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ORGANIC DERIVATIVES OF COPPER
AND SILVER

BY

M. JEWITT

A Thesis submitted for the degree of Master of
Science in the University of Durham.

1963.



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The author is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

FOREWORD

The work described in this thesis was carried out in the Chemistry Department of the Durham Colleges in the University of Durham, between 1958 and 1960.

The main effort was directed towards the formation of stable organo derivatives of copper and silver in which the metal is simultaneously co-ordinated to Π -bonding ligands, especially tertiary phosphines.

Two subsidiary topics were studied, both of which failed to develop into positive research problems. One was concerned with attempts to obtain substituted derivatives of nickelocene, and the other involved the use of alkali metal-hydrocarbon compounds, such as sodium naphthalene, as a means of introducing alkali metals into the graphite lattice. Both of these topics are reported, since a considerable amount of time was devoted to them.

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PART 1.

SUMMARY

ORGANIC DERIVATIVES OF COPPER

SUMMARY

The preparation of organo-copper compounds and subsequent attempts at stabilisation of these compounds by co-ordination with donor molecules is described. The organo-copper compounds used were:-

- (i) Phenyl copper
- (ii) Methyl copper
- (iii) Mesityl copper

Methyl- and phenyl copper have been described previously, while mesityl copper has not. The donor molecules used were mainly phosphines, such as phenyldiethylphosphine, PhPEt_2 , and triphenylphosphine, Ph_3P . All attempts at isolation of a co-ordination stabilised organo-copper compound failed, although there was evidence that co-ordination took place in solution, the complex formed evidently being too unstable to be isolated.

The most striking feature of the work is the isolation of a soluble organo-copper compound, which, although not fully characterised, appears to be mesityl copper. The soluble nature of this compound is in direct contrast to that of the insoluble methyl- and phenyl copper, over which the mesityl copper also shows increased stability.

In addition, reaction was attempted between excess of phenyl lithium and the phosphine-cuprous iodide complex $(\text{PhPEt}_2)_3(\text{CuI})_2$ in the hope that a phosphine stabilised phenyl copper compound would be produced, with elimination of lithium iodide. However, no evidence for the formation of an organo-copper compound was obtained, and indeed, the phosphine-cuprous iodide complex was recovered in high yield, being evidently far too stable to react under the conditions used.



ORGANIC DERIVATIVES OF SILVERSUMMARY

The attempted preparation of organo-silver compounds by reaction of the well known phosphine-silver iodide complexes or a silver halide with a Grignard or organo-lithium reagent in tetrahydrofuran, ether, or tetrahydrofuran-ether mixtures is described. In this way, mesityl magnesium bromide, mesityl lithium, and cyclopentadienyl lithium were used with a phenyldiethylphosphine complex of the type $(\text{PhPET}_2)_x\text{AgI}$, while mesityl lithium and styryl magnesium bromide were used with silver halides, followed by addition of phenyldiethylphosphine, PhPET_2 , in order to stabilise any organo-silver compound formed.

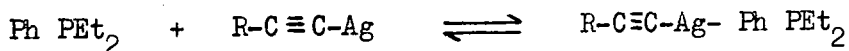
However, the phosphine-silver iodide complexes proved to be extremely unreactive towards organo lithium and Grignard reagents even in homogeneous solution, except in the case of methyl lithium, where extensive decomposition to metallic silver occurred at 0°C .

The conclusion reached is that the mildest conditions under which the phosphine-silver iodide complexes react also result in decomposition to silver, hence no stable organo-silver complexes of this type can be expected.

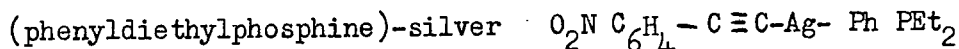
Of some interest was the fact that during purification of recovered phenyldiethylphosphine complexes by recrystallization, it was observed that phosphine was lost in successive stages, a range of compositions being found, only one of which, the 1:1 complex, has previously been described:-

	m.p.
$(\text{PhPEt}_2)_2 \text{AgI}$	$71^\circ - 72^\circ\text{C}$
$(\text{PhPEt}_2)_3(\text{AgI})_2$	$83^\circ - 84^\circ\text{C}$
$(\text{PhPEt}_2) \text{AgI}$	$138^\circ - 139^\circ\text{C}$
$(\text{PhPEt}_2)(\text{AgI})_2$	200°C

In contrast to the low stability of the aryl- or alkyl silver compounds, even when complexed to a phosphine, the analogous silver acetylides, which are polymeric, insoluble compounds, give, with phenyldiethylphosphine, crystalline solids, soluble in some organic solvents (related complexes of silver have previously been prepared).



The stability of these compounds appears to depend on the nature of the group R, and in general, reversible dissociation is possible. In some cases, e.g. with p-nitrophenylethynyl

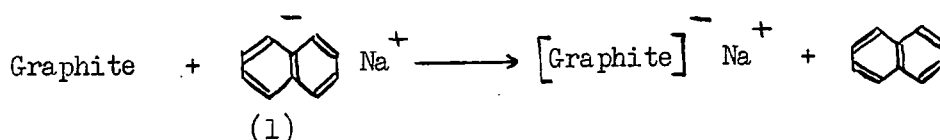


the tendency to dissociate was so great that satisfactory molecular weight determinations could not be performed. The phenyldiethylphosphine complex of phenylethynyl silver $\text{Ph-C}\equiv\text{C-Ag Ph PEt}_2$ was found to be dimeric in freezing benzene.

REACTION BETWEEN GRAPHITE AND ALKALI METAL-NAPHTHALENE COMPOUNDS

SUMMARY

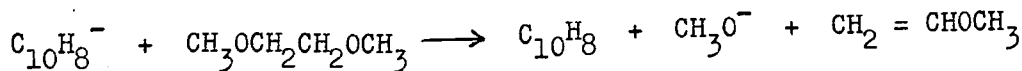
The main object of this work was the preparation of an intercalation compound of sodium with graphite, of which only one has been reported previously, by the reaction between dry graphite and alkali metal-naphthalene compounds (1) in specially purified ethylene glycol dimethyl ether:-



These reactions are described, together with subsequent analysis of the graphite products by several methods:-

1. Hydrolysis with water and titration with standard acid.
2. Acid hydrolysis and back titration of excess alkali metal-hydrocarbon with standard alkali.
3. Carbon and hydrogen analysis.
4. Sublimation of metal from the product, followed by hydrolysis and titration.
5. Vacuum line hydrolysis, and estimation of hydrogen evolved.
6. X-ray powder diffraction photographs.

Agreement between the different methods was not good, due to complication by the reaction between the alkali metal-naphthalene compound and the solvent, resulting in contamination of the products by insoluble alkali metal methoxides, which are completely inseparable:-



The extent of this contamination was investigated by numerous experiments which showed that contamination was greatest in those experiments conducted under more drastic conditions.

It was finally shown that the electron transfer from naphthalene to graphite will take place and in two cases, X-ray evidence indicated alteration of the basal spacing of graphite, although in only one of these cases was formation of a definite intercalation compound likely, while this compound did not show a similar X-ray analysis to that of the previous sodium graphite compound reported by Asher and Wilson.

It was also demonstrated fairly conclusively that the electron transfer reaction will not take place in the opposite direction, i.e. from graphite to naphthalene, by investigation of the reaction between the well known potassium graphite compounds and naphthalene, in ethylene glycol dimethyl ether.

SUMMARY

Biscyclopentadienyl nickel, (i) (nickelocene) was prepared by acknowledged methods and, in small yield, by two methods not previously described for this compound:-

1. From anhydrous nickel bromide and cyclopentadienyl sodium in ethanol in 20% yield.

2. From anhydrous nickel bromide and cyclopentadienyl lithium in tetrahydrofuran in 12% yield.



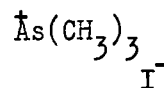
Ni



Ni



Ni



(i)



(ii)



(iii)

Lithiation of nickelocene was attempted using butyl lithium, usually in tetrahydrofuran-ether mixtures, in the hope of producing compound (ii), which could then be used to prepare a range of derivatives. Subsequent reaction of compound (ii) was generally attempted with cacodyl iodide, $(\text{CH}_3)_2\text{AsI}$, followed by methyl iodide, CH_3I , arriving at compound (iii); or by carbonation.

These attempts failed, the conclusion being drawn that butyl lithium will degrade nickelocene at temperatures close to -78°C , while at -100°C , no reaction occurs.

PART 2.

ORGANIC DERIVATIVES OF COPPER AND SILVER

ORGANIC DERIVATIVES OF COPPER AND SILVER

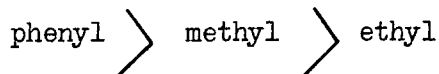
INTRODUCTION

All three elements of Group 1B form organic derivatives. With gold, auric and aurous compounds are known, all of which are stabilised by co-ordination to a suitable donor molecule. In contrast, the organic compounds of copper (I) and silver, apart from the characteristic acetylides, are few in number, unstable, and often poorly characterised. No organo-copper (II) compounds are known.

Copper

Copper (I) methyl, ethyl and phenyl have been described.

Stability of these compounds varies according to:-

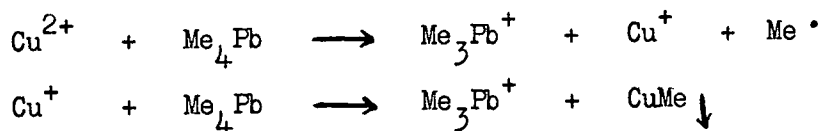


as is usually the case. The only suitable preparative method available is the reaction between an organo-lithium or Grignard reagent and a copper (I) halide. In this way, methyl copper¹ has been prepared as a yellow insoluble solid, from the reaction between methyl lithium and cuprous iodide at -15°C . The methyl copper decomposes in boiling ether, with formation of metallic copper, while methane and ethane are evolved. The dry solid will explode violently at room temperature. Addition of a further mole of methyllithium to an ethereal suspension of methyl copper results in the formation of an almost colourless solution, which gives a positive colour test (Mischler's ketone), and probably contains the solvated salt $\text{Li}^+(\text{CuMe}_2)^-$. Phenyl copper² can be prepared similarly as a grey powder from the reaction between copper (I) iodide, and phenylmagnesium iodide or phenyllithium. At about 80°C , this powder decomposes rapidly to metallic copper and biphenyl, and, although

insoluble in most organic solvents, will give a yellow solution in pyridine. Phenylcopper is slowly hydrolysed by water to copper (I) oxide and benzene, and is sufficiently reactive to form benzophenone from benzoyl chloride.

Methyl copper can be detected in the reaction between methyl chloride and copper at 350°C , as a stream of gas will redeposit a copper mirror on a glass tube. At 250°C the half-life of methyl copper is $2 \times 10^{-3} \text{sec.}^3$

Reaction between copper (II) nitrate and tetramethyl lead in ethanol at -60°C to -45°C , also results in formation of methyl copper in a two-stage reaction:-



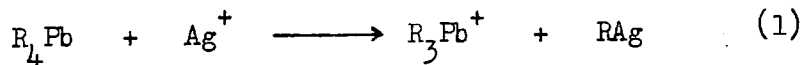
Attempted isolation of ethylcopper from the reaction of ethyl chloride with copper and silicon, and from the reaction between tetra ethyl lead and copper (II) salts, has led to the formation of ethane and ethylene, doubtless by the interaction of ethyl radicals.

Triethylphosphinecyclopentadienylcopper, $^4\text{C}_5\text{H}_5\text{CuPEt}_3$, formed by the addition of triethylphosphine to a suspension of copper (I) oxide in cyclopentadiene and petroleum ether, is the most stable of the organo-copper compounds. It reacts rapidly with ferrous chloride in tetrahydrofuran to give an almost quantitative yield of ferrocene. On the basis of this reaction, and of its spectra, it is regarded as a σ -complex.

Silver

The brown alkyl and aryl compounds of silver are all

thermally unstable, coloured solids, generally prepared by reaction of a tetra alkyl- or tetra aryl-lead compound with silver nitrate in ethanolic solution at low temperature⁵:-



The stability of the organo-silver compounds⁶ depends partly on the nature of the radical, R, more stable radicals giving less stable organo-silver compounds. Thus, while benzyl-silver has only a transitory existence above -100°C , phenyl-silver is comparatively stable.

It has been shown⁷ that the reaction (1) is not quantitative at -78°C , and that composition of the products is probably close to $(RAg)_2 AgNO_3$. Methyl, ethyl, and n-propyl silver have been prepared in this form as yellow solids, which decompose at about -60°C . Methyl silver^{5,7} is remarkable in that it decomposes to silver and ethane.

Complex salts, $(ArAg)_2 AgNO_3$ (Ar = phenyl or o-tolyl) are isolated as unstable yellow or orange solids from the reaction between alcoholic silver nitrate and various organo-lead, tin or bismuth compounds e.g. Ph_3PbEt .⁸

Compounds of the type, $RCH = CHAg$ ⁹ appear to show increased thermal stability, e.g. isobut-1-enyl silver, $(CH_3)_2C : CHAg$ is stable to about -30°C , while styrylsilver is reasonably stable at 0°C .

Impure phenyl silver, $PhAg$, has been isolated from the reaction between silver halides and cooled solutions of phenylmagnesium bromide. It is explosive when dry, and decomposes at about -18°C to silver and biphenyl.^{2,10}

Olefin complexes of copper and silver

All copper (I) and silver mono-olefinic complexes are comparatively

unstable. Ethylene and propene are absorbed by hydrochloric acid solutions of copper (I) chloride,¹¹ while the compound C_2H_4CuCl is isolated when ethylene reacts with solid copper (I) chloride at 60-62 atmospheres. Propene is not absorbed under comparable conditions.¹²

A pale yellow butadiene complex,¹³ C_4H_6CuCl (and the bromide) are formed from reaction between liquid butadiene and the copper (I) halide at $-10^\circ C$.

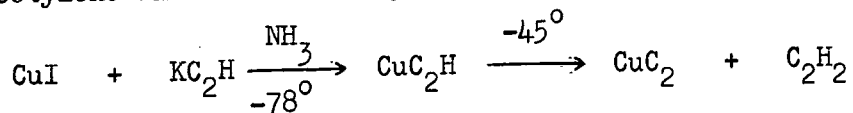
In the case of silver, a wide range of olefinic compounds forms 1:1 complexes which are usually too unstable to be isolated, evidence for their existence being available from experiments in solution.¹⁴ It is interesting to note that in the case of the cyclo-octadiene-silver complexes, the chelating 1,5-diene, $C_8H_{12}AgNO_3$, forms colourless needles, m.p. $135^\circ C$, and is stable to $90^\circ-100^\circ C$, while the 1,3, and 1,4 complexes have the composition $C_8H_{12}2AgNO_3$, and are considerably less stable, evolving the diene on warming.¹⁵ The stability of the olefine-silver complexes evidently depends mainly on steric effects, and partially on the presence of electronegative or electropositive groups conjugated with the double bond.

Copper and silver acetylene complexes

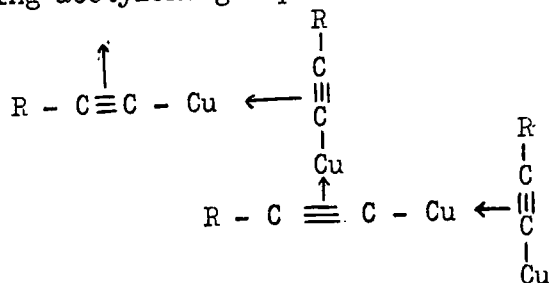
Almost all of these are acetylides, $MC\equiv CR$, but a few copper and silver complexes¹⁶ of disubstituted acetylenes, of the type $C_6H_{10}AgNO_3$ (formed by the slow reaction between silver nitrate and 3-hexyne), in which the triple bond is not greatly altered, are known.

The yellow, red, or brown copper (I) acetylides, and the

colourless silver compounds, are formed by the reaction between acetylene or mono-substituted acetylenes and copper or silver salts, usually in ammoniacal solution. The explosive compounds Cu_2C_2 and Ag_2C_2 have been long known, the dry silver compound being particularly shock-sensitive. From the low temperature reaction between copper (I) iodide and potassium acetylide in liquid ammonia the orange mono-copper (I) acetylide, CuC_2H can be isolated. Above -45° it decomposes into acetylene and the black crystalline copper (I) acetylide.¹⁷



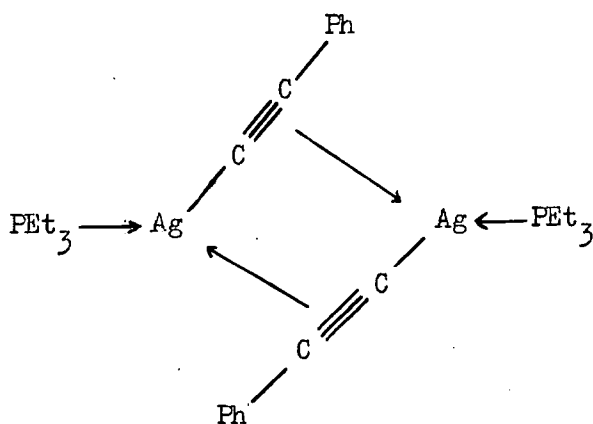
The mono acetylides of copper and silver are useful intermediates in the preparation of di-acetylenes from mono-acetylenes,¹⁸ but have been little investigated due to their insolubility, and the difficulty of obtaining single crystals for crystallographic work. They are evidently polymeric, the metal atom of one $\text{RC}\equiv\text{CM}$ unit combining with other acetylenic groups. It can be interpreted by the formation of two $\sigma(\text{sp})$ bonds by the metal atom, the extra electron being provided by a donating acetylene group:-



Back co-ordination from filled metal d-orbitals to empty antibonding Π -orbitals of both acetylene groups is possible, resulting in a near neutral metal atom. If another polymer chain was placed

above and below that illustrated above, then additional bonding between metal d-orbitals and acetylenic π -orbitals would result.

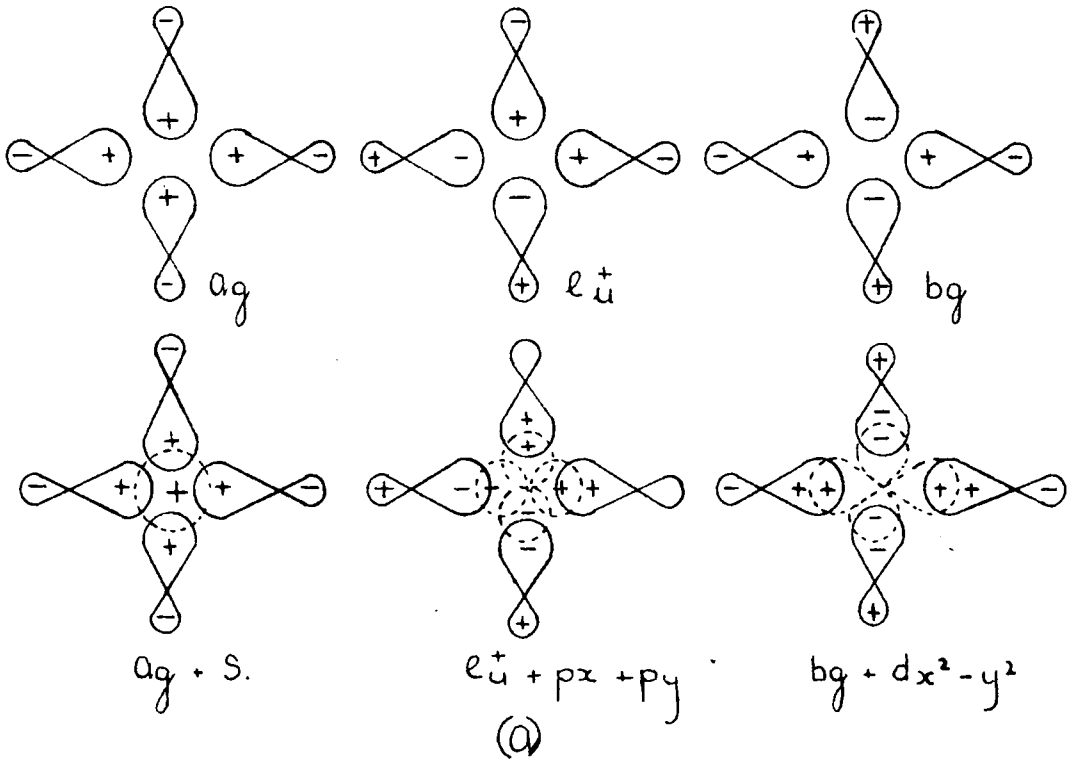
Several co-ordination complexes of copper and silver acetylides have been described. Phenylethynylcopper (I) will form a colourless, unstable ammine $\text{PhC}\equiv\text{CCuNH}_3$, but the use of stronger donor molecules, namely tertiary phosphines and arsines,¹⁹ results in the formation of more stable complexes. For example, $\text{PhC}\equiv\text{CCu}$ dissolves in a benzene solution of triethylphosphine, to give the yellow co-ordination compound $\text{PhC}\equiv\text{CCuPEt}_3$, which is associated in solution (2-4 times). The silver analogue, $\text{PhC}\equiv\text{CAgPEt}_3$ forms colourless crystals, and is reasonably stable in air. The suggested structure for the silver complex is:-



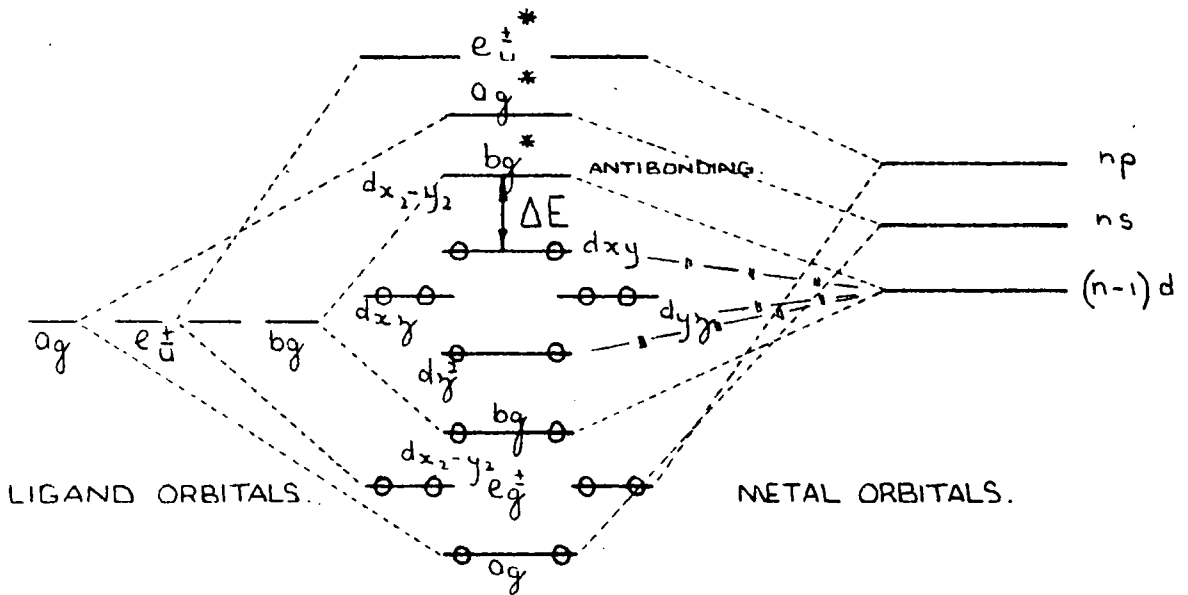
The tertiary butylethynyl copper (I) and silver compounds are exceptional in that they are not high polymers, being readily soluble in non-polar solvents,²⁰ while the copper compound appears to be octameric in freezing benzene.¹⁹

Factors affecting the stability of metal-carbon σ -bonds

A characteristic of the transition metals is the small energy difference which exists between the $(n-1)d$ orbitals, and the



LIGAND ORBITAL COMBINATIONS IN A SQUARE PLANAR COMPLEX AND MOLECULAR ORBITALS DERIVED THEREFROM.



ENERGY LEVELS OF MOLECULAR ORBITALS IN SQUARE PLANAR METAL COMPLEXES

FIG 1.

ns and np orbitals, this being evident in the square planar complexes of nickel, palladium and platinum, which use hybrid dsp_2 σ -orbitals.

The stability of the metal-carbon bonds depends on the ease with which an organic radical is formed; this radical then being free to react with neighbouring molecules, and the complex being irreversibly decomposed. In considering the stabilities of σ -bonded organic complexes, it is therefore necessary to find out how easily an electron transition will occur from the highest energy non-bonding orbital, to the lowest energy antibonding. Clearly, the smaller the energy difference between the two, the more easily will the transition take place.

Any factor which tends to increase this energy difference must result in stabilisation of the metal-carbon σ -bond. For a complex of the type $(R_3P)_2MR_2$, four possible combinations of ligand orbitals (two sp_3 of carbon and two sp_3 of phosphorous) exist, with correct symmetries for combination with metal orbitals. These are shown in Fig. 1 and are labelled ag , e_u^+ (one of a conjugate pair e_u^+) and bg .

The metal orbitals shown in dotted lines have the correct symmetries for bonding. The four bonding combinations of metal and ligand orbitals are therefore:-

$$ag + s$$

$$e_u^+ + px + py$$

$$bg + d_x^2 - y^2$$

Four antibonding orbitals are produced by reversing the signs of either the metal or ligand orbitals. For nickel, palladium and platinum, only the $dx^2 - y^2$ orbital is used in bonding, the other four being fully occupied. Relative energies of orbitals are shown in Fig. 1

If we take the four bonding orbitals as lying along the xy axes, then the energies of the non-bonding d-orbitals will depend on their positions relative to these regions of high electron density. The only non-bonding orbital in the xy plane is the d_{xy} orbital, and electrostatic repulsion between this and the bonding orbitals will be greater than for any other, the d_{xy} orbital thus being the highest energy non-bonding orbital. Thus, the lowest energy transition possible, ΔE , is from d_{xy} , and is shown in the diagram. ΔE may be increased by use of ligands which can form π -bonds with the d_{xy} orbital, and preferably also with the d_{xz} and d_{yz} , thereby reducing the energy of these orbitals. Of the π -bonding ligands (e.g. phosphines, arsines, and sulphides) the most suitable are tertiary phosphines, which combine strong donor character with π -bonding tendency. It might thus be expected that these considerations would apply for any organo-transition metal complex in which the highest energy non-bonding orbital is a d-orbital, i.e. almost certainly to those transition metals in which the d-orbitals are more than half-full.

In the aryl series of organo-nickel complexes, stability varies greatly with the nature of the aryl group, the most striking feature being the low stability of phenyl, and meta- and para- substituted phenyl derivatives, with ortho-substituted phenyl or other aryl groups. For example, the complex $(Et_3P)_2NiPh_2$, decomposes rapidly in ethanolic

solution and melts with decomposition at 125°-130°, while the complex $(Et_3P)_2Ni(mesityl)_2$, is much more stable, and melts at 148°-150°. The effect is purely steric, as stability is not greatly influenced by the electronic nature of the substituent. The bulky (chloride, methyl or larger) ortho substituents prevent free rotation of the aryl groups about the metal-carbon bonds, and, if the substituents are large enough, keep the plane of the aryl rings roughly perpendicular to the d_{sp^2} nickel bonds. Under these conditions, the π -electrons of the aromatic rings interact exclusively with the d_{xy} orbital of nickel, thereby lowering its energy, and further enhancing stability of the metal-carbon σ -bond.

It was hoped that both of the above factors would assist in stabilising any organo-copper or organo-silver compound formed.

Cuprous halide- and silver halide- phosphine complexes

Trialkyl phosphines will react with silver halides²¹ and copper (I) halides²² to form trialkylphosphine-metal halide complexes of the type $(R_3P \rightarrow AgI)_4$, the preparation being carried out by shaking the phosphine and metal halide in concentrated aqueous potassium iodide solution. X-ray evidence suggests that the silver halide complexes are tetrameric in the solid state, while the degree of association in freezing benzene is 3-4, some dissociation possibly occurring in solution:-

	M. Pt.
$(Et_3P AgI)_4$	208°-209°C
$(n.Pr_3P AgI)_4$	258°-265°C
$(n.Bu_3P AgI)_4$	43°C

Similar results were obtained for the alkyl phosphine-copper (I) iodide complexes $(R_3P \rightarrow CuI)_4$:-

R.	M. Pt.	n. in benzene
Et	236°-240°C	3.47 (ebullioscopic)
n.Pr	207°C	3.57)
n.Bu	75°C	3.36) cryoscopic
n.Am	27°C	3.62)

The co-ordination number of copper and silver in all of these compounds is thus four.

Work on phenyldialkylphosphine-metal halide complexes²³ showed that 3-co-ordination of copper (I) and silver in these complexes was possible, as some compounds of the type $(Aryl P Alkyl_2)_2 AgI$ were found to be monomeric in solution e.g.:-

	m.p.	Degree of association in nitrobenzene
$(PhPMe_2)_2 AgI$	114-5°C	0.93

Although this indicates a co-ordination number of 3, it gives no indication of the structures of the solids. Only one of the phosphines used, $(NMe_2C_6H_4PEt_2)$ afforded both types of complex (the tetrameric 1:1 and monomeric 2:1) with solubilities and stabilities adequate for molecular weight measurement, while one 3:1 complex was obtained $(CF_3C_6H_4PEt_2)_3 CuI$, which dissociates in solution.

In this work, molecular weight measurements on some of the complexes were impossible due to lack of solubility (in the case of copper (I)) and lack of stability in solution (in the case of silver).

It is presumably because of the lack of solubility, that little work has been done on complexes of the type $(R_3P - MI)_x$ where R=Me, Ph, and M=Cu, Ag, the only mention of a triphenylphosphine-copper (I) halide complex $(Ph_3P)_2 CuCl$, m.p. $173^{\circ}-175^{\circ}C$, being made in a paper on polymerization of acetylenes,²⁴ where it was used as a catalyst.

ORGANIC DERIVATIVES OF COPPERDISCUSSION

Since few organo-copper compounds, other than the acetylides or their complexes with donor molecules have been reported, the present work was undertaken to study the formation, and possible stabilisation of organic derivatives of copper. Although phenyl copper (1) and methyl copper (1) have been described, no co-ordination complexes of these compounds have been reported. It was proposed, therefore, to attempt stabilisation of these compounds, particularly phenyl copper, with donor molecules such as triphenylphosphine, triethylphosphine, phenyldiethylphosphine, and to a lesser extent, bipyridyl. In addition, the preparation of mesityl copper was to be attempted, using methods analogous to the preparation of phenyl copper, in the hope that the product may then be similarly stabilised by co-ordination.

Stabilisation of phenyl copper was attempted by direct reaction between a benzene solution of the donor molecule and phenyl copper as a solid or suspension, or as the ether-soluble solvated salt, lithium diphenyl copper, $\text{Li}^+(\text{CuPh}_2)^-$. The only exception to this procedure was one experiment in which the reaction of excess of phenyl lithium was attempted with the phosphine-cuprous iodide complex, $(\text{PhPEt}_2)_3(\text{CuI})_2$, in the hope that a phosphine stabilised phenyl copper would be formed. However, 80% of unreacted phosphine-cuprous iodide complex was recovered, and no evidence for the formation of an organo-copper compound was obtained.

Only one reaction involved the preparation of methyl copper, and will be dealt with separately.

