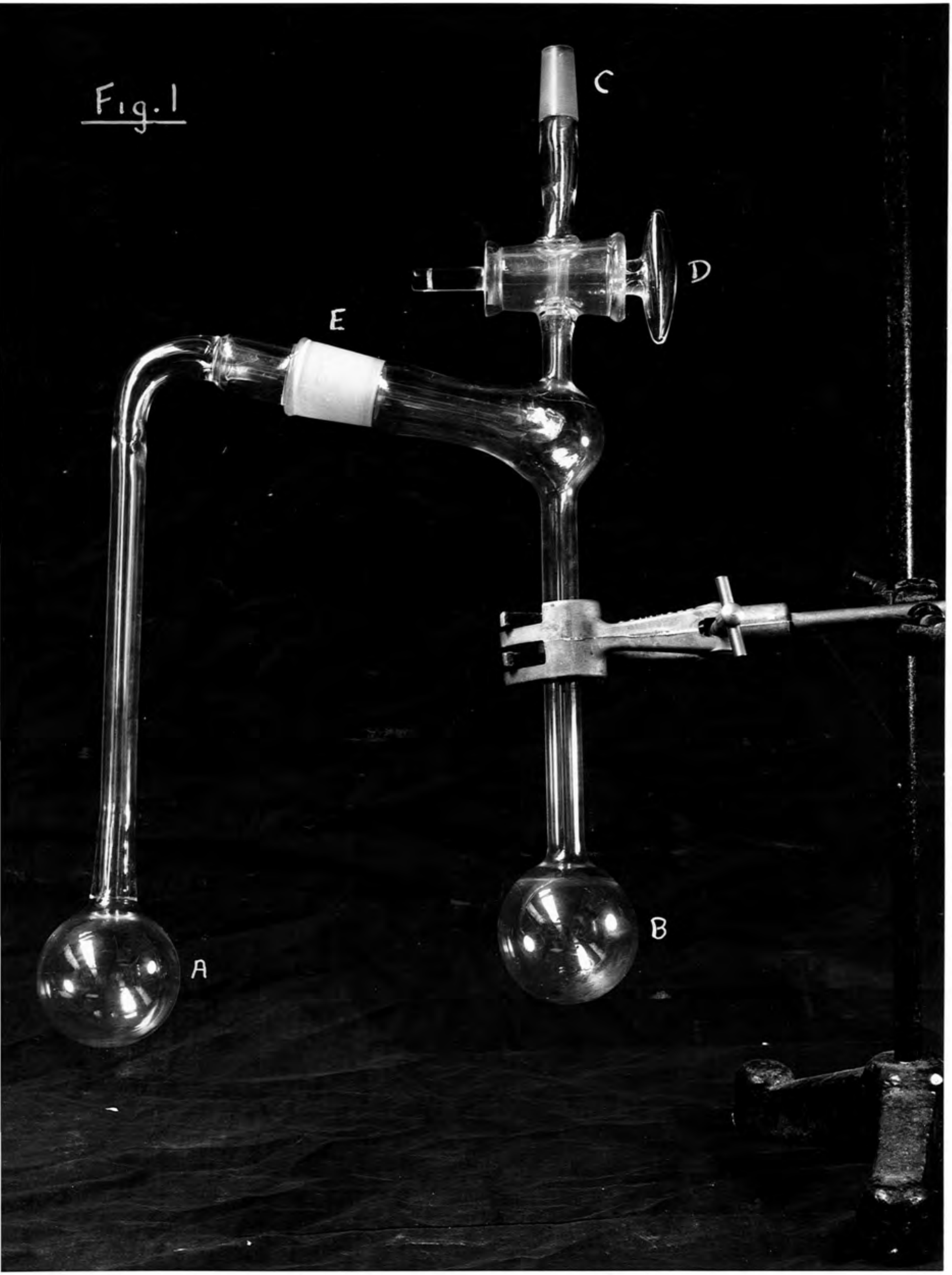


Fig. 2

Fig. 1



The acid solution was diluted to about 6N and titrated with standard ammonium thiocyanate solution, using 1 c.c. of a 40% solution of ferric alum as indicator.

Recovery of silver = 91%

(c) Isolation of Triethyllead Nitrate

Triethyllead nitrate was isolated in 94.6% yield from the decomposition of 0.0551 g. lead alkyl with silver nitrate, as previously described.[26] The nitrate was converted to triethyllead chloride by the method of Gilman and Woods.[15]

Found	C, 21.8 ;	H, 4.8 %
Calculated for $C_6H_{15}PbCl$,	C, 21.8 ;	H, 4.6 %

i.e. $$Et_3Pb\cdot CH_2\cdot C(CH_3):CH_2 + AgNO_3 \longrightarrow Ag + Et_3PbNO_3 + (CH_2:C(CH_3)\cdot CH_2\cdot)_2$$

$$Et_3PbNO_3 + HCl \longrightarrow Et_3PbCl + HNO_3$$

(d) Investigation of Volatile Products

In the investigation for volatile hydrocarbon products from the reaction of the lead alkyl with silver nitrate, standard vacuum techniques were employed. The reaction vessel requires a little more description and a diagram is shown in fig. 1.

A small quantity of the lead compound (0.65 g.) in ethanol (20 c.c.) was placed in bulb B of the reaction vessel, and a slight molar excess of silver nitrate (0.33 g.) in ethanol (20 c.c.) was placed in bulb A. The apparatus was connected to the vacuum apparatus by the joint C and pumped out. In order that solvent was not pumped off in sufficient quantity to cause precipitation of either silver nitrate or lead alkyl, the the bulbs were cooled in a CO_2/acetone trap after the initial de-gassing. The tap D was then closed and the pumps switched off. The two solutions were mixed at -78°C by rotation of the bulb A about the joint E. There was immediate precipitation of silver, even at this low temperature. The taps connecting the apparatus to the fractionating chain (fig. 2) were then opened, and about half the contents of the reaction vessel were condensed into the first bulb of the fractionating chain, by cooling it in liquid nitrogen. This fraction would contain all volatile products and ethanol. The solution was then fractionally condensed through a -78°C trap into a liquid nitrogen trap. This operation was repeated, and the more volatile fraction was transferred to a calibrated gas burette, via a -90°C trap, using a Töpler pump.

The first experiments yielded some volatile products, which on combustion proved to be a mixture of C_2 and C_4

hydrocarbons. The carbon dioxide formed was condensed in a liquid nitrogen trap and the excess oxygen pumped off. The carbon dioxide was then transferred to the gas burette, via a -78°C trap, and measured.

Typical Results

(i) Weight of lead compound = 0.65 g.
Volume of gaseous products = 52 c.c.
pressure = 31.07 m.m.
temperature = 22.1°C

Combustion
Volume of carbon dioxide = 122.2 c.c.
pressure = 31.07 m.m.
temperature = 22.1°C.

i.e. Carbon content of the gaseous material

$$= \frac{122.2}{52} = C_{2.35}$$

This result would be expected if an ethyl group had been cleaved, since:-

$$\begin{aligned} C_2H_5^{\bullet} &\longrightarrow C_2H_6 \\ 2C_2H_5^{\bullet} &\longrightarrow C_4H_{10} \\ 2C_2H_5^{\bullet} &\longrightarrow C_2H_6 + C_2H_4 \end{aligned}$$

On the assumption that 1 mole lead compound produces 1 mole C_2 hydrocarbon the volume of gaseous material obtained is equivalent to a 4.8% yield.

(ii) This experiment was repeated on the same sample of lead compound, with the same result. Yield of gaseous products = 4.9%.

(iii) The lead compound was redistilled twice more, rejecting the first 40% of the required fraction, in order to prevent tetraethyllead collecting in the sample. The freshly distilled sample was then used for a repeat experiment, when it was found that the yield of volatile compounds had fallen to 0.62%. It is clear that volatile hydrocarbons are produced due to tetraethyllead as an impurity.

$$Et_4Pb + AgNO_3 \longrightarrow Et\cdot + Et_3PbNO_3$$

Mole % tetraethyllead in the first sample of Compound I = 4.8

Mole % tetraethyllead in the redistilled sample = 0.62

(2) <u>Benzyltriethyllead</u>

(a) <u>Isolation of Dibenzyl</u>

An excess of silver nitrate (1.4 g.) in ethanol (70 c.c.) was added to benzyltriethyllead (2.33 g.) in ethanol (20 c.c.) at -78°C. Silver was slowly precipitated and filtered off. Water (600 c.c.) was added to the filtrate and the turbid solution extracted twice with 100 c.c. ether. The ether extracts were washed three times with water, dried, and distilled. The solid residue was recrystallised from aqueous alcohol, and gave dibenzyl (0.491 g.; 89% yield). Melting point and mixed melting point 52.5°C.

(b) Estimation of Silver

The precipitation of silver was carried out as in the case of Compound I.

Recovery of silver = 98.5%.

(c) Investigation of Volatile Products

This was carried out using the same procedure as for compound I. No C_2 or C_4 hydrocarbons were produced.

(3) Triethyl-p-trifluoromethylphenyllead

(a) Isolation of Organic Material

The isolation of organic material was effected in the same way as the isolation of dibenzyl in the previous case. After removal of ether from the ether extract, a small quantity of non-volatile, tarry oil (0.08 g.) was isolated. It is clear that volatile products, distilling in the ether, must have been formed; possibly benzotrifluoride. Isolation of a small amount of benzotrifluoride from the comparatively large volume of solvents necessarily involved, would be difficult. Since the reason for this reaction was to see if an ethyl group was cleaved by silver nitrate, isolation of any benzotrifluoride was not attempted.

(b) Estimation of Silver

The recovery of silver was 90%.

(c) Investigation of Volatile Products

This was carried out as before. On mixing the solution of lead compound (0.442 g.) in ethanol (20 c.c.) with silver nitrate (0.17 g.) in ethanol (20 c.c.) at -78°C, there was no immediate precipitation of silver. On warming slowly to room temperature, silver was slowly precipitated, with the formation of a transitory red colour. No volatile hydrocarbons were formed, i.e. there was no cleavage of an ethyl group.

(4) p-Dimethylaminophenyltriethyllead

(a) Isolation of Dimethylaniline

The red-brown precipitate obtained on addition of an excess of ethanolic silver nitrate to a solution of the lead compound (8.51 g.; 0.0206 mole) in ethanol (100 c.c.), was left overnight to decompose. The greyish solid (silver) was filtered and the filtrate reduced in volume to 50 c.c., by distillation. The ethanol solution was then extracted with ether and water. The dried ether extract yielded 0.8 g. of a dark red oily liquid, which on distillation gave 0.65 g. tar and 0.15 g. dimethylaniline, (characterised as the p-nitroso derivative; m.pt. and mixed m.pt. 85-86°C).

A second ether extraction yielded 0.1 g. dimethylaniline and 0.4 g. tar. A further 0.65 g. tar were obtained by ether extraction after making the solution strongly alkaline.

Total yield dimethylaniline = 0.25 g. (10%)

Total yield tar = 1.7 g.

100% yield of the radical $\cdot C_6H_4N(CH_3)_2 = 2.47$ g.

(b) Estimation of Silver

The recovery of silver was 110% based on the reaction

$$Et_3Pb\cdot C_6H_4N(CH_3)_2 + AgNO_3 \longrightarrow Ag\cdot C_6H_4N(CH_3)_2 + Et_3PbNO_3$$

$$Ag\cdot C_6H_4N(CH_3)_2 \longrightarrow Ag + \cdot C_6H_4N(CH_3)_2$$

In a similar reaction, in which the lead compound was in excess, there was a quantitative recovery of the silver used.

(c) Investigation of Volatile Products

Investigation of the formation of volatile products was carried out as in the previous cases. No volatile hydrocarbons (i.e. C_2 or C_4) are formed.

(d) Reaction of the Methiodide with Silver Nitrate

The methiodide of p-dimethylaminophenyltriethyllead was formed from 0.461 g of the lead compound and an excess of methyl iodide, in one limb of the reaction vessel used in the determination of volatile hydrocarbons. The excess methyl iodide was pumped off leaving the white, solid, methiodide. Reaction of this with two equivalents of silver nitrate in ethanol produced no volatile hydrocarbons. On mixing at -78°C a pale yellow precipitate (presumably silver iodide) was formed. On allowing the mixture to warm slowly upto room temperature a red-brown colouration was obtained, which slowly disappeared, accompanied by the deposition of metallic silver, on standing for several hours at room temperature.

$$\left[Et_3Pb\cdot C_6H_4\overset{+}{N}(CH_3)_3\right]I^- + AgNO_3 \longrightarrow \left[Et_3Pb\cdot C_6H_4\overset{+}{N}(CH_3)_3\right]NO_3^- + AgI$$

$$\left[Et_3Pb\cdot C_6H_4\overset{+}{N}(CH_3)_3\right]NO_3^- + AgNO_3 \longrightarrow \left[\cdot C_6H_4\overset{+}{N}(CH_3)_3\right]NO_3^- + Et_3PbNO_3 + Ag$$

(5) Triethyl-α-styryllead

(a) Isolation of Organic Products

Triethyl-α-styryl lead (20 g.) was added slowly, with stirring, to a solution of silver nitrate (9 g.) in alcohol (800 c.c.) at -78°C. The deep red precipitate (of silver styryl ?) formed was refluxed overnight in the ethanol solution, when it was apparent that decomposition had taken place. The solution was filtered, and the filtrate extracted with ether and water. The dried ether extract was brominated, when dibromostyrene, equivalent to 0.05 g. styrene, was isolated (1% yield). The precipitate was found to consist of silver and a large quantity of insoluble and evidently polymeric material, the exact nature of which was not elucidated. No distyryl was isolated.

(b) Examination of the Silver Styryl

In a similar experiment a little of the solution containing the deep red precipitate was cooled to -78°C and quickly centrifuged. The solution was decanted from the precipitate, which was then washed well with cold alcohol, and centrifuged again. The washed precipitate was pumped dry and weighed. During the pumping, decomposition of the precipitate occurred, and hence the weight obtained was of the decomposition products. The organic material was extracted with ether or benzene, and the silver estimated by conversion to the nitrate, and titrating with standard thiocyanate solution.

	Silver styryl (Decomposition)	Silver Found	Silver Estimated	Organic Material Found	Organic Material Estimated
1.	0.1033 g.	0.063 g.	0.0527 g.	- g.	0.0506 g.
2.	0.066	0.0313	0.0336	0.013	0.0324
3.	0.077	0.043	0.0393	0.013	0.0377

$Ag{\cdot}CH{:}CHC_6H_5$ requires 51% silver
found 56% silver

Although decomposition of the suspected silver styryl in solution results in the formation of a negligible amount of volatile material, decomposition of the near dry solid may result in the formation of a slightly larger amount of volatile material. On pumping this would be lost, and since the silver styryl was weighed as decomposed material, this would have the effect of increasing the silver content. This may well account for the difference of 5%.

The discrepancy between the organic material found, and that estimated, is due to the formation of an insoluble grey material, probably polymeric, and not extracted in ether or benzene.