1. Preparation of Copper Aryls.

(a) Phenyl copper, CuPh.

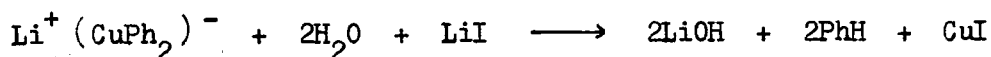
Phenyl copper was obtained as a grey powder from the reaction between anhydrous cuprous iodide and phenyl magnesium iodide in ether. The product was never halogen-free, and never showed the presence of excess Grignard reagent (Gilman colour test 1).

Phenyl copper was also obtained as a pale grey, green, yellow, or pink powder in 85%-90% yield from the reaction between anhydrous cuprous iodide and phenyl lithium in ether. The product once more was always contaminated with halide, not always in the form of iodide, although some unreacted cuprous iodide usually remained in the reaction flask after decantation of the lighter suspension of phenyl copper. The ethereal filtrate always contained excess of unreacted phenyl lithium (Gilman colour test 1). Purity of the washed and dried samples of phenyl copper seemed to vary considerably, since some could be weighed quickly in air with no apparent change, while others glowed red-hot on exposure. A sample of phenyl copper thus prepared decomposed rapidly above 80°C at 0.04 mm. Hg pressure to biphenyl and metallic copper.

(b) Lithium diphenyl copper, $\text{Li}^+(\text{CuPh}_2)^-$

It has been reported by Gilman that addition of an extra mole of methyl lithium to an ethereal suspension of methyl copper yields an almost colourless solution, giving a positive colour test, thought to contain the solvated salt $\text{Li}^+(\text{CuMe}_2)^-$. It may be expected that phenyl copper will behave similarly. Consequently, reaction of a

four-fold excess of phenyl lithium with cuprous iodide gave an ether soluble product, giving a positive colour test, no doubt containing lithium diphenyl copper $\text{Li}^+ (\text{CuPh}_2)^-$, as expected. This solution, although filtered to remove unreacted cuprous iodide, always gave a positive test after hydrolysis for water - in soluble iodide, which could only be cuprous iodide. It is probable, therefore, that cuprous iodide is being reformed on hydrolysis, the necessary iodide being obtained from the ether-soluble lithium iodide present in the solution. The hydrolysis may be broadly represented by:-

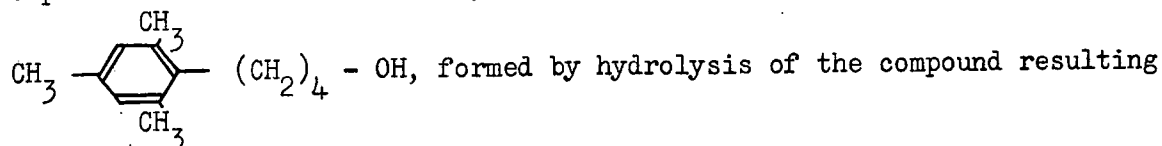


It may well be that some cuprous bromide is also formed from the lithium bromide originally present in the phenyl lithium solution.

(c) Mesityl copper.

Mesityl copper has not previously been reported, and, in the hope that it may be more susceptible to stabilisation by donor molecules than is phenyl copper, preparation was attempted from anhydrous cuprous iodide and mesityl magnesium bromide in tetrahydrofuran-ether mixture, and cuprous iodide and mesityl lithium in tetrahydrofuran. The original deep, red-brown solution of the Grignard eventually gave a deep green solution containing a grey or white suspension. The behaviour of the solid, which contained magnesium, iodine, and copper was consistent with that of a mixture of magnesium halide - tetrahydrofuran complexes and unreacted

cuprous iodide. In addition, presence of the compound



from attack of the tetrahydrofuran by mesityl lithium, was detected by its characteristic sweet sickly smell.

Analysis of two small samples of the deep green solution showed that 64.2% of the copper (precipitated as cuprous thiocyanate) originally used was now present in organic solution. Removal of most of the solid was effected in vacuo, the last traces being difficult to remove, no doubt due to retention in the form of magnesium halide-tetrahydrofuran complexes. The tacky, dark green, almost black mass was investigated:-

(i) Burned with a strikingly aromatic flame, and showed the presence of copper by the green flame colour. A red-brown residue was probably copper oxide.

(ii) Hydrolysis yielded copper oxide (by comparison of X-ray powder photographs), while the filtrate contained magnesium, which could be obtained as a white precipitate of its hydroxide, soluble in ammonia.

(iii) Thermal decomposition in vacuo at an oil bath temperature of 190°C gave a residue of metallic copper (again proved conclusively by X-ray powder photographs) with some impurity, certainly magnesium halides. The colourless distillate was shown to contain the alcohol mentioned previously, $\text{CH}_3 - \text{C}_6\text{H}_2(\text{CH}_3)_2 - (\text{CH}_2)_4 - \text{OH}$ (infra-red spectrum),

probably as a mixture with mesitylene, which has a very similar

infra-red spectrum.

It appears therefore, that a soluble organo-copper compound, namely, mesityl copper, has in fact been formed, and, from (iii), shows increased thermal stability over phenyl copper. However, the difficulty of removal of magnesium halides, held in complexes with tetrahydrofuran, increase the difficulties of a more rigorous qualitative analysis, and would appear to render quantitative analysis impossible.

Unfortunately, the above results were obtained only from the two initial preparations of mesityl copper and much time and effort was wasted in attempts to repeat the experiment successfully. The numerous subsequent attempts differed from the first two in that a buff-coloured Grignard solution was obtained instead of the red-brown solution mentioned previously. Large amounts, $\sim 80\%$, of unreacted cuprous iodide were always reclaimed, and furthermore, during working-up of the reaction mixtures, iodine was frequently liberated, presumably by oxidation of cuprous iodide, which seems highly improbable in what is primarily a reducing medium. In fact the only feasible explanation is that oxidation is being effected by peroxides present in the tetrahydrofuran. However, this possibility was eliminated, as, in one reaction, all of the tetrahydrofuran used was distilled directly from potassium diphenyl ketyl, $K^+ \text{ } ^-O-C-Ph_2$, into the reaction vessel, no alteration in the course of the reaction taking place. A sample of the mesityl magnesium bromide was also successfully carbonated to give mesitylene carboxylic acid in 74% yield. Despite rigorous precautions to ensure purity of all reactants and solvents, the

reaction could not be successfully repeated until the trouble was traced to the source of bromomesitylene used. It was found that only by using mesitylene supplied by L. Light and Co., Payle Trading Estate, Colnbrook, Bucks., could the deep green solution described previously be prepared.

This suggests that the reaction is being either encouraged or inhibited by a catalyst present in one of the two types of Grignard reagent used, and that this catalyst or the substance from which it is derived, is present in one or other of the samples of mesitylene.

Mesityl lithium, made from the same mesityl bromide used in the unsuccessful experiments described above, was used with cuprous iodide in attempts to prepare mesityl copper, no significant colour change being observed. Isolation of mesityl copper was not attempted, triphenylphosphine being added directly to the reaction mixture in order to stabilise by co-ordination, any organo-copper compound present. The results are discussed in the next section.

2. Reaction of Copper Aryls with Donor Molecules.

(a) Phenyl Copper

(i) Pyridine. As reported by Gilman, phenyl copper, like cuprous iodide, gave a yellow solution in pyridine.

(ii) Bipyridyl. An attempt to complex bipyridyl with phenyl copper was unsuccessful, merely resulting in recovery of bipyridyl, and inorganic copper.

(iii) Phenyldiethylphosphine. PPh Et₂.

Reaction of phenyldiethylphosphine with phenyl copper

resulted in recovery of copper in the form of a phosphine - cuprous iodide complex (either as $\text{PhP Et}_2 \cdot \text{CuI}$ or $(\text{PhP Et}_2)_3 (\text{CuI})_2$) in amounts of 21%-43% of the original cuprous iodide used. The amount of metallic copper formed on hydrolysis seemed to depend on the severity of conditions used, more being formed if the hydrolysis was carried out at higher temperatures, this being consistent with an increase of thermal, rather than hydrolytic dissociation. This was confirmed by the isolation of a small amount of biphenyl from one of the reactions.

Reaction of phenyldiethylphosphine with phenyl copper in the form of the solvated salt, lithium diphenyl copper, $\text{Li}^+ (\text{Cu Ph}_2)^-$ gave a 53% recovery of cuprous iodide as the phosphine - cuprous iodide complex $\text{PhP Et}_2 \cdot \text{CuI}$, together with some inorganic material containing copper, probably as cuprous oxide. This would again suggest that cuprous iodide is being reformed from lithium iodide and lithium diphenyl copper.

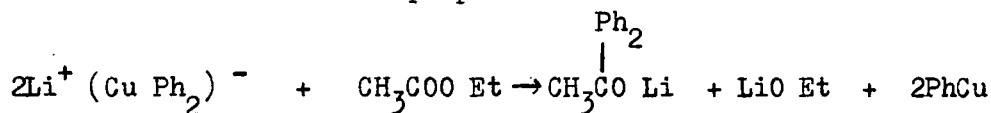
(iv) Triethylphosphine, PEt_3 .

Reaction between a benzene solution of triethylphosphine and solid phenyl copper resulted in formation of a solution from which only insoluble, copper-containing inorganic residue could be obtained, suggesting that, although co-ordination takes place sufficiently to enable solution of the phenyl copper, the complex formed is too unstable to be isolated.

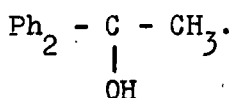
A 58% recovery of copper in the form of triethylphosphine monoiodo copper, $\text{PEt}_3 \text{CuI}$, was obtained by reaction of a solution of

lithium diphenyl copper with triethylphosphine.

In a further reaction of the latter type, ethyl acetate was used to remove excess of phenyl lithium, leaving the phenyl copper free for co-ordination purposes:-



Subsequent reaction with triethylphosphine, however, again resulted in isolation of $\text{PEt}_3 \text{CuI}$, cuprous oxide, and the carbinol



These experiments once more demonstrate the reformation of cuprous iodide. It is likely that this reformation takes place on hydrolysis, rather than on addition of the donor molecule, since cuprous iodide can be isolated from a solution of lithium diphenyl copper to which no donor molecule has been added (previous work).

(v) Triphenylphosphine, PPh_3 .

Reactions carried out between large (~four-fold) excess of benzene solutions of triphenylphosphine and benzene suspensions of phenyl copper generally resulted in formation of large amounts of inorganic, copper-containing decomposition product, especially if exposed to the atmosphere, together with small yields (~4%) of air-stable, colourless needles containing copper, bromine, and triphenylphosphine, thought to be a triphenylphosphine-cuprous bromide complex, m.p. $165^\circ\text{--}166^\circ\text{C}$. This compound will be discussed more fully at a later stage. Large recovery of triphenylphosphine, usually ~90% was effected in each case. Thus, once more, although

co-ordination must take place in solution, no organo-copper compound can be isolated.

At various stages during working up of the products, small yields of colourless materials were obtained, beginning to melt at lower temperatures than 165°C , often with decomposition, although otherwise identical (e.g. infra-red spectrum) to the triphenylphosphine-cuprous bromide complex above.

The low yield of phosphine-cuprous halide complex is easily explained if it is assumed that the sample of phenyl copper is fairly pure (a reasonable assumption, since, although halide could always be detected in the solid, it was not always in the form of iodide). Therefore, as the phenyl copper was normally washed and dried, only a small amount of halide would be available for complexing with the phosphine, hence the low yields.

(b) Mesityl Copper.

Reaction between mesityl copper and donor molecules was carried out after filtration of the deep green solution from any precipitated magnesium halide-tetrahydrofuran complexes and unreacted cuprous iodide.

(i) Triethylphosphine.

Reaction between triethylphosphine and mesityl copper resulted in a colour change from deep green to deep red. Hydrolysis led to extensive formation of cuprous oxide and recovery of free triethylphosphine, together with colourless crystals of triethylphosphine-cuprous bromide complex, $\text{PEt}_3 \text{Cu Br}$, while all

attempts at crystallization of a solid organo-copper complex merely resulted in isolation of magnesium halide-tetrahydrofuran complexes and triethylphosphine-cuprous halide complexes, once again indicating that although co-ordination may take place in solution, it is not strong enough to allow isolation of the solid complex.

Triphenylphosphine was added to a benzene solution from the reaction between triethylphosphine and mesityl copper, resulting in the slow formation of colourless needles, m.p. 167° - 168° C, found to be identical to those previously obtained from phenyl copper and triphenylphosphine.

(ii) Triphenylphosphine, PPh_3 .

Reaction between a benzene solution of triphenylphosphine and mesityl copper resulted once more in isolation of colourless needles, m.p. 170° C, containing copper, bromine, and triphenylphosphine, shown to be identical to those obtained from the reaction between triphenylphosphine and phenyl copper.

It is once more of interest to note that, although the copper was presumably in solution as mesityl copper, it was eventually obtained solid as cuprous bromide in a complex with triphenylphosphine. Moreover, the reformation of a cuprous halide, namely the bromide, shows that this reaction will take place without hydrolysis, the source of bromide probably being magnesium halide-tetrahydrofuran complexes, which are very difficult to remove completely.

The cuprous bromide-triphenylphosphine complex will be discussed in the next section.

3. Comparison of the products obtained from reaction of Triphenylphosphine with Phenyl Copper and with Mesityl Copper.

In each case, reaction of triphenylphosphine with either phenyl copper or mesityl copper resulted in formation of a compound whose melting point varied from 165°C to 170°C. The samples from each source were shown to possess identical infra-red spectra, both closely resembling that of triphenylphosphine and showing no aliphatic CH frequencies in the range 2900 cm^{-1} - 2850 cm^{-1} , which would be expected from the methyl groups of a mesityl ring. In addition, carbon and hydrogen analyses of both compounds were in agreement:-

	Carbon	Hydrogen	Copper
Sample from PhCu + Ph ₃ P	73.4%	5.5%	
Sample from Mesityl Cu + Ph ₃ P	(73.2% 73.4%)	5.6% 5.1%	6.26%
Required for: PPh ₃ Cu Br	53.3%	3.7%	15.2%
(PPh ₃) ₂ Cu Br	64.7%	4.5%	9.5%
(PPh ₃) ₃ Cu Br	69.8%	4.9%	6.8%
(PPh ₃) ₄ Cu Br	72.6%	5.0%	5.4%

It is immediately obvious that, although the compounds are identical, the analyses do not correspond to any of the cuprous bromide-triphenylphosphine complexes tabulated. When a sample of the compound, which had already been shown to contain copper, bromine, and triphenylphosphine, was thermally decomposed in vacuo, it gave only a sublimate of triphenylphosphine, and a pale yellow residue rich in copper and bromine (obviously mainly consisting of

cuprous bromide) with no trace of metallic copper, which would, of course, be expected if the crystals were those of an organo-copper compound.

The compound is obviously a triphenylphosphine-cuprous bromide complex, a more extensive investigation of its exact composition being outside the scope of this work.

It is of interest to note that in none of these reactions involving mesityl copper and phosphines was any phosphine-cuprous iodide complex formed, although large excesses of phosphine were often used. It may be explained by the fact that the magnesium iodide-tetrahydrofuran complexes are less soluble than the magnesium bromide-tetrahydrofuran complexes, the former thus being removed in the initial filtration of the mesityl copper solution. This, however, does not explain the fact that a cuprous bromide-phosphine complex was obtained from reaction between triphenylphosphine and phenyl copper, while cuprous iodide-phosphine complexes were obtained from reactions between phenyl copper and other phosphines, viz. triethylphosphine, phenyldiethylphosphine. An alternative explanation, adequate for reactions involving phenyl copper, may be that triphenylphosphine shows a tendency to complex with cuprous bromide rather than with cuprous iodide.

4. Reaction of Methyl Copper with Donor Molecules.

The yellow insoluble methyl copper dissolved in an ethereal solution of bipyridyl, but slowly deposited an inorganic decomposition product containing copper. Similarly, methyl copper dissolved in

ether when phenyldiethylphosphine, PhPEt_2 , was present. Hydrolysis of these solutions, however, resulted merely in extensive formation of cuprous oxide, and the isolation of a small amount of phenyldiethylphosphine monoiodo-copper, PhPEt_2CuI , doubtless formed from some unreacted cuprous iodide, while attempted crystallization of a product, avoiding hydrolysis, yielded only the highly explosive methyl copper.

In conclusion, it may be said that co-ordination must take place in solution with all of the donor molecules used, since the normally insoluble phenyl copper and methyl copper would dissolve in a solution of a donor molecule. Furthermore, the deep green colour of the soluble mesityl copper was usually changed in some way when a donor molecule was added, again suggesting that co-ordination has taken place. However, in all cases, isolation of a co-ordination stabilised organo-copper compound proved impossible, while slow decomposition, greatly accelerated by exposure to the atmosphere, or by hydrolysis, always took place in solution.

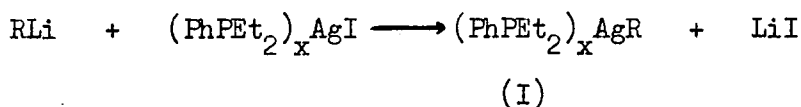
The most important factor to emerge from this work is the formation of mesityl copper, as a soluble compound, in direct contrast to phenyl copper and methyl copper. In addition, mesityl copper possesses greater thermal stability than either methyl or phenyl copper. From these considerations alone, it would appear to offer far more scope for stabilisation by co-ordination than the previously isolated organo-copper compounds, and there is obviously room for a more extensive study in this field.

aryl silver-phosphine complex. The reactions involving the possible formation of styryl silver were therefore carried out at 0°C. However, it was found that only in the reactions between styryl magnesium bromide and silver iodide could styryl silver have been formed, no reaction taking place when silver bromide or silver chloride was used.

Reaction between styryl magnesium bromide and silver bromide at room temperature led to extensive formation of silver over a prolonged period while use of silver chloride instead of silver bromide under similar conditions resulted in formation of only a small amount of silver, large amounts of silver chloride being recovered. These results give a very rough indication that the order of reactivity of silver halides towards styryl magnesium bromide is $\text{AgI} > \text{AgBr} > \text{AgCl}$, although this may easily be affected by a number of factors such as relative purity of samples. Although, in one case addition of phenyldiethylphosphine to what was apparently a solution of styryl silver in toluene resulted in a change of colour from deep red to yellow, the effect of the donor molecule on the stability of the organo-silver compound was never great enough to allow its isolation, since hydrolysis led to extensive decomposition. Support for the intermediate formation of an organo-silver compound comes from the appearance of varying amounts of silver, and isolation of a sample of bistyryl, probably formed by thermal decomposition of styryl silver, in solution.

Failure to prepare a relatively stable compound by this method led to another approach to the possible isolation of a co-ordination complex of the type (I), namely, by use of the well-known phosphine-silver iodide complexes. In a compound of this type, for example

$(\text{PhPEt}_2)_x\text{AgI}$, the silver atom is already bonded to a phosphine donor, and, by reaction with a Grignard or organo-lithium reagent, it was hoped that the required compound could be prepared:-



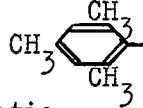
The reactions were carried out in tetrahydrofuran, ether, or tetrahydrofuran-ether mixtures, and involved the use of the phosphine-silver iodide complex $(\text{PhPEt}_2)_3(\text{AgI})_2$ (which is dealt with later in this work) with mesityl magnesium bromide, mesityl lithium, styryl magnesium bromide, methyl magnesium iodide, methyl lithium, and cyclopentadienyl lithium, while in one isolated case, reaction was attempted with cyclopentadienyl sodium in ethanol-benzene mixture. The latter reaction may be considered separately from the remainder.

In general, all of these reactions were carried out at low temperature ($\sim -60^\circ\text{C}$) and allowed to warm up slowly. The presence of organo-lithium or Grignard reagent was investigated using Gilman Colour Test 1, and immediately this test became negative, indicating that the reagent had been used up in some way, or at the first appearance of silver, due to thermal decomposition of the organo-silver compound, the reaction mixture was cooled down in order to stop further decomposition, hydrolysed, and rapidly worked up. However, in all reactions involving mesityl magnesium bromide, mesityl lithium, styryl magnesium bromide, or cyclopentadienyl lithium, large amounts of unreacted phosphine-silver iodide complex were recovered, and only small amounts of silver produced, indicating that little reaction had taken place, even in

experiments carried out over prolonged periods of time (~ 84 hours).

In the hope of speeding up the reactions, some were warmed up, and even refluxed, but, generally, little increase in the rate was noticed.

This technique involved increased difficulties, in that the rate of reaction of the organo-lithium or Grignard reagent with the solvent, particularly with tetrahydrofuran, is greatly increased with temperature, much of the reagents therefore being wasted, while working up was also complicated due to the presence of by-products from solvent attack.

Indeed, the presence of one of these by-products, CH_3  $(\text{CH}_2)_3 - \text{CH}_2\text{OH}$, a viscous oil, could be detected by its characteristic sweet smell, during the working up of all reaction mixtures involving use of mesityl magnesium bromide or mesityl lithium with tetrahydrofuran. In order to compensate rapid loss of Grignard or organo-lithium reagents by solvent attack, large excesses of these reagents were frequently used, but no improvement was found.

In the hope that any organo-silver compound formed would be additionally stabilised, excess of free phenyldiethylphosphine was used in some reactions, with the additional advantage of increasing solubility of the $(\text{PhPEt}_2)_3(\text{AgI})_2$, so that reaction could be carried out in homogeneous solution, even at low temperature, where previously the complex had tended to precipitate. The presence of excess of the free phosphine complicated use of the Gilman Colour Test 1, as excess of iodine must be added to oxidise the phosphine to phosphine oxide. When this was done, however, the test seemed far less reliable than under normal conditions, only very pale colours being obtained even when a

large excess of Grignard was known to be present.

Reaction of the complex $(\text{PhPEt}_2)_3(\text{AgI})_2$ with methyl magnesium iodide and methyl lithium, the latter in the presence of excess of free PhPEt_2 , yielded very similar results, both reaction mixtures being rapidly cooled on the first appearance of metallic silver (at 30°C and 7°C respectively) and both giving large recovery (90%+) of unreacted phosphine-silver iodide complex. This indicated that, although reaction had commenced, it was immediately followed by thermal decomposition of any methyl-silver compound. Reaction of $(\text{PhPEt}_2)_3(\text{AgI})_2$ with a twofold excess of methyl lithium, carried out entirely at 0°C , led to rapid and extensive decomposition to silver, a metallic mirror being formed on the walls of the flask. It thus appears that the presence of free phosphine in the reaction mixture results either in slightly increased stability of the organo-silver complex formed, although not sufficiently to allow its isolation, or in decrease of reactivity of the phosphine-silver iodide complex towards methyl lithium.

Attempted reaction between $(\text{PhPEt}_2)_3(\text{AgI})_2$ and cyclopentadienyl sodium in ethanol-benzene mixture was carried out at room temperature and 50°C , but large recovery of starting material was obtained in each case.

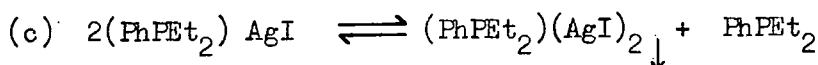
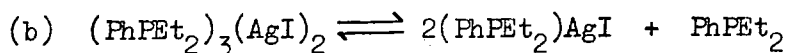
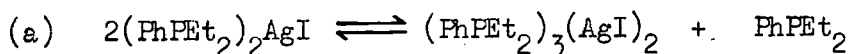
Recovery of starting material, $(\text{PhPEt}_2)_3(\text{AgI})_2$

The only phenyldiethylphosphine-silver iodide complex reported in the literature is the tetrameric 1:1 complex $((\text{PhPEt}_2)\text{AgI})_4$, m.p. $138^\circ-139^\circ\text{C}$, prepared by Cass, Coates, and Hayter.²³ However, preparation of this material, attempted by addition of excess of silver iodide to the steam distillate from a bulk preparation of

phenyldiethylphosphine, resulted in the isolation of colourless crystals, m.p. 83° - 84° C, which gave carbon and hydrogen analyses consistent with a formula of $(\text{PhPET}_2)_3(\text{AgI})_2$. Further, during purification by recrystallization of material recovered from the preceding experiments, it was observed that phenyldiethylphosphine was lost by the complex in successive stages, a range of compositions, including that of the 1:1 complex previously reported, being obtained:-

m. p.	Composition	Found		Required	
		Carbon	Hydrogen	Carbon	Hydrogen
71° - 72° C	$(\text{PhPET}_2)_2 \text{ AgI}$	42.6%	6.0%	42.4%	5.3%
83° - 84° C	$(\text{PhPET}_2)_3 (\text{AgI})_2$	37.9%	4.9%	37.2%	4.7%
138° - 139°	$\text{PhPET}_2 \text{ AgI}$	29.6%	4.2%	29.9%	3.7%
200° C	$\text{PhPET}_2 (\text{AgI})_2$	19.9%	2.6%	18.9%	2.4%

The first three were obtained as colourless crystals, while the last was obtained as a white, insoluble powder, although it was freely soluble in solutions containing phenyldiethylphosphine. Solutions of the first three complexes usually smelled of phenyldiethylphosphine, especially on warming, equilibria probably existing in solution. As no molecular weight determinations were attempted little evidence on these equilibria is available, but since no silver iodide was precipitated on recrystallization, they may be of the form:-



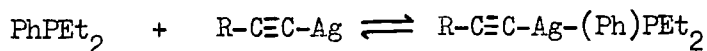
The 1:1 complex formed as a result of dissociation of $(\text{PhPET}_2)_3(\text{AgI})_2$ will be tetrameric $((\text{PhPET}_2)\text{AgI})_4$, as found by Cass et al, while the complex $(\text{PhPET}_2)\text{AgI}$ is probably monomeric in benzene, by analogy with the phenyldimethyl-silver iodide complex $(\text{PhPMe}_2)_2\text{AgI}$ isolated by Cass et al.

The above workers found that only one of the phosphines, viz $(\text{NMe}_2\text{C}_6\text{H}_4\text{PET}_2)$, afforded both the tetrameric 1:1 complex and the monomeric 2:1 complex with solubilities and stabilities adequate for molecular weight measurements, and in no case obtained a 3:2 complex.

B. Ethyne silver-phenyldiethylphosphine complexes

In direct contrast to the low stability of alkyl or aryl silver compounds, even when complexed to a phosphine, the analogous silver acetylides, which are polymeric, insoluble compounds, give, in some cases with phenyldiethylphosphine, crystalline solids, soluble in some organic solvents. (Related compounds have previously been prepared.)¹⁹

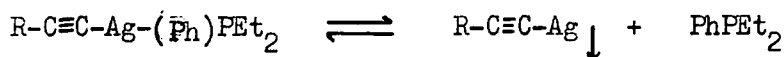
Preparation of the complexes was carried out in benzene or toluene solution:-



Only the complexes where R=phenyl, p-introphenyl, and tertiary butyl- were prepared. All were light-sensitive, decomposing to a dark oil with a smell of free phenyldiethylphosphine. The phenyldiethylphosphine complex of p-nitrophenylethyne silver was the most stable of the three to light and was obtained as yellow needles, while the tertiary butyl-ethynylsilver- and phenyl ethynylsilver- phenyldiethylphosphine

complexes were colourless.

The stability of these compounds in solution appears to depend on the nature of the group R- attached to the acetylenic carbon atom, and, in general, reversible dissociation is possible. This tendency is greatest in the case of the tertiary butyl silver acetylide-phosphine complex $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{Ag}-(\text{Ph})\text{PEt}_2$, and least in the case of the phenylethyne silver-phosphine complex $\text{PhC}\equiv\text{C}-\text{Ag}(\text{Ph})\text{PEt}_2$. Solutions of the complexes $p\text{-NO}_2\text{C}_6\text{H}_4\text{C}\equiv\text{C}-\text{Ag}(\text{Ph})\text{PEt}_2$ and $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{Ag}-(\text{Ph})\text{PEt}_2$ smelled of free phosphine, and eventually became cloudy due to reversible dissociation and formation of the insoluble acetylide:-



This dissociation renders purification difficult, as attempted recrystallization leads to the isolation, along with the crystalline complex, of traces of the insoluble acetylide. The formation of the acetylide can be inhibited, but not completely eliminated, by addition of a little free phenyldiethylphosphine to the recrystallizing solution. Consequently, figures for analyses were low in carbon due to the presence of free acetylide, this defect, as might be expected, being greatest in the case of the complex, $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{Ag}-(\text{Ph})\text{PEt}_2$.

Cryoscopic measurements

As a further result of the tendency to dissociate in solution, only the phenylethyne (phenyldiethylphosphine) silver, $\text{Ph}-\text{C}\equiv\text{C}-\text{Ag}(\text{Ph})\text{PEt}_2$ could be successfully used for a reasonably reliable molecular weight determination, and was found to be dimeric in freezing benzene. Attempts to obtain cryoscopic measurements on the other two complexes in both

nitrobenzene and benzene were almost impossible due to their lack of stability in both media.

One of the main obstacles in the use of the $p\text{-NO}_2\text{C}_6\text{H}_4\text{C}\equiv\text{CAg}(\text{Ph})\text{PEt}_2$ complex was the difficulty in making up a solution of reasonable strength, as dissociation tended to set in before solution was complete. Accordingly, four very dilute solutions (~ 0.01 molar) of the complex were made up in benzene, and used immediately to minimise dissociation. However the apparent molecular weights in solutions of approximately equal strength were found to vary considerably, giving values of 414; 465; 604; 297. These results may indicate that the complex (Empirical M.W. = 420) might be monomeric in benzene solution, but the solutions are so dilute, and the results so diverse, that little reliance may be placed upon them.

As mentioned previously, stability of the $p\text{-NO}_2\text{-C}_6\text{H}_4\text{C}\equiv\text{C-Ag}(\text{Ph})\text{PEt}_2$ complex in solution is enhanced by the presence of free phosphine, and in the hope that more information on the molecular weight of the complex might be obtained, the freezing points of solutions of the complex in benzene, in the presence of a known amount of free phenyldiethylphosphine were determined. A solution of phenyldiethylphosphine (1.0 ml) in benzene (100 ml) was made up accurately, and used to dissolve the $p\text{-NO}_2\text{C}_6\text{H}_4\text{-C}\equiv\text{C-Ag}(\text{Ph})\text{PEt}_2$ complex, only weak solutions being obtained. See Table 1 on following page.

The freezing point depression of the solutions containing the $p\text{NO}_2\text{-C}_6\text{H}_4\text{C}\equiv\text{C-Ag}(\text{Ph})\text{PEt}_2$ complex over that containing the free phosphine alone is much less than expected if simple solution was taking place.

TABLE 1

Weight of Solute	Vol. of Phosphine-Benzene Solution to Dissolve it	Freezing Point	Depression from Benzene Soln.	Apparent Molecular Weight
Pure Benzene	0.845°			
25 mls Phosphine-Benzene Soln.	0.486°			
0.1590g.	20 ml	0.474°	0.012°	4033
0.2671g.	20 ml	0.447°	0.039°	2084
0.5230g.	30 ml	0.450°	0.036°	2946

TABLE 2

Wt. of Solute	No. of Moles of Solute	Vol. of original Soln. made up to 50ml	No. of Moles of PnPhEt_2 per 25 ml	Moles PnPhEt_2 / Moles complex	Depression from pure Benzene	Depression caused by PnPhEt_2 alone (Calc.)	Depression caused by complex alone	Apparent Molecular weight of complex
0.1519g	3.617×10^{-4}	6 mls	3×10^{-4}	Pure Benzene	1.241°			
0.1259g	2.997 "	12 mls	6 "		0.131°	0.074°	0.057°	647.8
0.1347g	3.207 "	19.2 "	9.6 "		0.194°	0.146°	0.052°	585.1
0.1368g	3.257 "	26.1 "	13.05 "		0.274°	0.232°	0.042°	776.6
					0.620°	0.317°	0.303°	110.6

The results would appear to correspond to a phosphine:acetylide molar ratio of just less than 2:1 i.e. if it was $(\text{PhPET}_2)_2\text{Ag-C}\equiv\text{C-C}_6\text{H}_4\text{-NO}_2$ in solution, there would be no change in the number of molecules present in the solution, and would therefore be no additional freezing point depression.

Consequently, to obtain more information on the possibility of additional phosphine-acetylide co-ordination in solution, a series of freezing point determinations was carried out using solutions in which the phosphine: complex ratio was gradually increased:- See Table 2 on previous page.

The results thus obtained are obviously not due to simple solution of the acetylide-phosphine complex in the phosphine-benzene solvent; nor to any simple increase in the ratio of moles of phosphine complexing to one mole of acetylide. Indeed, the results would appear to defy a reasonably simple interpretation.

Infra-red measurements

The $\text{C}\equiv\text{C}$ stretching frequency shows up strongly in the infra-red absorption spectrum of non-symmetrically substituted acetylenic compounds, usually in the region $2000\text{-}2300\text{ cm}^{-1}$. Comparison of the position of this absorption band in the spectrum of a metal acetylide, e.g. $\text{p-NO}_2\text{-C}_6\text{H}_4\text{-C}\equiv\text{CAg}$, and the corresponding p-nitrophenylethynyl silver-phosphine complex, e.g. $\text{p-NO}_2\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-Ag(Ph)PET}_2$, shows a shift towards a higher frequency in the case of the phosphine complex. For example, in the case of the latter compounds, the shift is from 2042 cm^{-1} to 2070 cm^{-1} . It might be expected that if co-ordination took place between a silver acetylide-phosphine complex and additional molecules of free phosphine in solution,

then the absorption band may be moved to an even higher frequency. Therefore, in an attempt to explain the anomalous cryoscopic data, a series of solutions of the $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-Ag(Ph)PET}_2$ complex in benzene, with varying known amounts of free phenyldiethylphosphine present was made up, and the position of the $\text{C}\equiv\text{C}$ stretching frequency determined accurately in each case:-

$\frac{\text{Moles PhPET}_2}{\text{Moles complex}}$	(Pure Benzene) 0	0.57	1.16	1.93	2.88	3.86
$\text{C}\equiv\text{C}$ stretching frequency	$2095\text{-}\frac{1}{\text{cm}}$	$2095\text{-}\frac{1}{\text{cm}}$	$2095\text{-}\frac{1}{\text{cm}}$	$2095\text{-}\frac{1}{\text{cm}}$	$2095\text{-}\frac{1}{\text{cm}}$	$2095\text{-}\frac{1}{\text{cm}}$

It is immediately obvious that variation of concentration of free phenyldiethylphosphine in the solution has no effect on the $\text{C}\equiv\text{C}$ stretching frequency, no light being thrown on the possible additional co-ordination of phosphine with the p -nitrophenylethynyl (phenyldiethylphosphine)-silver, except that, if it does take place, the effect is very much less than that of the molecule of phosphine originally co-ordinated. It may be noted that the frequency obtained in benzene solution ($2095\text{-}\frac{1}{\text{cm}}$) is appreciably different from that obtained from the solid $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-C}\equiv\text{CAgPhPET}_2$ in a potassium bromide disc ($2070\text{-}\frac{1}{\text{cm}}$).

ORGANIC DERIVATIVES OF COPPEREXPERIMENTAL

Throughout this work, stirring of cuprous halide suspensions was effected with a tantalum wire Hershberg stirrer. All solvents used were carefully purified and stored over molecular sieve.

Preparation of Phenyl Copper1. From cuprous iodide and phenyl magnesium iodide

Magnesium turnings (1.4g, 0.0576 moles) and iodobenzene (10.2g, 0.05 moles) were used in ether (50 mls) to make phenyl magnesium iodide (0.049 moles, 98% yield). After filtration through a glass wool plug and estimation, the transparent light brown solution was transferred to a 250 ml, three-necked flask, and cooled to 0°C in an ice-water bath before addition of cuprous iodide (8g, 0.042 moles), the mixture being stirred vigorously with a Hershberg stirrer. Stirring was continued for 3 hours at 0°C, the colour changing from dark brown to dark green, a little unreacted cuprous iodide being present throughout. On allowing the solution to settle, a light coloured precipitate, phenyl copper, was observed above the heavier cuprous iodide. The phenyl copper was carefully decanted from the unreacted halide and filtered as a pale grey solid on a sintered glass disc (Grade 3), being washed several times with ether. The washings gave a negative result to Gilman Colour Test 1. The solid, as a slurry wet with ether, was then used for tests or reactions with donor molecules.

Excess of phenyl magnesium iodide was present in the reaction mixture throughout. The product always gave a negative colour test for Grignard and a positive Beilstein test for halogen.

2. From cuprous iodide and phenyl lithium

Lithium shot (1.6g, 0.23 moles) and bromobenzene (15.7g, 0.1 moles) were used to prepare phenyl lithium (0.0936 moles, 93.6% yield) in ether (90 mls), at room temperature and allowed to reflux. After filtration through a glass wool plug, the phenyl lithium solution was allowed to settle for a few hours before estimation, giving a clear red solution. This solution was then added over 30 minutes to a well stirred suspension of anhydrous cuprous iodide (16.1g, 0.085 moles) in ether (50 mls), previously cooled to 0°C, in a 500 ml, three-necked flask. During the addition, the colour of the mixture changed from white, through yellow and mustard, to dark green, being stirred at 0°C for additional periods of from 4 hours to 24 hours. On settling, a light coloured solid was observed, while unreacted cuprous iodide remained in some cases, probably due to coating by the product. In many cases, especially those stirred for longer periods, metallic copper was observed as a thin red-brown deposit on parts of the flask. The mixture was filtered, the phenyl copper appearing as a pale coloured grey, green, yellow or pink powder on the sintered glass disc. It was washed repeatedly with ether, being stirred with a glass rod during each washing. The filtrate was always a red or red-brown colour, often being fluorescent, invariably depositing metallic copper on standing and giving a positive test for phenyl lithium (Gilman Colour Test 1). The solid was pumped dry on the high vacuum pump and weighed, being ready for use in subsequent reactions. Yields were of the order of 85%-90%.

As mentioned previously, unreacted cuprous iodide remained in some cases, but the majority of this could be left in the reaction flask by decantation. It is not surprising, therefore, that the product always contained some halogen. In some cases, however, no iodine could be detected in the product, while Gilman Colour Test 1 was always negative.

Purity of the samples varied considerably; some could be weighed in air with little apparent change, while others glowed red-hot when exposed.

A sample of phenyl copper was heated in a cold finger apparatus in an oil bath, at a pressure of 0.04 mm mercury, and decomposed suddenly above 80°C, leaving a copper mirror, while biphenyl, m.p. 69-71°C, sublimed.

Preparation of Lithium Diphenyl Copper (I), $\text{Li}^+ (\text{CuPh}_2)^-$

Cuprous iodide (6g, 0.0316 moles) was added to a solution of phenyl lithium (0.1263 moles) in ether (110 mls) at 0°C, in a 250 ml three-necked flask, with rapid stirring, the very dark colour of the solution making observation difficult. Stirring was continued for periods of 1½ hours and 12 hours at 0°C in two cases, and for 12 hours at room temperature in another. Small portions (2 ml) of the solution were tested for the presence of water-insoluble iodide (i.e. cuprous iodide) at intervals throughout the preparation, being positive in every case, as was Gilman Colour Test 1.

In one instance, before reaction with donor molecules, the whole solution was filtered to remove any unreacted cuprous iodide, while in another case, ethyl acetate was added to the solution at 0°C to remove

excess phenyl lithium and leave the phenyl copper free for subsequent reaction with donor molecules:-



This reaction took place so vigorously, however, that about half of the solution was lost by boiling over.

Preparation of Mesityl Copper

Mesityl copper was made by reaction of mesityl magnesium bromide and cuprous iodide in tetrahydrofuran-ether mixture. The preparation was also attempted using mesityl lithium in tetrahydrofuran.

a. Preparation of Mesityl Magnesium Bromide

Mesityl magnesium bromide (0.0447 moles, 89.6% yield) was prepared from magnesium turnings (1.4g, 0.0576 moles) and bromomesitylene (9.93g, 0.0499 moles) in a mixture of ether (50 mls) and tetrahydrofuran (30 mls), being initiated at room temperature with ethylene bromide, and allowed to reflux. From the first two preparations, transparent, red-brown solutions were obtained after filtration through a plug of glass wool. Mesityl copper was successfully prepared from these solutions. Numerous subsequent preparations, using new batches of tetrahydrofuran, bromomesitylene, and magnesium metal, yielded a buff coloured solution, which would not give mesityl copper, although it gave mesitylene carboxylic acid, m.p. 152°C, in 74% yield, when carbonated by pouring on to a dry ice-ether slurry. The preparation of mesityl copper, was however eventually repeated and it was discovered that the successful preparations used bromomesitylene which had been made from mesitylene supplied by L. Light & Co., Payle Trading Estate, Colnbrook, Bucks., while the unsuccessful preparations were attempted using two different batches of

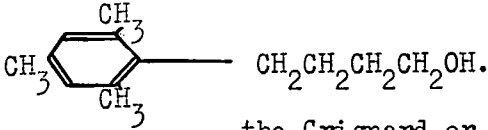
bromomesitylene from another source.

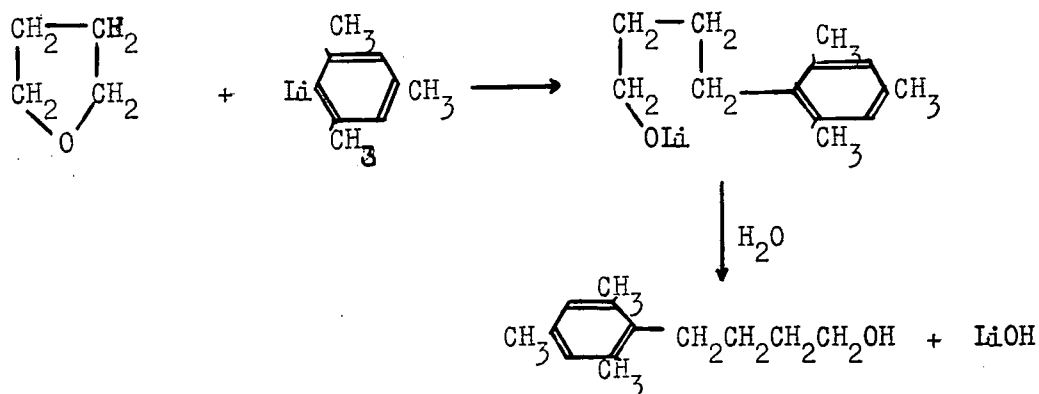
b. Preparation of Mesityl Lithium in tetrahydrofuran

Lithium shot (0.9g, 0.128 moles) in tetrahydrofuran (50 mls) was used with a solution of bromomesitylene (9.95g, 0.05 moles) in tetrahydrofuran (50 mls) to prepare mesityl lithium as a deep red solution, the reaction being initiated at room temperature. The addition of aryl halide was carried out at -60°C or -30°C over periods of from one to three hours, stirring being continued for a further $1\frac{1}{2}$ hours to ensure completion of the reaction. Yields varied from 48% to 96%, increasing in proportion to the time of reaction. The cooling bath had to be removed at intervals to ensure that the reaction was proceeding.

c. Reaction of cuprous iodide with mesityl magnesium bromide

The deep red-brown solution of mesityl magnesium bromide (0.036 moles) in tetrahydrofuran-ether mixture, was added to a well stirred suspension of cuprous iodide (6g, 0.0316 moles) in ether (30 mls), previously cooled to 0°C , in a 500 ml flask. The colour of the mixture changed slowly from pale greenish-brown to very dark green. At this stage, Gilman Colour Test 1 was positive. Stirring was continued for 30 minutes in one case, and overnight in others, before filtering through a sintered glass disc (Grade 3), a grey or white solid, and a deep green filtrate being obtained. The solid was washed with ether until the washings were colourless, and the solid examined. It was found to contain magnesium, iodine and a small amount of copper. On allowing a little of this solid to stand in air, or on hydrolysis of a small sample, a smell of tetrahydrofuran was noticed, together with a sweet smell, often noticed after use of mesityl lithium or mesityl magnesium bromide in tetrahydrofuran,

and thought to be:-  This would be formed by reaction of the Grignard or organo-lithium compound with tetrahydrofuran:-



The behaviour of the solid is therefore consistent with that of a mixture containing magnesium halide-tetrahydrofuran complexes and unreacted cuprous iodide.

The deep green filtrate was therefore analysed for copper:-

Two samples (10 mls) of the solution (total volume = 194 mls) were withdrawn, the solvent pumped off, and the copper estimated as cuprous thiocyanate:-

Weight of CuSCN	Moles of copper per 10 mls solution	Total Moles of copper in solution
0.1272g	1.047×10^{-3}	0.0203
0.1274g	1.048×10^{-3}	0.0203

It was thus shown that 64.2% of the total copper used was present in this deep green organic solution.

The solvent was pumped off under high vacuum, the tetrahydrofuran being reluctant to do so in the later stages, as it was probably being held in a complex with magnesium halides, leaving a tacky dark green, almost black, mass. This was investigated:-

1. It burned on a nickel spatula with a strikingly aromatic flame, also giving a green copper colour. A red-brown residue, probably of cuprous oxide, was obtained.

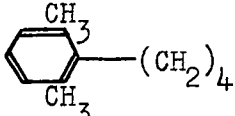
2. A small amount was dissolved in benzene, being freely soluble. On addition of a few drops of water, it was slowly hydrolysed, a yellowish precipitate being obtained. This was filtered, washed, pumped dry, and an X-ray powder photograph taken. Comparison of this with a similar photograph of cuprous oxide showed the two to be identical. The colourless filtrate from this hydrolysis contained magnesium, which could be precipitated as its hydroxide, which dissolved in ammonia.

3. A further sample was heated in a cold finger apparatus under high vacuum to an oil bath temperature of 190°C , a colourless liquid distilling off to leave a red-brown metallic looking residue, containing copper and magnesium. An X-ray powder photograph, using copper $K\alpha$ radiation, was performed on a sample of this material, and compared with a photograph of precipitated copper - see Table on opposite page.

Only the bands from the copper photograph coinciding with those in the decomposition product are shown, but these include all of the strong bands of copper, the extra lines no doubt being due to the presence of magnesium halides.

Very little of the colourless sweet-smelling distillate was

isolated, and an infra-red spectrum performed on it. The spectrum resembled that of mesitylene, but contained a strong OH stretching frequency at 3390 cm^{-1} . It was thought to be a mixture of mesitylene and the reaction product of mesityl magnesium bromide with tetrahydrofuran,

namely:- CH_3  $(\text{CH}_2)_4 - \text{OH}$ and, indeed, the infra red spectrum was

found to be identical to that of a product isolated by other workers in this department after use of mesityl magnesium bromide in tetrahydrofuran.

The bulk of the deep green solid was then taken up in benzene (30 mls), and hexane (20 mls) was added to reduce solubility of magnesium halide-tetrahydrofuran complexes. The liquid was decanted off, the small amount of dark residue being washed with benzene-hexane mixture (10 mls), and the solvents pumped off at room temperature, the dark green solid being used for reaction with donor molecules.

As mentioned previously, the reaction succeeded only when the Grignard reagent was prepared using the bromomesitylene made from mesitylene supplied by L. Light & Co., Payle Trading Estate, Colnbrook, Bucks. In the other attempts, no reaction with cuprous iodide took place:-

Mesityl magnesium bromide (0.0518 moles) in tetrahydrofuran-ether mixture (100 mls) was added to a suspension of cuprous iodide (6g, 0.0316 moles) in ether (50 mls) exactly as previously, no reaction taking place, even after stirring at room temperature for two days, at which stage Gilman Colour Test 1 was still slightly positive. It was therefore filtered and the pale residue washed with tetrahydrofuran-ether mixture, the washings containing iodine, presumably formed by oxidation

of cuprous iodide. The pale solid was dried and weighed (5g) being soluble in strong potassium iodide solution. This was obviously cuprous iodide and had therefore been at least 83% unreacted.

Despite rigorous precautions to ensure that all reactants and solvents were pure and dry, the preparation of mesityl copper could not be repeated using this bromomesitylene.

Mesityl magnesium bromide (0.10 moles) prepared from this bromomesitylene, gave mesitylene carboxylic acid, m.p. 152° (12g, 74.2% yield).

The production of iodine during working up of these reaction mixtures was very strange, but would be explained by the presence of peroxides in the tetrahydrofuran. However, one reaction was carried out in which all tetrahydrofuran used was distilled from potassium diphenyl ketyl, $K^+ \bar{O}-CPh_2$, directly into the reaction flask, before preparation of the Grignard solution. However, this did not alter the course of the reaction. The original cuprous iodide was tested for possible contamination by cupric iodide, which would decompose to give cuprous iodide and iodine, by simply adding water, no change being apparent.

d. Reaction between cuprous iodide and mesityl lithium and subsequent reaction with triphenylphosphine

All reactions of this type were carried out using the batches of bromomesitylene which were unsuccessfully used in the attempted preparations of mesityl copper from cuprous iodide and mesityl magnesium bromide.

(i) Mesityl lithium (0.036 moles) in tetrahydrofuran (100 mls), was added with vigorous stirring to a suspension of cuprous iodide (6g, 0.0316 moles) in ether (50 mls), at 0°C, the addition taking 1 hour. On allowing to stand for 1 hour, a dark deposit settled out from the deep red solution, and in addition, a small deposit of metallic copper had formed where the mesityl lithium solution had made direct contact with the flask below the dropping funnel. The solution was filtered through a sintered glass disc (Grade 3), giving a dark-coloured, inorganic, copper-containing residue, and a red filtrate. To the filtrate, was added a solution of triphenylphosphine (8.3g, 0.0316 moles). After standing overnight, the solvent was removed in vacuo, leaving a black, sticky residue. Benzene (100 mls) was added, and the solution hydrolysed, filtered (hyflo super cel), and separated, the benzene solution yielding a yellow crystalline material (7.5g), which contained triphenylphosphine, copper and iodine. A small sample of this material was recrystallized from benzene-hexane mixture to give white crystals which melted with decomposition at 225°-230° to give a clear brown solution. An infra red spectrum closely resembled that of triphenylphosphine, while carbon and hydrogen analysis gave:-

	C	H
Found	57.6%	4.0%
Required for (a) $(\text{Ph}_3\text{P})\text{CuI}$	47.7%	3.32%
(b) $(\text{Ph}_3\text{P})_2\text{CuI}$	60.6%	4.21%
(c) $(\text{Ph}_3\text{P})_3(\text{CuI})_2$	55.6%	3.86%

This analysis was not really satisfactory for any of the

complexes shown, its composition being closest to compound (c), and probably consisting of a mixture. For comparison, cuprous iodide (0.6g, ~ 0.00316 moles) was shaken with a solution of triphenylphosphine (3.6g, ~ 0.0137 moles) in ether (25 mls), and the white insoluble precipitate was filtered off, washed thoroughly with ether, and pumped dry. Its infra-red spectrum was found to be identical to that of the compound above, while a carbon and hydrogen analysis gave C=57.8%, H=4.3%, very similar to that of the last compound.

(ii) In a similar reaction, carried out at lower temperature ($\sim -70^\circ\text{C}$) 12.8g of material identical to that obtained in the last experiment was isolated (confirmed by infra-red spectrum and melting point).

Reaction between phenyl lithium and tris-(phenyldiethylphosphine) bis-moniodocopper $(\text{PhPEt}_2)_3 (\text{CuI})_2$

A solution of phenyl lithium (0.0264 moles) in ether (40 mls) was added dropwise, with vigorous stirring, to a suspension of $(\text{PhPEt}_2)_3 (\text{CuI})_2$ (10g, 0.0114 moles) in ether (70 mls) at -50°C , Gilman Colour Test 1 being positive after complete addition. The mixture was stirred for 2 hours at this temperature being periodically tested for organically combined iodide, by hydrolysis of a small sample, the organic phase being washed well with water, dried, and the solvent removed, the residue being tested for iodine in the usual way. As the test was positive, more phenyl lithium (0.0143 moles) in ether (20 mls) was added, and the solution kept at -78°C overnight. It was then allowed to warm up, the suspension dissolving at -20°C . After stirring for 2 hours at room temperature, some phosphine-cuprous iodide complex still remained

in solution. It was split into two parts, the first being stirred with a four fold excess of phenyl lithium, and the second refluxed overnight. However, in neither case did the reaction proceed, starting material being isolated as white crystals, m.p. 59°C - 615°C , in a combined yield of 8g, 80%. The crystals were subjected to carbon and hydrogen analysis:-

	Carbon	Hydrogen
Found	41.0%	5.2%
Calculated (for $(\text{PhPEt}_2)_3 (\text{CuI})_2$)	41.0%	5.13%

Reaction of copper aryls with donor molecules

1. Mesityl copper

Only three preparations were performed in which the deep green mesityl copper was produced and these will be discussed separately. The reaction with donor molecules was normally carried out after the initial filtration of the deep green solution from precipitated magnesium halide-tetrahydrofuran complexes and any unreacted cuprous iodide.

(i) Triethylphosphine (4.66 mls, 0.0316 moles) was added to the deep green filtrate containing mesityl copper (0.0316 moles based on 100% yield) in tetrahydrofuran-ether mixture (200 mls). After standing overnight, the resulting deep red solution was split into two equal parts and treated separately:-

Part 1. This was hydrolysed with distilled water, an orange, inorganic, copper-containing solid, probably cuprous oxide, appearing in the aqueous layer, while a pale green organic layer was formed. The ethereal layer was washed thoroughly with water, and after being filtered, separated, dried, and pumped down, yielded a yellow oil with some yellow solid present in it.

This mixture smelled strongly of triethylphosphine and had an infra-red spectrum identical to that of the triethylphosphine-cuprous iodide complex, PEt_3CuI . The whole mixture was transferred to a small double Schlenke tube in pentane solution, cooled to -40°C and the pentane poured through the sinter, leaving a pale yellow solid, which was washed once more with pentane at -40°C . This solid contained copper and halogen and smelled of triethylphosphine when burned, while its infra-red spectrum was identical to that of triethylphosphine-moniodocopper, PEt_3CuI . However, in contrast to the latter (m.p. $\sim 240^\circ\text{C}$), the yellow compound began to melt at 140°C , darkening, and not melting completely over a considerable range of temperature. The compound could not be recrystallized satisfactorily, being insoluble in most organic solvents. It was analysed in duplicate for carbon and hydrogen:-

	Carbon	Hydrogen
Found	(27.4%	5.9%
	(27.0%	5.7%
Required for PEt_3CuBr	27.5%	5.7%
PEt_3CuI	23.4%	4.9%

It is thus triethylphosphinemonobromo copper, accounting for the difference in melting point.

The pentane solution which had been removed from the above solid, on pumping down, yielded a brown oil, smelling strongly of triethylphosphine and having an infra-red spectrum identical with that of the compound above. It was therefore thought to consist largely of triethylphosphine with a little dissolved phosphine-cuprous halide complex.

Part 2. The solvent was removed from this portion of the solution under high vacuum leaving a red viscous copper-containing oil which was washed with benzene containing some pentane to inhibit solubility of magnesium halide-tetrahydrofuran complexes, into a double Schlenke tube. The dark residue was pumped dry leaving a pale green powder, white in parts, which did not burn, but contained copper, magnesium and iodine. Repeated attempts at recrystallization on the solution in the Schlenke tube gave only an oil, so the solvent was removed in vacuo to give a viscous, pale green oil which looked brown on the sides of the tube. Addition of dry hexane gave a red-brown solution, and precipitated an off-white solid, which was filtered and washed with hexane. The small amount of solid contained copper, magnesium, halogen, and smelled of triethylphosphine when burned, and was thought to be a mixture of magnesium halides and triethylphosphine-cuprous halide complex.

The red hexane solution gave colourless, almost insoluble crystals, containing copper, halogen, and triethylphosphine. These crystals began to melt at 115°C to give a dark coloured semi-solid over a considerable range of temperature, and were once more thought to be a triethylphosphine-cuprous halide complex.

2. a. Triethylphosphine

Triethylphosphine (0.5 mls, 0.0034 moles) was added to a solution of the dark green solid (0.5g, 0.00274 moles, assuming it to be mesityl copper) in benzene (30 mls), forming a pale yellow solution with some pale, insoluble, flocculent material present. The solid was thought to be a trace of magnesium halide and was filtered off. The

benzene was removed in vacuo, leaving a pale yellow oil with a small amount of yellow solid present. This mixture contained copper and halogen, and smelled of triethylphosphine, probably consisting of a little phosphine-cuprous halide complex in an excess of free phosphine. Repeated attempts at removal of free phosphine by washing with hexane, hexane-benzene mixtures, and by pumping at 10^{-3} mm Hg pressure and 40°C were unsuccessful, each step resulting in formation of more dark brown decomposition product.

A further sample of mesityl copper (1g), after similar treatment, finally was obtained as a dark brown benzene solution, to which a little triphenylphosphine was added. On standing for seven days, colourless needles, m.p. 167° - 168°C , separated. These were air-stable, contained copper, triphenylphosphine, and bromine, but no iodine. They were eventually shown to be the same compound as that obtained in the next section.

b. Triphenylphosphine

A solution of triphenylphosphine (1.44g, 0.0055 moles) in benzene (10 mls) was added to a solution of mesityl copper (1.0g, 0.0055 moles) in benzene (20 mls), the deep green colour persisting, and a few white needles coming out of solution. Addition of more triphenylphosphine (2.0g, 0.00764 moles) resulted in formation of more needles, but still did not discharge the green colour. The crystals were filtered and washed with a small amount of benzene to remove the last traces of green colour. More triphenylphosphine (2.0g, 0.00764 moles) was added to the green filtrate with no further effect. The crystals,

m.p. 168° - 169° C contained copper, triphenylphosphine and bromine, but did not contain iodine. A sample recrystallized from benzene gave colourless needles, m.p. 170° C, whose infra-red spectrum contained no aliphatic CH frequencies in the range 2900 cm^{-1} - 2850 cm^{-1} , which would be expected from the methyl groups of the mesityl ring in a compound of the type: Mesityl-Cu-PPh₃. Indeed, the spectrum closely resembled that of triphenylphosphine and was almost identical to that of a triphenylphosphine-cuprous iodide complex. Carbon and hydrogen analysis gave:-

	Carbon	Hydrogen
Found	73.2%	5.6%

A small sample of the compound was heated under high vacuum at 230° C for 1 hour in a cold finger apparatus, a pale yellow residue containing copper and bromine, obviously consisting mainly of cuprous bromide, remaining. The sublimate was triphenylphosphine, m.p. 78° C. The remainder of the compound was used up when an attempted copper analysis failed.

3. Triphenylphosphine (16.55g, 0.0632 moles) in benzene (50 mls) was added to a filtered solution of mesityl copper (0.0158 moles assuming 100% yield), and after partial removal of the benzene in vacuo, colourless crystals, m.p. 169° - 170° C were obtained. These were identical to those obtained from the last experiment (infra-red spectrum). A sample was recrystallized from benzene and tested:-

a. A sodium fusion was carried out on a small sample, the solution giving a faint precipitate with silver nitrate, indicating the presence of halogen.

b. A further sample of sodium fusion solution, on heating with a

little chromic acid, evolved bromine, which turned fluorescein paper red.

c. Carbon and hydrogen and copper analyses were performed:-

	Carbon	Hydrogen	Copper
Found	73.4%	5.1%	6.28%
			6.24%
Required for PPh_3CuBr	53.3%	3.7%	15.2%
$(\text{PPh}_3)_2\text{CuBr}$	64.7%	4.5%	9.5%
$(\text{PPh}_3)_3\text{CuBr}$	69.8%	4.9%	6.84%
$(\text{PPh}_3)_4\text{CuBr}$	72.6%	5.0%	5.36%

2. Phenyl Copper

a. Pyridine As reported by Gilman, phenyl copper, like cuprous iodide, gave a yellow solution in pyridine.

b. Bipyridyl A solution of bipyridyl (2.5g, 0.016 moles) in benzene (50 mls) was added to phenyl copper (2.21g, 0.0158 moles), a deep red solution, with a dark flocculent precipitate being formed. On working up, the reaction mixture yielded only bipyridyl (2.5g, 100% recovery) together with dark coloured residue containing inorganic copper.

c. Phenyldiethylphosphine

(i) A solution of phenyldiethylphosphine (4.6 mls, 0.0263 moles) in benzene (30 mls) was added to phenyl copper (0.0263 moles, assuming 100% yield), as a slurry wet with ether, to give a dark coloured, opaque solution. Once more, inorganic copper was obtained in dark coloured residues, while cuprous iodide was recovered (0.0114 moles, 43.3%) as yellow crystals of the complex, $(\text{PhPEt}_2)_3(\text{CuI})_2$, (5g), m.p. $59^\circ\text{-}61.5^\circ\text{C}$.

(ii) In other experiments, the phenyl diethylphosphine was added directly to the reaction mixture from the preparation of phenyl copper, once at room temperature, and once at -60°C . The first of these was hydrolysed at room temperature after stirring for 10 minutes, becoming hot, and extensive decomposition to metallic copper taking place. Working up of the hydrolysate yielded a mixture (3g) of biphenyl and phosphine-cuprous iodide complex. The lower temperature reaction was allowed to warm up, being stirred for 90 minutes at room temperature. The dark green solution was then cooled to -5°C and hydrolysed, some metallic copper forming. Working up yielded phenyldiethylphosphinemonoiodo-copper (2g, 0.00562 moles), m.p. $149^{\circ}-151^{\circ}\text{C}$, recrystallized from ethanol, representing a 21.4% recovery of cuprous iodide.

(iii) Phenyldiethylphosphine was also added to phenyl copper as a filtered solution of lithium diphenyl copper (I), $\text{Li}^+ (\text{CuPh}_2)^-$, at -50°C , being allowed to warm to room temperature, stirred for 1 hour, cooled to -20°C , and hydrolysed with a mixture of water (20 mls) and THF (50 mls). Very little insoluble inorganic material was obtained on filtering, the aqueous layer having a distinct cupric colour. White crystals of phenyldiethylphosphinemonoiodo-copper, m.p. $149^{\circ}-151^{\circ}\text{C}$ (6.0g, 0.0168 moles, 53.2%) were obtained, being confirmed by a carbon and hydrogen analysis:-

	Carbon	Hydrogen
Found	33.7%	4.3%
Required for PhPEt_2CuI	33.8%	4.22%

d. Triethylphosphine

(i) A solution of triethylphosphine (4.66 mls, 0.0316 moles) in benzene (80 mls) was added to solid phenyl copper (0.0316 moles assuming 100% yield), giving a very dark brown opaque solution, a small amount of dark solid being filtered off. The benzene was pumped off, a dark brown oil containing copper and triethylphosphine being left. All attempts at crystallization, mainly with benzene-ligroin mixtures, failed, each attempt yielding more dark coloured, inorganic, copper containing residue.