(c) Estimation of Volatile Products

Using the same procedure,as previously described,a variable quantity of volatile material was isolated, which, on combustion, was found to have a carbon content of $C_{2.2}$, in the order of that expected from the production and reaction of ethyl radicals in ethanol. The amount of gaseous product was found to be greater in samples stored at -78°C for several days. Repeated distillation, using a molecular still, and using the sample immediately after distillation, reduced the yield of volatile hydrocarbons from 15% to 4%. It is fairly obvious that the production of volatiles is due to the formation of tetraethyllead by decomposition of triethyl-α-styryllead, either by storing at -78°C or on distillation. Every distillation of this compound resulted in the formation of some lead.

$$Et_3Pb.CH{:}CHC_6H_5 + AgNO_3 \longrightarrow Et_3PbNO_3 + Ag.CH{:}CHC_6H_5$$

$$Ag.CH{:}CHC_6H_5 \longrightarrow Ag + 1\%\ CH_2{:}CHC_6H_5 + \text{insoluble, polymeric material}$$

4. Polymerisation Experiments

(1) Polymerisation of Styrene

Styrene was freed from it's inhibitor by vacuum distillation. 10 c.c.s of the freshly distilled styrene were added, in turn, to 3 two necked flasks (50 c.c.), one containing triethyl-2-methylprop-2-enyllead (0.33 g.), one containing an equimolar quantity of tetraethyllead

(0.305 g.), and one empty. 12 c.c. of a solution of silver nitrate (0.6 g.) in ethanol (36 c.c.) were added to each flask, causing instant precipitation of lead in those flasks containing lead compounds. After standing overnight, the contents of the flasks were filtered. The silver residues were extracted with hot benzene, and the benzene extracts added to the first filtrates. The same volume of benzene was added to the blank. Polystyrene (infra red identification) was precipitated and coagulated by the addition of methanol. The polymer was filtered, dried, and weighed. The whole experiment was carried out under nitrogen.

It was found that the blank produced no polystyrene, whereas appreciable amounts were obtained from the reaction of Compound I, and tetraethyllead with silver nitrate

Weight of polystyrene from tetraethyllead = 0.75 g.
Weight of polystyrene from Compound I = 0.05 g.

In the same way compounds II and IV were found to produce small quantities of polystyrene.

Ratio of polystyrene from tetraethyllead: Compound I = 15:1

Ratio of polystyrene from tetraethyllead: Compound II = 13.5:1

Ratio of polystyrene from tetraethyllead: Compound IV = 12:1

(II) Polymerisation of Acrylonitrile

In exactly the same way a small quantity of polyacrylonitrile was obtained from triethyl-2-methylprop-2-enyllead.

5. Reactions to show the Production of Free Radicals from the Reaction of Triethyl-2-methylprop-2-enyllead and Silver Nitrate

(I) Reaction with n-Butyl Mercaptan

(a) Compound I (0.44 g.) was dissolved in 5 c.c. of n-butyl mercaptan and placed in one limb of the reaction vessel (fig. 1). A slight excess of silver nitrate (0.27 g.) in n-butyl mercaptan (10 c.c.) was placed in the other limb. On standing at room temperature for about 20 minutes it was found that the originally clear solution of lead compound in mercaptan had become coloured greenish-yellow with the formation of a brown-yellow precipitate. On cooling to -78°C, prior to mixing with the silver mercaptide, a yellow solid was brought out of solution. On mixing the two solutions no precipitate of silver was produced. Reaction had already taken place.

(b) Although this reaction could not now be used to test for the production of free radicals by the action ~~action~~ of silver nitrate on Compound I, a reaction between the lead compound (0.741 g.) and an excess of n-butyl mercaptan was carried out in the same way as described above. It was found that reaction did not take place at -78°C, but on allowing to stand at room temperature, overnight, a grey solid, in which could be seen yellow crystalline material, was formed.

A large volume (35.21 n.c.c) of gaseous material, which on combustion analysed to $C_{1.9}$, was also produced.

Yellow place crystals, containing lead and sulphur, were isolated from the solid products by extracting the grey material with chloroform. These yellow crystals proved to be highly insoluble in most organic solvents, and were crystallised from dimethylformamide, when they melted at 195-197°C, with decomposition.

On attempting to recover the grey material from the chloroform solution by distillation, a black solid was precipitated, evidently by decomposition of the grey material.

A similar reaction occurs between tetraethyllead and n-butyl mercaptan. The reaction was found to be highly photo-sensitive.

This topic was not pursued.

(II) Reaction with n-Butyl Disulphide

Reaction of Compound I with silver nitrate in the presence of n-butyl disulphide to show the formation of free radicals by breakage of the S-S bond, could not be carried out, since both silver nitrate and the lead compound each react separately with the disulphide.

(III) Reaction with Chloranil $C_6Cl_6O_2$

The lead compound (3 g.) in benzene (10 c.c.) was added to a solution of chloranil (2.1 g.) in a benzene/ methanol mixture (200 c.c.; 10% methanol). A deep red solution was immediately produced, and addition of silver nitrate in methanol produced no precipitation of silver. Reaction had already taken place between the quinone and the lead compound.

Tetraethyllead behaves in a similar manner, and at least two different yellow-brown, amorphous solids, both containing lead and both, in part, organic, were isolated by evaporation of the benzene solution. The nature of these solids is not known, and since the reaction did not give any added information of free radicals from the reaction between the lead compound and ethanolic silver nitrate, this topic was not pursued.

PART 1B

THE LOW TEMPERATURE REACTIONS OF SOME ORGANO-METALLIC REAGENTS WITH LEAD HALIDES

SUMMARY

The reactions of phenyl lithium, phenyl magnesium bromide, and mesityl magnesium bromide with lead bromide in tetrahydrofuran are described.

Evidence is presented, which corroborates the idea, put forward by Gilman, Summers, and Leeper,[4] of an equilibrium between diphenyllead and triphenyllead lithium,

i.e. $Ph_2Pb + PhLi \rightleftharpoons Ph_3PbLi$

This reaction is shown to proceed at -78°C in tetrahydrofuran.

The analagous Grignard reactions, involving the formation of triphenyllead- and trimesityllead magnesium bromide, are described, and the evidence suggests the existence of an equilibrium,

i.e. $Ph_2Pb + PhMgBr \rightleftharpoons Ph_3PbMgBr$

and $Ms_2Pb + MsMgBr \rightleftharpoons Ms_3PbMgBr$

(Ms = mesityl)

The experimental evidence also suggests that diorganolead compounds are hydrolysed with water, and are only formed in equilibrium with the triorgano-lead lithium and triorgano-lead magnesium bromide compounds. It is

suggested that this latter factor is responsible for the fact that no diorgano-lead compounds were isolated from these reactions.

DISCUSSION

The isolation of diaryllead compounds, from the reaction between lead chloride and a Grignard reagent, must seem rather suspect, as has already been pointed out in part IA of this thesis (page 4). Since Krause[3] first isolated diphenyl- and di-o-tolyllead from the reaction of the appropriate Grignard reagent and lead chloride in ether at 2°C, not only has this work never been repeated but all attempts by other methods[8,9] have met with no success.

Gilman[4] suggested that diphenyllead may be present in the reaction between lead chloride and phenyl lithium in ether at -10°C, but none was ever isolated.

This present work began with the idea of preparing diaryllead compounds by a method which would give reproducible results. If it can be considered that diaryllead compounds are thermally unstable, and quite reactive, then it will be appreciated that the best yields would be obtained at low reaction temperatures. It was thought that the use of tetrahydrofuran as the solvent would enable these reactions to proceed at much lower temperatures, ensuring that any diaryllead compound would not decompose.

It was also hoped that these reactions would help to explain the reaction mechanism involving the formation of diaryl and tetraaryllead compounds[2]

$$\text{e.g.}\quad \begin{aligned} 2RMgX + PbCl_2 &\longrightarrow R_2Pb + MgXCl \\ 3R_2Pb &\longrightarrow R_6Pb_2 + Pb \\ 2R_6Pb_2 &\longrightarrow 3R_4Pb + Pb \end{aligned}$$

1. Reaction of Phenyl Lithium with Lead Halides

The ease of cleavage of tetrahydrofuran by phenyl lithium necessitates that the solution is kept cold. Hence it was found more convenient to add lead chloride to the phenyl lithium solution, and not vice-versa. Several reactions were tried, and it was found that even at -78°C reaction was complete, as signified by Colour test I, after a few minutes. The reaction products, from reactions in which a 2:1 molar ratio of phenyl lithium to lead chloride was used, appeared to be green in colour, and on hydrolysis and extraction with benzene, at low temperature, only a pale yellow benzene solution was obtained. It was expected that if diphenyllead is formed in these reactions, then a deep red solution would be obtained.

These pale yellow benzene solutions yield only a small quantity of hexaphenyldilead, generally not more than 1 to 2%, although in one case a 20% yield was recorded. The majority of the lead is recovered in some inorganic form, precipitated from solution on hydrolysis. This inorganic compound was later found to be an oxybromide, $3PbO.PbBr_2.(1-3H_2O)$, established by X ray powder photographs.

The low recovery of organic material is puzzling, and it can only be concluded that phenyl groups form a compound not easily isolated from the organic solvents used, the most obvious compound being benzene. In fact 6% benzene was estimated by using an ultra-violet spectrum on a cyclohexane extract. The yield is low, and could be ascribed to the hydrolysis of excess phenyl lithium, even though Colour Test I was negative, since this test in tetrahydrofuran is known to be slightly less sensitive than in ether. Another possibility is that benzene is washed out of the cyclohexane extract, which had to be freed from tetrahydrofuran by numerous water washings.

In all experiments conducted with phenyl lithium in tetrahydrofuran, there was no evidence for the formation of lead. Hence it is difficult to see how the formation of hexaphenyldilead is brought about, if the mechanism proposed by Krause[2] is correct. Hence this point calls for further explanation.

Gilman[4] prepared triphenyllead lithium by the action of phenyl lithium on lead chloride in ether at -10°C. The mechanism suggested is

$$2PhLi + PbCl_2 \longrightarrow Ph_2Pb + 2LiCl$$

$$PhLi + Ph_2Pb \rightleftharpoons Ph_3PbLi$$

and it is more than probable that the analogous reaction in tetrahydrofuran would proceed at lower temperature, as found in these experiments.

The problem is now twofold:-

(1) How is hexaphenyldilead formed

and (2) Why, if an equilibrium is postulated between diphenyllead and triphenyllead lithium,

$$Ph_2Pb + PhLi \rightleftharpoons Ph_3PbLi$$

is no diphenyllead isolated.

(1) It is difficult to see, if there is no formation of lead, how hexaphenyldilead is formed from any source other than triphenyllead lithium, and the following mechanism is tentatively suggested.

$$Ph_3PbLi + H_2O \longrightarrow Ph_3PbH + LiOH$$

$$2Ph_3PbH \longrightarrow Ph_3Pb.PbPh_3 + H_2$$

or $$2Ph_3PbH \xrightarrow{[O]} Ph_3Pb.PbPh_3 + H_2O$$

There is also another possibility involving the formation of $[Ph_3Pb.PbPh_3]^{2-}\ 2Li^+$.

$$[Ph_3Pb.PbPh_3]^{2-}2Li^+ + 2H_2O \longrightarrow Ph_3Pb.PbPh_3 + 2LiOH + H_2$$

Gilman's experiment was repeated, in ether, as for the preparation of triphenyllead lithium, although lead bromide was used instead of lead chloride. Atmospheric oxygen was rigorously excluded, and the product was hydrolysed in a vacuum apparatus. There was no production of hydrogen, and only a small quantity of hexaphenyldilead (0.1 g.) was isolated.

An identical experiment was performed, this time filtering off the grey suspension. Hexaphenyldilead, in appreciable yield, was isolated on extraction of the solid with chloroform, after first washing with water in air. However a small quantity of hexaphenyldilead was also isolated from the filtrate, which was maintained under nitrogen. Hence it is difficult to draw any conclusions from these experiments. It would seem that the presence of oxygen is necessary, but in all experiments carried out in tetrahydrofuran oxygen was excluded. It is true that only small quantities of hexaphenyldilead were isolated (except in one case), and traces of oxygen may be sufficient for these small amounts.

The situation is even more complicated, since it is by no means certain that small quantities of lead are not formed during the reaction. Finely divided lead could react to give the hydroxide or oxybromide on hydrolysis. Gilman suggests that a small quantity of lead is formed in the reaction. If lead is formed then no argument can be proposed against the mechanism suggested by Krause,

$$3Ph_2Pb \longrightarrow Ph_3Pb.PbPh_3 + Pb$$

other than the fact that it is difficult to imagine 3 such unstable molecules reacting together at the same time. One point which was clarified, however, was the formation of large quantities of lead oxybromide, $3PbO.PbBr_2(1\text{-}3H_2O)$, not reported by Gilman.

(2) If the postulation of an equilibrium,

$$PhLi + Ph_2Pb \rightleftharpoons Ph_3PbLi$$

is correct, then addition of water should drive the equilibrium to the left, as phenyl lithium is hydrolysed. If only 2 moles of phenyl lithium are used to 1 mole of lead bromide then reaction should stop at the diphenyllead stage, at low temperature. Krause[3] reports that diphenyllead is stable to water. Since no diphenyllead is isolated, either diphenyllead is not stable to water, or the equilibrium between it and triphenyllead-lithium does not exist. The evidence obtained in this and later sections points to the fact that diphenyllead is water sensitive. It is difficult to suggest a method other than the hydrolysis of diphenyllead, whereby lead oxybromides are formed, and this point is made clearer in the next section. It is also possible that another stage to the reaction exists,

i.e. 1. $PhLi + PbBr_2 \longrightarrow PhPbBr + LiBr$

2. $PhLi + PhPbBr \longrightarrow Ph_2Pb + LiBr$

3. $PhLi + Ph_2Pb \rightleftharpoons Ph_3PbLi$

Water hydrolysis of phenyllead bromide could also account for the presence of lead oxybromides. It is found that when equimolar quantities of phenyl lithium and lead bromide or chloride react, approximately half the lead halide is recovered unreacted. This points to the reaction stopping at stage 2, or to a complicated equilibrium between phenyllead bromide, diphenyllead and triphenyllead lithium. Evidence that the final stage, Ph_3PbLi, was reached in this reaction, was obtained when a 28% yield of benzyltriphenyllead was obtained on addition of benzyl chloride.

It is tentatively suggested that there is co-existence of various species in solution, in the low temperature reaction between phenyl lithium and lead halides.

2. Reactions of Mesityl Magnesium Bromide with Lead Bromide

The reactions of phenyl lithium in tetrahydrofuran point to the high instability and high reactivity of diphenyllead, in as much as it was never isolated. Hence it was decided that the larger, more hindered mesityl group may cause an increase in stability of the diaryl compound; it has already been found[3] that di-o-tolyllead is more stable than diphenyllead. In view of the low yields of mesityl lithium[33] it was decided to use the Grignard compound in tetrahydrofuran. This involves the use of much better reaction techniques, since, relieved of the necessity for keeping the active organometallic solution cold, the Grignard solution could be added, dropwise, to a vigorously stirred suspension of lead bromide at -20 to -30°C.

Addition of 2 moles of mesityl magnesium bromide to 1 mole of lead bromide produces an intense deep red colour. Hydrolysis causes the immediate discharge of this colour, and the precipitation of lead hydroxybromide, $Pb(OH)Br$ or $PbO.PbBr_2.H_2O$, confirmed by X ray analysis. The only organic material isolated was an oil, probably produced by attack of the Grignard reagent on solvent.