(ii) Triethylphosphine was also added to phenyl copper in the form of the filtered solution of lithium diphenyl copper (I), $\text{Li}^+(\text{CuPh}_2)^-$, in ether at -60°C , the solution being allowed to warm up to room temperature and stirred for 2 hours, before cooling to -20°C for hydrolysis with THF-water mixture (~ 100 mls, 2:1). Filtration of the solution yielded triethylphosphinemono-iodocopper, m.p. 240°C + (3.0g) as a white, insoluble powder. The blue aqueous layer, no doubt containing cupric copper, was discarded, the organic layer yielding more phosphine-cuprous iodide (2.7g) complex, found to be identical with the first by its infra-red spectrum and melting point. A carbon and hydrogen analysis of this sample confirmed its composition:-

	Carbon	Hydrogen
Found	22.1%	4.9%
Required for PEt_3CuI	23.4%	4.9%

Recovery of cuprous iodide was thus 0.0185 moles, 58.5%.

(iii) Ethyl acetate (10g, 0.1134 moles) was added at 0°C to a solution of lithium diphenyl copper (I), made by adding excess of phenyl lithium (0.1263 moles) to cuprous iodide (6g, 0.316 moles) in ether, as described previously. A violent reaction, which caused loss of about half of the reaction mixture, took place. After 30 minutes, a solution of triethylphosphine (4.66 mls, 0.0316 moles) in ether (30 mls) was added at 0°C and the solution hydrolysed at this temperature. Working up as usual, yielded a little cuprous oxide, triethylphosphine-monoiodocopper (2.0g, 0.0065 moles, 20.5%), identified by its melting point, 240°C, and infra-red spectrum; and the carbinol $\text{Ph}_2\text{-C-CH}_3$, m.p. 82°C, (4.5g, 0.0288 moles), purified by sublimation in vacuo.

e. Triphenylphosphine

(i) A solution of triphenylphosphine (3.8g, 0.01450 moles) in benzene (50 mls) was added to a suspension of phenyl copper (2g, 0.01428 moles) in benzene (10 mls), the original red colour of the solution, probably due to the presence of some colloidal copper, changing to deep green. The solution was kept overnight at -78°C, allowed to warm to room temperature, and more triphenylphosphine (3.8g, 0.0145 moles) added with shaking, and the solution allowed to stand for 1 hour. The solution was filtered from some dark decomposition product, probably cuprous oxide, and the benzene was pumped off, leaving a brown, semi-crystalline material (8g). This was dissolved in benzene, and the solution concentrated, some pale yellow crystalline solid (1g) being obtained. A hot benzene solution of this material deposited long colourless needles (0.5g), m.p. 165°-166°C, on cooling. They were unstable in benzene solution in the air, giving a brownish-red deposit,

almost certainly cuprous oxide, but the needles themselves were completely stable, containing copper, triphenylphosphine, and bromine, but no iodine. They were identical to the compound obtained from triphenylphosphine and mesityl copper (infra-red and carbon and hydrogen analysis):-

	Carbon	Hydrogen
Found	73.4%	5.5%
Found (for compound for mesityl copper)	73.2%	5.6%

Addition of hexane to the mother liquors precipitated triphenylphosphine (5.6g, 0.0214 moles, ~74%). No diphenyl was found in the final hexane-benzene mother liquors.

(ii) In all of the later experiments, a four-fold excess of triphenylphosphine over phenylcopper was used, the reaction mixture becoming warm in at least one case when the phosphine solution was added. Attempted crystallization usually led to extensive decomposition in solution, especially if carried out in the air. Small amounts of pure samples (~0.7g) were eventually obtained by taking up the solid in warm benzene, filtering, and allowing the solvent to evaporate slowly in a stream of nitrogen. Even so, to remove large quantities of dark green or brown decomposition products, (probably cuprous oxide), the recrystallization had to be repeated, large losses of material were encountered at each stage. Yields of the colourless needles, m.p. 165°-166°C, were usually very low (~4%), while recovery of triphenylphosphine was high (90%+).

At various stages during recrystallization, samples of material

were isolated, which began to melt, sometimes with decomposition at temperatures ranging from 140°C to 160°C , none of which gave a clear solution at any temperature up to 190°C , and which were otherwise identical to the higher melting compound.

The crystals melting at 165° - 166°C had an identical infra-red spectrum to the compound obtained from the reaction between mesityl copper and triphenylphosphine.

Preparation of methyl copper and subsequent reaction with donor molecules

1. To a well stirred suspension of cuprous iodide (19.05g, 0.1 moles) in ether (50 mls), at -15°C , was added a solution of methyl lithium (0.1 moles) in ether (100 mls), a bright yellow precipitate of methyl copper being formed. Small portions (~ 1 ml) of the reaction mixture were withdrawn and examined:-

(i) A sample (1 ml) was added to a solution of bipyridyl (0.05g, 0.03 moles) in ether (5 mls) at room temperature, a yellowish solid, turning red-brown on standing, being produced. This solid was filtered and found to be inorganic, containing copper, probably as cuprous oxide.

(ii) Another sample was added to a solution of PhPET_2 (1 ml) in ether (5 mls) and a greyish solid, which did not change on standing, being produced.

To the bulk of the solution at -20°C was added phenyldiethylphosphine (17.5 mls, 0.101 moles), the dark brown solution being kept at -78°C overnight. A white solid was then present in the solution, but on stirring at -15°C for 15 minutes, the solution became uniformly black, filtration giving only a small amount of black residue. The clear brown filtrate was hydrolysed, large amounts of gas being

evolved, and a large amount of dark coloured inorganic decomposition product, containing copper, being formed.

2. In a similar reaction, phenyldiethylphosphine (17.5 mls, 0.101 moles) was added to the suspension of methyl copper (0.1 moles) at -20°C , a clear brown solution being obtained. The solution was then concentrated to a small volume by removal of the ether in vacuo, when benzene (15 mls) was added, and the process repeated, the sticky residue being dark green in colour. Samples were withdrawn and tested:-

(i) Shaking with a small volume of benzene-ether mixture (1:1) in air at room temperature caused fairly rapid decomposition to a brown product, probably cuprous oxide.

(ii) Similar treatment in an inert atmosphere caused less rapid decomposition.

(iii) A further small sample, allowed to dry in the air at room temperature, decomposed with a violent explosion, a characteristic of methyl copper.

Ether (50 mls) was added to the bulk of the solution, and the solution hydrolysed at room temperature, large volumes of gas, and large amounts of cuprous oxide being formed. The organic layer yielded a few white crystals of phenyldiethylphosphinemoniodocopper, m.p. 139°C , formed by a little unreacted cuprous iodide.

ORGANIC DERIVATIVES OF SILVEREXPERIMENTAL

All solvents used were carefully purified and all work carried out in an atmosphere of dry nitrogen, unless otherwise mentioned. When a phosphine-silver iodide complex is expressed in moles, it is with respect to gramme-atoms of silver present.

A. Preparation of Grignard, organo-lithium, and organo-sodium reagents

1. Preparation of mesityl magnesium bromide in tetrahydrofuran

Mesityl magnesium bromide (0.047 moles, 94% yield) was prepared from bromomesitylene (9.9g, 0.0497 moles) and magnesium turnings (1.4g, 0.0576 moles), as a brownish red solution in tetrahydrofuran (100 mls). The reaction was initiated by ethylene dibromide, and the solvent allowed to reflux. The yields estimated by titration (85%-96%) were much higher than those by carbonation (67%-74%) to mesitylene carboxylic acid, m.p. 151°C.

2. Preparation of mesityl lithium

The preparation of mesityl lithium in tetrahydrofuran is described under the section on organo-copper compounds. One preparation was attempted in a benzene-ether mixture, but gave only 14% yield, and was subsequently abandoned.

3. Preparation of methyl magnesium iodide

Methyl magnesium iodide was prepared from methyl iodide (2.50 mls, 0.04 moles) and magnesium turnings (1.2g, 0.0495 moles) in ether (80 mls). The reaction was initiated by addition of a little iodine. The solution was not estimated.

4. Preparation of methyl lithium in ether

Methyl lithium (0.04 moles) was prepared from a solution of

methyl iodide (2.5 mls, 0.04 moles) in ether (40 mls), and lithium shot (1.0g, 0.144 moles) in ether (40 mls). The reaction was initiated by ethylene dibromide and allowed to reflux. The solution was not estimated, as methyl lithium was normally used in large excess.

5. a. Preparation of styryl magnesium bromide in tetrahydrofuran

Styryl magnesium bromide (0.11 moles, 92% yield) was prepared from magnesium turnings (4g, 0.165 moles) and ω -bromostyrene (22g, 0.12 moles) in tetrahydrofuran (200 mls), as a dark red or dark green solution. The reaction was initiated by ethylene dibromide; addition of the halide-tetrahydrofuran solution took 1 hour at 0°C, with stirring for a further 15 minutes before filtration and estimation.

b. Preparation of styryl magnesium bromide in ether

Styryl magnesium bromide (0.117 moles, 78%) was prepared as a dark brown solution from ω -bromostyrene (27.5g, 0.1500 moles) and magnesium turnings (11g, 0.45 moles) in ether (160 mls). The reaction was initiated by refluxing in the presence of a little iodine, and addition of the ethereal solution of ω -bromostyrene took 1 hour, with continuous refluxing and stirring. The solution was refluxed for a further 15 minutes to complete the reaction.

6. Preparation of cyclopentadienyl sodium

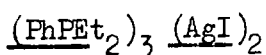
Freshly distilled cyclopentadiene (6.6g, 0.10 moles) was added dropwise to a stirred solution of sodium ethoxide, prepared from sodium (2.3g, 0.1 moles) and dry ethanol (100 mls), a yellow solution of cyclopentadienyl sodium being formed.

7. Preparation of cyclopentadienyl lithium in tetrahydrofuran

A solution of freshly distilled cyclopentadiene (8.1 mls, 0.1 moles)

in tetrahydrofuran (40 mls) was added dropwise to lithium shot (2g, 0.288 moles) in tetrahydrofuran (50 mls), the reaction starting immediately, a yellow colour spreading throughout the solution from the surface of the lithium. Addition of the cyclopentadiene solution took 1 hour at 0°C. The brownish yellow solution was stirred for a further hour before filtration from excess metal; no estimation was necessary, since a large excess of cyclopentadienyl lithium was used in each case.

B. Reaction of Grignard, organo-lithium, and organo-sodium reagents with tris(phenyldiethylphosphine)-bis(moniodosilver),



Preparation of phenyldiethylphosphine and phenyldiethylphosphine-silver iodide complex, $(\text{PhPEt}_2)_x \text{AgI}$

Phenyldiethylphosphine had been prepared in these laboratories from PhPCl_2 (4 moles) and EtMgBr (8 moles). After hydrolysis, steam distillation was carried out, the initial part of the distillate being extracted with ether and redistilled (56°C at 0.05 mm pressure) to give phenyldiethylphosphine, PhPEt_2 (385g, 2.32 moles). To the remainder of the steam distillate was added silver iodide (excess) being stirred for two days before being washed with water and recrystallized from alcohol, (the excess silver iodide thus being removed), to give white crystals (300g) m.p. 83°-84°C. A carbon and hydrogen analysis gave:-

	C	H
Found	37.6%	5.1%
Required for $(\text{PhPEt}_2)_3 (\text{AgI})_2$	37.2%	4.7%

Total yield of phenyldiethylphosphine is therefore 3.25 moles, 81%.

1. Reaction between mesityl magnesium bromide and $(\text{PhPEt}_2)_3(\text{AgI})_2$ in tetrahydrofuran

A solution of mesityl magnesium bromide (0.047 moles) in tetrahydrofuran (80 mls) was added dropwise to a well-stirred suspension of the phosphine-silver complex, $(\text{PhPEt}_2)_3(\text{AgI})_2$, (16g, 0.0332 gm. atoms Ag) in tetrahydrofuran (50 mls) at -15°C , with no apparent change. After stirring for 15 minutes, it was allowed to warm to room temperature, when the phosphine-silver iodide complex dissolved. The solution was stirred overnight, and, on standing, a grey solid, probably a mixture of magnesium halide-tetrahydrofuran complexes coated with silver, was observed. Since a test sample showed that large amounts of the phosphine-silver iodide complex were unreacted, the temperature was gradually raised until the solvent refluxed, during which time only a little more silver was produced. Gilman Colour Test 1 remained positive throughout. Hydrolysis of the solution was carried out at 0°C , no additional silver being produced. Ether (100 mls) was added to the filtered solution (hyflo super cel), and the yellow organic layer separated, dried, and distilled, the last traces of solvent being removed in vacuo. A yellow oil (15.7g) which crystallized partly on standing, was obtained. Crystallization from ether, yielding colourless crystals (8g), which, when recrystallised from ethanol, were found to be phenyldiethylphosphinemonoiodosilver, PhPEt_2AgI , m.p. $138^\circ-139^\circ$ (0.0199 moles). The mother liquors, on cooling in dry ice-acetone, gave a yellow crystalline solid (4g) which was recrystallized from petroleum ether to give colourless crystals of the starting material, $(\text{PhPEt}_2)_3(\text{AgI})_2$, m.p. $83^\circ-84^\circ$, (0.0083 moles). This represented a

total recovery of starting material of 0.0282 moles, 85%.

The petroleum ether was pumped off from the final mother liquors, leaving a yellow oil with the characteristic sweet smell thought to be associated with the compound:- Mesityl- $(\text{CH}_2)_3\text{-CH}_2\text{OH}$, formed by reaction of mesityl magnesium bromide with tetrahydrofuran. The main fraction of the yellow oil, distilling at $164^\circ\text{-}171^\circ\text{C}$, was characterized as mesitylene (b.p. 164.6°C). The yellow semi-solid residue from the distillation gradually darkened on heating, and smelled of phenyldiethylphosphine, probably consisting of a small amount of silver iodide-phosphine complex which had not been removed by the low temperature treatment.

(ii) The reaction was also carried out using as much as a sixfold excess of mesityl magnesium bromide, the Grignard solution being added at temperatures as low as -60°C . The mixture was always allowed to warm up, at least to room temperature, while some reaction mixtures were even refluxed overnight.

(iii) Similar reactions were performed in the presence of a threefold excess of free phenyldiethylphosphine, in the hope that any organo silver compound produced would be additionally stabilised. A further advantage was that because of the increased solubility of the phosphine-silver iodide complex in the presence of excess phosphine, the reaction could be carried out in homogeneous solution, even at low temperatures. In order to make Gilman Colour Test 1 work in the presence of free phosphine, excess of iodine was added to oxidise the phosphine to phosphine oxide. However, the test seemed less reliable under these conditions; only pale colours being obtained.

Hydrolysis of a reaction mixture was usually carried out with distilled water at 0°C, but some were done as low as -40°C.

Working up of reactions was carried out as quickly as possible in the air, but, in all cases, no appreciable reaction had taken place; small amounts of silver, and large amounts of starting material (70%-90%) being obtained.

Four phenyldiethylphosphine-silver iodide complexes of different compositions were isolated from reaction mixtures during working up only one of which, PhPEt_2AgI , has previously been described. These were characterised:-

m.p.	Composition	Found		Required	
		C	H	C	H
71°-72°C	$(\text{PhPEt}_2)_2\text{AgI}$	42.6%	6.0%	42.4%	5.3%
83°-84°C	$(\text{PhPEt}_2)_3(\text{AgI})_2$	37.9%	4.9%	37.2%	4.7%
138°-139°C	PhPEt_2AgI	29.6%	4.2%	29.95%	3.7%
200°C	$\text{PhPEt}_2(\text{AgI})_2$	19.9%	2.6%	18.9%	2.4%

The first three were obtained as colourless crystals, while the last was usually obtained as a highly insoluble white powder, which melted at 200°C to give a cloudy liquid, turning yellow at 250°C. Solubility decreased in the series towards the compound of highest silver iodide content, i.e. $\text{PhPEt}_2(\text{AgI})_2$ which was, nevertheless, freely soluble in solutions containing phenyldiethylphosphine. Solutions of the first three compounds usually smelled of phenyldiethylphosphine, especially on warming. All four compounds possessed identical infra-red

spectra, very closely resembling that of the free phosphine.

2. Reaction between mesityl lithium and tris(phenyldiethylphosphine)-bis(moniodosilver), $(\text{PhPEt}_2)_3(\text{AgI})_2$, in tetrahydrofuran and in tetrahydrofuran-ether mixture

(i) A solution of the phosphine-silver iodide complex, $(\text{PhPEt}_2)_3(\text{AgI})_2$, (9.68g, 0.02 moles) in tetrahydrofuran (70 mls), was added dropwise to a well-stirred solution of mesityl lithium (0.042 moles) in tetrahydrofuran (90 mls) at -60°C , the phosphine-silver iodide complex being precipitated. During the addition, the red-brown colour of the mesityl lithium solution changed to dark brown. During warming to 0°C , the solution became even darker in colour, and consequently was cooled to -20°C and hydrolysed, a little silver being produced as a grey-black powder. Working up in the usual way yielded crystals of starting material, (9.0g, 93%), confirmed by melting point ($83^\circ-84^\circ\text{C}$) and infra-red spectrum.

(ii) A further reaction was carried out between mesityl lithium (0.0741 moles) and the complex $(\text{PhPEt}_2)_3(\text{AgI})_2$, (6g, 0.0124 moles), as previously, but after mixing at -60°C , ether (150 mls) was added, and the solution allowed to warm up to room temperature. The deep port wine-coloured solution was stirred overnight. Despite a considerable colour change, almost to orange, large amounts of the phosphine-silver iodide complex were still present in solution. It was therefore refluxed for one hour, cooled to 0°C , and hydrolysed, a small amount of silver being formed. Working up of the organic layer gave a 75% recovery of starting material, as a mixture of the phenyldiethylphosphine complexes:-

$(\text{PhPEt})_3(\text{AgI})_2$, m.p. $83^\circ-84^\circ$, and $\text{PhPEt}_2 \text{AgI}$, m.p. $136^\circ-137^\circ$.

(iii) A reaction using a two-fold excess of mesityl lithium was stirred at 0°C for 84 hours, giving a dark green, opaque solution. Hydrolysis at 0°C produced a small amount of metallic silver, while subsequent working up recovered 67% of starting material, $(\text{PhPEt}_2)_3(\text{AgI})_2$, identified by melting point ($83^\circ-84^\circ\text{C}$) and infra-red spectrum.

3. Reaction between styryl magnesium bromide and tris-(phenyldiethylphosphine) bis-(monoiodosilver), $(\text{PhPEt}_2)_3(\text{AgI})_2$ in ether.

Styryl magnesium bromide (0.117 moles) in ether (150 mls) was added to a well-stirred solution of tris-(phenyldiethylphosphine), bis-(monoiodosilver) (18.8g, 0.039 moles) in ether (80 mls) at room temperature. A white precipitate was formed initially, but addition of more Grignard reagent caused formation of what appeared to be a black crystalline precipitate. Hydrolysis at 0°C resulted in formation of some silver, and a white precipitate, which proved to be soluble in benzene, to give a yellow solution. On removal of benzene and recrystallization of the residual pale yellow solid (6g, 0.015 moles), from ethanol, white needles, m.p. 139°C , of phenyldiethylphosphine monoiodocopper were obtained, together with a small amount of the highly insoluble complex, $\text{PhPEt}_2 (\text{AgI})_2$, m.p. $\sim 200^\circ\text{C}$. The ethereal solution yielded unchanged starting material (4.1g, 0.0085 moles), m.p. $83^\circ-84^\circ$, giving a total recovery of 0.0235 moles (60%).

4. Reaction between methyl magnesium iodide and $(\text{PhPEt}_2)_3 (\text{AgI})_2$ in benzene-ether mixture

A solution of methyl magnesium iodide was added to a solution of $(\text{PhPEt}_2)_3(\text{AgI})_2$ (9.64g, 0.02 moles) in 50-50 benzene-ether mixture

(80 mls) at 0°C . On allowing the mixture to warm to room temperature, it changed from yellow, then orange, to a brown colour, and when warmed to 30°C silver began to form. It was therefore quickly cooled to -10°C before hydrolysis and working up, starting material (9g) being reclaimed (93%).

5. Reaction between methyl lithium and $(\text{PhPEt}_2)_3(\text{AgI})_2$, in ether

(i) A solution of methyl lithium (0.08 moles) in ether (100 mls) was added to a well-stirred suspension of the phenyldiethylphosphine-silver iodide complex, $(\text{PhPEt}_2)_3(\text{AgI})_2$, (9.68g; 0.02 moles) in ether (100 mls), at -70°C , and stirring continued overnight below -55°C . Large amounts of the phosphine-silver iodide complex were still present in solution, no silver or smell of free phosphine being detected on hydrolysis of a small sample. The reaction mixture was allowed to warm up slowly, phenyldiethylphosphine (10 mls, 0.0572 moles) being added at -40°C . At 7°C , the solution began to darken slowly, and was therefore quickly cooled to -10°C and hydrolysed, little silver being formed. Crystals of starting material (8.8g, 91%), identified by melting point (82° - 83°C) and infra-red spectrum, were recovered on working up. Gilman Colour Test 1 remained positive throughout.

(ii) In another reaction, addition of a solution of methyl lithium (~ 0.24 moles) in ether (100 mls) to a well-stirred suspension of tris-(phenyldiethylphosphine) bis-(monoiodosilver), (9.68g, 0.02 moles) in ether (100 mls) at 0°C , led to rapid and extensive decomposition, a silver mirror being formed on the walls of the flask.

6. Reaction between cyclopentadienyl lithium and $(\text{PhPET}_2)_3(\text{AgI})_2$ in tetrahydrofuran

(i) A solution of cyclopentadienyl lithium (0.10 mls) in tetrahydrofuran (100 mls) was added, with vigorous stirring, to a suspension of the phenyldiethylphosphine-silver iodide complex, (20g, 0.0413 moles) in tetrahydrofuran (100 mls) at -60°C , the mixture becoming progressively darker during the addition. It was allowed to warm up to -10°C and stirred for 1 hour at this temperature, before being hydrolysed, no silver or free phosphine being detected, and tris-(phenyldiethylphosphine) bis-(monoiodosilver), m.p. $83^\circ-84^\circ\text{C}$ being recovered in 80% yield (16g), by recrystallization from propanol, together with a brown, insoluble, organic powder, (1.6g), probably polymerised cyclopentadiene.

(ii) In a reaction carried out, using exactly the same quantities, but at room temperature, the same progressive darkening of the solution was observed as the cyclopentadienyl lithium solution was added. Hydrolysis at 0°C , followed by working-up in the same way as above, yielded starting material (15g, 75%), and a similar brown polymeric powder (2g). At no time during working up was a smell of free phosphine noticed.

7. Reaction of cyclopentadienyl sodium with $(\text{PhPET}_2)_3(\text{AgI})_2$ in ethanol-benzene

To a yellow solution of cyclopentadienyl sodium (0.1 moles) in ethanol (100 mls), was added a solution of phenyldiethylphosphine-silver iodide complex, $(\text{PhPET}_2)_3(\text{AgI})_2$, (20g, 0.0413 moles) in benzene (50 mls), at room temperature. The mixture was heated at 50°C for

4 hours. Working up of the brown solution isolated what was probably a mixture of silver, polymerised cyclopentadiene (0.7g) and unreacted phosphine-silver iodide complex (14.3g, 71.5%) m.p. 83° - 85° C.

C. Reaction of Grignard and organo-lithium reagents with silver halides, and subsequent reaction with donor molecules

1. Reaction of mesityl lithium with silver iodide in tetrahydrofuran

Silver iodide (9.5g, 0.0405 moles) was added, with vigorous stirring, to a solution of mesityl lithium (0.081 moles) in tetrahydrofuran (170 mls), at -60° C. The mixture was allowed to warm up slightly, and at -50° C went a very dark colour, although unreacted silver iodide was still present. The solution was divided roughly in half and treated separately:-

Part 1:- A solution of phenyldiethylphosphine (8.5g, 0.052 moles) in ether (90 mls) was added at -60° C. The dark brown solution was allowed to warm up to room temperature, stirred overnight, and hydrolysed. Working up yielded unreacted silver iodide (4.5g, 47.4%) (soluble in strong potassium iodide solution), coated with silver (insoluble in dilute but soluble in concentrated nitric acid), and colourless crystals, m.p. 72° - 73° , of bis-(phenyldiethylphosphine)-monoiodosilver, (3.5g, 0.0062 moles, 15.3%).

Part 2:- A solution of bipyridyl (6.25g, 0.04 moles) in ether (100 mls) was added, with stirring, to the deep red solution at -60° C, the solution warmed up to room temperature, stirred overnight, and hydrolysed.

Isolated from the reaction mixture were silver iodide, (2g, 21%), coated

with silver, and bipyridyl (4.5g, 72%), m.p. 72°C , purified by sublimation in vacuo.

Total recovery of silver iodide was therefore 83%.

2. Reaction of styryl magnesium bromide with silver halides in tetrahydrofuran

a. Silver Iodide

(i) A solution of styryl magnesium bromide (0.10 moles) in tetrahydrofuran (200 mls), was treated at 0°C with excess of finely powdered silver iodide (30g, ~ 0.128 moles), and stirred for 4 hours at this temperature, Gilman Colour Test 1 being negative. At this stage, a greyish solid settled out, probably a mixture of tetrahydrofuran-magnesium halide complexes coated with silver. The supernatant liquid was a deep green colour, and, after standing overnight at 0°C , samples were tested as follows:-

- a. Hydrolysis produced a dark brown solid, insoluble in toluene. The solid, on heating, turned almost white, with only slight burning.
- b. Addition to toluene gave a deep red solution, which became pale yellow on addition of excess phenyldiethylphosphine.

The bulk of the solution was treated as in (b) after decantation from most of the excess AgI, much silver being present. The filtered solution was hydrolysed, and on working up, phenyldiethylphosphine-monoiodosilver, m.p. 138° - 139° , was obtained as colourless crystals (6.5g, 0.0162 moles) by recrystallization from ethanol, together with the highly insoluble phosphine-silver iodide complex, $\text{PhPEt}_2(\text{AgI})_2$, m.p. 200°C (0.5g, ~ 0.002 moles with respect to silver).

(ii) Silver iodide (4.3g, 0.0183 moles) was added with vigorous stirring, to a solution of styryl magnesium bromide (0.11 moles) in tetrahydrofuran (190 mls) at 0°C, being stirred overnight at this temperature. A greyish solid had settled out once more from the dark solution, and hydrolysis of a small sample produced more grey solid. Phenyl-diethylphosphine (3.20 mls, 0.0183 moles) was added, the colour of the solution being impossible to distinguish. After stirring for 1 hour, Gilman Colour Test 1 was still positive. Hydrolysis was performed at 0°C, working up yielding unreacted silver iodide (~3g, 70%), which had probably been protected by coating with silver, and a small amount of $\text{PhPEt}_2 \text{ AgI}$ (~0.4g) m.p. 138°C.

Styryl magnesium bromide (0.138 moles) was reacted with silver iodide (8.1g, 0.0344 moles) at 0°C, a small amount of metallic silver being formed. Phenyl-diethylphosphine (7 mls, ~0.0404 moles) was added, and the solution was hydrolysed, a mixture of basic magnesium halides and unreacted silver iodide being obtained as residue. Gilman Colour Test 1 was positive throughout. Working up of the reaction mixture yielded a little (~0.7g) of the insoluble phenyl-diethylphosphine-silver iodide complex, $\text{PhPEt}_2 (\text{AgI})_2$, m.p. ~200°C, and yellow crystals (~1g, 0.0485 moles) of bistyryl, (1,4, - diphenyl butadiene, m.p. 149°-150°C).

b. Silver Bromide

Finely powdered silver bromide (6.0g, 0.032 moles), was reacted with styryl magnesium bromide (0.14 moles), in the same way as was silver iodide above. After stirring for 30 hours at 0°C, the silver bromide was coated with silver, while there was no evidence for the presence of styryl

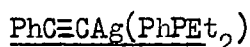
silver in the solution. Stirring was continued for a further 48 hours at room temperature, when extensive decomposition to silver, appearing as a grey-black powder, occurred. Samples were withdrawn, treated with phenyldiethylphosphine, and hydrolysed, but no evidence for formation of an organo-silver complex was obtained. Gilman Colour Test 1 was positive throughout. Hydrolysis of the main bulk of the reaction mixture yielded styrene, and an intractable brown tar.

c. Silver chloride

Styryl magnesium bromide (0.12 moles) and silver chloride (2.87g, 0.02 moles) were reacted as above, unreacted silver chloride (2g, 70%) being recovered, together with a little metallic silver. No evidence for an organo-silver compound was obtained.

D. Ethynyl silver-phenyldiethylphosphine complexes

1. Preparation of phenylethynyl (phenyldiethylphosphine)-silver



A solution of phenyldiethylphosphine (13.9 mls, 0.08 moles) in toluene (30 mls), was added to a well-stirred suspension of phenyl silver acetylide, (16g, 0.077 moles), (prepared from excess of ammoniacal silver nitrate and phenyl acetylene), in toluene (80 mls). The acetylide dissolved to give a yellow solution, which was stirred for 15 minutes, before addition of hexane (100 mls). Repeated attempts at crystallization by cooling the solution in dry ice-acetone, gave a white solid, which formed an oil as it warmed up. The solution was therefore cooled to -78°C , quickly centrifuged, and the supernatant liquid poured off. The white solid melted to form an oil, smelling of phenyldiethylphosphine, which

crystallized partially on standing, to give off-white crystals (3.5g, 0.009 moles, 11.7%), m.p. 52° - 54° . These were filtered and washed with a small volume of hexane. Repeated attempts at crystallization of the remainder of the oil were unsuccessful. Carbon and hydrogen analyses and identical infra-red spectra showed that the oil and the crystals had the same composition:-

	Carbon	Hydrogen
Found Crystals	57.0%	5.3%
Found Oil	57.9%	5.8%
Required for $\text{Ph-C}\equiv\text{CAgPhEt}_2$	57.7%	5.4%

Both were light sensitive, decomposing to a dark red oil smelling of phosphine. The crystals were soluble in benzene and acetone, but decomposed to phenylethynyl silver when solution was attempted in hexane.

A molecular weight determination was carried out cryoscopically in benzene:-

Wt. of solute	Depression in $^{\circ}\text{C}$	Molecular Weight	Degree of Association
0.1372g	0.054°	635	1.69
0.2624g	0.100°	637	1.69
0.4797g	0.162°	718	1.92
0.7969g	0.252°	763	2.04

Empirical molecular weight = 375 ($\text{Ph-C}\equiv\text{CAgPhEt}_2\text{P}$)

The solutions were made up by successive additions of the crystals to 25 mls of benzene, the number of moles being obtained from a calibration graph for diphenyl in 25 mls of benzene.

2. Preparation of p-nitrophenylethynyl (phenyldiethylphosphine)-silver, p-nitrophenyl - C≡CAgPhPEt₂

To a suspension of the yellow, insoluble para-nitrophenylethynyl silver (3.0g, 0.0118 moles) (prepared from p-nitrophenylacetylene and excess of ammoniacal silver nitrate) in benzene (40 mls), in one arm of a double Schlenke tube, was added phenyldiethylphosphine (2.21 mls, 0.0127 moles). It was shaken for one hour, a deep red solution being formed. Addition of hexane to the filtered solution resulted in the formation of yellow needles (4.5g, 0.0107 moles, 91%), which were filtered and washed with a small volume of hexane. The crystals began to darken above 110°C and melted 115°-117°C. A carbon and hydrogen analysis gave:-

	Carbon	Hydrogen
Found	49.9%	4.6%
Required for No ₂ C ₆ H ₄ C≡CAgPhPEt ₂	51.4%	4.6%

Cryoscopic measurements of molecular weight could not be carried out in either benzene or nitrobenzene, as the compound tended to dissociate into the free phosphine, of which its solutions smelled, and the insoluble p-nitrophenyl ethynyl silver. The low figure for the carbon content was thus probably due to the presence of a little of the p-nitrophenylethynyl silver, despite the fact that a small volume of phenyldiethylphosphine was added to the recrystallizing solution. The p-nitrophenyl ethynyl silver-phenyldiethylphosphine complex was much more stable to light than PhC≡CAg(PhPEt₂).

3. Preparation of tertiary butyl ethynyl (phenyldiethylphosphine)-silver
(CH₃)₃C.C≡CAgPhPEt₂

Phenyldiethylphosphine (2.89 mls, 0.0166 moles) was added to a

well stirred suspension of tertiary butyl ethynyl silver, (3g, 0.0159 moles) (prepared in the usual way), in benzene (70 mls). After stirring for 15 minutes, some of the solvent was pumped off, and off-white crystals, (5.6g, 0.158 moles, 99%), appeared on standing. Recrystallization, in the presence of a little excess phosphine, was carried out from benzene-hexane mixture, yielding light-sensitive colourless crystals, melting at 95°C to a cloudy solution, which blackened above 110°C. A carbon and hydrogen analysis gave:-

	Carbon	Hydrogen
Found	49.1%	6.4%
Required for $(\text{CH}_3)_3\text{C}\equiv\text{C}\text{Ag}(\text{Ph})\text{PEt}_2$	54.1%	6.5%

The low carbon figure can once more be ascribed to the presence of some insoluble acetylide, as the complex dissociated very readily in solution, a molecular weight determination again being impossible.

4. Cryoscopic measurements on p-nitrophenylethynyl-(phenyldiethylphosphine)-silver

Molecular weight determinations were carried out in a standard type of cryoscopic apparatus. Molecular sieve was added to absorb traces of water, and a nitrogen atmosphere was maintained.

(i) As mentioned previously, the complex $\text{p-NO}_2\text{-C}_6\text{H}_4\text{C}\equiv\text{C}\text{Ag}(\text{Ph})\text{PEt}_2$ tends to dissociate in solution, but is stabilised by the presence of excess of free phosphine. Consequently, it was hoped that some data on its molecular weight might be obtained by determining the freezing points of solutions of the complex in benzene, in the presence of a known quantity of free phenyldiethylphosphine.

A solution of phenyldiethylphosphine (1 ml, 0.00572 moles) in

benzene (100 mls) was made up accurately, and used to dissolve weighed amounts of p-nitrophenylethynyl (phenyldiethylphosphine)-silver. The freezing points of these solutions, the phosphine-benzene solution, and pure benzene, were determined. Despite the presence of free phenyldiethylphosphine, only dilute solutions of the complex could be obtained.

Weight of Solute	Volume of Phosphine-Benzene sol ⁿ . to dissolve it	Freezing Point	Depression from F.Pt. of Phosphine-Benzene Sol ⁿ .	Apparent M.W.
P U R E B E N Z E N E		0.845°		
25 mls PHOSPHINE-BENZENE SOLN.		0.486°		
0.1590g	20 mls	0.474°	0.012°	4033
0.2671g	20 mls	0.447°	0.039°	2084
0.5230g	30 mls	0.450°	0.036°	2946

The depression caused by solution of the phosphine alone gives the molecular weight of the phosphine as 163 (C.A. 166 calculated), which is quite good agreement.

(ii) In the hope that some information would be obtained concerning possible co-ordination of additional molecules of free phosphine to the complex, p-NO₂C₆H₄C≡CAg(PhPEt₂) in solution, a further series of freezing points of similar solutions was performed, in which the ratio

$\frac{\text{moles PhPEt}_2}{\text{p-NO}_2\text{C}_6\text{H}_4\text{C}\equiv\text{CAg(PhPEt}_2)}$ was varied:-

Phenyldiethylphosphine (0.01 moles) was diluted to 100 mls with pure benzene. Aliquots of this solution were made up to 50 mls,

and 25 mls of this resulting solution was used to dissolve accurately weighed amounts of the complex.

The results obtained, shown on opposite page, are obviously not due to simple solution of the acetylide-phosphine complex in the phosphine-benzene solvent; various equilibria probably being present.

(iii) An approximate value for the molecular weight of $p\text{-NO}_2\text{C}_6\text{H}_4\text{C}\equiv\text{CAg}(\text{PhPEt}_2)$ in benzene solution was sought by determination of the freezing points of a series of very dilute solutions. Each was made up and used as quickly as possible, to minimise dissociation to the insoluble *p*-nitrophenylethynyl silver.

Wt. of Solute	Vol. of Benzene Used	Freezing Point	Depression	No. of Moles	Molecular Weight
		PURE BENZENE 0.865°			
0.0828g	25 mls	0.815°	0.050°	0.00020	414
0.1110g	25 mls	0.800°	0.065°	0.00026	465
		PURE BENZENE 1.235°			
0.0798g	25 mls	1.202°	0.033°	0.00013	604
0.0713g	25 mls	1.175°	0.060°	0.00024	297

Empirical molecular weight of $p\text{-O}_2\text{NC}_6\text{H}_4\text{C}\equiv\text{CAg}(\text{PhPEt}_2) = 420$.

These results indicate that the complex may be monomeric, but the solutions used are so dilute that little reliance may be placed upon them.

Two phenyldiethylphosphine-benzene solutions were made up:-

Solution A. Phenyldiethylphosphine (0.20 mls, 0.00115 moles) was made

up to 100 mls with benzene.

Solution B. Phenyl-diethylphosphine (0.40 mls, 0.0023 moles) was made up to 100 mls with benzene.

These solutions were then diluted as required, 5 mls of the final solutions being used to dissolve the small weighed amounts of

$\text{pNO}_2\text{C}_6\text{H}_4\text{C}\equiv\text{CAg}(\text{PhPET}_2)$ ($\sim 0.01\text{g}$):-

The C≡C stretching frequency of the p-nitrophenylethynyl silver-phenyl-diethylphosphine complex was then determined accurately in each case:-

Wt. of complex used	Moles of complex used if monomeric	Vol. PhPET ₂ sol ^{n.2} used	Vol. made up to	Moles PhPET ₂ per 5mls	Moles $\frac{\text{PhPET}_2}{\text{Moles complex}}$	C≡C freq.
0.0085g	2.020×10^{-5}	5mls Sol ⁿ A	25mls	1.15×10^{-5}	0.57	2095cm^{-1}
0.0083g	1.977 "	10mls Sol ⁿ A	25mls	2.30 "	1.16	"
0.0100g	2.380 "	40mls Sol ⁿ A	50mls	4.60 "	1.93	"
0.0081g	1.930 "	15mls Sol ⁿ B	25mls	6.70 "	2.88	"
0.0100g	2.380 "	20mls Sol ⁿ B	25mls	9.20 "	3.86	"
0.0072g	P U R E B E N Z E N E					"

PART 3.

REACTION BETWEEN GRAPHITE AND ALKALI METAL-NAPHTHALENE COMPOUNDS

INTRODUCTION

Graphite, one of the two modifications of elemental carbon, is interesting in its reactions, in that it is able, under certain conditions, to take up atoms, ions, or molecules into its lattice, the essential structure of the graphite remaining largely unchanged. The formation and composition of these intercalation compounds, may be explained in terms of the structure of graphite, and the type of bonding encountered within it.

Graphite crystallizes in a layer lattice, each layer consisting of regular sheets in which the carbon atoms are linked hexagonally. These sheets are displaced relative to one another, and in the stable hexagonal modification alternate sheets are situated above one another, giving a layer sequence A,B,A,B. (Fig. 1).

Another rhombohedral form of graphite, having the layer sequence A,B,C,A,B,C is known to exist, but seldom occurs in synthetic graphite, while in natural graphite it can be present to the extent of 30%.

Within the graphite layers, each carbon atom is linked to three neighbours, at a distance of 1.41 \AA , by a strong homopolar bond. In contrast, the distance between layers is 3.35 \AA , corresponding to much weaker bonding, and indeed, the fourth valency electrons of the carbon atoms are completely delocalised, and as with the π - electrons of an aromatic molecule, are shared by the

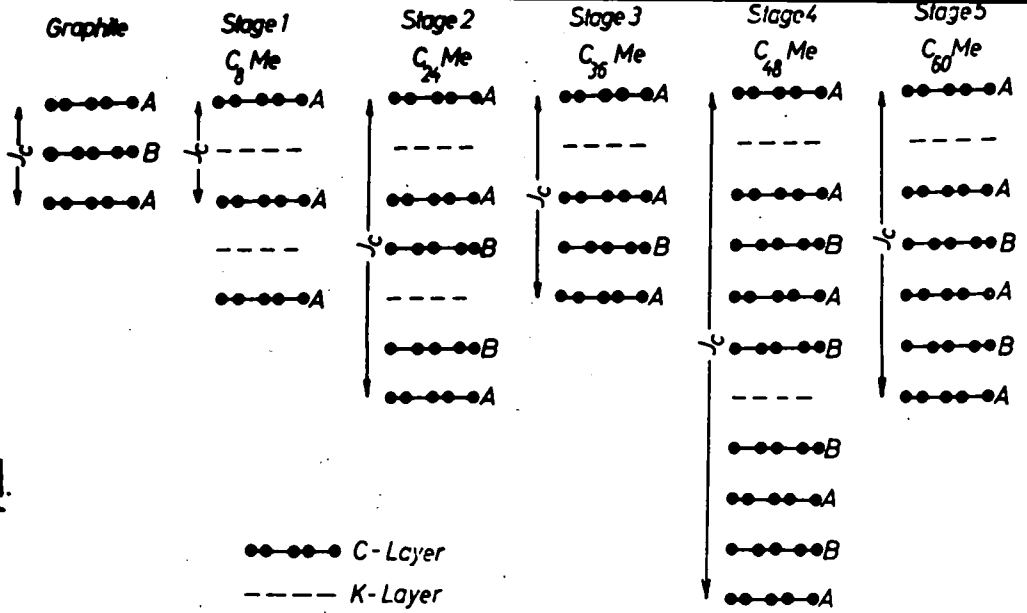


Fig. 1.

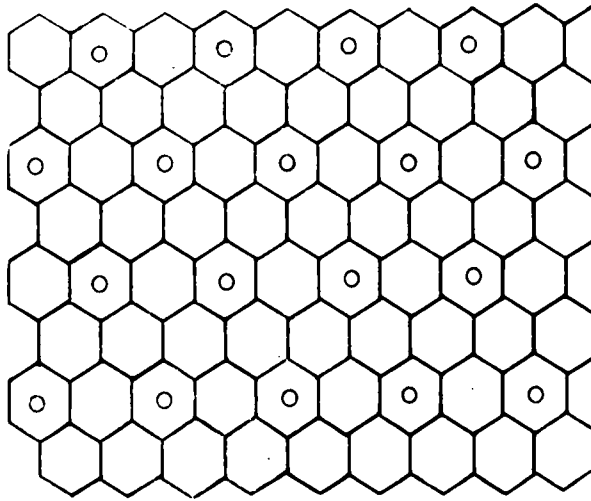
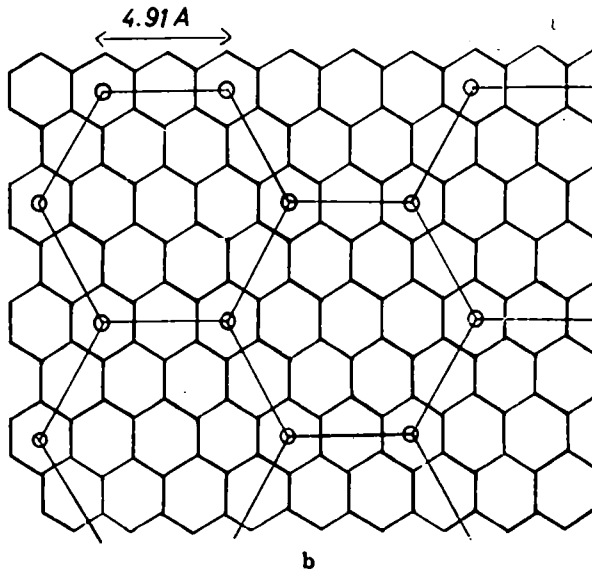


Fig. 2.



layer as a whole. To these 'free' electrons graphite owes its high electrical and thermal conductivity. It follows that a relatively energetic reaction is needed to break the homopolar bonds within the layers, while suitable reactants are able, under reasonably mild conditions to alter the electron distribution between the layers and become intercalated between the planes. The carbon planes themselves remain unaltered, merely being pushed further apart, the formation of intercalation compounds always being linked with swelling of the graphite in a direction perpendicular to the basal planes.

The bonding in some of the intercalation compounds of graphite is not yet fully understood, but the compounds may be divided into two classes, according to the nature of the bond. In the first class, including such compounds as graphite oxide, carbon monofluoride, and tetracarbon monofluoride, homopolar bonding takes place between the intercalated atoms and the carbon atoms, while in the second class, to which the majority of intercalation compounds belong, the bonding is of polar character.

1. Graphite compounds with homopolar bonding.

As this group of compounds does not immediately concern the present work, it will be dealt with very briefly.

Graphite oxide. Also known as graphitic acid, graphite oxide is probably the most fully studied graphite compound, but its constitution is still not fully known. It can be prepared by oxidation of graphite with a mixture of potassium chlorate and

concentrated sulphuric and nitric acids. Products vary in colour, but no correlation with composition can be found. Graphite oxide is thermally unstable, possesses oxidising properties, and can be reduced by reducing agents, although never completely, to graphite. The C:O ratio in well-oxidized preparations varies from 2.4 to 2.9, while in less oxidized preparations, the ratio is 3.5-4, both groups showing the same characteristic properties.

Graphite will undergo swelling, water and organic liquids with polar groups causing a reversible change in the inter-planar spacing. In weakly alkaline solutions, the interplanar distance of graphite becomes so great that it can no longer be measured by X-rays.

By analysis, hydrogen found in graphite oxide cannot be attributed solely to water taken up in the swelling process, since it is always present, even in thoroughly dried specimens. The hydrogen has in fact been attributed to the presence of weakly acidic -OH and more strongly acidic -COOH groups, and comprehensive studies of the proportions and points of attachment of these groups have been carried out, but, as mentioned previously, the constitution of the compound is by no means clear, and it has been proposed by Ruess¹ that the carbon planes are puckered, and no longer possess their aromatic character.

Carbon monofluoride. Compounds of composition $CF_{0.68}$ - $CF_{0.995}$ are formed when graphite reacts with fluorine in the narrow temperature range 420° - $460^{\circ}C$. The colour of the compounds lightens

with increasing fluorine content, while electrical conductivity falls in the same direction, the white, fluorine-rich preparations being practically non-conducting.

The formation of graphite monofluoride is catalysed by gaseous hydrogen fluoride, and explains the destruction of graphite anodes in the space above the electrolyte, in the electrolysis of potassium fluoride - hydrogen fluoride melts. Carbon monofluoride is very inert, and is even unaffected by concentrated acid or alkali.

The proposed structure for graphite monofluoride is based on homopolar bonding between carbon and fluorine atoms, the sp_3 hybridisation of the carbon atoms causing the graphite layers to be puckered, no aromatic character being retained, while the distance apart of the layers varies from 6.6 \AA to 8.8 \AA . Proof of the presence of a C-F bond has recently been furnished by infra-red evidence,² this structure readily explaining the low reactivity, the absence of electrical conductivity, and the formation of low molecular weight carbon fluorides on thermal decomposition.

Tetracarbon monofluoride. A compound of composition $C_4F - C_{3.6}F$ is formed when a fluorine-hydrogen fluoride mixture is passed over graphite at room temperature, rate of reaction depending on the composition of the gas mixture. At $80^\circ - 100^\circ \text{C}$, no reaction occurs.

Tetracarbon monofluoride, appearing velvet-black,

sometimes with a bluish tinge, is, like carbon monofluoride, very inert, although it is less stable thermally. The compound does have an electrical conductivity, although it is appreciably lower than that of graphite itself. Tetracarbon monofluoride contains no hydrogen fluoride, but, once again, the gas plays an important role in the synthesis, as rate of reaction is affected by the partial pressure.

The properties of tetracarbon monofluoride are consistent with the formation of a C-F homopolar bond, while the existence of three 'free' electrons for every four carbon atoms explains the electrical conductivity. The hexagonal carbon network remains, the C-C distance being practically the same as that of graphite. The structure differs from that of graphite in that the layers are in identical positions above one another, giving the sequence A,A,A,A. The distance apart of the planes varies from 5.34 \AA° (C_4F) to 5.50 \AA° ($\text{C}_3.6\text{F}$). The fluorine atoms from two layers, above and below each carbon plane, and, assuming a regular distribution, form a triangular network with an F-F distance of 4.9 \AA° .

2. Graphite compounds with polar bonding.

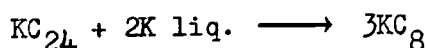
In this class of compounds, occupation of the inter-layer spacings takes place in a characteristic series of steps or 'stages', the reactant entering the space in the lattice between each set of basal planes, or that between each second, third, fourth, and so on. The separate compounds, clearly distinguishable from one another by analysis or X-ray investigation, are called stages 1,2,3, etc. This group of compounds will be studied with

particular reference to the alkali metal-intercalation compounds, as it was with these compounds that the work carried out was solely concerned, while other compounds possessing polar bonding will only be very briefly mentioned.

a. Preparation, composition, and properties.

The molten alkali metals, potassium, rubidium, and caesium, or their vapours, react readily with graphite to give alkali metal-graphite compounds. Depending on the temperature of the reaction, and the alkali metal vapour pressure, products of different colour were obtained, and were the same for all three metals. The compound richest in alkali metal, and of approximate composition MeC_8 , was bronze-red in colour and was prepared by carefully distilling off, in vacuo, the excess alkali metal used in the preparation. Further heating results in removal of some of the alkali metal to give a steel-blue compound, at first thought to be MeC_{16} , but later found to be MeC_{24} by the X-ray work of Rüdorff and Schulze.^{3,4} This was further confirmed by the work of Herold,⁵ whose isobaric breakdown curve for potassium graphite showed the first clear break at KC_{24} . By heating the blue compound strongly, all the alkali metal may be finally removed.

For the heat of formation of KC_8 , Fredenhagen obtained a value of 12 k.cal./mole, while Quartermann and Primak⁶ obtained 7.8 k.cal./mole. Herold⁷ calculated from vapour pressure measurements that ΔH for the reaction:-

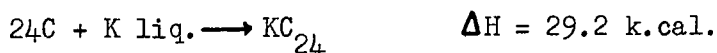


was -6.8 k.cal., while the corresponding rubidium and

caesium values are -11.6 k.cal. and -20.2 k.cal. respectively.

Using Fredenhagen's value for the heat of formation of KC_8 ,

we obtain:-



If Quartermann's value is used, $\Delta\text{H} = -16.6 \text{ k.cal.}$

The alkali metal-graphite compounds are highly reactive, as they will ignite in air, and may react explosively with water. In controlled reaction with water or alcohol, the only products are hydrogen and the alkali metal hydroxide. Mercury will remove the alkali metal from the lattice, while treatment of MeC_8 with liquid ammonia results in the loss of one third of the alkali metal and its replacement by two molecules of ammonia.

b. Structure.

For the compound richest in alkali metal, or the stage one compound, MeC_8 , a layer of alkali metal atoms exists between each pair of carbon planes, while in the blue, second stage compound, MeC_{24} , this occurs between alternate pairs of carbon planes. The interplanar distance is increased by potassium to 5.41 \AA , by rubidium to 5.61 \AA , and by caesium to 5.95 \AA .

In the first stage, the alkali metal atoms form a triangular net, the Me-Me distance being 4.91 \AA , twice as long as the hexagonal 'a' axis of the hexagonal carbon net (Fig. 2a). Fully occupied, the first stage compound thus has a composition of MeC_8 . The recently determined structure⁴ of this compound is shown in Fig. 3, and differs from the original crystal structure by Schleede and Wellmann⁸ in that

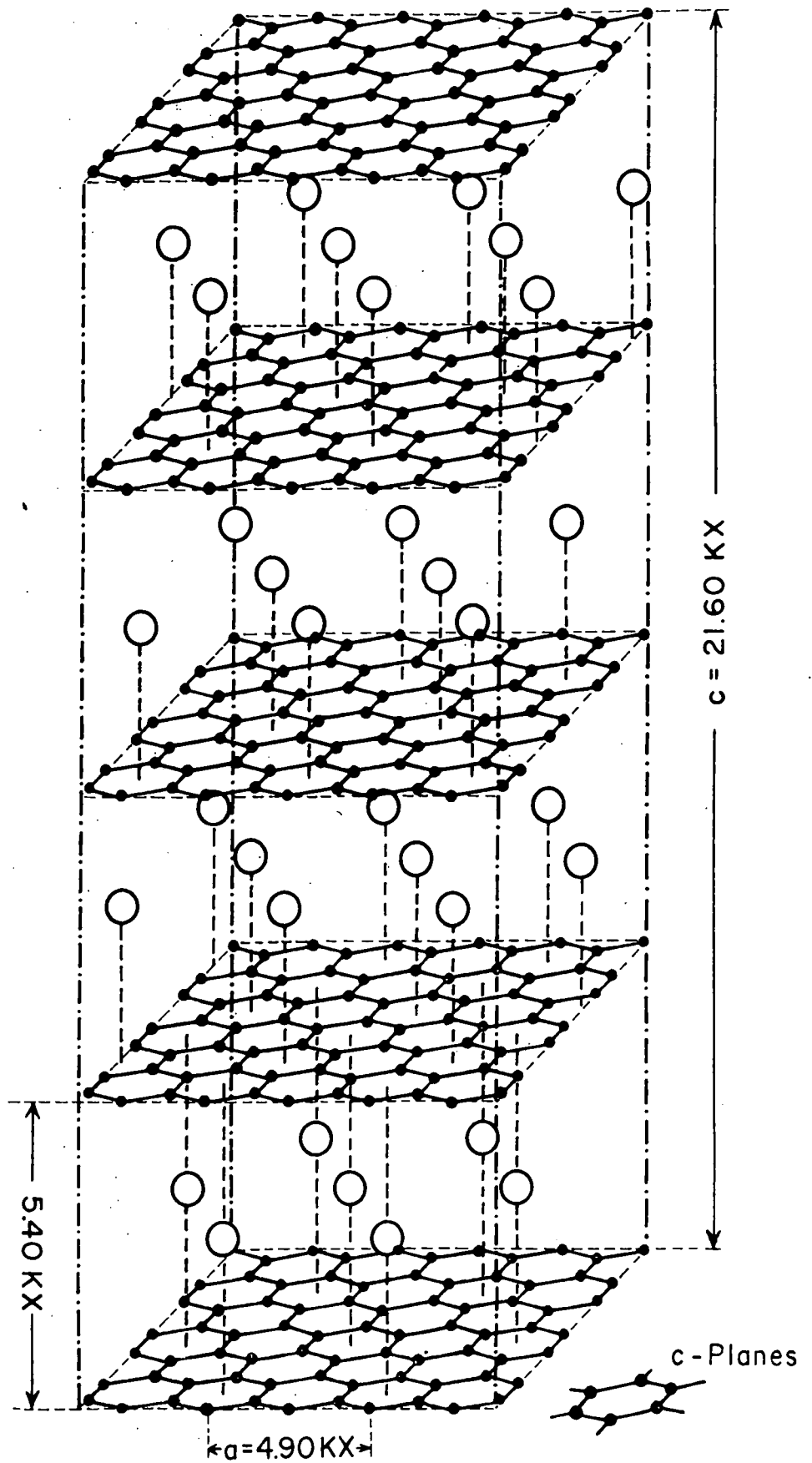


FIG. 3.

instead of being in the hexagonal modification of graphite (i.e. in the sequence A,B,A,B,), the carbon planes are identically situated above one another (i.e. in the sequence A,A,A,A,) and consequently, the alkali metal atoms, instead of lying between one carbon atom in one plane and the middle of a hexagon in another, all lie between the middle of a hexagon of carbon atoms. This seems much more likely, as each alkali metal atom now has twelve carbon atoms equidistant from it (in the case of KC_8 , at 3.07 \AA) instead of one carbon atom from one layer, and six from another, at different distances.

In the stage two compound, if the layers were just as densely occupied, a composition of MeC_{16} would result, as there would now be half as much alkali metal present as in the stage one compound. In fact, Schleede arrived at this formula under this assumption. However, as the composition is MeC_{24} , then the alkali metal layers must be more sparsely occupied, and removal of every third alkali metal atom leads to a hexagonal net (Fig. 2b) in which the Me-Me distance is again the same as in the triangular net of the stage one compound. This arrangement corresponds to a composition of $C_{24}Me$ for stage two.

In addition, W. Rüdorff^{4, 9} has pointed out that other alkali-poor stages exist, and by studying potassium - and rubidium - graphite, showed that five stages occur in the range $MeC_8 - MeC_{60}$, the compositions of which are shown in Table 1:-

Stage and Composition	Lattice Constant C for Potassium Graphite in Å ^o
1st stage MeC ₈	5.41 = 5.41
2nd " MeC ₂₄	8.76 = 5.41+(1x3.35)
3rd " MeC ₃₆	12.12 = 5.41+(2x3.35)
4th " MeC ₄₈	15.48 = 5.41+(3x3.35)
5th " MeC ₆₀	18.83 = 5.41+(4x3.35)

It is obvious that for stages two to five, the same hexagonal net of alkali metal atoms must be present, as their compositions are merely multiples of 12:1. When large deviations from the ideal formula exist, for example, in an attempted preparation of a compound of composition MeC₁₆, a mixture of the two stages, in this case one and two, result, the transition between stages occurring discontinuously.

From Table 1, it is also obvious that introduction of the layer of metal atoms always causes the same increase in interplanar distance. In addition, the arrangement of carbon atoms in adjacent planes is always identical, so that introduction of a layer of metal atoms, besides causing an increase in interplanar distance, also causes a lateral displacement of carbon planes, in order that each metal atom may be surrounded by twelve carbon atoms at equal distances.

c. Intercalation of sodium and lithium.

The ease with which potassium, rubidium, and caesium enter the graphite lattice is in direct contrast to the behaviour of sodium

and lithium. Herold⁷ studied the reaction between lithium and graphite and found that, for long periods of reaction at 500°C and above, only the carbide Li_2C_2 results. At intermediate stages, he obtained products differing in properties from the carbide. A product of overall composition LiC_4 , harder than graphite, gave a golden yellow powder when broken up, while, on increasing the Li:C ratio, first black, grey, and then white substances result. These compounds are stable in dry air. On hydrolysis, hydrogen and acetylene are evolved, the proportion of acetylene increasing to 100% when the Li:C ratio is increased to 0.5. No X-ray study of these very peculiar compounds has yet been performed.

Sodium was found to react with soot, but not with graphite by Fredenhagen,^{10 11} while Tamman and Sworykin¹² observed attack by sodium vapour on small rods of retort carbon between 500° and 900°C. This attack led to disintegration of the carbon and the formation of products which ignite in air, this being attributed to the formation of a solid solution of sodium in carbon at higher temperatures. Despite this, attempts to prepare a definite compound were unsuccessful until Herold⁷ was able to intercalate sodium and caesium together by reaction between graphite and a sodium-caesium alloy. The Na:Cs ratio in the product was, however, only 0.12.

More recently, Asher and Wilson^{13 14} report that when graphite is heated with about 3% sodium to 400°C in an atmosphere of pure argon or helium, a deep violet product is formed, whose composition is NaC_{53} - NaC_{66} by X-ray analysis. The formation of a stage eight

compound was proposed by the authors, but despite a wide variation of experimental conditions, no further compounds were obtained. It is thus obvious that a great difference in behaviour towards graphite exists between sodium and the heavy alkali metals, potassium, rubidium, and caesium. Attempts by Hennig to prepare the compound obtained by Asher and Wilson were unsuccessful.

4. Bonding in the alkali metal-graphite compounds.

The alkali metal-graphite compounds can be considered as intermetallic compounds possessing a certain polar character, the limiting structure of the bond being $\text{Me}^+ \text{Graphite}^-$.

This concept may also be used to explain the stereochemical interpretation of the alkali metal-graphite compounds. If the volume of graphite is subtracted from the molecular volume of the compound MeC_8 , the difference, or alkali metal increment, can be shown to approximate to the values for the metal ions, as found in salts (see Table 2):-

Compound	Alkali Metal Increment	Atomic Volume Me in Metals	Ionic Volume Me^+ in Salts
KC_8	25.7	43.4	16
RbC_8	30.3	53.1	20
CsC_8	33.6	66.0	26

Formation of the compound MeC_8 from the metal is therefore associated with an appreciable contraction, greatest for caesium, probably because in that case, the polar character is most pronounced.

Studies on the electrical conductivity of potassium graphite

of various compositions¹⁵ showed that increase of conductivity occurs with intake of potassium and that the temperature coefficient of conductivity, as with a true metal, is negative. This signifies increase in the number of electrons available, which must have come from the potassium.

The polar character of the bond also explains the regular sequence of metal and graphite layers in compounds of different composition, as the electropositive metal layers, because of mutual repulsion, will tend to distribute themselves as uniformly as possible.

The magnetic properties of these compounds will not be described here, all of the stages of potassium graphite to stage five showing weak paramagnetism⁴.

5. Other intercalation compounds of graphite.

The alkali metals and the alkaline earth metals both form ammoniates with graphite. These compounds can be made by reaction of the blue solution of the metal in liquid ammonia with graphite, and resemble the alkali metal-graphite compounds in both structure and properties. Removal of absorbed ammonia results in compounds corresponding approximately to the formula $\text{MeC}_{12}(\text{NH}_3)_2$. The potassium, rubidium, and caesium compounds may also be obtained by treatment of MeC_8 with liquid ammonia. Instead of ammonia, amines can be used to form similar compounds.

Graphite, in the presence of concentrated acids, may be oxidised by oxidising agents or by anodic oxidation to the 'graphite salts'. The name is justified in that the graphite behaves as a true metal, and packing again takes place in stages.

The behaviour of the halogens towards graphite shows marked differences within the group. Bromine and chlorine give unstable graphite complexes with limiting composition C_8X , which are only suitable under the saturation pressure of the halogen. Iodine, as yet, has not been found to react with graphite, but fluorine forms the homopolar-bonded C_4F and CF dealt with previously.

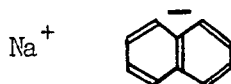
Compounds are also formed when graphite is heated with a metal chloride, the intercalated chloride being given off again at a sufficiently high temperature. The constitution of the wide range of metal chloride-graphite compounds is not yet clear.

Oxides and sulphides of polyvalent elements in higher oxidation states are capable of intercalation in graphite, and whether intercalation of any substance in a layer lattice will take place, is said by Croft¹⁶ to depend on whether or not an electronic interaction can take place between the host lattice and the intercalated substance, and that the host lattice has room to take up the latter.