Addition of more than 2 equivalents of Grignard reagent to lead bromide leads to fading of the deep red colour, and after addition of 3 to 6 equivalents the colour is orange to red-brown. Hydrolysis of this product results in the intermediate return of the deep red colouration, followed by its' discharge and precipitation of lead hydroxybromide. If the product from the addition of 6 equivalents of Grignard reagent to lead bromide is refluxed overnight, then small quantities of organo-lead compounds are formed. The analyses, although not good, point to tetramesityllead, particularly since this melts at 210°C, whereas it is reported that hexamesityldilead decomposes above 325°C.[7b]

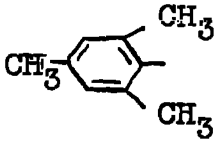
Refluxing benzyl chloride with the product, from the addition of 3 equivalents of mesityl magnesium bromide to lead bromide, results in the formation of benzyltrimesityllead.

The stability of species in the mesityl series is quite marked. Even in reactions where heating was continued overnight, there was no sign of the formation of lead.

These results are consistent with the following mechanism:-

1. $MsMgBr + PbBr_2 \longrightarrow MsPbBr + MgBr_2$
2. $MsMgBr + MsPbBr \longrightarrow Ms_2Pb + MgBr_2$
3. $MsMgBr + Ms_2Pb \rightleftharpoons Ms_3PbMgBr$

Ms =



The existence of an equilibrium between trimesityllead magnesium bromide and dimesityllead is postulated, since it fits with experimental observations and is analagous to the diphenyllead-triphenyllead lithium system. Evidence for the presence of trimesityllead magnesium bromide is based on the formation of benzyltrimesityllead,

$$Ms_3PbMgBr + PhCH_2Cl \longrightarrow Ms_3PbCH_2Ph + MgBr\ Cl$$

and it is difficult to visualise any other mechanism.

Addition of water to the reaction product, from the addition of 3 or more equivalents of Grignard reagent to lead bromide, results in the intermediate formation of the deep red colour, associated with the addition of 2 equivalents of Grignard reagent to lead bromide. This suggests that the reaction is being driven back along the same path, i.e. indicative of an equilibrium. The discharge of the red colour is accompanied by precipitation of lead hydroxybromide, Pb(OH)Br. Since it is difficult to envisage the hydrolysis of, $Ms_3PbMgBr$, producing lead hydroxy bromide, it was thought that mesityllead bromide was responsible, i.e. $MsPbBr + H_2O \longrightarrow MsH + Pb(OH)Br$.

This would mean that the red colouration is due to mesityllead bromide and not to dimesityllead. Hence either dimesityllead is not formed (and it is hard to see how a compound like trimesityllead magnesium bromide can be formed without postulating a dimesityllead intermediate) or dimesityllead reacts preferentially with the Grignard reagent as soon as it is formed. This hardly seems justified, since there is no good reason why dimesityllead should be more reactive than mesityllead bromide. However it was found that lead hydroxide reacts with magnesium bromide in water/tetrahydrofuran solution to produce the more insoluble lead hydroxybromide. Hence the most probable mechanism is that dimesityllead is hydrolysed by water to lead hydroxide,

$$2H_2O + Ms_2Pb \longrightarrow 2\ MsH + Pb(OH)_2$$

and lead hydroxide reacts with halides in solution to give the hydroxy bromide

$$Pb(OH)_2 + MgBr_2 \longrightarrow Pb(OH)Br + Mg(OH)Br.$$

Mesitylene was isolated from a reaction in which excess Grignard may have been present. Attempts to verify the presence of mesitylene by the use of ultra-violet spectrometry on a cyclohexane extract, met with no success due to the presence of impurities. However the presence of mesitylene would be expected from the hydrolysis of the Grignard reagent,

i.e. $Ms_2Pb + MsMgBr \rightleftharpoons Ms_3PbMgBr$

An attempt was made to isolate dimesityllead, in the absence of water, by addition of dioxane to precipitate all magnesium salts. Ethyl acetate was first added to the reaction products in the hope that this would result in the removal of all excess Grignard reagent from solution, thus driving the equilibrium to the left. The return of the red colour from the red-brown colour of the reaction products was not certain, and it may be that mesityl magnesium bromide does not react sufficiently well with ethyl acetate, even at room temperature. Addition of dioxane then caused the discharge of the red or red-brown colour, and the product ultimately obtained was tetramesityllead together with magnesium impurities, which were still present.

It is suggested that it may be profitable to repeat this experiment, since the purity of the dioxane was questionable. However it may be found that the red colour will still disappear, since its presence may be due to the dimesityllead-trimesityllead magnesium bromide system, and not to dimesityllead alone. In this case precipitation of magnesium, by dioxane, would destroy the system and the colour.

3. Reactions of Phenyl Magnesium Bromide with Lead Bromide

The results of reactions between phenyl magnesium bromide and lead bromide at -25°C show great similarity to those involving mesityl magnesium bromide. Addition of Grignard to lead bromide shows the same colour changes,

i.e. yellow ——→ red ——→ red-brown.

(1 equiv. PhMgBr) (2 equiv.) (3 or more equiv.)

Furthermore, on hydrolysis the red colour again returns momentarily, followed by it's discharge and precipitation of lead hydroxy bromide.

i.e. $PhMgBr + PbBr_2 \longrightarrow PhPbBr + MgBr_2$

$PhMgBr + PhPbBr \longrightarrow Ph_2Pb + MgBr_2$

$PhMgBr + Ph_2Pb \rightleftharpoons Ph_3PbMgBr$

Even when 3 equivalents of Grignard reagent are used, sufficient for the formation of triphenyllead magnesium bromide, lead hydroxybromide (92%) is precipitated. Hence it would be expected that the possible mechanism

$$Ph_3PbMgBr + H_2O \longrightarrow Ph_3PbH + LiOH$$

$$2Ph_3PbH + [O] \longrightarrow Ph_3Pb.PbPh_3 + H_2O$$

would have little effect, since it is obvious that the water is reacting preferentially with the Grignard reagent. This is observed, since only small quantities of hexaphenyldilead are isolated, and it must be pointed out that this may be due to other causes.

The complexity of species in solution is borne out by experiments with benzyl chloride. Addition of 1 to 3 equivalents of phenyl magnesium bromide to lead bromide, followed by heating with benzyl chloride, results in the formation of benzyltriphenyllead.

i.e. 1. $PhMgBr + PbBr_2 \longrightarrow x\ Ph_3PbMgBr$

2. $3PhMgBr + PbBr_2 \longrightarrow y\ Ph_3PbMgBr.$

$$Ph_3PbMgBr + PhCH_2Cl \longrightarrow Ph_3PbCH_2Ph + MgBrCl$$

Since, for the formation of benzyltriphenyllead, the intermediate, $Ph_3PbMgBr$, is postulated, then this compound must be present in solution in both cases (1 and 2).

1. $PhMgBr + PbBr_2 \longrightarrow PhPbBr + MgBr_2$
2. $PhMgBr + PhPbBr \longrightarrow Ph_2Pb + MgBr_2$
3. $PhMgBr + Ph_2Pb \rightleftharpoons Ph_3PbMgBr$

Furthermore when 1 equivalent of phenyl magnesium bromide is added to lead bromide (1 mole) some 45% lead bromide is recovered unreacted. Hence it is clear that the immediate products, of the reaction between lead bromide and the Grignard reagent, react more readily with more Grignard than does lead bromide. Since only 50% lead bromide reacts with 1 equivalent of Grignard reagent it would be expected that diphenyllead is the ultimate product,

$$PhMgBr + PbBr_2 \longrightarrow PhPbBr + MgBr_2$$
$$PhMgBr + PhPbBr \longrightarrow Ph_2Pb + MgBr_2$$

and this would fit in with the expected reactivity of the species, PhPbBr. Whether the species $Ph_3PbMgBr$ is present in solution under these conditions is not certain. Addition of benzyl chloride at -20°C produces no benzyltriphenyllead, until the temperature is raised to reflux point. However, if this were true, no equilibrium would exist (since there would be no free Grignard), diphenyllead would be isolated, and triphenyllead magnesium bromide would not be formed, even at higher temperatures. It is quite probable that benzyl chloride does not react with triphenyllead magnesium bromide at -20°C.

An attempt was made to isolate any diphenyllead formed, by removal of tetrahydrofuran, and addition of methylene chloride to precipitate all inorganic salts. However the orange-red solid obtained from this solution still contained magnesium, and it is evident that triphenyllead magnesium bromide (probably as a T.H.F. complex) is soluble in methylene chloride.

In conclusion it can be said that the nature of species present in solution, from the reaction of phenyl lithium and Grignard compounds in tetrahydrofuran, is quite complex. It is suggested that experimental evidence points to a system in which at least two species are always present in solution, (i.e. diphenyllead and triphenyllead magnesium bromide in the case of phenyl magnesium bromide), whatever the ratio of Grignard, or lithium compound, to lead bromide (although, as the proportion of Grignard reagent increases, the equilibrium will become more and more in favour of triphenyllead magnesium bromide). The evidence also corroborates Gilman's postulation of the equilibrium:[4]

$$Ph_2Pb + PhLi \rightleftharpoons Ph_3PbLi$$

and its extension to the phenyl magnesium bromide and mesityl magnesium bromide series, hitherto unreported. It is tentatively suggested that no diorgano-lead compounds have been isolated due to this equilibrium, and the fact that the diorgano-lead compounds in these reactions, only exist because of such an equilibrium. Furthermore the experimental evidence points to the water sensitivity of the diorgano-lead compounds. The idea of the existence of organo-lead halides is postulated as a convenient first stage in the reaction.

EXPERIMENTAL

In all experiments described in this section, stirring of lead halide suspensions was effected by means of a tantalum wire Hershberg stirrer. The whole of the work was conducted under nitrogen, unless otherwise stated.

1. Reactions of Phenyl Lithium with Lead Chloride in Tetrahydrofuran

(I) Phenyl lithium[34] was made from bromobenzene (15.7 g., 0.1 mole) in tetrahydrofuran (100 c.c.), and lithium shot (approx. 0.5 g. atoms) in tetrahydrofuran (50 c.c.) at -65°C. After complete addition of the bromobenzene the deep red solution was stirred overnight at -78°C, and filtered.

Polythene tubing, normally used for filtrations under nitrogen, was not used here, since it is rapidly attacked by phenyl lithium in tetrahydrofuran. Instead, a length of glass tubing, having a B.19 male joint at one end, was bent to form an L shape, and the tube was blocked with a small, quartz wool plug. The phenyl lithium solution was poured, and blown, through the tube, with a good stream of nitrogen, into one neck of a flask, having a counter-stream of nitrogen blowing from it. This technique proved to be quick and convenient, resulting in no appreciable loss in yield of phenyl lithium, and was used throughout this work.

A sample (2 c.c.) of the filtered solution was hydrolysed in water and titrated with standard acid.

Yield of phenyl lithium = 0.092 mole (92%). Lead chloride (12.5 g., 0.045 mole), oven-dried and stored in a desiccator, was added in small amounts, over a period of ½ hour, to the stirred solution of phenyl lithium at -60°C. After the addition of lead chloride was completed, there was no apparent change in colour of the mixture, but on stirring for a few minutes at -40°C, it was noticed that the colour had changed to green. After stirring overnight the green solution was hydrolysed with water, at -30°C, under nitrogen, and extracted with water and benzene. The yellow benzene extract was washed and dried, after filtering free from solid material. The benzene was pumped off, when a yellow solid (2 g.) was obtained. This solid was dissolved in benzene (10 c.c.) and added to ethanol (50 c.c.) under nitrogen. Colourless crystals of hexaphenyldilead (0.4 g., 3%; decomposes 155°C; infra-red spectrum identical with that of known compound) were obtained.

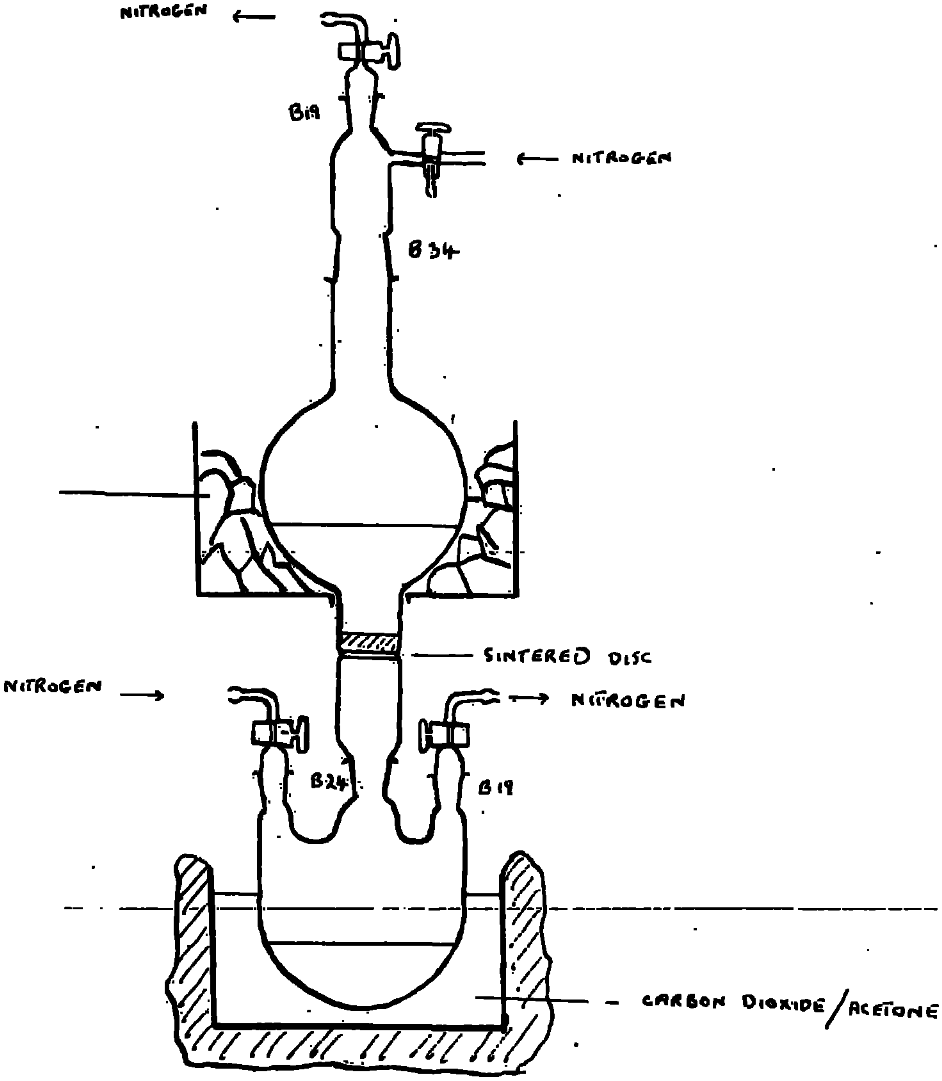

NITROGEN
B19
NITROGEN
B34
SOLID CARBON DIOXIDE
SINTERED DISC
NITROGEN
NITROGEN
B24
B19
CARBON DIOXIDE/ACETONE

Fig. 4

The solid (12 g.), filtered off after hydrolysis, proved to be inorganic, containing lead, chlorine, and bromine, and was insoluble in hot water. Addition of dilute hydrochloric acid produces lead chloride. These facts are consistent with the formation of a basic lead halide on hydrolysis.

(II) In a similar experiment, lead chloride (13.47 g., 0.0484 mole) was added to phenyl lithium (0.088 moles) in tetrahydrofuran (150 c.c.) at -60°C. On warming to -40°C, it was found that the Gilman Colour Test I was negative.

The solution was filtered under nitrogen, keeping the temperature low with solid carbon dioxide (Fig. 4). The orange-yellow filtrate was divided into three parts.

Part I was allowed to warm up to room temperature, when a small quantity of a white solid was precipitated. On still further gentle warming (30 to 40°C) the still yellow solution decomposed, depositing lead.

Part II was hydrolysed, as in the previous experiment. A yellow solid was produced, which was partly soluble in benzene giving an orange-red solution, and partly inorganic, insoluble in benzene, and presumed to be a basic lead halide, since lead chloride was produced on reaction with hydrochloric acid. On standing at room temperature for about an hour, the orange-red benzene solution faded to a pale yellow colour, and a small quantity of hexaphenyldilead (0.1 g., $< 1\%$) was subsequently isolated from this solution.

Part III was maintained at -40°C, and benzyl chloride (1.27 g., 0.01 mole) in tetrahydrofuran (10 c.c.) was added. The mixture was stirred for 2 hours at -25°C, and then hydrolysed. No organic lead derivatives were isolated. Only inorganic lead compounds, and unreacted benzyl chloride were obtained.

(III) Lead chloride (24 g., 0.086 mole) was added, all at once, to phenyl lithium (0.086 mole) in tetrahydrofuran (150 c.c.) at -78°C. The mixture was stirred for 10 minutes, when Colour Test I was negative. Stirring was continued overnight at -78°C, and then for two hours at -20°C. The product was filtered, with cooling, as previously described, and chloroform (150 c.c. at -30°C) was added to the filtrate, which was then hydrolysed with water at -30°C. More water (approximately 300 c.c.) was added, keeping the temperature at -10°C, and the almost colourless, chloroform layer was separated, dried over anhydrous magnesium sulphate, and filtered under nitrogen.

The chloroform extract was pumped at high vacuum, at a temperature of between -10 to -20°C, until the volume had been reduced to about 30 c.c.s. The colourless crystals so formed, were filtered off under nitrogen, and were found to be hexaphenyldilead (1.5 g.)

Found	C 49.6%	H 3.7%
$C_{36}H_{30}Pb_2$ requires	C 49.3%	H 3.45%

The remaining chloroform solution was added to cold ethanol (100 c.c. at -10°C), when a further quantity of hexaphenyldilead (1 g.) slowly crystallised from solution.

Yield hexaphenyldilead = 20%.

(IV) Lead chloride (20 g., 0.0718 mole) was added, all at once, to phenyl lithium (0.06 mole) in tetrahydrofuran (150 c.c.) at -78°C. After 5 minutes Colour Test I was negative, and benzyl chloride (4.2 g., 0.033 mole) in tetrahydrofuran (20 c.c.) was added over a period of 10 minutes.

The resulting mixture was allowed to come to room temperature and then refluxed for 1.5 hours. The mixture was then grey-black in colour, evidently containing lead. After cooling, the products were hydrolysed with a large quantity of water and filtered in air. The solid residue was extracted with hot ethanol when triphenylbenzyllead (3 g., 28%) was obtained (m.pt. and mixed m.pt. 92.5°C). Extraction with benzene yielded tetraphenyllead (2.5 g., 32% based on phenyl; m.pt. and mixed m.pt. 223°C).

(V) Lead chloride (25.75 g., 0.0925 mole) was added to phenyl lithium (0.09 mole) in tetrahydrofuran (150 c.c.) at -60°C. The reaction products were filtered cold, and the filtrate hydrolysed with water.

Unreacted lead chloride (13 g., 0.0466 mole 50.5%) was isolated from the residue.

After hydrolysis the filtrate was again filtered, and extracted with water and cyclohexane. The solid (8.7 g., 31.6%) was found to be a lead oxybromide, $3PbO.PbBr_2.(1-3H_2O)$, by X ray analysis. The cyclohexane was washed well with water to remove tetrahydrofuran, and an ultra-violet spectrum on the dried, and distilled, extract proved the presence of benzene (6%).

2. Reactions of Phenyl Lithium with Lead Bromide in Ether

(I) Phenyl lithium (0.1 mole) in ether (100 c.c.) was added slowly to a vigorously stirred suspension of lead bromide (12.2 g., 0.033 moles) in ether (100 c.c.) at

-20°C, according to the reaction of Gilman, Summers, and Leeper.[4] The reaction products were filtered cold (Fig. 4), under nitrogen. The pale yellow filtrate was hydrolysed with water, when a pale yellow solid was precipitated. The solid proved to be a lead oxybromide, whilst the ether solution yielded hexaphenyldilead (0.4 g., 2.8%).

The grey residue from the reaction was opened to the air and extracted with hot water, when lead bromide (0.2 g.) was obtained. Extraction with chloroform yielded hexaphenyldilead (3 g., 20%), and the residual inorganic solid (5 g., 60%) was found to be a lead oxybromide, $3PbO.PbBr_2.(1-3H_2O)$ (confirmed by X ray powder photograph).

(II) In a similar experiment, the product of reaction between phenyl lithium (0.1 mole) and lead bromide (12.2 g., 0.033 mole), in ether (200 c.c.), was attached to a standard vacuum apparatus, the ether de-gassed, and the flask evacuated of all gaseous material. A water/tetrahydrofuran mixture was condensed onto the reaction products, and the whole mixture left to attain room temperature. During the warming up of the flask, good stirring was effected by the ether boiling at low pressure. No gaseous products were obtained, which could not be condensed in a liquid air trap.

The products of hydrolysis were removed from the vacuum apparatus, under nitrogen, and filtered at room temperature. More water was added to the filtrate, and the ether layer separated, and dried. The ether extract yielded hexaphenyldilead (0.2 g., 1.4%) and a small quantity of diphenyl (0.1 g., m.pt. and mixed m.pt. 70-71.5°C).

The solid, obtained by the filtration was extracted with chloroform, under nitrogen. No organic material was extracted. The solid was then opened to the air and re-extracted with chloroform, when again no organic material was isolated. The grey solid was, in fact, found to be a lead oxybromide $3PbO.PbBr_2(1-3H_2O)$ by X ray analysis.

3. Reactions of Mesityl Magnesium Bromide with Lead Bromide

(I) Mesityl magnesium bromide was prepared in the usual way from magnesium (2.6 g., 0.107 g. atoms) and mesityl bromide (19.9 g., 0.1 mole) in tetrahydrofuran (100 c.c.). After filtration, a sample of the Grignard solution was hydrolysed with an excess of standard acid, the excess being estimated by titration with standard sodium hydroxide solution.

Yield = 0.093 mole (93%)

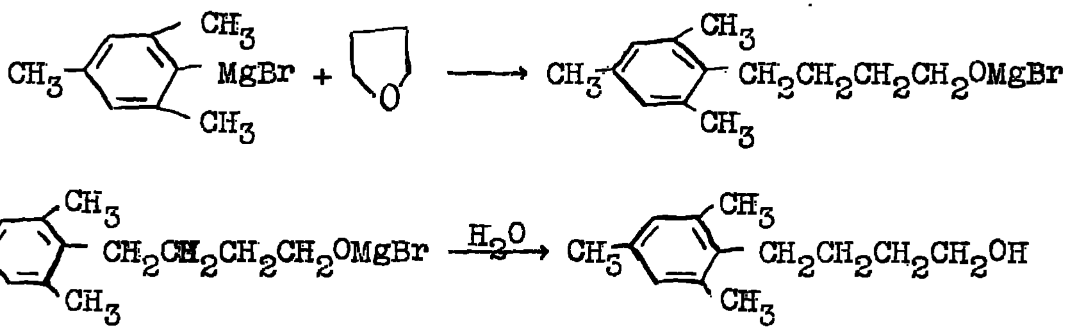
The Grignard solution was added dropwise to lead bromide (17.1 g., 0.0465 mole) in tetrahydrofuran (150 c.c.), under nitrogen, at -25 to -30°C. Addition of the first drop produced a localised deep red colouration, which quickly dispersed, producing a uniform pale yellow colour. This colour deepened as addition proceeded. It was noticed that if the rate of addition was increased then the deep red-brown colour persisted until addition was stopped, when the yellow colour quickly returned. On completion of the addition of Grignard, the colour was deep red.

The reaction products were filtered until nitrogen, keeping the temperature below -20°C, as previously described in section 1. The deep red filtrate was hydrolysed carefully with water, when it was found that the deep colour was instantly discharged, with the first few drops of water, producing a cream white precipitate, and an almost colourless supernatant solution. Chloroform and more water were added and the whole mixture filtered.

The precipitate (11 g., 78%) was found to be a lead hydroxy bromide, $Pb(OH)Br$, or $PbO.PbBr_2.H_2O$, by X ray identification. It was found that the X ray powder photograph corresponded exactly with that of the listed standards. Furthermore lead bromide (61.8%) was crystallised from a dilute nitric acid solution ($PbO.PbBr_2.H_2O$ requires 62% lead bromide; $PbO.PbBr_2.H_2O + HNO_3 \longrightarrow PbNO_3 + PbBr_2$).

The chloroform extract yielded a dark coloured, viscous oil (0.8 g.). This was distilled in a micro-distillation apparatus, when a clear pale yellow distillate (B.pt 100°C/0.1 mm) was obtained. The infra-red spectrum of this oil was consistent with the product expected from attack of mesityl magnesium bromide on solvent,

i.e.



However no good analysis could be obtained.

Found	C 75.8%	H 10.3%
$C_{13}H_{20}O$ requires	C 81.2%	H 10.5%

No other organic compounds were isolated from this reaction. Unreacted lead bromide (0.1 g.) and some inorganic lead salt, which yielded lead bromide (2.2 g.) on treatment with dilute hydrobromic acid, were isolated from the residue of the reaction, obtained by filtration before hydrolysis.

(II) A repeat experiment under the same conditions gave approximately the same results, i.e.

1.	organic oil	1.4 g.	
2.	lead hydroxy bromide	.11 g.	78%
3.	unreacted lead bromide	0.9 g.	5%
4.	product yielding lead bromide on treatment with hydrobromic acid	1.8 g.	

(III) Mesityl magnesium bromide (0.187 mole) in tetrahydrofuran (200 c.c.) was added slowly to a vigorously stirred suspension of lead bromide (11.4 g., 0.031 mole) in tetrahydrofuran (60 c.c.), under nitrogen, at a temperature of between -20 to -25°C. After addition of approximately 2 equivalents of Grignard, a deep red colour was observed, which gradually faded on addition of more Grignard. The final colour, on addition of 6 equivalents of Grignard, was orange-red.

The products of this reaction were filtered cold, as before, and the filtrate divided into two parts.

Part 1. was hydrolysed at -20°C with water, and treated as in the first experiment of this section. Lead hydroxy bromide (5.31 g.) contaminated with basic magnesium halides was isolated.

lead content = 45%.

$Pb(OH)Br$ requires 68% lead.

i.e. this product is 66% pure.

The ether extract of the filtrate yielded mesitylene (2 g., infra-red identification).

Part 2 was refluxed for 3 hours when no apparent change was observed. This solution was divided into 2 parts:

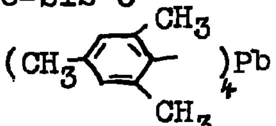
(a) The first part was hydrolysed with water, when the pale orange-brown colour changed to deep red, and then to pale yellow, with precipitation of a cream-white solid. This solid proved to be an inorganic lead compound, similar to lead hydroxy bromide but not identical; it was presumed to be one of the many basic lead halides.

Extraction of the filtrate with ether produced a pale yellow solid, and a further small quantity was extracted from the inorganic precipitate with chloroform. This yellow solid (1 g.) was organic, contained lead, and could not be crystallised. After precipitation from acetone it had a melting point of 210-218°C, with decomposition, and its' infra-red spectrum was consistent with a mesityl-lead compound.

(b) The second part was hydrolysed with alcohol, when the initial white precipitate redissolved on addition of more alcohol. A clear yellow solution was produced. On adding water a white solid was precipitated from solution. The products were filtered, and the solid proved to be another basic lead halide, not the same as the previous sample, and not lead hydroxy bromide. The chloroform extract of the filtrate produced a pale yellow solid (2 g.), which had an infra-red spectrum almost identical with that obtained in the previous case, (m.pt. 210-212°C). Analyses of these compounds were unsatisfactory.

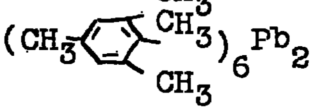
i.e. M.pt. 210-212°C Pb 30.8%; C 58.2%; H 6.3%

Calculated for



$((CH_3)_3C_6H_2)_4Pb$ Pb 30.25%; C 63.3%; H 6.48%

" "



$((CH_3)_3C_6H_2)_6Pb_2$ Pb 36.74%; C 57.5%; H 5.9%

(IV) Mesityl magnesium bromide (0.135 mole) in tetrahydrofuran (150 c.c.) was added to lead bromide (16.5 g., 0.045 mole) in tetrahydrofuran (50 c.c.) at -20°C. Benzyl chloride (6 g., 0.0475 mole) in tetrahydrofuran (20 c.c.) was added to this reaction product. After allowing the mixture to come to room temperature, the products were refluxed overnight. There was no precipitation of lead, and, on cooling the clear yellow solution, long needle crystals, presumably a magnesium halide-tetrahydrofuran complex, were obtained.

Water was added, when the crystals were found to dissolve. The solution was extracted with benzene, and the dried benzene extract pumped under high vacuum. A semi-solid, glass like material, containing lead, was obtained. This solid was soluble in petroleum ether, chloroform, benzene, hexane, carbon tetrachloride, and somewhat less soluble in ethanol and methanol. All attempts at crystallisation resulted in the production of the same semi-solid material.

Attempted distillation of this compound resulted in decomposition to lead at 160-180°C/0.001 mm.

The infra-red spectrum showed a close similarity to that of the suspected tetramesityllead, previously isolated. Furthermore, there was additional evidence of the presence of $-CH_2-$ groups.

Found C, 62.3%; H, 6.1%

Trimesitylbenzyllead, $C_{36}H_{40}Pb$, requires C, 63.9%; H, 6.7%

(V) Mesityl magnesium bromide (0.1 mole) in tetrahydrofuran (150 c.c.) was added to lead bromide (12.2 g., 0.033 mole). Ethyl acetate (2.94 g., 0.033 mole) in tetrahydrofuran (50 c.c.) was added to the red-brown product, and stirred overnight at 0°C.

After filtration, the tetrahydrofuran was removed using a high vacuum pump, and dioxane (100 c.c.) was added to the sticky red-brown solid. The red-brown colour faded, leaving an orange dioxane solution and an off-white solid containing magnesium. The filtered dioxane solution was pumped with a high vacuum pump, when a soft sticky solid was obtained. This material was extracted with hexane, giving an insoluble yellow solid, partly organic, and containing lead and magnesium. The clear orange hexane solution was pumped down leaving a low softening orange solid, which on purification with ethanol had an orange-yellow colour, with a melting point 60-110°C. The infra-red spectrum was consistent with tetramesityllead, and a molecular weight determination in benzene gave the result as 695 (tetramesityllead has m.wt. 684).