The alkali metal-hydrocarbon addition compounds.

Aromatic hydrocarbons containing two or more aromatic rings, joined (biphenyl), conjugated (1,4, diphenylbutadiene), or fused (naphthalene) will react with the alkali metals to form addition compounds, no loss of hydrogen taking place. These compounds are all strongly coloured, and their ease of formation depends to a large extent on the reaction medium. These compounds are not to be confused with alkali metal-hydrocarbon substitution compounds, typified by benzylna⁺ or triphenylmethyl sodium, also strongly coloured compounds. Both groups have the negative charge delocalised in the organic system.

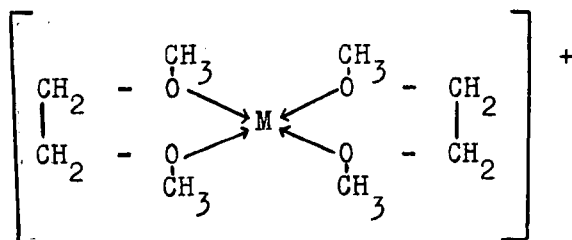
For instance, sodium naphthalene, the addition compound of sodium and naphthalene, may be formulated as:-



17 18

Early work on these addition compounds was carried out in diethyl ether, in which medium anthracene, α , ω diphenyl-polyenes, and polyarylethylenes will add sodium, although low solubility of the products and relative inaccessibility of starting materials restricted their application. Some aromatic cyanides and ketones were observed to behave similarly, the latter forming ketyls, benzophenone and sodium, for example, forming the deep blue sodium diphenyl ketyl $\text{Ph}_2\text{C}-\bar{\text{O}} \text{Na}^+$. These ketyls are very air and water-sensitive and are used in solvent purification.

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The discovery that these addition compounds could be prepared much more easily in ethers with a high O:C ratio greatly widened the scope of their application. Naphthalene will add sodium in dimethyl ether and methyl ethyl ether, but these are inconvenient due to their low boiling points, and in fact, the addition takes place particularly easily in ethylene glycol dimethyl ether (B.P. 84°C). This solvent, because of its strong donor character, reduces the energy of the alkali metal ion by solvation:-



Another good solvent for these compounds is tetrahydrofuran,

which, although cheaper than ethylene glycol dimethyl ether, suffers from the disadvantage that it forms peroxides more readily than the latter, and will not give such concentrated solutions.

Lithium will add to aromatic hydrocarbons rather more readily than will sodium, slowly dissolving in solutions of naphthalene in diethyl ether.

Sodium naphthalene solutions in glycol dimethyl ether are dark green in colour and have a relatively high electrical conductivity.¹⁹ Both glycol dimethyl ether and tetrahydrofuran have greater dielectric constants (6.8 and 7.3) than diethyl ether.²⁰ Solutions of these addition compounds undoubtedly consist of solvated alkali metal cations and hydrocarbon anions, as they are paramagnetic in the two solvents mentioned above, as would be expected for anions with an odd number of electrons. Supporting this is the fact that electrical conductance of solutions of these compounds shows the presence of ion pairs (in triplets in the case of di-negative anions), and the ions are separated by at least one layer of solvent molecules, it being quite likely that the anions are also solvated to some extent. Ion solvation increases with decrease of temperature, corresponding to increase of dielectric constant of the solvent.

The reaction between an alkali metal and naphthalene results in transfer of an electron from the sodium into the lowest vacant orbital of the naphthalene molecule. The lowest vacant orbital in benzene is at too high an energy level for this transition to take place, while in naphthalene, it can take place, but only if the energy of the resulting sodium ion is lowered by solvation in an

ether of high donor character. In anthracene, the first available orbital is at an even lower level than in naphthalene, and the formation of the $C_{14}H_{10}^-$ anion will consequently take place even in diethyl ether.

The presence of this extra electron also explains the deep colour of the compounds. The longest wavelength light absorptions of both naphthalene and anthracene lie in the ultra-violet, but with the anions the longest wavelength absorptions lie at a much longer wavelength, and are in fact in the visible region at 7550 \AA and 7250 \AA respectively.

The paramagnetism of the compounds is also explained by this odd electron, and, should a second electron transfer take place (i.e. formation of R^{2-}), then, in the case of naphthalene and anthracene, since the singly occupied orbitals are non-degenerate, a diamagnetic compound would be formed, as both electrons would be in the same orbital, with spins paired. Naphthalene, except when in liquid ammonia solution, does not readily accept a second electron. Anthracene does, however, and the anthracene²⁻ anion has been shown to be diamagnetic in solution.²² At the same time, the electron spin resonance spectrum, characteristic of 'odd-electron' molecules has been shown to have disappeared.

Paramagnetic, coloured solutions containing low concentrations of anions derived from benzene, toluene, and the three xylenes with potassium have been observed in ethylene glycol dimethyl ether at -80°C , but decompose rapidly above this temperature.²³

It becomes clear that stability of the hydrocarbon anions is

in the order:- $C_{14}H_{10}^- > C_{10}H_8^- > C_6H_6^-$

or similarly, the hydrocarbons, in order of electron affinity are

$C_{14}H_{10} > C_{10}H_8 > C_6H_6$. The hydrocarbon of lowest electron affinity

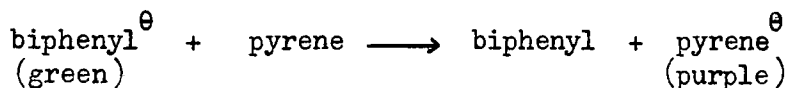
capable of forming an anion with sodium in ethylene glycol dimethyl

ether is biphenyl, so addition of a solution of sodium biphenyl in

this solvent to a solution of any other hydrocarbon of greater electron

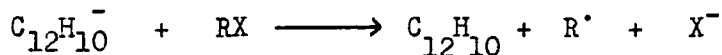
affinity results in an electron transfer, and may be accompanied by a

colour change, e.g.:-



These exchanges have been studied quantitatively in this way by potentiometric titration in ethylene glycol dimethyl ether and in tetrahydrofuran, a scale of reduction potentials of aromatic hydrocarbons and their univalent anions being drawn up against sodium biphenyl as zero. In this way, the reduction potentials of naphthalene and anthracene in ethylene glycol dimethyl ether have been found to be 0.09 and 0.78 volts respectively.

Solutions of sodium naphthalene and other compounds are strongly reducing, behaving as solutions of electrons. The halogen of organic halides is thus reduced to halide:-



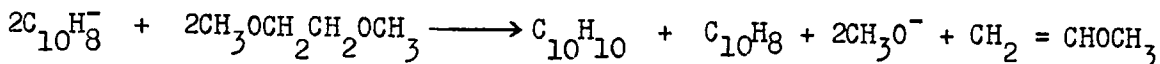
The free radicals produced react with solvent, hydrocarbon, hydrocarbon anion, or dimerize, but the halide ion may be quantitatively extracted

by water. The estimation of halogen in organic compounds may be reliably carried out by decomposition with a solution of sodium

biphenyl in glycol dimethyl ether. This is added to a solution of

the organic compound in di-isopropyl ether until a green colour persists.

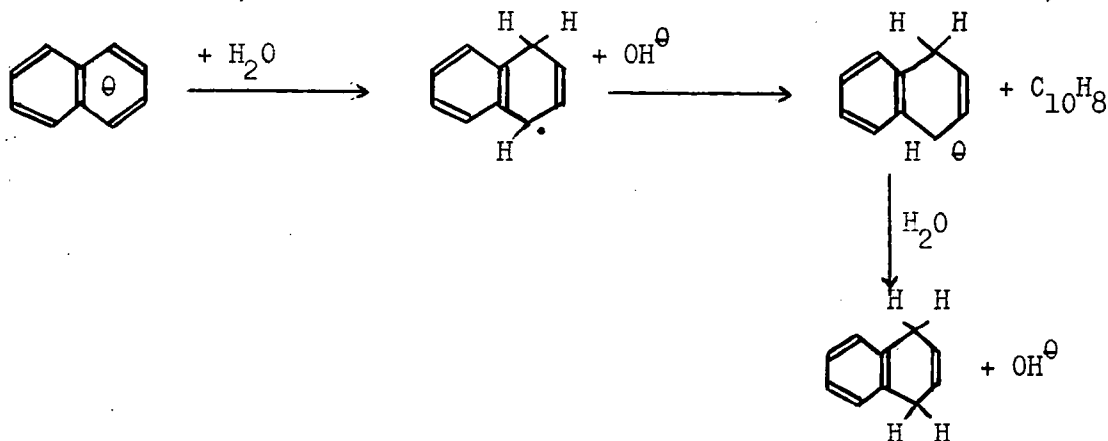
These reagents are not stable at room temperature, as the ether is slowly attacked:¹⁹



The products of this attack are thus, a mixture of naphthalene, dihydronaphthalene, methyl vinyl ether, and the alkali metal methoxide.

Sodium naphthalene will reduce a solution of cobalt (II) chloride in tetrahydrofuran to colloidal cobalt, while, with mercury, it will give a sodium amalgam and reform naphthalene.

With water, alcohol, or almost any source of acidic hydrogen, sodium naphthalene will give 1,4,-dihydronaphthalene,¹⁹ and will give a mixture of the 1,2- and 1,4- isomers of dihydronaphthalene carboxylic acid with carbon dioxide. The fact that dihydro derivatives are formed is not indicative of the presence in solution of di-sodium derivatives of naphthalene, evidence against this being strong. In reactions of this type, half of the naphthalene present as the anion is reconverted to the hydrocarbon:-



Di-sodium adducts of naphthalene are present in liquid ammonia, giving red solutions.

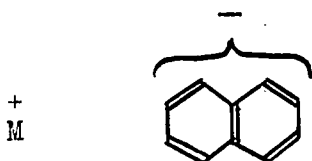
The more reactive sodium-aromatic complexes such as sodium naphthalene, have found application as anionic polymerization catalysts, for instance, if styrene is added to a dilute solution of sodium naphthalene in tetrahydrofuran, the colour changes from green to red. Polymerization may be initiated by an electron transfer reaction:-



Polymerization then takes place, one end growing as a free radical, and the other as a carbanion. Eventually, radical ends join, and polymerization continues only by the anionic process, and goes on until all of the monomer is used up, and even then, addition of more monomer, whether it be styrene or another monomer, results in further polymerization, as there is no chain terminating mechanism.

DISCUSSION

Although the intercalation compounds of potassium with graphite are well-known, as mentioned previously, only one such compound has been reported to be formed by sodium, and this by direct reaction of sodium with graphite at 400°C. It was hoped to prepare compounds of this type by reactions using alkali metal-naphthalene compounds (formulated as in (1)) with graphite in specially purified ethylene glycol dimethyl ether.



(1)

The electron affinity of graphite is much greater than that of naphthalene, and hence it might be expected that an electron transfer

reaction would take place, namely:-



It would seem that this is likely to occur, but it is difficult to say whether intercalation would take place, or whether the sodium ions would remain on the surface of the graphite.

In general, solutions of alkali metal-naphthalene compounds were treated with dried synthetic graphite for different times under varying conditions, the insoluble graphitic products being separated from excess alkali metal hydrocarbon by filtration. Analysis of the products was carried out by six general methods:-

- (a) Direct hydrolysis of the product, followed by titration with standard acid.

TABLE I

Experiment No.	Alkali Metal Used	Reaction of Alkali Metal			Reaction of Alkali Metal			Reaction of Alkali Metal			Reaction of Alkali Metal			Volume of Solvent Used	Approximate Molality of Solution		
		Time of Reaction	Temperature of Reaction	Yield of Product (%)	Time of Reaction	Temperature of Reaction	Yield of Product (%)	Time of Reaction	Temperature of Reaction	Yield of Product (%)	Time of Reaction	Temperature of Reaction	Yield of Product (%)				
1	Na	3hrs	30°C		3hrs	-30°C	Na ₂ C ₂₀								200ml	0.26	
2	Na	"	0°C		"	0°C	Na ₂ C ₂₀	81.9	97	1.9	0				150ml	0.35	
3	Na	"	"		"	"	Na ₂ C ₂₀	79.0	94	2.1	0				200ml	0.26	
4	Na	1hr	17°C		"	"	Na ₂ C ₂₃								"	"	
5	Na	"	"		"	"	Na ₂ C ₂₆								"	"	
6	Na	"	"		"	"	Na ₂ C ₂₉								180ml	0.29	
7	Na	"	"		"	"	Na ₂ C ₃₂								200ml	0.26	
8	Na	"	"		"	"	Na ₂ C ₃₇								150ml	0.35	
9	Na	"	"	0.03mole/l	"	17°C	Na ₂ C ₃₆	81.5	94.5	1.4	0				GW.	160ml	0.23
10	Na	"	"	0.03mole/l	"	"	Na ₂ C ₃₅	85.6	95	1.3	0				"	150ml	0.25
11	Na	"	"	0.04mole/l	"	"	Na ₂ C ₃₅	77.4	95	1.4	0				"	140ml	0.29
12	Na	"	"	0.03mole/l	"	83°C	Na ₂ C ₃₆	64.0	89.5	1.7	0				"	130ml	0.30
13	Na	"	"	0.05mole/l	"	"	Na ₂ C ₃₆								"	140ml	0.37
14	Na	"	"	1.00%	"	~17hrs	Na ₂ C ₃₀								"	0.37	
15	Na	3hrs	0°C	0.05mole/l	"	"	Na ₂ C ₂₈								"	0.37	
16	Na	1hr	17°C		"	"	Na ₂ C ₂₅								S.D.	200ml	0.26
17	K	3hrs	30°C	0.03mole/l	"	3hrs	K ₂ C ₂₀								"	0.13	
18	K	"	17°C	0.04mole/l	"	2hrs	K ₂ C ₂₄	67.7	90	2.3	0				GW.	170ml	0.23
19	K	"	"	0.04mole/l	"	~17hrs	K ₂ C ₂₄	54.0	79.3	2.4	0				"	160ml	0.28
20	K	"	"	0.03mole/l	"	"	K ₂ C ₁₇	56.2	78.1	3.1	0				"	100ml	0.37
21	Li	2hrs	"		"	3hrs	Li ₂ C ₂₂								S.D.	200ml	
22	Li	15hrs	"		"	~17hrs	Li ₂ C ₂₄								"	"	
23	Li	1hr	"		"	"	Li ₂ C ₂₄								"	"	
24	K	3hrs	"		"	"	K ₂ C ₂₁								GW.	0.26	
25	K	"	"		"	3hrs	K ₂ C ₂₂								S.D.	"	

- (b) Hydrolysis with standard acid of excess alkali metal-naphthalene and back-titration with standard alkali.
- (c) Carbon and hydrogen analysis.
- (d) Sublimation of alkali metal from the product in vacuo, followed by hydrolysis and titration with standard acid.
- (e) Acid hydrolysis of the product in a vacuum system and estimation of hydrogen evolved.
- (f) X-ray powder diffraction photographs.

The results are set out broadly in Table 1, but will be discussed in more detail later.

Alkali metal-naphthalene compounds.

The alkali metal-naphthalene compounds formed by sodium, potassium, and lithium were used in reactions with graphite at -30°C , 0°C , and 83°C (refluxing ethylene glycol dimethyl ether) for times of $2\frac{1}{2}$ hrs, 3 hrs, or 17 hrs (overnight). The majority of the reactions were carried out using sodium naphthalene.

ESTIMATION

In the early course of the work, it was hoped that the composition of the product, obtained by the method of direct hydrolysis and titration, could be checked by hydrolysis of the unreacted sodium naphthalene with excess standard acid, and back-titration with standard alkali. From the amount of sodium naphthalene used in reaction with graphite, the composition of the product was calculated. Initially, however, agreement between these two methods was very poor, for example:-

TABLE 3

No. of Experiment	Result by Direct Hydrolysis (Method 1)	Result by Back Titration (Method 2)
(9)	NaC _{32.6}	NaC ₆₅
(10)	NaC _{35.8}	NaC ₁₅₆
(11)	NaC ₃₅	NaC ₈₃

The results from the back-titration method thus show that less sodium has remained with the graphite than does the result by direct hydrolysis. This means that more alkali is being found in the filtrate than expected, i.e. assuming that the original estimation of the sodium naphthalene and the direct hydrolysis result are correct, alkali is being gained during the experiment. This result is, of course, absurd, and the error was eventually found to occur in the initial estimation of the sodium naphthalene solution, which was done by withdrawing aliquots, hydrolysing, and titrating with standard acid. The hydrolysis of the aliquots was normally performed by allowing the sodium naphthalene solution to run into distilled water in the air, but on hydrolysis under nitrogen using de-aerated water, an immediate increase in yields of sodium naphthalene was observed. Apart from one experiment (Experiment (12), in which the former method of hydrolysis was used), this corresponded to increased reliability of the results from the back-titration method, in the sense that they indicated loss of alkali during the experiment, which is more to be

TABLE 4

No. of Expt.	Alkali Metal	Conditions of Reaction between Metal and Naphthalene		Yield of Alkali Metal-Naphthalene Compound	Molarity	Comp ⁿ . of Product by back-titration	Comp ⁿ . of Product by Direct Hydrolysis	Method of Hydrolysis (in estimation of Alkali Metal-Naphthalene)
		Time	Temp.					
9	Na	1 hr	17°C	0.036 moles 70%	0.225	NaC ₆₅	NaC _{32.6}	In air
10	"	"	"	0.0376 " 72.3%	0.251	NaC ₁₅₆	NaC _{35.8}	"
11	"	"	"	0.0407 " 78%	0.29	NaC ₈₃	NaC ₃₅	"
12	"	"	"	0.0384 " 74%	0.295	NaC _{14.2}	NaC ₁₆	"
13	"	"	"	0.052 " 100%	0.37	NaC _{8.4}	NaC _{16.9}	In nitrogen
14	"	"	"	0.0518 " 99.5%	0.37	NaC _{5.5}	NaC ₁₀	"
15	"	3 hrs	"	0.052 " 100%	0.37	NaC _{4.8}	NaC _{8.6}	"
D	"	1 hr	"	0.052 " 100%	0.26	-	-	"
19	K	3 hrs	"	0.0445 " 85.5%	0.278	KC ₅	KC _{12.4}	"
18	"	3 hrs	"	0.0392 " 75.4%	0.23	-	KC _{29.4}	"
20	"	3 hrs	"	0.0365 " 70%	0.365	-	KC _{11.7}	"
A	"	1 hr	"	0.0328 " 63%	0.328	-	-	"

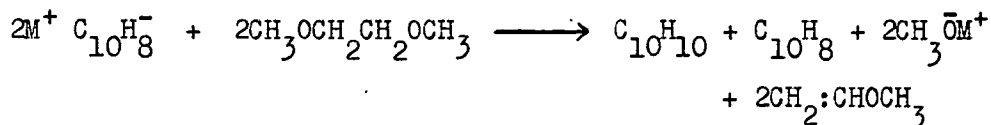
expected. These points are illustrated by the table on the previous page. Another factor emerging from Table 4 is that the formation of potassium naphthalene appears to be much slower than that of sodium naphthalene. Formation of sodium naphthalene was complete (Expts. 13, 14, D) in one hour at room temperature, while formation of potassium naphthalene was not complete in three hours at the same temperature (Expts. 18, 19, 20, A). This apparently slow rate of formation could not be due to decreased solubility of potassium naphthalene in ethylene glycol dimethyl ether, as it is in 0.365 M solution (Expt. 20), while the strongest sodium naphthalene solution in Table 4 is 0.37 M.

Lithium naphthalene, from the limited amount of work carried out, appears to be even slower to form than either of the others. In a reaction between lithium naphthalene and graphite at reflux overnight (Expt. 22), total decomposition of the lithium naphthalene took place and an estimate of the lithium naphthalene present initially was obtained by analysis of the graphitic products, of apparent composition $\text{LiC}_{12.4}$. This showed that the yield of lithium naphthalene, after standing for $1\frac{1}{2}$ hours at room temperature, was only 0.0168 moles (32.3%), much lower than yields of sodium or potassium naphthalene under comparable conditions.

Reaction with solvent.

The analysis of the graphitic products, outlined previously, is complicated by the fact that, at room temperature, a slow reaction between the alkali metal-naphthalene¹⁹ and ethylene glycol dimethyl

ether, takes place:-



This reaction results in the formation of naphthalene, dihydronaphthalene, methylvinyl ether, and the alkali metal methoxide. The first three products do not affect the analysis in any way, methylvinylether being a low boiling liquid, while naphthalene and dihydronaphthalene were removed by washing with ethylene glycol dimethyl ether. Sodium methoxide, however, was found to be completely insoluble in the solvent, and was therefore isolated along with the graphitic products, from which it is completely inseparable.

The fact that this reaction was taking place was confirmed by an experiment in which lithium naphthalene was refluxed overnight in ethylene glycol dimethyl ether. From a cold trap connected to the effluent nitrogen, was obtained a small sample of an unsaturated volatile liquid which could be brominated, almost certainly methyl vinyl ether, while the 3, 5, dinitrobenzoate m.p. 108°C , of methyl alcohol was prepared from the hydrolysate of the alkaline, insoluble residue, which therefore contained lithium methoxide. The colour of the ethylene glycol dimethyl ether filtrate was a pale, transparent red-brown, and proved to be alkaline on hydrolysis, suggesting that the reaction may be complicated by side reactions. Lithium naphthalene seemed to be the most reactive with solvent, sodium

TABLE 2

Experiment	NUMBER OF EXPERIMENTS IN TABLE 1.	ALKALI METAL USED	REACTION OF ALKALI METAL WITH NAPHTHALENE			REACTION WITH SOLVENT			INSOLUBLE ALKALINE MATERIAL ISOLATED (MOLES)	ALKALINE MATERIAL PRESENT IN THE FILTRATE	TOTAL ALKALI ACCOUNTED FOR	REACTION WITH GRAPHITE		INSOLUBLE MATERIAL ISOLATED IN GRAPHITE (MOLES)	INITIAL METHOD OF PREPARATION OF THE REFINED METAL	VOLUME OF SOLVENT USED	APPROXIMATE MOLECULARITY OF SOLUTION
			TIME OF REACTION	TEMPERATURE OF REACTION	YIELD OF ALKALI METAL-NAPHTHALENE (MOLES)	TIME OF REACTION	TEMPERATURE OF REACTION	QUANTITY OF GRAPHITE USED				TEMPERATURE OF REACTION					
A		K	1hr.	17°C	0.0328 (6.3%)	~17hrs.	83°C	0.0235 (7.17%)	0.0086mols (26.8%)	0.0313mols (98.5%)				G.W.	100ml.	0.33	
B		K	3hrs.	-30°C	0.052 (100%)	3hrs.	-30°C	0.00146 (281%)			1.25g			S.D.	180ml.	0.29	
C	17	K	"	"	0.026 (")	"	"	0.00314 (12%)		0.0104mols (96.5%)	0.0104mols	3hrs.	-30°C	0.00372	"	200ml.	0.13
D		Na	1hr.	17°C	0.052 (100%)	~17hrs.	83°C	0.0398 (766%)	0.0104mols (20.0%)	0.0502mols (96.5%)	2.50g			G.W.	200ml.	0.26	
E	2	Na	3hrs.	0°C	0.052 (100%)	3hrs.	0°C	0.00115 (2.21%)			0.208mols	3hrs.	0°C	0.00349	S.D.	150ml.	0.35
F		Na	"	"	"	"	"	0.000099 (1.9%)						"	200ml.	0.26	
G		Na	"	"	"	"	"	0.00115 (2.21%)						"	400ml.	0.13	
H		Na	1hr.	17°C	"	"	83°C	0.023 (44.2%)						G.W.	200ml.	0.26	
I	3	Na	3hrs.	0°C	"	"	0°C	0.00105 (20.2%)			2.50g	3hrs.	0°C	0.00698	S.D.	200ml.	"
J		Na	1hr.	17°C	"	"	17°C	0.00377 (7.26%)			2.50g			G.W.	160ml.	0.33	
K	4	Na	"	"	"	"	0°C	0.00136 (2.66%)			0.208mols	3hrs.	0°C	0.00269	"	200ml.	0.26

naphthalene the most stable, and potassium naphthalene intermediate between the two. From Table 2 (Expts. B and C) it can be seen that the amount of insoluble alkaline material (2.8% and 12% of total alkali) formed by reaction between potassium naphthalene and ethylene glycol dimethyl ether at -30°C for three hours, is greater than that formed by sodium naphthalene (Average = 2.19% of total alkali) under more severe conditions (Expts. E, F, G, I and K), i.e. three hours at 0°C .

Nature of the graphite products.

As the majority of the work was conducted using sodium naphthalene, the general discussion will apply to sodium, while any interesting points relating to potassium or lithium will be mentioned specifically.

Direct Hydrolysis:

Direct hydrolysis, assuming that all of the alkali is present as metal, led to the range of compositions of NaC_{8-77} , those products richest in alkali being obtained from reactions carried out under the most prolonged and severe conditions. For potassium, the compound richest in alkali would have a composition of $\text{KC}_{11.7}$ if it were present as potassium metal. If this was the case, then it would be expected to contain a high proportion of the well-known potassium graphite compound KC_8 , and therefore to possess the bronze-red colour characteristic of this compound. However, in no case did the appearance of the products differ appreciably from that of graphite, suggesting that all of the alkali was not present as the free metal. This was in fact borne out

TABLE 5

Conditions of Reaction		Actual Experiment with Graphite		Control Experiment		
Time	Temperature	No. of Expt. from Table 1	Composition by Direct Hydrolysis	No. of Moles of Insoluble Alkali	Corresponding Composition Using 0.208 moles Graphite	No. of Expt. from Table 2
3 hrs	0°C	2, 3, 4, 5, 6, 8	Av. NaC _{48.7}	Av. 0.00114	Av. NaC _{182.5}	E, F, G, I, K
3 hrs	17°C	9, 10, 11	Av. NaC _{34.5}	0.00377	NaC _{55.2}	J
2½-3 hrs	83°C	12, 13	Av. NaC _{16.4}	0.023	NaC ₉	H
17 hrs	83°C	14, 15	Av. NaC _{9.3}	0.0398	NaC _{5.2}	D
3 hrs	-30°C	17	KC _{38.3}	0.0023	Av. KC ₉₀	B, C
17 hrs	83°C	20	KC _{11.7}	0.0235	KC _{8.8}	A

'Av.' indicates an average result from the experiments shown.

by control experiments, in which solutions of alkali metal-naphthalenes in ethylene glycol dimethyl ether were used under identical conditions to those in the actual experiments, except for the complete exclusion of graphite. The amount of insoluble alkaline material, namely sodium methoxide, produced by reaction between sodium naphthalene and the solvent, was then obtained by hydrolysis and titration with standard acid. The results obtained are set out in Table 2. The results from the control experiments are compared with the results from actual experiments in Table 5 on previous page.

Where several experiments were carried out under the same conditions, the average composition of the compound formed, or, in the case of the control experiments, the average composition of the compound which would be formed if graphite was present (0.208 moles), is shown. This shows that, in the case of experiments carried out at reflux temperature (83°C) all of the alkali present is accountable as methoxide; in the others, the proportion of alkali accountable as methoxide varies from 26.7% (for sodium, 3 hours at 0°C) to 62.5% (for sodium, 3 hours at 17°C), and is 42.6% for potassium (3 hours at -30°C).

The validity of these results is uncertain, as the composition of the products formed under a given set of conditions varied a great deal. For example, in experiments carried out between sodium naphthalene and graphite (Experiments 2-8, Table 1), for 3 hours at 0°C , the range of compositions was NaC_{37-77} . A possible explanation

TABLE 6

Expt. No. Table 2	Alkali Metal	Time	Temperature	Reaction with Solvent			Reaction with Graphite			
				Insoluble Alkali (Moles)	Corresponding Composition if Reacted with Graphite	Insoluble Alkali (Moles)	Composition by Direct Hydrolysis	Molarity of Sodium Naphthalene		
E	Na	3hrs	0°C	0.00115	NaC ₁₈₁	0.00349	NaC _{59.6}	0.35		
I	Na	3hrs	0°C	0.00105	NaC ₁₉₈	0.00698	NaC _{29.8}	0.26		
K	Na	3hrs	0°C	0.00136	NaC ₁₅₃	0.00269	NaC _{77.3}	0.26		

for this wide range may at first appear to be due to inefficient filtration of the sodium naphthalene solution before reaction with graphite. Initially, this filtration was done using a glass wool plug, and it is quite possible that this may allow the passage of small pieces of sodium, broken off from the sodium wire, or any sodium methoxide formed, to pass into the reaction flask, while in another case more efficient filtration may take place. These insoluble alkaline impurities would then be isolated with the graphite and give a greatly erroneous alkaline content.

Probably the most reliable results along these lines were obtained from experiments (E,I,K, Table 2) in which sodium naphthalene was first filtered through glass wool, allowed to react with ethylene glycol dimethyl ether under given conditions, and the insoluble alkaline material estimated after filtration on a sintered glass disc. The filtrate was then allowed to react with graphite under exactly similar conditions. The results obtained from these experiments are shown in Table 6.

Again this wide diversity of results for the composition of the graphite products is apparent, and this time cannot be due to contamination by, e.g. pieces of sodium escaping filtration. On the contrary, where we would expect possible interference from this source, that is, in the initial estimation of insoluble alkali obtained from reaction with the solvent, the results are far more consistent (0.00105 moles - 0.00136 moles). In fact, the most striking point about these results is that, in every case (at 0°C for 3 hours) more

TABLE 7

No. of Expt. (Table 1)	Composition of Compound by Direct Hydrolysis	Found.		Required. Assuming all alkali present as metal		Required. Assuming all alkali present as methoxide	
		Percentage Carbon	Percentage Hydrogen	Percentage Carbon	Percentage Hydrogen	Percentage Carbon	Percentage Hydrogen
2	NaC _{59.6}	81.9	1.9	97	0	94.5	0.39
3	NaC _{29.8}	79.0	2.1	94	0	89.0	0.78
9	NaC _{32.6}	81.5	1.4	94.4	0	90.6	0.67
10	NaC _{35.8}	85.6	1.3	95	0	91.3	0.62
11	NaC ₃₅	77.4	1.4	95	0	91.1	0.63
12	NaC ₁₆	64.0	1.7	89.5	0	82.9	1.22
18	KC _{29.4}	67.7	2.3	90	0	85.1	0.77
19	KC _{12.4}	54.0	2.4	79.3	0	69.1	1.32
20	KC _{11.7}	56.2	3.1	78.1	0	67.5	1.68

insoluble alkali was produced while the sodium naphthalene was in contact with graphite than when no graphite was present. This leads to the conclusion that, under these conditions either, the graphite is acting as a catalyst for the reaction between sodium naphthalene and ethylene glycol dimethyl ether, or the required electron transfer reaction is taking place.

In support of the latter theory, it was noted that samples of the products richest in alkali would glow red hot on exposure to air, behaviour similar to that of the known potassium graphite compounds.

Carbon and Hydrogen analysis.

Carbon and hydrogen analysis was carried out on the products from several of the early experiments, and the observed results (Table 1) were always lower in carbon and higher in hydrogen, than expected. They are summarised in Table 7.