Found	Pb 29.8%;	C, 59.7%;	H, 6.4%
$C_{36}H_{44}Pb$ requires	Pb 30.25%;	C, 63.3%;	H, 6.48%

4. Reactions of Phenyl Magnesium Bromide with Lead Halides

Phenyl magnesium bromide (0.2 mole) in tetrahydrofuran was added to a vigorously stirred suspension of lead chloride (42 g., 0.15 mole) in tetrahydrofuran (50 c.c.), at -40°C. The products were stirred overnight at -78°C, and the resultant yellow-green solution was extracted with benzene and water, and filtered under nitrogen.

The precipitate was found to correspond to a mixture of lead hydroxy bromide and chloride (X ray evidence).

The benzene extract yielded a small quantity, (0.1 g.) of hexaphenyldilead.

The product of reaction between the Grignard and lead chloride decomposes to lead on standing for long periods at 0°C, and on standing at room temperature overnight.

(II) Phenyl magnesium bromide (0.15 mole) in tetrahydrofuran (120 c.c.) was added to lead bromide (18.35 g., 0.05 mole) in tetrahydrofuran (50 c.c.) at -20°C. The colour of the products passed through a deep red stage (at approximately 2 equivalents Grignard) to a final yellow-brown colour. The mixture was allowed to warm up to -10°C, and hydrolysed with water. It was found that the slow addition of water, caused the colour to return, momentarily, to the deep red colour observed during the addition.

The products of hydrolysis were filtered under nitrogen, and the filtrate extracted with benzene and water. The white solid residue, which contained no organic material, was found to be lead hydroxy bromide (14 g., 92%, based on lead) by X ray analysis.

The dried benzene extract yielded a small quantity (0.1 g.) of tetraphenyllead (m.pt. and mixed m.pt. 234-236°C. corr.) on evaporation.

(III) Phenyl magnesium bromide (0.162 mole) in tetrahydrofuran (150 c.c.) were added to lead bromide (19.98 g., 0.0545 mole) in tetrahydrofuran (100 c.c.) at -20°C. Benzyl chloride (6.7 g., 0.053 mole) in tetrahydrofuran (20 c.c.) was added to the reaction product. After warming to room temperature the reaction mixture was refluxed overnight. Some decomposition to lead occurred, and the lead (3.6 g., 32%) was filtered off. Benzene (100 c.c.) was added to the filtrate, which was then hydrolysed with water producing a white solid.

This white solid was filtered and extracted with chloroform, when tetraphenyllead (6 g., m.pt. and mixed m.pt. 233°C. corr.) was obtained. The remaining solid (0.9 g.) was inorganic, and found to be lead hydroxy bromide.

Evaporation of the benzene extract yielded a further quantity of organo-lead compounds. After extraction with alcohol, and recrystallisation from alcohol, benzyltriphenyllead (2.5 g., 9%; m.pt. and mixed m.pt. 92.5°C) was obtained as a crystalline solid. A further quantity of tetraphenyllead (1 g.) was also isolated. Total yield tetraphenyllead = 7 g. i.e. 33% (based on phenyl).

(IV) The above experiment was repeated with phenyl magnesium bromide (0.1 mole), lead bromide (36.7 g., 0.1 mole), and benzyl chloride (5.06 g., 0.04 mole). After addition of the Grignard to lead bromide the reaction products were bright yellow, and, after filtration, the filtrate was orange-red, and the residue white. Benzyl chloride was refluxed with the filtrate overnight.

Recovered:-	tetraphenyllead	8.5 g.	66% Yield
	benzyltriphenyllead	1.5 g.	8.5%
	lead	2.5 g.	
	unreacted lead bromide	16.7 g.	
	other inorganic lead salts + lead	5.3 g.	

(Yields based on phenyl)

(V) Magnesium bromide, from ethylene dibromide and magnesium in tetrahydrofuran, was shaken, in tetrahydrofuran/water solution, with an equimolar quantity of lead hydroxide (from lead nitrate and ammonia). It was found that lead hydroxy bromide was formed (X ray evidence).

i.e. $Pb(OH)_2 + MgBr_2 \longrightarrow Pb(OH)Br + Mg(OH)Br$

(VI) Phenyl magnesium bromide (0.1 mole) in tetrahydrofuran (100 c.c.) was added to a vigorously stirred suspension of lead bromide (18.35 g., 0.05 mole) in tetrahydrofuran (50 c.c.), under nitrogen, at -25°C. Tetrahydrofuran was removed under vacuum from the orange solution, dry, cold methylene chloride was added, and the resulting orange solution filtered. Methylene chloride was removed from the filtrate at 0°C under vacuum, when an orange-red solid, containing lead and magnesium, was obtained.

Addition of benzene produced two layers, one a yellow-orange layer containing lead and magnesium, and a deep red layer, which, on removal of benzene under vacuum, produced a dark coloured, sticky solid. This dark coloured solid still contained lead and magnesium, decomposed to a yellow powder in air, and addition of water produced lead hydroxy bromide and a small quantity of hexaphenyldilead.

PART 2

THE CHEMICAL REACTIONS OF ALKALI METAL AROMATIC COMPOUNDS

SUMMARY

The reaction of a unique type of alkali-metal aromatic compound, potassium graphite, with various organic halides is described.

Potassium and graphite form a series of compounds[2], KC_8, KC_{24}, KC_{36}, KC_{48}, KC_{60}, in which potassium atoms are accommodated interstitially in the graphite layers. In nearly all reactions the compound, KC_8, was used, with a view to determining,

(i) the order of reactivity

and (ii) whether the reaction products differ from those expected from a normal Wurtz reaction.

Reaction with the following halides is described:-

(i) the phenyl halides,

(ii) benzyl chloride and benzyl bromide,

(iii) α-chloroethylbenzene, diphenylchloromethane, and triphenylchloromethane,

(iv) benzoyl chloride,

and (v) dipropylboron chloride and triphenyltin bromide.

The reaction products do not differ significantly from those expected from a normal Wurtz reaction. All

products are consistent with the formation of free radicals, either directly or via an intermediate organo-potassium compound, RK. In some cases the products could be accounted for without postulating the presence of free radicals.

$$RX + K \longrightarrow R\cdot + KX$$

Reactions with benzoyl chloride and triphenyltin bromide are described, in which organic material may be strongly attached to the residual potassium graphite structure, either as benzoyl and triphenyltin radicals, or, in the case of the tin compound, as $\left[Ph_3Sn{-}Sn{-}Ph_3\right]^{--}2K^{++}$.

An interesting steric effect, produced by the graphite layer structure, is demonstrated by the comparative reactivities shown by the phenyl halides, and other organic halides, towards potassium graphite. The relative rates of reaction are

$$PhCl \gg PhCH_2Cl \gg Ph_2CHCl$$

and $$PhF < PhCl > PhBr > PhI$$

A steric factor is also demonstrated by the reaction of the phenyl halides, in solution, with potassium shot, whereby the normal sequence of reactivities is reversed; i.e. the relative rates of reaction are:-

$$PhF > PhCl > PhBr > PhI$$

INTRODUCTION

Alkali metal-organic compounds can be divided into four groups.

(I) Lithium compounds, which, although predominantly covalent in nature, have a partial negative charge on the organic radical, resulting in high reactivity, e.g. C_6H_5Li

(II) Organic derivatives of the other alkali metals, in which there is no means whereby the negative charge on the organic radical can be delocalised. The resulting localisation of almost a full negative charge on the organic radical, is the seat of the intense reactivity of these compounds, e.g. $C_6H_5^-Na^+$

(III) Derivatives of the alkali metals, in which there is no localisation of the negative charge on the carbanion, e.g. $[C_6H_5\dot{C}H_2]^-Na^+$, $[Ph_2C\cdot CPh_2]^=Na_2^{++}$

(IV) Derivatives of the alkali metals, in which there is no localisation of negative charge on the carbanion, and in which the alkali metal is not substituted, or added onto a double bond. There is simply an electron transfer from the metal to the organic molecule, e.g. $[C_6H_5-C_6H_5]^-Na^+$, sodium diphenyl.

This present work involves the reactions of a compound, potassium graphite, in which there is electron transfer from the metal to the graphite layers. Hence potassium graphite may be regarded as belonging to this last type of alkali metal-aromatic compounds.

Graphite crystallises in a layer lattice structure, in which each layer is separated by a distance of 3.355Å. Each layer is a regular sheet of linked hexagons, in which each carbon atom is linked by a strong covalent type bond to its three neighbours, all carbon-carbon bond distances within the layer being 1.41Å. The electrons representing the fourth valency of the carbon atoms are not localised in any definite bond, but are shared by the whole layer, as is the case of the π electrons in large aromatic molecules. These electron sheets explain the high electrical conductivity of graphite. The weakness of the interlayer bonding explains the reason why graphite forms a large number of intercalation compounds, in which the interlayer spacing can, if needed, be extended from 3.355 to 10 or 11Å.

Graphite forms two types of intercalation compounds:-

(I) In which the intercalated atoms are linked by strong homopolar bonds. In this case the intercalated atoms are not easy to remove, and,if this were possible, it would result in the breakdown of the graphite structure. Examples of this type are graphite oxide and the graphite-fluorine compounds.

(II) In which the intercalated atoms are linked by polar bonds. The majority of graphite compounds, including the alkali metal compounds, fall into this class. Here it is comparatively easy to remove the foreign atoms and regain the graphite structure. Other examples of this type are the halogen compounds (not fluorine), the metal halide compounds, and the graphite salts.[1]

Graphite reacts readily with the alkali metals, potassium, rubidium, and cesium, in the molten or vapour state, to produce graphite-alkali metal compounds. Fredenhagen et al[2] obtained compounds differing in colour according to the temperature and vapour pressure of the metal. The first compound corresponded to a formula MC_8, and was said to have a bronze-red colour. On heating it was found that metal is lost and a steel blue product is obtained. On further heating all the metal can be distilled off, leaving graphite.

The composition of the blue compound was, at first,[3] thought to be MC_{16}, but it was later shown,[4,5] by X ray data and analysis, that the composition is, in fact, MC_{24}. This result was supported by the work of Hérold,[6] who found that sudden breaks in the curve of temperature against composition, for the potassium-graphite system,

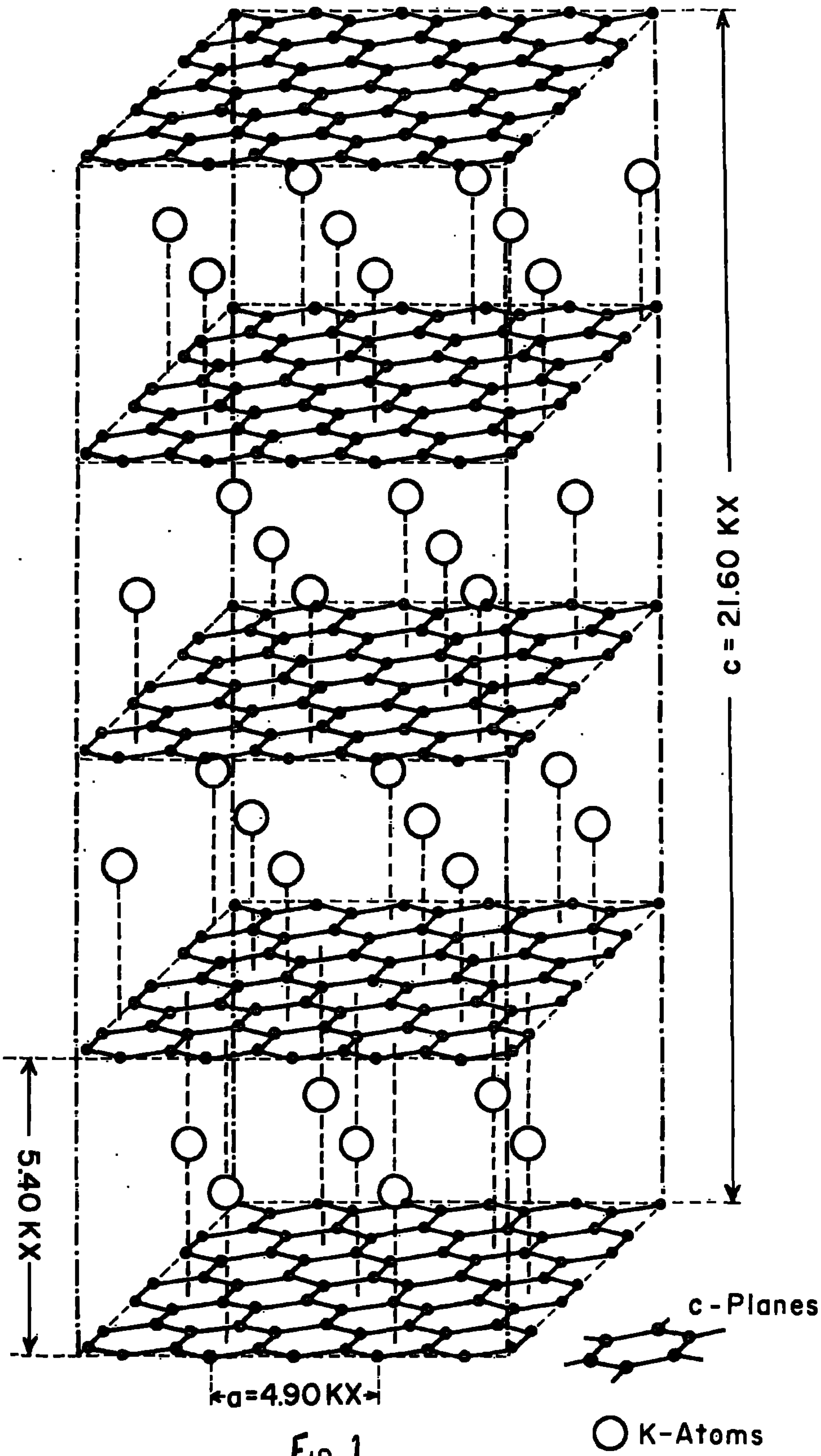


Fig. 1

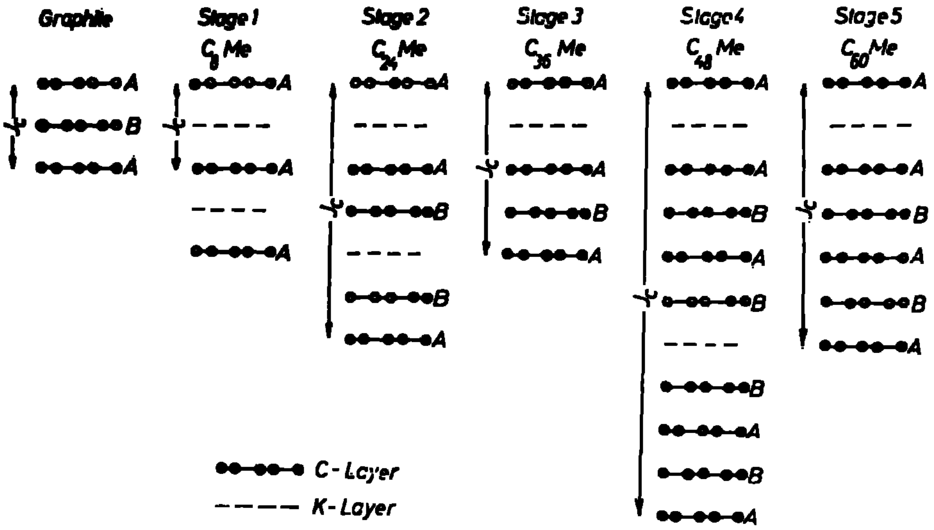

Graphite
Stage 1
C_8Me
Stage 2
$C_{24}Me$
Stage 3
$C_{36}Me$
Stage 4
$C_{48}Me$
Stage 5
$C_{60}Me$
A
B
c
C-Layer
K-Layer

Fig. 2

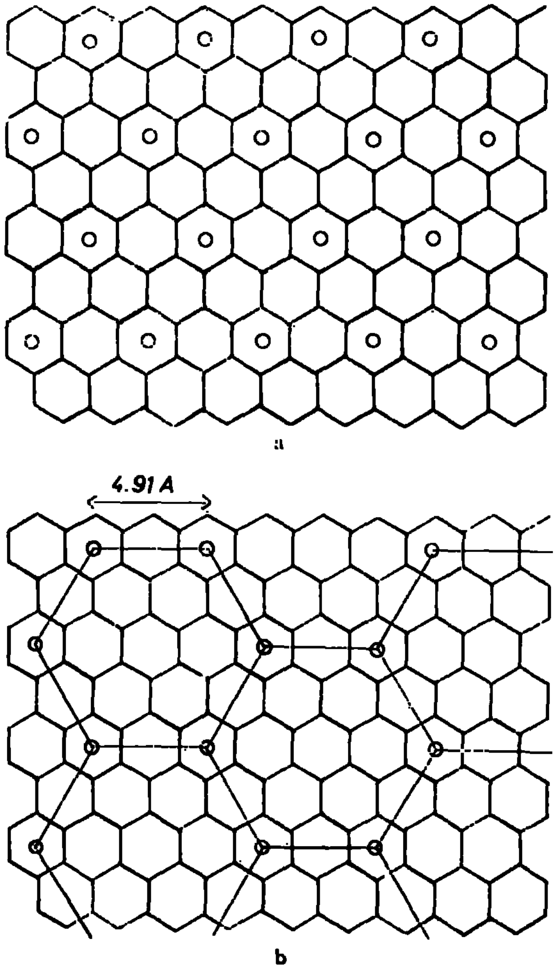

a
4.91 A
b

Fig. 3

indicated the existence of KC_8, KC_{24}, and KC_{40}.

The following range of compounds was obtained by Rüdorff and Schulze:-[4]

MC_8, MC_{24}, MC_{36}, MC_{48}, MC_{60}

The structure of the MC_8 compounds (Fig. 1), involves the intercalation of metal atoms, between each graphite layer, in the form of a triangular net, of edge 4.91Å, (Fig. 3a) exactly twice that of the hexagonal "a" axis of the carbon net. Furthermore the stacking, sequence of layer planes changes from ABAB, in graphite itself, to AAAA, resulting in each metal having 12 carbon atoms equidistant from it.

The compound, MC_{24} (Fig. 2), has only alternate interlayer spacings occupied. It is now easy to understand how a formula, KC_{16}, is arrived at, since occupation of alternate layer spacings would give this formula. However in MC_{24} every third metal atom is removed from the triangular net, resulting in the formation of a hexagonal net, (Fig. 3b).

In the remaining compounds described, MC_{36}, MC_{48}, and MC_{60}, in which the formulae are whole number multiples of C_{12}, (M being constant), this hexagonal network is present, but more interlayer spacings are unoccupied (Fig. 2).

Whilst potassium, rubidium, and cesium enter the lattice very readily, sodium and lithium do not appear to form the same type of compounds. Fredenhagen[2] found that sodium reacts with soot but not with graphite. Hérold[7] managed to intercalate sodium with cesium, using a sodium-cesium alloy, but the ratio of sodium to cesium was only 0.12. Recently Asher and Wilson[8] obtained a deep violet compound corresponding to a composition, $C_{64}Na$, by heating sodium and graphite in a glove box, under a helium atmosphere.

Hérold reports that heating lithium with graphite at 500°C, the ultimate product is the carbide, LiC_2, but at intermediate stages, yellow products result, which give hydrogen as well as acetylene on hydrolysis with water. However no definite interstitial lithium compound has been reported.

The bonding in graphite-alkali metal compounds can be considered as intermetallic, with a limiting structure of M^+ graphite$^-$. This is evident in the great increase in electrical conductivity as metal atoms are intercalated,[9] i.e. as electrons are added to the conducting bands of the graphite layers.

Although a considerable amount of physical data has been obtained, little attempt has been made to investigate the chemical reactivity of these compounds. They react vigorously with water to give hydrogen, potassium hydroxide, and graphite; no acetylene is formed, i.e. they are not acetylides. The compounds MC_8 spark in the air, and lower compounds sometimes generate sufficient heat to make the whole mass glow. This air sensitivity makes it necessary to handle these compounds in nitrogen.

Reaction with liquid ammonia produces compounds of the type, $C_{12}M(NH_3)_2$,

$$3C_8M + 4NH_3 \longrightarrow 2C_{12}M(NH_3)_2 + M$$

Similar compounds are formed with methylamine and other amines. The interlayer spacing in these compounds is determined by the amine and not the metal. The spacing in the compounds containing ammonia is approximately 6.6Å for all the metals. Sodium and lithium form these compounds, from graphite and a solution of the metal in liquid amine.

The only organic reactions reported are the polymerisation of ethylene and the alkylation of certain aromatic hydrocarbons. Podall and Foster[10] found that ethylene is polymerised, under pressure, and at a temperature of 300°C, by potassium graphite, KC_8. It is suggested that this is due to the intermediate formation of ethyl potassium. Ethyl potassium is formed from diethyl zinc and potassium graphite,

$$Et_2Zn + KC_8 \longrightarrow EtK$$

$$Et_2Zn + KC_8 \longrightarrow KEt_3Zn$$

When aromatic hydrocarbons were used as solvents in these polymerisation experiments, alkylation of the benzene nucleus occurred, giving a variety of substituted benzenes.

No other reactions involving alkali metal-graphite compounds have been reported. This present work deals with the reaction of potassium graphite with various organic halides.

DISCUSSION

The present work began with the idea that the normal course of the Wurtz type of reaction might be modified, if the reaction between potassium graphite and organic halides occurs essentially at the graphite surface. For example, whereas a diorgano-boron halide reacts with potassium to give mainly the triorgano-boron[21] and degradation products, potassium graphite may react to give a tetraorgano-diboron, $R_2B\text{-}BR_2$, if the reaction were modified by the graphite surface.

Since no data is available on the reaction of potassium graphite with organic halides, it was decided, initially, to investigate the reaction of various organic halides with potassium graphite, with a view to determining

(i) the order of reactivity

and (ii) whether the reaction products differ significantly from those expected from a normal Wurtz reaction.

(1) Order of Reactivity

The first reactions were carried out with benzyl chloride, and benzyl bromide, in methylcyclohexane. It was found, using a concentration of potassium equivalent to KC_8, and a molar ratio of potassium to halide of approximately 3:1, that 50% of the benzyl chloride was recovered, unreacted, after refluxing for 64 hours. This is a comparatively slow reaction, and it may appear that the graphite is merely acting as a diluent in the reaction.

When this reaction was repeated using chlorobenzene, it was immediately noticed that reaction appeared to take place far more quickly. As a purely visual aid in estimating the extent of reaction, the blackening of the bronze colour of KC_8 proved to be quite useful. In the experiment with potassium graphite it was found that the formation of the blue-black colour of KC_{16} (actually a mixture of KC_8 and KC_{24}) appeared to be complete in only 3 hours.

These observations were verified in later experiments, and are quite surprising. It would be expected that benzyl chloride, with a C-Cl bond strength less than that of chlorobenzene, would react more rapidly.

D.$PhCH_2$-Cl	68	K.cals/mole[14]
D.Ph-Cl	85.6	K.cals/mole.

It is clear that some considerable steric effect must be present, and that this must be due to the structure of potassium graphite.

To clarify the situation a series of rate determination reactions was completed, using chlorobenzene, benzylchloride, α-chloroethylbenzene, diphenylchloromethane, and triphenylchloromethane. It must be pointed out that no attempt was made to measure absolute reaction rates. Indeed, it is doubtful if the simple experimental techniques used would lend themselves to accurate, absolute determinations. However the reaction conditions were duplicated as faithfully as possible, in each experiment, so that comparative reaction rates were as accurate as possible. It is noted that loss of solvent (B.pt. 100°C) must occur to some extent, on prolonged refluxing, even using a good water condenser, thus altering the halide concentration. However the important results are so striking in their differences, that it is unlikely that the probable loss of solvent has any significance.

The results are summarised on page 146, and show the striking difference in the reactivities of chlorobenzene and benzyl chloride. As expected, diphenylchloromethane reacts even more slowly than does benzyl chloride;

i.e. the reactivity $PhCl > PhCH_2Cl > Ph_2CHCl$.

The case of α-chloroethylbenzene must seem somewhat anomalous, since, although initially it reacts more slowly than the smaller molecule, benzyl chloride, the results suggest that the rate of reaction increases, and in the later stages it reacts more quickly than benzyl chloride. A possible explanation may be found in the fact that polystyrene is isolated from this reaction in 80% yield, hence it is possible that a dehydrohalogenation reaction takes place, as well as a dehalogenation reaction. If the dehydrohalogenation reaction is slow to start, but then proceeds quite rapidly, then this would offer some explanation for the results obtained.

The reactivity exhibited by triphenylchloromethane also does not fit in with the postulated steric effect. This large molecule should react very slowly with potassium graphite, but in fact it reacts more rapidly than does diphenylchloromethane. However the stability of the triphenylmethyl radical is such that it may well outweigh any steric considerations. In a reaction of the type

$$RX + K \longrightarrow R^{\bullet} + KX$$

the rate of reaction may be governed by either

(i) the strength of the R-X bond,

(ii) the stability of the radical R•,

or (iii) the accessibility of the potassium to the halide.

Only in the case of the triphenylmethyl radical does the stability of the radical appear to outweigh the steric effect.

The nature of the steric effect, itself, is probably fairly obvious. In potassium graphite, the graphite layers are 5.41Å apart, and the potassium atoms (or ions) are screened by the graphite layers. Hence the halide must attack, via the edges of the layer planes of the graphite crystal. This, in itself, would offer some hindrance to reaction, but other factors may well contribute to produce a substantial steric effect.

(1) Access to the potassium ions, further from the surface, may be inhibited by adsorbed, or bonded, organic reaction products. There is no reason to suspect that potassium halides, formed in the reaction, are intercalated, thus blocking further reaction. No potassium halide intercalation compound has, in fact, been reported, and it is unlikely that the temperature of these reactions would be high enough for the formation of such a compound.

(ii) It has also been suggested[15] that when an intercalated atom is leached out, near the edge of the graphite crystal, the interplaner distance reverts to about the value of graphite itself, before the reactant can penetrate into the crystal, and before the intercalated compound can diffuse out. This is evident in the heterogeneity of leached preparations, in which the crystal is composed of undecomposed material surrounded by a thick skin of graphite.

It will be appreciated that the steric hindrance caused by such a phenomenon would be considerable.

Experiments were also carried out with the phenyl halides, and the results, summarised on page 147, show that halide size influences the reaction rate. The relative rates of reaction are:

$$PhI < PhBr < PhCl > PhF.$$

The result, that reaction proceeds more rapidly with chlorobenzene than with fluorobenzene is not very conclusive. They do react at comparable rates, and it may well be that at this point the greater bond strength of the C-F bond, and the greater steric effect, caused by the larger chlorine atom, tend to balance.

In order to compare these results with the reactivities shown towards potassium, similar experiments were carried out with the phenyl halides, and benzyl chloride, and potassium shot. It was found that, with the halides in solution and potassium in a fine shot form, the relative reactivities were found to be quite the reverse of those quoted in text books,

i.e. $PhI < PhBr < PhCl < PhF$.

Since the bond strength, C-X, certainly decreases from fluorine to iodine, some inhibition process must occur. In a heterogeneous reaction of this type, it is difficult to imagine any significant inhibition process other than the coating of the potassium shot with potassium halide. The reaction rate is then dependent on penetration of this halide layer, or its removal by vigorous stirring. There seems to be no reason why one potassium halide should be removed, from the potassium surface,more quickly than another, and hence it seems that the most likely factor is the penetration of the halide coating. This would then explain the results obtained, for it would be expected that the larger phenyl iodide would have the greatest difficulty in penetrating the halide coating, and the smaller fluoride the least difficulty.

However it was found that benzyl chloride does, in fact, react slightly more rapidly with potassium, than does chlorobenzene. This emphasises the steric effect produced by the graphite layers in potassium graphite, as previously described.

(2) Reaction Products

To summarise this section, it can be said that the products of reaction are essentially those expected from the reaction of potassium itself, either by the direct production of free radicals,

$$\text{i.e.} \quad RX + K \longrightarrow R\cdot + KX$$

or by the production of an intermediate organo-potassium compound.

A brief discussion on free radicals is presented in Part I of this thesis (page 13) and no attempt will be made to enlarge on this here.

Bryce Smith[16] concludes, from experiments with alkyl halides and alkali metals, and their organo compounds, that the normal course of the Wurtz reaction in solution is via the organo-metal derivative, i.e.

$$\begin{array}{lll}
(1) & RI + 2M \longrightarrow & RM + MI \\
(2) & RM + RI \longrightarrow & 2R\cdot + MI \\
(3) & 2R\cdot \longrightarrow & R\cdot R \\
 & \longrightarrow & R(-H) + R(+H) \\
(4) & R\cdot + \text{solv} \longrightarrow & RH + \text{solv}\cdot \\
(5) & RM + RI \longrightarrow & R\text{-}R + MI \\
(6) & RM + RI \longrightarrow & R(-H) + R(+H) + MI
\end{array}$$

Evidence is presented[16] to show that free radicals are only produced to any appreciable extent when lithium is used, and then by reaction 2. When sodium and potassium are used the normal course of the reaction is via 5 and 6.

In the present work no attempt was made to find out if the reaction proceeds via a potassium-organo compound or by the direct production of free radicals. The work of Bryce-Smith would seem to point to the intermediate formation of an organo-potassium compound. However it must be borne in mind that the work of Bryce-Smith was confined to the alkyl series. When the more resonance stabilised, aromatic radicals are used (e.g. benzyl), it might be expected that the direct production of free radicals plays a more prominent role.

The corresponding gas phase reactions[17] do involve the production of free radicals, unlike the Wurtz reactions in solution. Bryce-Smith suggests that in the gas phase, free metal atoms, at high temperature and low pressure, are not so likely to capture free radicals, as is the case with bulk metal in solution (Bryce-Smith used metal wire). In potassium graphite, potassium ions are dispersed uniformly in the graphite lattice, so that there is no bulk metal present. In this case it may be that there is a certain 'gas phase' character present, resulting in the direct formation of free radicals, in reaction with organic halides.