The observed results were found to be lower in carbon and higher in hydrogen than the corresponding mixtures would be, if all the alkali was present as sodium or potassium methoxide. Even if complete hydrolysis of sodium methoxide, by atmospheric water vapour, to sodium hydroxide and methyl alcohol took place before weighing, the alteration in composition would not account for the large differences in carbon analysis. The extreme values for the range of 'sodium graphite' products are shown on the next page:-

TABLE 8

Expt. No.	Composition by Direct Hydrolysis	Found		Required, allowing for complete Hydrolysis of Alkali	
		% Carbon	% Hydrogen	% Carbon	% Hydrogen
2	NaC _{59.6}	81.9	1.9	92.3	0.63
12	NaC ₁₆	64.0	1.7	77.3	1.9

It appears, therefore, that either, impurities other than those mentioned above are present, or, the analyses are unreliable.

Sublimation of Metal.

The fact that the products did contain free sodium was shown beyond doubt in several cases, the metal being sublimed in vacuo, although any quantitative measurement was rarely attempted. A notable feature of at least one of these graphitic products (Experiment 15) was that, even after sublimation of sodium was apparently complete, the residue glowed red-hot when exposed to air, suggesting that sodium metal may still be present, despite the fairly severe conditions used in the sublimation. This may be explained if the sublimed metal was merely present as a dispersion on the surface of the graphite, while that remaining behind was intercalated in the graphite lattice, thereby being more tenaciously held.

Hydrolysis and estimation of the sublimed metal gave an approximate range of compositions of NaC₂₀₀₋₄₇₀. In two experiments,

the amount of involatile alkali present was estimated by hydrolysis and titration, and, assuming that it was all present as sodium methoxide, the compositions due to sublimed metal alone were calculated:-

TABLE 9

Expt. No.	Composition by Direct Hydrolysis	Composition by Estimation of Sublimed Metal	Composition Assuming all Involatile Alkali is Sodium Methoxide
15	NaC _{8.6}	NaC ₄₇₄	NaC ₂₇₂
4	NaC _{77.3}	NaC ₂₅₅	NaC ₂₄₁

The presence of alkali metal in the graphitic products, whether as a random distribution on the surface of the graphite, or as intercalated ions, or both, has now been established. However, besides the postulated electron transfer reaction, the occurrence of sodium with the graphite could possibly be explained more simply. Sodium naphthalene does not exist other than in solution, and, if washing of the products with ethylene glycol dimethyl ether was incomplete, then removal of the solvent would result in the re-formation of sodium and naphthalene, and the detection of the free metal in the graphite. Therefore, sodium naphthalene was mixed with graphite (in an amount corresponding to a composition of NaC₄₅₂) and subjected to the same drying process used for all of the products, naphthalene easily being detectable as it sublimed on the sides of the drying tube, a phenomenon

not observed in any of the actual experiments. However, should this dissociation to sodium and naphthalene occur before washing is complete, then subsequent washing may remove the naphthalene before the addition compound can re-form, thus leaving only sodium behind. Precautions were taken against this eventuality by ensuring that the graphite residue was always wet with ethylene glycol dimethyl ether until filtration and washing were complete.

The remaining possibility that small pieces of free sodium, broken away from the sodium wire used in the preparation of the sodium naphthalene, had escaped filtration and contaminated the graphite, was very unlikely, in that sodium could be sublimed from products of reactions (Experiments 4, 7, 8) using sodium naphthalene which had itself been filtered through a grade three sintered glass disc before use.

Vacuum Line Hydrolysis.

The control experiments, carried out between sodium naphthalene and ethylene glycol dimethyl ether, especially in the case of the reactions carried out at 83°C , give very little data on the relative amounts of free metal and other alkaline impurities in the graphite. The results obtained by estimation of sublimed metal, too, seem to be of little value in ascertaining the true metal:graphite ratio, as it appears that not all of the metal is removed under the conditions used.

The most reliable method of unequivocally determining the amount of alkali metal in a given sample would appear to be by vacuum

line hydrolysis, and estimation of the hydrogen evolved. Experiments along these lines led to results in the range $MC_{516-2380}$, not allowing for the presence of material other than graphite and alkali metal. Even so, these results are much lower in alkali than anticipated by sublimation figures. These results were most peculiar, since Fredenhagen and Cadenbach¹⁰ had successfully determined the composition of alkali metal-graphite lamellar compounds by measuring the volume of hydrogen evolved on passage of a stream of moist nitrogen. Accordingly, a trial determination performed on a potassium graphite compound of known composition (KC_{75} by direct hydrolysis and titration), made by direct reaction of potassium and graphite, gave good agreement (KC_{76}), showing that little was wrong with the technique employed.

Another surprising aspect of these results is that a product which would glow red-hot on exposure to air (Experiment 16) prepared at $83^{\circ}C$, and one which would not (Experiment 7), evolved comparable amounts of hydrogen when treated as above, the results corresponding to compositions of NaC_{1138} and NaC_{935} respectively, whereas the former product would be expected to contain much more free sodium. The random nature of the results from the vacuum line hydrolysis is exemplified in the case of Experiment 7, in which three determinations on samples of the product gave results of NaC_{1138} , 1690 and 2380. These results, in fact, indicate that a very small amount of alkali metal is present as a random distribution, as no explanation of the apparent loss of hydrogen either by its use in reduction or by absorption seems possible. However, the evidence from sublimation experiments, and the

TABLE 10

Copper Radiation			Cobalt Radiation
d in A° Graphite	d in A° Experiment 12 2½ hrs. at 83°C	d in A° Experiment 15 17 hrs. at 83°C	d in A° Sodium Methoxide
			13.18
			11.26
			8.23
			6.53
	5.28		
			4.32
			4.03
(1) 3.74 β	3.76 β	3.74 β	
			3.62
(2) 3.37	3.38	3.39	3.38
		2.98	
			2.90
	2.78		2.78
	2.68		
		2.62	
		2.54	2.53
	2.48		
	2.38	2.37	2.40
			2.29
(3) 2.26	2.25	2.26	
		2.18	
(4) 2.12	2.13		
(5) 2.03	2.03	2.04	
		1.95	
		1.88	
(6) 1.85			
	1.79		
		1.71	
(7) 1.69	1.69	1.68	1.70
	1.62		
(8) 1.36			
(9) 1.28			1.27
(10) 1.23	1.23		1.23
			1.20
(11) 1.16	1.16		
			1.06
(12) 0.99			

β = due to unfiltered β radiation

fact that some of the alkali-rich products are so air sensitive, does indicate that more sodium metal is present than is shown by the vacuum line experiments, and that all of this metal may not simply be present as a surface distribution. The only way to discriminate between the two possibilities is by X-ray diffraction measurements, and powder photographs were taken of many samples.

The X-ray work described subsequently was carried out as a qualitative indication of the presence of lamellar compounds of graphite, and is not to be interpreted as an attempt at detailed structural analysis.

X-ray investigation.

X-ray powder photographs were taken using copper $K\alpha$ or cobalt $K\alpha$ radiation, the results from early experiments showing little promise. Those experiments conducted under mild conditions were usually identical to graphite, while those conducted under more severe conditions, although containing many extra lines, showed no alteration of the 002 line of graphite, i.e. no alteration in the basal spacing of graphite, which must be taken as the criterion for formation of a lamellar compound. Typical results for experiments performed under more severe conditions are shown on the previous page, compared with the d spacings for graphite and a sample of sodium methoxide. Table 10.

For simplicity in explanation, the lines showing up on the graphite photograph are numbered 1-12, line 2, at 3.74\AA being due to the main basal spacing of the graphite layers. The product from Experiment 12 shows eight lines coincident with graphite (1, 2,

3, 4, 5, 7, 10 and 11), while that from Experiment 15 has five coincident lines (1, 2, 3, 5 and 7). The graphite lines which are not reproduced on these photographs are, without exception, weaker lines, which do not appear, probably due to relative overall intensity of the photographs. There is in fact, no doubt that a large amount of unchanged graphite is present in each of the above products, and, if any of the required lamellar compound is present, then it is in so small an amount as to be undetectable (approximately 10%), as no alteration of the basal line of graphite has taken place.

Experiment 12 shows coincidence with sodium methoxide in the case of five lines, three of which, at 3.38° , 1.69° and 1.23° also occur in graphite, while the other two occur at 2.38° and 2.78° , thus including one of the two very strong lines of sodium methoxide (8.23° and 2.40°). Experiment 15, carried out for a longer period at 83°C , produced lines coinciding with those of sodium methoxide at 3.39° , 1.68° , 2.54° and 2.37° , the first two of which also occur in graphite. Again, the line at 2.37° agrees with the very strong sodium methoxide line at 2.40° . In addition to the lines which can be accounted for in terms of either graphite or sodium methoxide, both photographs include more lines which are different in the two photographs. The two products therefore consist largely of unchanged graphite, some sodium methoxide and other impurities. These impurities, perhaps consisting of a little sodium oxide or hydroxide probably account for many of the extra lines appearing between 3.37° and 2.26° observed in the majority of the products obtained from reactions carried out at 83°C .

TABLE 11

Radiation Used	Copper	Copper	Cobalt	Copper	Cobalt
NaC ⁵³⁻⁶⁶ by Asher d in A ^o	Expt. 12 d in A ^o	Expt. 6 d in A ^o	Expt. 7 d in A ^o	Graphite d in A ^o	Sodium Methoxide d in A ^o
					13.18
					11.26
					8.23
			5.38		6.53
	5.28				
					4.32
					4.03
	3.76 β			(1) 3.74 β	
					3.62
3.50		3.50	3.53		
	3.38		3.38	(2) 3.37	3.38
		3.30			
3.12					
					2.90
	2.78	2.77	2.78		2.78
	2.68		2.70		
					2.53
	2.48		2.48		
	2.38	2.40	2.39		2.40
					2.29
	2.25			(3) 2.26	
2.13	2.13	2.13	2.14	(4) 2.12	
2.06					
2.02	2.03	2.03	2.04	(5) 2.03	
1.96					
				(6) 1.85	
	1.79				
1.75					
	1.69	1.68	1.69	(7) 1.69	1.70
1.65					
	1.62		1.62		
1.54					
				(8) 1.36	
				(9) 1.28	
1.23	1.23	1.23	1.23	(10) 1.23	
1.16	1.16	1.15	1.16	(11) 1.16	
1.14					
1.12					
1.06					
				(12) 0.99	

By far the most striking X-ray results were those obtained from Experiments 6 and 7, both conducted at 0°C for 3 hours, using sodium naphthalene previously filtered through a grade three sintered glass disc, in reaction with graphite. The values for the d spacings obtained from these experiments are tabulated on the previous page, together with those from Experiment 12, graphite, sodium methoxide and those published by Asher and Wilson for NaC_{53-66} . Table 11.

Attempts to prepare a sample of the sodium graphite compound made previously by Asher were unsuccessful (as had been reported by Hennig²²).

In Experiment 6 the basal line of graphite (at 3.37A°) has disappeared completely and is replaced by two new lines of equal intensity at 3.50A° and 3.30A° , on either side of the original position. The graphite lines, 3, 6, 8, 9 and 12, do not show up in the photograph from Experiment 6, but these are such weak lines that they are probably missing because the photograph has a lower overall intensity. The strong graphite lines (4, 5, 7, 10 and 11) are all present, and in addition, two other lines (at 2.77A° and 2.40A°), both of which correspond to lines in Experiments 12, 7 and in sodium methoxide. The line at 2.40A° corresponds to the very intense line of sodium methoxide, which is certainly present. The product, almost certainly a lamellar compound of sodium and graphite, does not show the structural features exhibited by Asher's sodium graphite compound, except in the position of the first line, at 3.50A° .

In Experiment 7, some interference with the basal spacing of

graphite again appears to have taken place, an additional line, less intense than the original line at 3.38\AA° , being present at 3.53\AA° . Considerable blurring of the film had occurred between these two lines. Once again, all of the strong lines of graphite were present, two of these (at 3.38\AA° and 1.69\AA°) together with two more (at 2.78\AA° and 2.39\AA°) corresponding to lines shown by sodium methoxide. The film from Experiment 7 differed from that from Experiment 6 in the appearance of lines at 5.38\AA° , 2.70\AA° , 2.48\AA° and 1.62\AA° , three of which correspond to lines appearing in the product from Experiment 12, thus showing the presence of the same impurities.

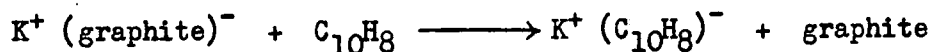
It thus seems obvious that, at least in the case of Experiment 6, an intercalation compound of sodium with graphite has been formed, especially as an X-ray film of a sample of the product which had been exposed to air, was identical with graphite itself (in that the position of the 002 line was restored). The blurring of the main basal line of graphite occurring in Experiment 7 indicates some interference with the graphite layer structure, but suggests that it is more likely in the form of a random distribution of sodium ions than in formation of a definite compound.

An interesting result is obtained if allowance is made for the presence of alkaline impurities from reaction between sodium naphthalene and ethylene glycol dimethyl ether, in calculating the composition of the compound from Experiment 6 ($\text{NaC}_{48.6}$ by direct hydrolysis). From Table 2, the average amount of alkaline insoluble impurities produced in this way at 0°C in three hours (Experiments E, F, G, I and K), is 0.001121 moles. The formula of the compound when

this is taken into consideration, reduces to $\text{NaC}_{65.8}$, within the range of compositions quoted by Asher for his sodium graphite compound, NaC_{53-66} . This result may be significant and it is possible that, in this experiment, the optimum conditions for the reaction were reached, the electron transfer reaction taking place to a sufficient extent, to allow formation of an intercalation compound, while excessive formation of alkaline impurities, which may hinder detection of the compound, did not take place.

Reaction between potassium graphite and naphthalene in pure ethylene glycol dimethyl ether

Because of the high electron affinity of graphite, it was thought unlikely that potassium graphite and naphthalene would react to form potassium naphthalene in ethylene glycol dimethyl ether, as this would involve an electron transfer from graphite to naphthalene:-



When naphthalene was allowed to react with the potassium graphite compound, KC_8 , in carefully purified ethylene glycol dimethyl ether, potassium naphthalene was formed. However, in this case, due to experimental difficulties, no quantitative measurement of the extent of the reaction was made. In any case, the formation of the sodium naphthalene may have taken place by reaction of the naphthalene with free potassium, present in a non-homogeneous mixture of the metal and potassium-graphite compounds. A similar experiment, in which a product of composition $\text{KC}_{13.5}$ (therefore a mixture of KC_8 and KC_{24})

was reacted with excess of naphthalene, led to formation of some potassium naphthalene. However, estimation of the potassium naphthalene solution formed showed that only 8.5% of the metal originally used (0.00193 moles) was present in this form.

Furthermore, a sample of the graphitic residue from this reaction would not react with more naphthalene in ethylene glycol dimethyl ether, while another sample was found to contain potassium, which could be sublimed out in vacuo. It thus appears that naphthalene will react under these conditions either with potassium metal which has not previously reacted with the graphite, or only with potassium graphite compounds with a K:C ratio above a certain value. The former explanation would appear to be more likely, although several careful experiments would have to be carried out to determine conclusively whether or not this is so.

EXPERIMENTAL

Since most of this work involved the use of air and water-sensitive compounds, it was carried out completely in an atmosphere of dry nitrogen, unless otherwise mentioned. All solvent used was purified by distillation from potassium diphenyl ketyl, and stored over molecular sieve in an atmosphere of dry nitrogen.

A. Preparation of alkali metal-naphthalene compounds in ethylene glycol dimethyl ether

1. Sodium Naphthalene

Excess of sodium wire (3g, 0.13 moles) was pressed directly into a solution of naphthalene (6.7g, 0.052 moles) in pure, dry ethylene glycol dimethyl ether (150 mls), an immediate deep green colour spreading from the surface of the metal throughout the solution. It was allowed to stand for 1 hour at room temperature, or 3 hours at 0°C or -30°C, before filtration from excess sodium, through a glass wool plug. Two aliquots (2 ml) were withdrawn, hydrolysed, and estimated, a yield of 0.036 moles (70%) being obtained.

In later preparations, it was found that a much higher titration figure was obtained if the hydrolysis was carried out in de-aerated water under nitrogen, all subsequent estimations being carried out in this way. Once the yields became consistently high, however, estimation of the solutions was discontinued.

Most of the preparations were performed at room temperature, and in several cases, the solution was filtered, under nitrogen, through a filtration apparatus containing a sintered glass disc (grade three) to ensure complete removal of insoluble alkaline impurities.

This technique was rendered very difficult with the preparations carried out at lower temperature, because of increased viscosity, decreased solubility of the sodium naphthalene, and the fact that the filtration apparatus could not be conveniently cooled to temperatures other than -78°C . In a few instances, blocking of the sintered glass disc caused the preparation to be abandoned.

The reaction conditions used and yields obtained are shown in Table 1. (See Discussion)

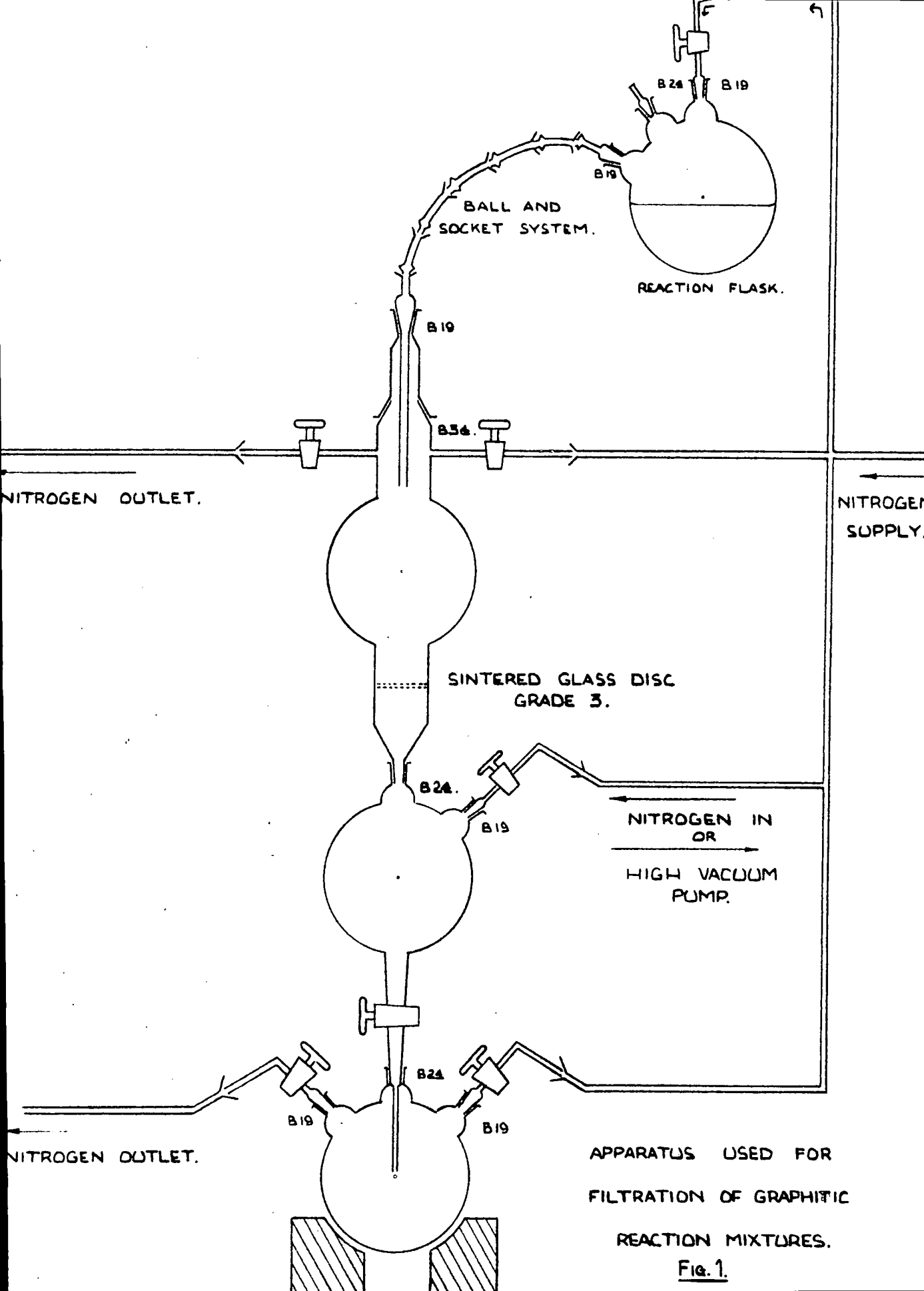
2. Potassium Naphthalene

Potassium metal ($\sim 2.5\text{g}$, 0.064 moles) was powdered by stirring in refluxing ethylene glycol dimethyl ether (100 mls), b.p. 83°C , a very pale transparent blue solution being obtained, with much excess potassium present. After cooling, naphthalene (6.7g, 0.052 moles) was added with stirring, a deep-coloured solution, appearing green or red-brown, being formed immediately. It was stirred for 3 hours, filtered and estimated as above, a yield of 0.0392 moles of potassium naphthalene (75.4%) being obtained. Yields varied from 70%–85%.

The preparation was also carried out at -30°C , but was not estimated in this case. Potassium naphthalene appeared to be less soluble than sodium naphthalene, some difficulty in filtration through a plug of glass wool being encountered, even at room temperature, due to the presence of a black sludge.

3. Lithium Naphthalene

Naphthalene (6.7g, 0.052 moles) was added to lithium shot (0.5g, 0.072 moles) in ethylene glycol dimethyl ether (200 mls),



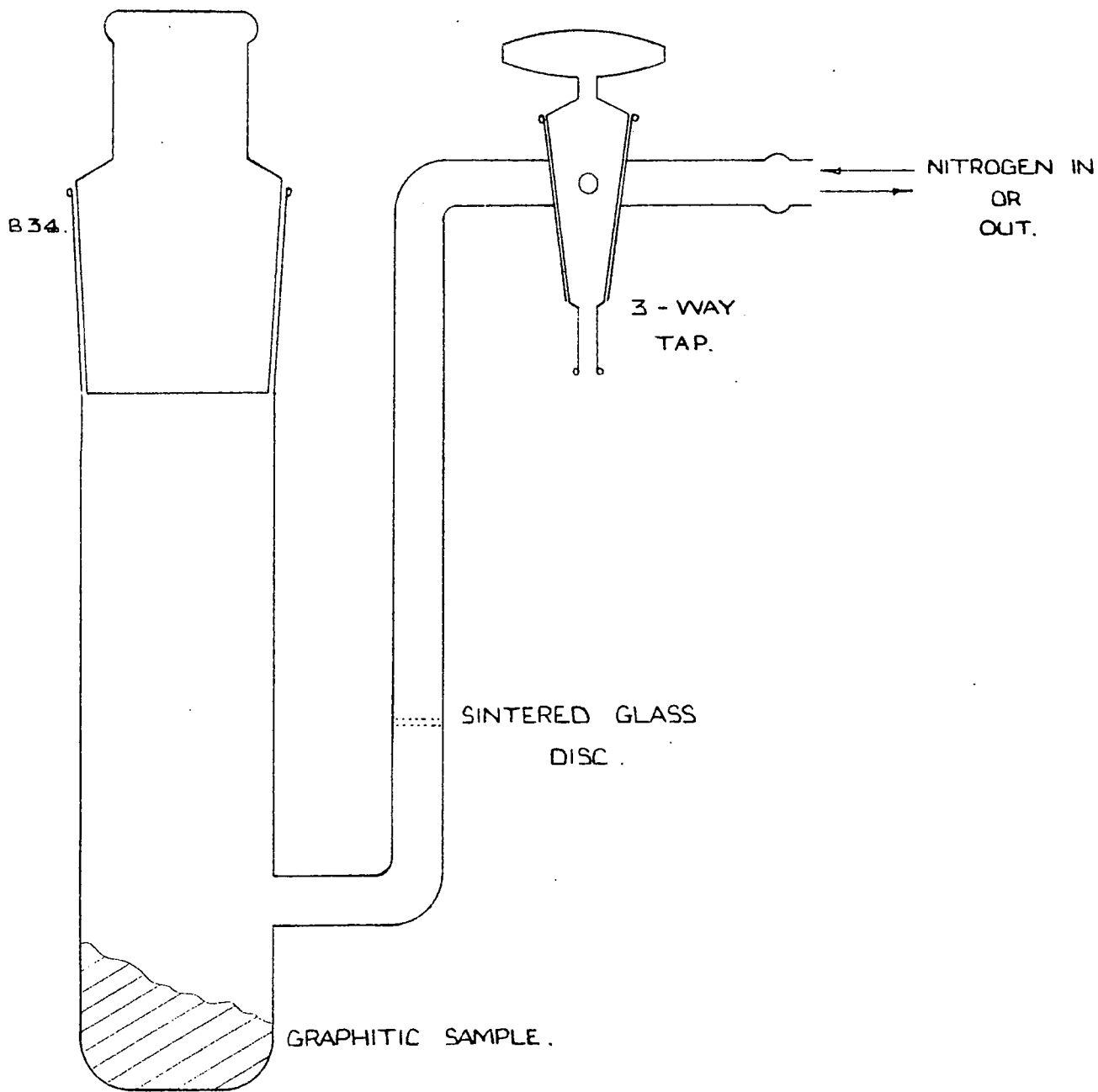
and stirred for $1\frac{1}{2}$ hours, before filtering through the apparatus shown in Fig. 1, the sintered glass disc (grade three) being covered with a layer of quartz wool to minimise blocking. Lithium naphthalene appeared to be much less soluble than either sodium or potassium naphthalenes, filtration taking at least 2 hours at room temperature. The filtrate was not estimated, but from subsequent reactions, it was calculated that the greatest amount of lithium naphthalene in solution was 0.0168 moles (32.3%). It was also noticed that yields seemed to increase directly in proportion to the time the naphthalene solution was in contact with the lithium metal.

B. Reaction between alkali metal-naphthalene compounds and graphite

Immediately before use, each sample of graphite was pumped under high vacuum for ten minutes in a small flask, being constantly shaken, and warmed with a gentle bunsen flame.

1. Reaction between sodium naphthalene and graphite

A solution of sodium naphthalene (0.036 moles) in ethylene glycol dimethyl ether (150 mls) was added with rapid stirring, to powdered, dry, synthetic graphite (2.5g, 0.208 moles). Stirring was continued for periods varying from $2\frac{1}{2}$ hours to 17 hours, at temperatures ranging from -30°C to 83°C (reflux temperature), before filtration through a sintered glass disc under intermittent suction from a high vacuum pump. During filtration, the green solution often looked red at the edges of the meniscus. The residue on the sintered glass plate (grade three) was washed thoroughly with pure, dry solvent, being stirred each time with a clean glass rod, until the washings were



APPARATUS USED FOR DRYING GRAPHITIC REACTION PRODUCTS.

FIG. 2.

colourless. At no time throughout filtration and washing was the residue allowed to become dry of solvent. The graphitic residue was then pumped partially dry under high vacuum to facilitate its direct transference to the drying tube shown in Fig. 2. This tube was then immersed partially in a silicone oil bath, and all traces of solvent removed by pumping under high vacuum at 220°C for 5 hours, the tube being shaken periodically.

In several of the later reactions, the sodium naphthalene solution, previously filtered through a glass wool plug, was subjected to identical reaction conditions as above, but in the complete absence of graphite. The solution was then filtered again through the sintered glass disc, a black sludge, turning almost white when pumped dry, being obtained. This residue was hydrolysed and titrated against standard acid, while the filtrate was either estimated, or used for reaction with a sample of graphite as above.

A preparation was attempted in which sodium naphthalene solution was to be added to graphite (2.5g, 0.208 moles) until a permanent green colour was obtained. However, the reaction seemed very slow, and colour changes were so difficult to distinguish, that it was modified, the reaction being carried out as usual.

A summary of the conditions and results of reactions between sodium naphthalene and graphite is shown in Table 1, while the reaction conditions and yields of insoluble alkaline material obtained from solutions of sodium naphthalene alone, are shown in Table 2.

The tabulated compositions of the products were calculated assuming that all of the alkali present is in the form of the metal.

It may also be mentioned that the experiments are not shown in chronological order. The method of filtration of the alkali metal naphthalene solution is also indicated by S.D. or G.W. in Tables 1 and 2, referring to the use of a sintered glass disc, or a plug of glass wool, respectively, the former method, of course, being the most efficient.

In none of the above reactions, despite careful observation during pumping or drying of the product, was any trace of free naphthalene observed.

None of the products differed appreciably from graphite in appearance, but their stability on exposure to air varied a great deal. The products from reactions under mild conditions remained apparently unchanged, but those produced under more severe conditions, e.g. at 83°C overnight, would glow red-hot in air.

2. Reaction between potassium naphthalene and graphite

A solution of potassium naphthalene (0.0392 moles) in ethylene glycol dimethyl ether (100 mls) was reacted with graphite (2.5g, 0.208 moles) at reflux temperature (83°C) for periods of $2\frac{1}{2}$ hours and 17 hours, using the same experimental technique as above.

In a further preparation at -30°C , the potassium naphthalene solution was used at twice the dilution, to alleviate filtration difficulties at this temperature. After filtration through a glass wool plug, the solution was allowed to stand for 3 hours at -30°C , before filtration through a sintered glass disc, the residue appearing as a dark sludge, with a few bright spots of metallic potassium, which

must have escaped the first filtration. It was cautiously hydrolysed and estimated, to give a maximum value for insoluble alkaline material produced under these conditions. This is included in Table 2, Expt. C. The filtrate, containing the excess potassium naphthalene, was then used for reaction with graphite under the same conditions (3 hrs at -30°C).

The products were treated identically to those obtained using sodium naphthalene, again being very similar to graphite in appearance, while those produced from the reactions under more drastic conditions would once again glow red-hot on exposure to air. The results obtained are shown alongside those for sodium.

3. Reaction between lithium naphthalene and graphite

A filtered solution of lithium naphthalene (~ 0.052 moles), made as described previously, but not estimated, was stirred with graphite (2.5g, 0.208 moles), at room temperature ($\sim 17^{\circ}\text{C}$) for 3 hours in one case, and at reflux temperature (83°C) for 17 hours in two other cases, the same technique as described for sodium and potassium being used. Filtration of the mixture after refluxing overnight, gave in both cases, a pale green, almost colourless filtrate, which indicated that all of the lithium naphthalene had reacted either with graphite or with the solvent.

Analysis of the products from these two reactions gave compositions of $\text{LiC}_{12.4}$ and $\text{LiC}_{47.4}$, although reaction conditions were very similar. The only difference lay in the fact that, in the first case, the lithium and naphthalene had been in contact for

$1\frac{1}{2}$ hours at room temperature before filtration and reaction with graphite, whereas in the second, they were only in contact for $\frac{1}{2}$ hour. This implies that the reaction between lithium and naphthalene in ethylene glycol dimethyl ether is slow, and indeed, the composition of the $\text{LiC}_{12.4}$ product indicates that the greatest amount of lithium naphthalene in solution is ~ 0.0168 moles (32.3% yield), although poor solubility of the lithium naphthalene itself may contribute to this low figure.

The products were once more very similar to graphite in appearance, and the results are shown with those of sodium and potassium in Table 1.

C. ANALYSIS OF PRODUCTS

The analysis of the products is described in detail for sodium, but are, in general, equally applicable to lithium and potassium.

Throughout these analyses, invaluable use was made of a small glove-box, purged continuously with oxygen-free nitrogen, and kept dry with fresh phosphorous pentoxide.