(3) Formation of Free Radicals

The reaction of phenyl halides with potassium graphite produces benzene, and diphenyl, together with a small amount of tar. These products are consistent with the intermediate formation of phenyl radicals. However the yield of diphenyl is surprisingly high, some 20-30%, and this would seem to point to the Bryce-Smith mechanism

$$K{\cdot}Ph + PhX \longrightarrow KX + Ph\text{-}Ph.$$

Even so, phenylcyclohexane has been isolated from reactions in cyclohexane, and 4,4'-dimethyldicyclohexyl, or an isomer, has been isolated from reaction in methylcyclohexane. These products are almost certainly formed by radical attack on solvent.

$$\mathrm{Ph\cdot + C_6H_{12} \longrightarrow PhH + C_6H_{11}\cdot}$$
$$\mathrm{Ph\cdot + C_6H_{11}\cdot \longrightarrow Ph{-}C_6H_{11}}$$
$$\mathrm{Ph\cdot + CH_3C_6H_{11} \longrightarrow PhH + CH_3C_6H_{10}\cdot}$$
$$\mathrm{2CH_3C_6H_{10}\cdot \longrightarrow CH_3C_6H_{10}\cdot C_6H_{10}CH_3}$$

High yields of dibenzyl (80%) are obtained from the reaction of benzyl chloride with potassium graphite. This, too, is consistent with the formation of free radicals. High yields of dimer would be expected from a resonance stabilised radical, such as benzyl.

$$\mathrm{PhCH_2Cl + KC_8 \longrightarrow PhCH_2\cdot + KCl}$$
$$\mathrm{2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph}$$

2,3-diphenylbutane and 1-phenyl-1-cyclohexylethane were isolated from the reaction with α-chloroethylbenzene.

$$\mathrm{PhCH(CH_3)Cl + KC_8 \longrightarrow Ph\dot{C}H(CH_3) + KCl}$$
$$\mathrm{2Ph\dot{C}H(CH_3) \longrightarrow PhCH(CH_3)\cdot CH(CH_3)Ph}$$
$$\mathrm{Ph\dot{C}H(CH_3) + C_6H_{12} \longrightarrow PhCH_2CH_3 + C_6H_{11}\cdot}$$
$$\mathrm{C_6H_{11}\cdot + Ph\dot{C}H(CH_3) \longrightarrow PhCH(CH_3)\cdot C_6H_{11}}$$

Ethylbenzene was not isolated, but the small quantity formed would probably have distilled in the cyclohexane, and its recovery would prove difficult.

A good yield of 1,1,2,2-tetraphenylethane (48%) was isolated from the reaction with diphenylchloromethane,

$$Ph_2CHCl + KC_8 \longrightarrow Ph_2CH\cdot + KCl$$

$$2Ph_2CH\cdot \longrightarrow Ph_2CH\cdot CHPh_2$$

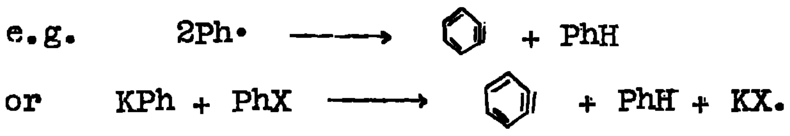
and a mixture of ethane and ethylene was obtained from the reaction with ethyl bromide.

$$C_2H_5Br + KC_8 \longrightarrow C_2H_5^{\bullet} + KBr$$

$$2C_2H_5^{\bullet} \longrightarrow C_2H_6 + C_2H_4$$

Butane, too, is undoubtedly formed, but its separation from pentane, the reaction solvent, was not attempted.

It is recognised that these products could also have been formed by the mechanism of Bryce-Smith. However it is suggested that when the highly stabilised, aromatic radicals are involved, it is equally probable that free radicals are directly formed. In the case of phenyl and ethyl the Bryce-Smith mechanism seems more likely. The possibility also exists of the formation of the benzyne intermediate, for which there is now considerable evidence.[18,19]



(4) Reaction with Benzoyl Chloride

Reaction of potassium graphite with benzoyl chloride proved to be rather complicated, and a variety of products were obtained. The products isolated from the solvent extraction proved to be varieties of $(PhCO)_n$. Both cis (1-2%) and trans isobenzil, $(PhCO)_4$, were isolated, the trans always in greater yield (1-5%). A yellow polymeric material, analysing approximately to $(PhCO)_n$ was isolated, and attempts to crystallise this compound met with no success. On heating in vacuum, this compound gave a hard glassy tar. High yields of dark, solid, tarry material were also isolated.

Probably the most interesting feature to these reactions, are the products obtained on hydrolysis of the graphite residues with ethanol. Using KC_8 appreciable quantities of solid tarry material are isolated, but when the reaction is repeated using KC_{16} (actually a mixture of KC_{24} and KC_8) then benzoic acid (10-20%) is obtained in addition to tar. Hitherto only small quantities of tar had been obtained on hydrolysis of the graphite residues. This was the first product obtained, which could be characterised. It seems probable that benzoyl groups are bonded to the graphite structure in some way, and are removed, as potassium benzoate, on hydrolysis. It is difficult to understand why benzoic acid is produced only when KC_{16} is used in the reaction.

(5) Reaction with Organo-Metal Compounds

Reaction of KC_8 with triphenyltin bromide resulted in only milligram quantities of hexaphenylditin being isolated in solvent extraction with cyclohexane and benzene. However after ethanolic hydrolysis an appreciable quantity of hexaphenylditin (43%) was obtained. Here again this may suggest that triphenyltin radicals are attached to the graphite surface, and only removed on hydrolysis. It is also possible that a salt of the type, $[Ph_3Sn{\cdot}SnPh_3]^{--}2K^{++}$, is formed.

Reaction with dipropylboron chloride results in the formation of tripropylboron and tarry material. The mechanism for this reaction is not known, and it can only be suggested that the intermediate formation of tetrapropyldiboron is involved. Decomposition then results in the formation of tripropylboron. This result is essentially the same as obtained from the reaction of diphenylboron chloride[20] and potassium, with the exception that less tarry material is formed.

In conclusion it can be said that the products of reaction do not differ from those expected in the normal Wurtz type of reaction, in solution, except in those cases where organic groups are attached to the graphite surface in some way. The most interesting point emerging is the steric effect produced by the graphite layers. It may be profitable to investigate the polymerisation of olefines, in those cases where organic material has been found to adhere to the graphite surface.

EXPERIMENTAL

1. Preparation of Potassium Graphite, KC_8

The potassium graphite used in most of these experiments was prepared from powdered, synthetic graphite (25 g.), and clean potassium (9 g.), according to the method of Podall and Foster.[10]

The graphite was placed in a 500 c.c. three necked flask, having one of the side necks about 20 cm. longer than the others, and stirred by means of a tantalum wire, Herschberg stirrer. The graphite was flamed dry in a good stream of nitrogen, before heating to a bath temperature of 300°C, in a Wood's metal bath. Small pieces of potassium, rinsed in cyclohexane, were added down the long limb of the flask, over a period of 30 minutes, maintaining vigorous stirring throughout the addition.

The product, consisting mainly of KC_8, with a small percentage of KC_{24}, was bronze-red in colour.

2. Preparation of Organic Halides

(i) Diphenylchloromethane, $(C_6H_5)_2CHCl$, was prepared according to the method of Ferinacci and Hammett[12], by passing dry hydrogen chloride through a solution of benzohydrol (75 g.) in a benzene/petroleum ether mixture (300 c.c.), in the presence of anhydrous calcium chloride

Distillation of the organic layer gave diphenylchloromethane, (B.pt. 90°C/0.1 mm; bath temperature, 140°C).

Found, Cl 17.5%

Calculated for $C_{13}H_{11}Cl$, Cl 17.5%

(ii) <u>α-Chloroethylbenzene</u>,[13] $C_6H_5CH(CH_3)Cl$, was prepared by passing dry hydrogen chloride into styrene at room temperature. Distillation gave α-chloroethylbenzene, (B.pt. 72°/11 mm).

Found, Cl 24.5%

Calculated for C_8H_9Cl Cl 25.2%

(iii) <u>Dipropylboron chloride</u>, Pr_2BCl, was prepared by saturation of tripropylboron with boron trichloride, and distilling, from the same flask, in a stream of boron trichloride, (B.pt. 124-128°C).

3. Purification of Solvents

<u>Cyclohexane</u> and <u>methylcyclohexane</u>, for use in these experiments, were dried with sodium wire.

Cyclohexane and methylcyclohexane, for use in ultraviolet work, were obtained free from olefines and other impurities by the following method. Two litres of solvent were stirred vigorously with concentrated sulphuric acid (200 c.c.) until the acid was coloured brown. Fresh lots of acid were used, until only a faint yellow colouration was observed on prolonged stirring. The solvent was separated from acid, washed, dried over anhydrous magnesium sulphate, and finally distilled over sodium.

4. Reaction of Potassium Graphite with Organic Halides

(i) Reaction with Benzyl Bromide and Benzyl Chloride

Benzyl bromide (30 g., 0.175 mole) in methylcyclohexane (150 c.c.) was added to potassium graphite, made from graphite (25 g., 2.08 mole) and potassium (9 g., 0.23 mole) as previously described. There appeared to be no initial reaction, and the mixture was refluxed for 2.5 hours under nitrogen.

The reaction products were transferred under nitrogen, by means of polythene tubing, to a soxhlet thimble, placed inside a nitrogen purged, soxhlet extraction apparatus. The graphite residues were then extracted with hot methylcyclohexane for several hours.

The solvent was distilled through a good column (30 cm., packed with glass helices), and the residual brownish coloured liquid distilled through a 15 cm, indented column, under a water pump vacuum. Benzyl bromide (20 g., 67%) was recovered, and the dark viscous residue in the distillation pot slowly crystallised on cooling,to give dibenzyl (2.5 g., 15.6%), which on recrystallising from alcohol had a melting point and mixed melting point of 52.5°C.

The results of other experiments, carried out in the same way, with the same quantity of potassium graphite, are summarised below.

Halide	Reflux Time	Recovered Halide	Dibenzyl
Benzyl bromide (30 g., 0.176 mole)	2.5 hrs	67%	15.6%
Benzyl bromide (30 g., 0.176 mole)	40	40	31
Benzyl bromide (15 g., 0.088 mole)	44	-	81
Benzyl chloride (11 g., 0.087 mole)	64	50	40

(ii) Reaction with Phenyl Halides

(a) Bromobenzene (15 g., 0.0955 mole) in methylcyclohexane (100 c.c.) was added to potassium graphite (25 g. graphite; 9 g. potassium), when a slight initial exothermic reaction was noticed. After 2 hours refluxing it was noticed that the bronze-red colour of KC_8 had given way to the blue-black of KC_{24}. After a total of 16 hours refluxing the products were transferred to a soxhlet, and extracted as previously described.

On distillation, no excess bromobenzene was recovered, but diphenyl (2.5 g., 34%) was sublimed from the dark tarry residue (3.5 g.). Diphenyl was characterised by melting point and mixed melting point, 70-71°C.

In a similar experiment a high boiling oil (0.2 g.) was distilled from the tarry residue, (after sublimation of diphenyl (1.5 g., 20%)), using a microdistillation apparatus. An infra-red spectrum, of a redistilled sample of this oil, showed a strong resemblance to that of 1,2-dicyclohexylethane, but the presence of methyl groups was also indicated. This suggests an isomer, e.g. 4,4'-dimethyldicyclohexyl.

Found	C,	86.6%	H,	13.5%
Calculated for $C_{14}H_{26}$	C,	86.5%	H,	13.5%

The results of experiments, carried out in a similar way, are summarised below.

Halide	Reflux Time	Recovered Halide	Diphenyl	Other Products
Bromobenzene (0.0955 mole)	16 hrs.	- %	34%	1 g. tar
Bromobenzene (0.0955 mole)	24	-	20	0.9 g. tar 0.2 g. oil
Chlorobenzene (0.106 mole)	24	-	27	0.5 g. tar
Fluorobenzene (0.105 mole)	3	-	29	0.3 g. tar

(b) Detection of benzene

Infra-red spectra of the methylcyclohexane distillates of the reactions in the previous section, indicated the presence of benzene. The solvent used, however, was found to be unsatisfactory for obtaining ultra-violet spectra, and reactions were therefore carried out in solvent, especially purified for ultra-violet absorption work.

(i) Bromobenzene (15 g., 0.0955 mole) in cyclohexane (100 c.c.), was refluxed for 16 hours with potassium graphite (25 g. graphite; 9 g. potassium). After extraction and distillation, an ultra-violet spectrum, identical with that of benzene (American Petroleum Institute, Project 44, Serial No. 1), was obtained from the distillate. Using a value of, $\xi = 230$, for the extinction coefficient at 255 μ (Gillam and Sterne, "Electronic Absorption Spectra"), a 40% yield of benzene (2.98 g.) was obtained.

Also isolated were diphenyl (1 g., 13%), and phenylcyclohexane (approximately 1.5 g., 9%). The diphenyl and phenylcyclohexane were partially separated by distillation in a microdistillation apparatus, using a good vacuum. It was found that diphenyl sublimed onto the cold surface of the cold finger, whereas phenylcyclohexane tended to run into the cup attached at the bottom of the cold finger. Although pure diphenyl was obtained by recrystallisation of the sublimate from alcohol, it was found impossible to remove traces of diphenyl from the oil. However an infra-red spectrum was found to be identical with that of phenylcyclohexane, except for slight shifts in the third order, due, presumably, to the diphenyl impurity.

(ii) The following results were obtained in a similar experiment with iodobenzene (20 g., 0.098 mole), on refluxing with potassium graphite (25 g. graphite; 9 g. potassium) for 6 hours.

Compounds isolated:-

1.	Bromobenzene	0 g.	0% Yield
2.	Benzene	0.2 g.	2.6%
3.	Diphenyl	1.0 g.	13.6%
4.	Tarry material	0.1 g.	
5.	4,4'-dimethyldicyclohexyl	2.2 g.	

(iii) Reaction with Benzoyl Chloride

(a) Benzoyl chloride (14 g., 0.1 mole) in methylcyclohexane (80 c.c.) was added to potassium graphite (25 g. graphite, 9 g. potassium), under nitrogen. After a slight initial exothermic reaction was detected, the mixture was refluxed for 115 hours, and extracted as before.

Distillation of the solvent produced a sticky tarry residue (7 g.; 100% yield PhCO• = 10.5 g.). Extraction of this material with alcohol produced a yellow amorphous solid (1.5 g.), which could not be crystallised, but was precipitated from ethanol solution by slow evaporation of the ethanol. After chromatographing (alumina column) it was found to darken at 163°C, melting to a red sticky liquid at 172-176°C.

Found	C, 81.0%	H, 5.1%
$(PhCO)_n$ requires	C, 80 %	H, 4.8%

After precipitation of the yellow material from the ethanol solution, ethyl benzoate (1 g.) was isolated from solution by distillation in a microdistillation apparatus. The ester was characterised by hydrolysis.

After extraction with ethanol the residual tarry material was subjected to sublimation in a good vacuum, when benzoic acid (1.3 g., m.pt. and mixed m.pt., 121-122°C) was obtained.

The remaining tarry material was subjected to chromatography in benzene/hexane solution (approximately 1/1), using a 50 cm. column, 1.5 cm. in diameter, packed with activated alumina. After the first 100 c.c. solvent had been collected, two fractions, each of 50 c.c., were obtained.

The first of these fractions produced long needle crystals (0.3 g.), which, after recrystallisation from benzene/hexane solution, had a melting point of 186-187°C.

Found	C, 80.4%	H, 4.8%
$(PhCO)_n$ requires	C, 80.0%	H, 4.8%

This is consistent with trans-isobenzil (m.pt., 185-187°C; Staudinger and Binkert, Hev. 5, 709). The infra-red spectrum of this compound was almost identical with that of cis-isobenzil, with certain marked intensity differences, of the type expected in the spectra of two sterio-isomers.

The second of the two fractions yielded more needle crystals of trans-isobenzil (0.2 g.), together with a small quantity (0.15 g.) of smaller, more closely packed, crystal conglomerates. The two crystal forms were separated mechanically, and each recrystallised from benzene/hexane solution. The smaller crystals proved to be cis-isobenzil (m.pt. and mixed m.pt., 157-158°C; infra-red identification).

Finally, on eluting the column with chloroform, a quantity (2.5 g.) of tarry material was isolated.

Recovery:-		Weight	% Yield
1.	Trans-isobenzil	0.5 g.	4.8
2.	Cis-isobenzil	0.15g.	1.4
3.	Benzoic acid	1.3 g.	10.7
4.	Ethyl benzoate	1.0 g.	6.6
5.	Yellow amorphous material	1.5 g.	
6.	Tar	2.5 g.	

(b) The above reaction was repeated with benzoyl chloride

(14 g., 0.1 mole) in cyclohexane (60 c.c.). During the extraction and 'working up' processes, alcohol and water were rigorously excluded.

On allowing the cyclohexane extract to cool, a yellow solid (0.7 g.) was precipitated from solution. This solid had no definite melting point, but softened between 97° to 120°C, to a dark brown, viscous liquid. Sublimation did not occur at 200°C/0.01 mm, but on cooling, the dark brown melt set to a hard, glassy tar. The infra-red spectrum of the yellow solid was found to be similar to that of *iso*benzil.

After evaporation of cyclohexane, the products were subjected to the same chromatographic technique as was previously used. The results are summarised below.

Fraction	Product	Amount	% Yield
1 and 2	Trans-*iso*benzil	0.1 g.	1%
3	Benzoyl Chloride	2.0	14
5	Yellow solid	0.5	
Elution with chloroform			
6	tarry material	3.0	

The graphite residues were then hydrolysed with ethanol. The ethanol extract was acidified, extracted with water and ether, and the dried ether extract yielded a dark brown, solid tar (1.0 g.), which could not be sublimed. However milligram quantities of benzoic acid were sublimed from the tar.

(c) A similar experiment was carried out with benzoyl chloride (7 g., 0.05 mole) in cyclohexane (75 c.c.), and potassium graphite, KC_{16}, (4.5 g. potassium; 25 g. graphite).

After 11 days refluxing, the following products were isolated from the solvent extraction:-

(i)	Tarry material	(1 g.)
(ii)	Trans-*iso*benzil	(m.gm. quantities)

After ethanolic hydrolysis of the graphite residues, the following products were isolated by ether extraction:-

(i)	Solid tar	(1 g.)
(ii)	Benzoic acid	(1.1 g., 18% yield)

(d) The above experiment was repeated, taking rigorous precautions to exclude moisture and oxygen, and with a slightly larger volume of cyclohexane (100 c.c.). The following products were isolated from the solvent extract:-

(i)	Trans-*iso*benzil	(0.2 g., 3.8%)
(ii)	Cis-*iso*benzil	(0.1 g., 1.9%)

(iii)	Yellow solid material	(0.3 g.)
(iv)	Tarry products	(1.7 g.)

and after ethanolic hydrolysis:-

(i)	Benzoic acid	(0.8 g., 13%)
(ii)	Solid tar	(2.0 g.).

(IV) Reaction with Organo-Metallic Halides

(a) Reaction with Dipropylboron Chloride

Dipropylboron chloride (10 g., 0.0755 mole) in cyclohexane (150 c.c.) was refluxed for 65 hours with potassium graphite, KC_{16}, (15 g. graphite, 3 g. potassium), and the graphite residues extracted, as before, under nitrogen. Distillation of the cyclohexane extract yielded two clear fractions (B.pt. $50^{\circ}C/0.1$ mm.).

The second of these fractions (4 g.) had an infra-red spectrum identical with that of tripropylboron. Furthermore the crystalline oxidation product had an infra-red spectrum identical with that obtained by the atmospheric oxidation of tripropylboron.

The first fraction (approximately 5 g.) proved to be a mixture of cyclohexane and tripropylboron (infra-red evidence).

A small amount (0.5 g.) of tarry material was obtained, as a residue, after distillation of the tripropylboron and cyclohexane.

(b) Reaction with Triphenyltin Bromide

Triphenyltin bromide (10 g., 0.0233 mole) in cyclohexane (200 c.c.) was refluxed for 69 hours with potassium graphite (15 g. graphite, 5.5 g. potassium) under nitrogen. After extraction, under nitrogen, first with ether, and then with benzene, only milligram quantities of some solid were obtained.

The graphite was hydrolysed with alcohol and filtered. Addition of water to the alcohol extract produce a small quantity of white solid (0.2 g.), which had an infra-red spectrum similar to that of diphenyltin oxide. The substance was, in part, organic, contained tin, and did not melt below 360°C.

The alcohol/water solution was acidified and extracted, first with ether, and then with chloroform. The ether extract yielded hexaphenylditin (0.8 g.), and the chloroform extract yielded a small quantity of tarry material (0.05 g.), together with a further quantity of hexaphenylditin (2 g.). Extraction of the hydrolysed, graphite residues afforded yet a further quantity of hexaphenylditin (1.5 g.), which was characterised by a melting point and mixed melting point (231.5-232.5°C).

Total yield hexaphenylditin = 4.3 g. (53%).

(V) Reaction with Other Organic Halides

(a) Reaction with α-Chloroethylbenzene, $C_6H_5CH(CH_3)Cl$

α-Chloroethylbenzene (15 g., 0.107 mole) in cyclohexane (150 c.c.) was refluxed for 96 hours with potassium graphite (25 g. graphite, 9 g. potassium) under nitrogen. The cyclohexane extract was distilled, when a thick,viscous liquid (15 g.) was obtained. On pumping this liquid the remaining cyclohexane was removed, and an extremely viscous, pale yellow material (11 g.) was obtained.

It was attempted to distil this material, in a larger version of the microdistillation apparatus (cold finger type), in a good vacuum. It was found that a certain amount of crystalline material formed on the cold surfaces, whilst a small quantity of liquid collected in the cup. The crystalline material (0.4 g., 3.6%) was recrystallised from ethanol, when the melting point, 125-127°C, corresponded to 2,3-diphenylbutane (quoted 126°C, Beilstein, 5, 617).

Found	C, 91.3%;	H, 8.8%.
$C_{16}H_{18}$ requires,	C, 91.3%;	H, 8.7%.

The liquid (0.2 g.) was redistilled and found to have an infra-red spectrum identical to that of 1-phenyl-1-cyclohexylethane (American Petroleum Institute, Project 44, Nos. 517, 527, 1919).

The glass-like, solid residue of the vacuum distillation (9 g., 81%) was found to be polystyrene (infra-red identification).

(b) Reaction with Triphenylchloromethane

Triphenylchloromethane (27.88 g., 0.1 mole) in cyclohexane (200 c.c.) was refluxed for 13 days with potassium graphite (25 g. graphite; 9 g. potassium), under nitrogen. On allowing the golden-yellow, cyclohexane extract to cool, a yellow solid (1.5 g.) was precipitated from solution (m.pt. 138-142°C). On distillation of the extract to half volume, a further quantity (1.5 g.) of the same yellow solid was precipitated.

This yellow compound could not be crystallised, but a deep yellow powder (m.pt. 244-255°C) was precipitated from benzene solution by addition of petroleum ether. On precipitation from carbon tetrachloride solution a melting point of 155-180°C was obtained.

The remaining cyclohexane extract was subjected to chromatography on an alumina column. The column was eluted with benzene, and a number of fractions (50 c.c.) taken.

Fraction 1, yielded a white solid (7.7 g.), which on repeated crystallisation from benzene gave triphenylmethane (3 g., 13%; m.pt. and mixed m.pt., 92-93°C).

Fractions 2 and 3 yielded a cream-white solid (5 g.), which after recrystallisation from hexane, and then from carbon tetrachloride, gave triphenylcarbinol (2 g., 8%; m.pt. and mixed m.pt., 160-162°C). A small quantity (0.2 g.) of triphenylmethane was also obtained.

Further fractions yielded a yellow, amorphous powder (3 g.), and a red-brown, phenolic smelling tar (5 g.). The yellow compound could not be crystallised, and repeated precipitation caused the softening point to be raised from approximately 110°C to the 200°C region. It was found that this compound liberates iodine from acidified potassium iodide solution, and dissolves in concentrated sulphuric acid to form a deep red solution. Both of these properties are indicative of a peroxide.

100% yield of $Ph_3C\cdot$ = 24.3 g.

Total recovery of material = 23.7 g.

(c) Reaction of Diphenylchloromethane

Diphenylchloromethane (20.3 g., 0.1 mole) in cyclohexane (150 c.c.) was refluxed with potassium graphite (25 g. graphite; 9 g. potassium), under nitrogen, for

10 days. On allowing the cyclohexane extract to cool, long needle crystals (5.1 g.) were obtained. After recrystallisation from chloroform these crystals had a melting point of 215-216°C (corr.), corresponding to 1,1,2,2-tetraphenylethane. This was verified by a mixed melting point with an authentic specimen.

After filtration of the crystals, the cyclohexane extract was distilled, when a sticky, semi-solid residue (9 g.) was obtained. This material was subjected to chromatography, in benzene solution, using an alumina column. Three fractions (50 c.c.) were taken before eluting the column with chloroform.

Fraction 1 consisted of benzene only, but the second and third fractions yielded a sticky tar (7 g.). This tarry material was distilled under a good vacuum, when a certain quantity of liquid was obtained, leaving a tarry residue (3 g.). The liquid was redistilled in a microdistillation apparatus, and three fractions were taken.

(i) upto 130°C/0.1 mm.
(ii) 130-145°C/0.1 mm.
(iii) 145-180°C/0.1 mm.

The infra-red spectra of all these fractions were very similar, and were consistent with a mixture of unreacted diphenylchloromethane and diphenylmethane.

Elution of the column with chloroform gave diphenylcarbinol (1.5 g., 8%; m.pt. and mixed m.pt., 67-68°C).

The graphite residues were hydrolysed with ethanol, and extracted with chloroform. This procedure gave a further quantity (3 g.) of 1,1,2,2-tetraphenylethane. The total yield of tetraphenylethane was 8.1 g., i.e. 48%.

(d) Reaction with <u>Ethyl Bromide</u>

Ethyl bromide (10.9 g., 0.1 mole), in pentane (200 c.c.), was refluxed with potassium graphite for 4 hours, under nitrogen. A carbon dioxide/acetone condenser was used, in addition to a water condenser, to prevent pentane passing over in the nitrogen stream. The gaseous products were passed through a cold trap (-78°C), and condensed in liquid air. The contents of the liquid air trap were transferred to a vacuum apparatus and fractionated, as described in Part I of this thesis (page 51).

The gaseous material analysed to $C_{2.07}H_{5.8}$, on combustion with excess oxygen. The infra-red spectrum was consistent with a mixture of ethane and ethylene. The fine structure of the spectrum of ethylene was particularly observed.

(VI) Reactivity of Halides towards Potassium Graphite

(a) The following experimental procedure was adopted for chlorobenzene, benzyl chloride, α-chloroethylbenzene, diphenylchloromethane, and triphenylchloromethane, and the results obtained are summarised below.

The halide (0.1067 mole) was dissolved in methylcyclohexane (200 c.c.), and a 2 c.c. sample was taken. The remaining solution was added to potassium graphite (25 g. graphite; 9 g. potassium) and quickly brought to reflux temperature. After refluxing for 30 minutes, stirring was stopped for 2 minutes, and a 2 c.c. sample was taken from the clear, supernatant liquid. Further samples were taken as reaction proceeded at reflux temperature.

In order that conditions were as standard as possible, the same pipette (2 c.c.) was used throughout these experiments. Likewise the same settings on the thermostatic heating controls were used.

The samples were presented for organic halide analysis, the first sample giving the initial concentration of the halide. Ignoring the amount of solvent removed, the quantity of halide reacted was calculated.

Time	% Reacted				
	PhCl	$PhCH_2Cl$	$PhCH(CH_3)Cl$	Ph_2CHCl	Ph_3CCl
0.5 hr	66%	16%	11%	13%	24%
1.75	86	20		17	51
17.5	100	36	25	35	
22.5		38	33		55
25				39	
41.5		55	59	45	72
64		76	82	54	81
89					96
92				58	
114		100		62	

The analyses in the case of triphenylchloromethane could not be carried out in the usual way, due to it's insolubility in *iso*propyl ether, the solvent used in the halogen analysis technique. In this case the samples were hydrolysed with aqueous acetone (50%), over a period of several hours. The aqueous extracts were made up to 100 c.c. of solution, and 10 c.c. aliquots were titrated with standard sodium hydroxide solution.

(ii) Similar experiments were carried out with the phenyl halides (0.1067 mole) in cyclohexane (200 c.c.) and potassium graphite (25 g. graphite; 9 g. potassium). The results are shown below.

Time	% Reacted			
	PhI	PhBr	PhCl	PhF
0 mins				
20	13	39	55	49
50	22	66	82	76
90	23	90	88	93
120	37	95	98	97
180	54	100	100	100

5. Reaction of Organic Halides with Potassium

Potassium (7.8 g., 0.2 mole) was heated to melting under methylcyclohexane (100 c.c.) in a 250 c.c., three necked flask, purged with nitrogen, and fitted with a Herschberg stirrer (tantalum wire). The source of heat was removed and vigorous stirring applied until the potassium was broken into a fine shot form. Stirring was continued until the first signs of coagulation of the shot, when stirring was promptly stopped. The flask was maintained at 25°C in a thermostat.

The halide (0.05 mole) in methylcyclohexane (10 c.c.) was added quickly from a dropping funnel, and washed through with a further quantity (10 c.c.) of solvent.

After stirring for one minute, the potassium was allowed to settle. A 2 c.c. sample was removed from the clear, supernatant liquid and filtered under nitrogen, the filter disc being washed with solvent (10 c.c.).

Other samples were taken as reaction proceeded, and presented for analysis. The results obtained are summarised below.

Time	% Reacted				
	PhI	PhBr	PhCl	PhF	$PhCH_2Cl$
2 min	0%	0%	0%	0%	0%
110	5	4	29	49	25
4.25 hr	6	20	57	64	78
7.25		30	80	78	94
19.25	24	65	91	96	97

A calculation on the titration figures for chlorobenzene, establishes the fact that only 0.001 mole react in the first 2 minutes.

At 0°C these reactions proceed extremely slowly. Bromobenzene and iodobenzene do not react appreciably in 24 hours, whilst only 20% chlorobenzene reacts.

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