The results are shown in Table 1.

(a) Direct hydrolysis of the product

Accurately weighed amounts, ($\sim 0.5\text{g}$), of the graphitic residue, introduced into weighed, two-necked flasks (50ml) in the glove-box, were hydrolysed with distilled water and filtered, the residue being extracted repeatedly with boiling water, until the washings gave no colour with phenolphthalein. The filtrate was

then titrated with standard acid. The whole analysis was performed in triplicate, good agreement being obtained in all cases.

(b) Back titration of excess alkali

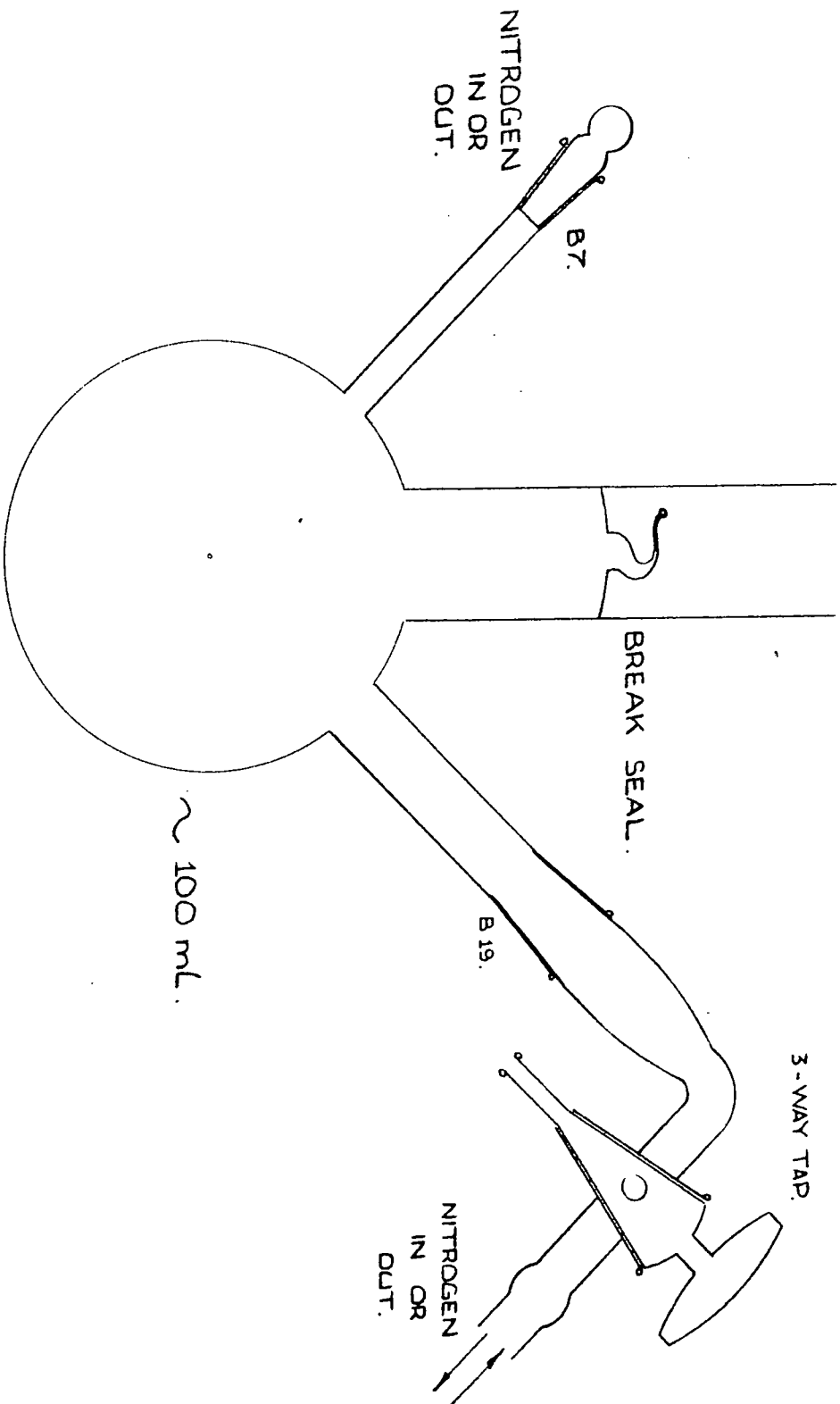
The filtrate from reaction of sodium naphthalene with graphite was run directly into an excess of standard acid, and back-titrated with standard alkali. As the amount of sodium naphthalene present initially was known, the amount used in reaction with graphite or with ethylene glycol dimethyl ether, was calculated. In the first few experiments, agreement between this method and method (a) was poor. This was found to be due to an inaccurate initial estimation of sodium naphthalene, but once this had been improved, and reasonable agreement obtained, (Expt. 12,) this method was discontinued. A further difficulty encountered was that even after the filtrate had been hydrolysed by excess of standard acid, a red-brown or green fluorescent colour partially, and in some cases, completely, masked the end point. This colour was particularly troublesome in the case of the potassium naphthalene experiments.

(c) Carbon and hydrogen analysis

Carbon and hydrogen analyses were performed on the products from early preparations, the carbon analysis always being too low, and the hydrogen analysis always too high, almost certainly due to the presence of sodium methoxide in the product.

(d) Sublimation of metal from the product

A sample of the product ($\sim 2g$) was transferred to a weighed silica flask in the glove-box, and the exact weight of the sample determined. The material was then pumped under high vacuum, while the flask was heated with a bunsen flame until it glowed red.



FLASK USED FOR VACUUM LINE HYDROLYSIS OF GRAPHITIC PRODUCTS.

FIG. 3

Metallic sodium was sublimed out, and, after the residual graphitic material had been tipped out, the sublimate was dissolved in ethanol, a little distilled water added, the solution being titrated against standard acid. Naturally, it was difficult to effect complete removal of the residue, so that we would expect the titration figure to be high if the residue contained alkali. In fact, the composition of the compound calculated by this method was always much poorer in alkali than by direct hydrolysis. Consequently, in some cases, the residue was hydrolysed and estimated, being found to contain most of the alkali, good agreement with the results by direct hydrolysis then being obtained.

Other residues from sublimations of this type were extracted with ether and filtered, but after removal of the ether, no naphthalene was detected. In at least one instance, even after prolonged sublimation treatment, in which sodium was sublimed out, the non-volatile residue glowed red on exposure to air, suggesting that some metal had remained unsublimed.

(e) Vacuum line hydrolysis and estimation of hydrogen produced

A sample of the product (~ 0.5 g) was introduced, in the dry box, to the weighed flask shown in Fig. 3, fitted with a break-seal, and the flask weighed again. A paper funnel was used to introduce the sample, to avoid getting any of the product on the side arm of the flask. With nitrogen passing into the B.7 arm, the B.19 arm was thickened so that it could be easily sealed off under vacuum. Then, with nitrogen passing the other way, the B.7 arm was sealed off completely, and the nitrogen removed from the flask by pumping on the vacuum line. A small amount (10 ml) of a 50% mixture of dilute

hydrochloric acid and propanol, previously stored in the vacuum line, was then condensed into the flask by cooling in liquid air, and the B.19 arm was sealed off. The flask was then immersed in boiling water for $2\frac{1}{2}$ hours, a B.19 joint sealed on to the neck with the break-seal, and the space above the break-seal evacuated. The seal was then broken, the gas evolved passing through a liquid air trap, before being Töplered and measured. The volume of gas evolved was always very small, and gave the apparent composition of products to be much lower in alkali than expected by other methods of analysis.

In one case, with a product obtained by refluxing potassium naphthalene with graphite in ethylene glycol dimethyl ether for 17 hours, (Expt. 25,) potassium metal was sublimed out of the sample before hydrolysis on the vacuum line, but the result was of the same order as previous determinations.

The method was checked by doing a determination of gas evolved on hydrolysis of a potassium graphite compound of known composition (KC_{75} by direct hydrolysis and titration) prepared directly from the elements, and giving good agreement (KC_{76} by estimation of gas evolved).

(f) X-ray powder diffraction photographs

Preparation of capillary tubes for X-ray powder photographs was done in the glove-box, the tubes being sealed off using a small coil of resistance wire. This technique, rendered difficult by the frailty of the capillaries and the clumsiness of the rubber gloves, was proved effective by production of a good photograph of the very air-sensitive, copper-coloured potassium graphite compound, KC_8

(prepared by the direct action of potassium on graphite).

In some cases, for comparison purposes, a sample of the product was deliberately exposed to the air before preparation of a specimen for X-ray.

A sample of sodium methoxide was also prepared for a powder photograph.

D. Reaction between alkali metal-naphthalene compounds and ethylene glycol dimethyl ether

Alkali metal-naphthalene compounds are known to react slowly with ethylene glycol dimethyl ether,¹⁹ to form the alkali metal methoxide and vinyl methyl ether.

(i) A solution of sodium naphthalene (0.052 moles) in ethylene glycol dimethyl ether (200 mls) was refluxed overnight, the effluent nitrogen being passed through a cold trap at -78°C . Filtration of the solution through a sintered glass disc gave a black residue, turning to an off-white colour as it was pumped dry. This was hydrolysed and estimated, amounting to 0.0398 moles (76.6%) of the total alkali. Hydrolysis and estimation of the filtrate gave 0.01042 moles (20%) of alkaline material, the other 0.00178 moles (3.6%) being accredited to experimental error. Dropwise addition of a solution of bromine (10%) in carbon tetrachloride, to the residue in the cold trap showed the presence of an unsaturated compound, almost certainly vinyl methyl ether.

(ii) In a similar reaction using a solution of potassium naphthalene (0.0328 moles) in ethylene glycol dimethyl ether (100 mls), after refluxing overnight, insoluble alkaline material (0.0235 moles, 71.7%)

was filtered off, while the filtrate contained 0.0088 moles (26.8%) of potassium as potassium naphthalene. Vinyl methyl ether was once more obtained in the cold trap.

(iii) A filtered solution of lithium naphthalene was prepared as described previously, in ethylene glycol dimethyl ether (200 mls), and was not estimated. The solution was refluxed, and even after one hour, had changed to a predominantly brown colour. After refluxing overnight, filtration gave a white insoluble alkaline residue, and a pale transparent red-brown filtrate, which proved alkaline on hydrolysis, but nevertheless suggested that extensive decomposition had taken place.

The white residue was hydrolysed with a small volume of water and distilled, the fraction boiling below 100°C being collected. This was then re-distilled, and a 3, 5, dinitrobenzoate derivative, m.p. 107°C , prepared from the fraction distilling below 70°C . This confirms the presence of methyl alcohol, (3, 5, dinitrobenzoate, m.p. 108°C) in the hydrolysate, and hence lithium methoxide in the white residue.

(iv) Mention has already been made in the section on the reaction between graphite and the alkali metal-naphthalenes, of isolation and estimation of insoluble alkaline materials, formed by reaction between the solvent and e.g. sodium naphthalene, under varying conditions. These reactions are essentially the same as those described immediately above, except that in most of the reactions, the filtrate was used in reaction with graphite. The conditions used, and the results obtained, together with those above, are summarised in Table 2. (See Discussion)

Solubility of sodium methoxide in ethylene glycol dimethyl ether

A small sample ($\sim 1\text{g}$) of sodium methoxide was added to refluxing ethylene glycol dimethyl ether, and stirred for 30 minutes. Filtration, followed by hydrolysis of the filtrate and addition of phenolphthalein showed that no alkali was present, sodium methoxide being completely insoluble.

Detection of a small amount of naphthalene in a mixture of graphite and naphthalene

(i) Naphthalene (0.0808g, 0.000631 moles) was mixed intimately with graphite (1g, 0.0834 moles), and subjected to the same drying process as used for the products, in the drying tube illustrated in Fig. 2. The naphthalene readily sublimed out and was easily detectable on the sides of the tube.

(ii) A solution of sodium naphthalene (0.00046 moles) in ethylene glycol dimethyl ether (3 mls) was added to graphite (2.5g, 0.208 moles), corresponding to a composition of NaC_{452} , and pumped under high vacuum in a small flask, warmed by a bunsen flame. Naphthalene sublimed out readily, but no sodium could be detected.

E. Preparation of lamellar compounds of potassium and graphite by direct reaction

(i) Dry graphite (15g, 1.25 moles) was stirred with a Hershberg stirrer in a 500 ml. flask on a Wood's metal bath maintained at 300°C . Freshly cut potassium metal ($\sim 0.8\text{g}$, 0.0204 moles) was added in small amounts, stirring being continued for 5 hours at 300°C to ensure homogeneity. After cooling, samples of the product were analysed by direct hydrolysis and titration (KC_{75}) and by vacuum line hydrolysis

and estimation of hydrogen evolved (KC_{76}), giving good agreement.

A preparation performed identically, apart from the fact that it was stirred for only 30 minutes, gave a non-homogeneous product.

(ii) A further preparation using graphite (25g, 2.08 moles) and potassium (10.1g, 0.26 moles) was carried out in the same way, being stirred at $350^{\circ}C$ for 5 hours. The bronze red product, of composition KC_8 , was very air sensitive, and even blackened slightly on the surface during standing in a slow stream of nitrogen.

(iii) In another experiment, a product of composition $KC_{13.5}$ was prepared, using graphite (3.7g, 0.308 moles) and potassium (0.89g, 0.0228 moles) under the same conditions as above. The product, a mixture of KC_8 and KC_{24} , was a deep blue colour.

F. Reaction of potassium graphite with naphthalene in ethylene glycol dimethyl ether

(i) Ethylene glycol dimethyl ether (~ 300 mls) was distilled directly from potassium diphenyl ketyl, $K^+ \bar{O}-CPh_2$, (prepared by adding benzophenone to excess of potassium metal in the refluxing solvent) into the reaction flask containing KC_8 ($\sim 35g$, 0.26 moles) cooled to $0^{\circ}C$ in an ice-bath. Naphthalene (33.3g, 0.26 moles) was added and the mixture stirred for 1 hour at $0^{\circ}C$, the deep green colour of potassium graphite being evident. The solution was then filtered in the apparatus shown in Fig. 1, but, due to the large bulk of material used, causing filtration and washing difficulties, no quantitative estimation of the extent of reaction could be performed.

(ii) In a similar experiment, ethylene glycol dimethyl ether (200 mls) was distilled from potassium diphenyl ketyl, into the reaction flask containing $KC_{13.5}$ (4.69g, 0.0228 moles) at $0^{\circ}C$. After stirring for 30 minutes at this temperature, the supernatant liquid was seen to be a pale blue colour. A small amount of solvent was filtered through a sintered glass disc, and appeared colourless, a small amount of graphite remaining on the disc. On hydrolysis, the filtrate showed no alkalinity (phenolphthalein). To the bulk of the mixture was added dry naphthalene (3.5g, 0.0273 moles), and stirring maintained for 1 hour. The reaction mixture was filtered as previously, a deep green filtrate being obtained. The graphitic residue was washed carefully with pure, dry solvent, being stirred on the sinter with a long glass rod during each washing. Several washings were performed even after the filtrate became colourless. The filtrate was hydrolysed and titrated with standard acid. Samples of the graphitic residue were withdrawn under nitrogen and tested:-

(a) A small sample was added to a solution of dry naphthalene in pure ethylene glycol dimethyl ether and allowed to stand for thirty minutes, no green colour of potassium naphthalene being produced.

(b) A small sample was transferred to a silica flask, and, on heating with a bunsen flame in vacuo, potassium metal could be sublimed out.

The sublimed potassium metal, and the total graphitic residues were hydrolysed, boiled with distilled water, and the

solutions combined, filtered, and titrated with standard acid.

Results are shown below:-

Alkali in filtrate	=	0.00193 moles
Alkali in residue	=	<u>0.01375</u> moles
Total alkali recovered	=	0.01568 moles
Total alkali used	=	0.0228 moles
Alkali unaccounted for	=	0.0071 moles

The result for the filtrate gives a composition, for the residue, of $KC_{14.7}$, while the result for the residue gives a composition of $KC_{22.4}$, some error being involved in the first result because of the slight inaccuracy in the weight of potassium originally used, while both may be affected by the probable reaction of potassium naphthalene with the solvent.

G. Attempted preparation of NaC_{64}

A freshly cut piece of metallic sodium (0.125g, 0.00546 moles), was added to dry graphite (4.2g, 0.3495 moles), in a 250 ml. flask, maintained at $400^{\circ}C$ on a Wood's metal bath. Stirring was continued for 30 minutes at this temperature and the whole allowed to cool, no colour change being apparent. The reaction was done in an atmosphere of argon. Samples were prepared for X-ray powder diffraction photographs, but analysis of the compound showed that the product must be non-homogeneous:-

Sodium metal was sublimed out from a weighed sample, ($\sim 1.5g$), equivalent to a composition of NaC_{710} , while hydrolysis and estimation of the residue from this sample gave a total alkaline content equivalent to a composition of NaC_{200} . This preparation could probably be

improved by more efficient stirring and a longer reaction period.

PART 4.

ATTEMPTED PREPARATION OF A SUBSTITUTED DERIVATIVE OF NICKELOCENE

INTRODUCTION

Since the discovery of ferrocene in 1951 by two completely independent groups of workers, a great deal of work has been done on this compound, and on the cyclopentadienides of many other metals. Since several excellent reviews on these compounds are readily available, they will be dealt with very briefly here.

The methods of preparation of the metal cyclopentadienyls may be summarised as follows:-

1. Interaction of metals and cyclopentadiene.
2. Interaction of metal salts and cyclopentadienyl magnesium bromide.
3. Interaction of alkali metal salts of cyclopentadiene and metal halides.
4. Interaction of metal halides and cyclopentadiene.
5. Interaction of metal carbonyls and cyclopentadiene.

It may be noted at this stage, that not all of the above methods can be applied to any cyclopentadienyl-metal compound, the use of the cyclopentadienyl Grignard and a metal salt (Method 2) being most generally applicable. At the same time, special methods are available for the preparation of particular compounds (e.g. ferrocene and cyclopentadienyl thallium).

Dicyclopentadienyl nickel, or nickelocene, with which this work will be concerned, has been made by the reaction of the Grignard reagent with nickel (II) acetylacetonate, or from potassium cyclopentadienide and

the ammine $(\text{Ni}(\text{NH}_3)_6)(\text{SCN})_2$ in liquid ammonia. The compound exists as dark green crystals, subliming at $80^\circ\text{--}90^\circ$ and melting in nitrogen at $173^\circ\text{--}4^\circ\text{C}$ with decomposition. Nickelocene is slowly oxidised by air, unaffected by cold water, and soluble in organic solvents. Oxidation yields an orange-yellow solution containing the ion $(\text{Ni}(\text{C}_5\text{H}_5)_2)^+$; stable for a short time in weakly acidic media, and can be precipitated as the reineckate or tetraphenyl borate.

Ferrocene forms orange needles, m.p. 172°C , is insoluble in water, stable in the air, and soluble in organic solvents. Oxidising agents such as ferric or silver salts, convert it into the blue cation $(\text{Fe}(\text{C}_5\text{H}_5)_2)^+$; an easily reversible process. Ferrocene, as its name implies has an organic chemistry very similar to that of benzene, undergoing most reactions of an aromatic character. The hydrogen atoms of the cyclopentadienyl rings of ferrocene can thus undergo a whole series of substitution reactions. The only other cyclopentadienyl compounds which have so far been reported to undergo this reaction are those of ruthenium and osmium, and in one reference to the

$(\text{Co}(\text{C}_5\text{H}_5)_2)^+$ ion.

Structure

The structure of the ferrocene-like dicyclopentadienyl derivatives, including that of nickel, has been established by X-ray methods as a



Fe



pentagonal antiprism. In ferrocene the rings, normally fixed as shown, become freely rotating at 360°C , and stereoisomers of ring-substituted derivatives have been obtained.

9 10

Bonding

The nature of the bonding in these compounds is still the subject of much discussion, despite the fact that they have been known for many years. It is fairly certain that the saltlike alkali, alkaline earth, and rare earth metal cyclopentadienyl compounds possess essentially ionic bonding between the metal atom and the ring, while the main group metal compounds, e.g. those of zinc, mercury, tin, lead and bismuth are of an intermediate nature, their structures not yet being fully understood.

In the transition metal-cyclopentadienyl complexes, concepts of the bonding depend on the sterically central position of the metal atom with the cyclopentadienyl rings. Wilkinson, Woodward, and their co-workers¹¹ associated five π -electrons with each five membered ring, which, together with the eight available electrons of the central Fe(0) atom, built up the electron shell of the latter to the inert gas configuration of eighteen. Fischer and Pfab,¹² however, postulated a completely new type of penetration complex, in which the parallel aromatic cyclopentadienyl anions each possess three pairs of π -electrons, the central Fe²⁺ ion interacting with each pair to form six co-ordinate covalencies, in a trigonal antiprism. This concept was strengthened by the theoretical studies of Ruch¹³ and by the fact that the aromatic nature of the rings is retained. Two other proposals also lead to the krypton configuration^{14,15} for ferrocene.

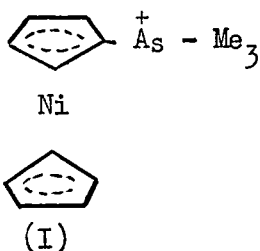
In opposition to this are comprehensive theoretical studies, suggesting a single $d\pi-p\pi$ bond between the metal and the ring in all transition metal compounds,¹⁶ but on this basis, ferrocene would show only

a closed 3d shell. Four electrons would then remain in the rings which could be considered as radicals without taking part in the bonding.

The fact that hydrogenation of the six-membered ring in di-indenyl compounds¹⁷ results in the taking up of only four hydrogen atoms seems to indicate that the third pair of π -electrons of the benzene ring are being drawn into the five-membered ring to form the complex, while the stability of the $[\text{Co}(\text{C}_5\text{H}_5)_2]^+$ cation (iso-electronic with ferrocene) towards ozone in acetic acid again indicates the use of the π -electrons in complex formation.¹⁸ The gradation in stability of the complexes is consistent with this theory, maximum stability occurring when the unchanged compound possesses the inert gas configuration, i.e. ferrocene, ruthenocene, and osmocene. It can be seen that the only difference between ferrocene and nickelocene is the presence of two extra electrons in the latter, these lying outside the inert gas configuration, and it is upon these two electrons that the difference in stability and chemistry of the two compounds must depend.

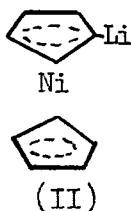
DISCUSSION

Nickelocene, as outlined in the introduction, is far less stable chemically than the iron analogue, ferrocene, being oxidised by the air either as solid or in solution, and undergoing attack by organic solvents, e.g. acetone. Since this lack of stability is undoubtedly connected with the two extra electrons possessed by nickelocene, attempts were made to introduce an electron-attracting substituent into the cyclopentadienyl ring of nickelocene, in an effort to prepare a compound of formula:-



If this was possible, then the effect of such a group may well be to enhance stability of the complex.

All attempts at substitution were made using butyl lithium, in the hope that the lithiated derivative of nickelocene, formulated in (II) would be produced:-



This could then be used with the appropriate halide, in this case cacodyl iodide, Me_2AsI , followed by methyl iodide, to prepare the required substitution product (I).

Preparation of Nickelocene

The preparation of nickelocene was carried out by the method of Fischer and Jira from nickel hexammine thiocyanate, $(\text{Ni}(\text{NH}_3)_6)(\text{SCN})_2$ and cyclopentadienyl sodium, $\text{C}_5\text{H}_5\text{Na}$, in liquid ammonia, and by two methods not previously used for nickelocene:-

1. Nickelocene, purified by sublimation in vacuo, was obtained in 30% yield from reaction of cyclopentadienyl sodium with a solution of anhydrous nickel bromide in pure ethanol. The reaction was immediate and better yields could probably be obtained by improved working up techniques. A similar preparation attempted using solid anhydrous nickel bromide gave only a minute yield of the required product, due to the slow solubility of anhydrous nickel bromide in ethanol. The speed of reaction was probably further hampered by the fact that nickelocene is unstable in alcoholic solution. The insoluble decomposition products produced would then coat the nickel bromide, rendering further reaction impossible. This method of preparation has been used to prepare ferrocene.

2. Dicyclopentadienyl nickel, again purified by sublimation, was made in 12% yield by gently refluxing cyclopentadienyl lithium with finely powdered nickel bromide in tetrahydrofuran-diethyl ether mixture.

Attempted lithiation of nickelocene

Lithiation of nickelocene was attempted at temperatures ranging from -100°C to room temperature, using butyl lithium in ether-tetrahydrofuran mixtures. Besides reaction with cacodyl iodide and methyl iodide mentioned previously, carbonation of some of the reaction mixtures was attempted.

1. Reaction with cacodyl iodide, followed by methyl iodide

Lithiation of nickelocene as above was attempted at room temperature, followed by reaction with cacodyl iodide and methyl iodide, but no organic nickel products could be isolated.

In a similar reaction, carried out at -78°C , a brown solid containing nickel, iodine, and arsenic was obtained, but was found to consist of a mixture of decomposition products, and could not be purified, dissolving with decomposition in most solvents.

2. Reaction with carbon dioxide

Carbonation of reaction mixtures from attempted lithiation reactions carried out at -78°C and -100°C were performed using dry ice. The reaction carried out at -78°C yielded a trace of unreacted nickelocene, much inorganic nickel-containing decomposition product, valeric acid (formed by carbonation of excess butyl lithium) and a small amount of acidic, yellow, crystalline solid, which did not contain nickel. From the lower temperature reaction was recovered 50% nickelocene, a little inorganic nickel-containing residue, and valeric acid. In neither case was any acidic nickel-containing compound isolated.

Since some decomposition of nickelocene always occurs in solution, some of this substance is always lost during working up and it thus appears that, while nickelocene is largely degraded by butyl lithium at temperatures close to -78°C , it is almost unaffected at -100°C , and lithiation of nickelocene is likely to be impossible.

EXPERIMENTAL

The whole of this work was carried out in an atmosphere of nitrogen, unless otherwise stated.

1. Preparation of nickelocene

a. From cyclopentadienyl sodium and nickel bromide in ethanol

(i) Freshly distilled cyclopentadiene (30g, 0.462 moles) was added dropwise, at room temperature, to a stirred solution of sodium ethoxide, made by dissolving sodium (11.5g, 0.5 moles) in absolute alcohol (300 mls), a yellow, orange, and then deep red solution of cyclopentadienyl sodium being formed. A green solution, appearing yellow when dilute, of anhydrous nickel bromide (20g, 0.0915 moles), made via nickel hexamine bromide, in dry ethanol (130 mls) was added with stirring, an immediate deep green colour being formed. Ether (400 mls) was added, the green organic layer being washed several times with water to remove alcohol, in which nickelocene is unstable, and left over magnesium sulphate overnight. After filtration, the ether was distilled off under water pump vacuum, at 25°-30°C, the last traces being removed under high vacuum. Some decomposition to a brown product occurred during the distillation. The product was then sublimed under high vacuum at 80°C, nickelocene being obtained as air-sensitive, deep green crystals (6.7g, 0.0355 moles, 38.9%). Much brown decomposition product remained as residue.

(ii) Another preparation, attempted using solid nickel bromide, gave a much slower reaction, a minute yield (2%) of nickelocene being

obtained. This was probably due to the slow solubility of anhydrous nickel bromide in ethanol, and subsequent decomposition in the alcohol, of most of the nickelocene formed. These decomposition products would, in turn, coat the undissolved nickel bromide and prevent further reaction, while the large excess of very fine nickel bromide greatly hampered working up of the product.

b. From cyclopentadienyl lithium and nickel bromide in tetrahydrofuran-ether mixture

A pale green or yellow solution of cyclopentadienyl lithium (0.5 moles) was prepared by dropwise addition of a solution of freshly distilled cyclopentadiene (32.5g, 0.5 moles) in tetrahydrofuran (100 mls), to a solution of methyl lithium (0.5 moles) in ether (150 mls), at room temperature. After stirring for 30 minutes, more tetrahydrofuran (250 mls) was added. To this solution, with vigorous stirring, was added finely powdered, anhydrous nickel bromide (54.7g, 0.25 moles), in successive small portions over $2\frac{1}{2}$ hours. After stirring for a further 4 hours with no apparent change, the solution was gently refluxed for 6 hours. Much unreacted nickel bromide was present. The deep green supernatant liquid was quickly decanted and filtered, working up as previously yielding nickelocene (5.8g, 0.0308 moles, 12.3%) as deep green crystals, m.p. $173^{\circ}-4^{\circ}\text{C}$ (in a sealed tube).

c. From nickel hexamine thiocyanate and cyclopentadienyl sodium in liquid ammonia

Nickel tetrammine thiocyanate (60.75g, 0.25 moles), forming the hexamine in liquid ammonia, was added with vigorous stirring, to a

solution of cyclopentadienyl sodium (0.5 moles) in liquid ammonia. Due to great difficulty encountered in filtering the solution, the ammonia was allowed to evaporate, and nickelocene was sublimed directly from the reaction mixture, being obtained once more as deep green crystals (11g, 0.0584 moles, 23.4%). The yield would have been appreciably higher, but for extensive decomposition of the hot reaction mixture, which occurred when air was accidentally sucked in during the sublimation.

2. Attempted metallation of nickelocene by butyl lithium

a. Preparation of butyl lithium in ether

A solution of butyl chloride (2.9g, 0.034 moles) in ether (20 mls), was added dropwise at -30°C to a stirred slurry of lithium shot (0.7g, 0.11 moles) in ether (50 mls), stirring being continued for 15 minutes after complete addition. The reaction was initiated at room temperature by the addition of a few drops of ethylene dibromide. The solution of butyl lithium was filtered from excess lithium through a plug of glass wool before estimation. Yields were $\sim 70\%$.

b. Attempted lithiation, and subsequent carbonation of nickelocene

(i) A solution of butyl lithium (0.037 moles) in ether (75 mls) was added dropwise at -78°C , to a well-stirred solution of nickelocene (2g, 0.0106 moles) in tetrahydrofuran (50 mls), the green solution becoming red-brown in colour. Gilman Colour Test 2 was negative at this stage. After stirring for 15 minutes, the solution was carbonated by pouring on to a dry ice-ether slurry, and the resulting dark brown solution was hydrolysed. The aqueous layer was made more alkaline with sodium hydroxide, filtration of the solution giving a brown, non-acidic

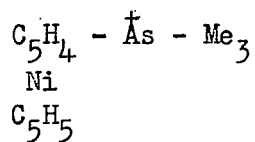
residue (0.8g), from which a few crystals of nickelocene could be sublimed, the remainder consisting of inorganic, nickel-containing material. The layers were separated, the organic layer being washed with alkali and water, dried, and distilled, leaving a dark brown, sweet smelling, oily residue (0.3g) which contained nickel, probably as a decomposition product of nickelocene. The aqueous layer was acidified and extracted several times with ether. Evaporation of the dried ethereal washings gave a mixture (2.5g) of a brown oil and a yellow solid. The solid was filtered and washed with petroleum ether, to give an acidic, yellow, crystalline solid (0.4g), which did not contain nickel. The sharp-smelling, brown oil (1.5g, 0.0147 moles), distilling at 184° - 186°C to a colourless liquid, was valeric acid, b.p. 186°C , formed by carbonation of excess butyl lithium.

(ii) In a further experiment, butyl lithium (0.0475 moles) in ether (100 mls), was added with stirring, to a solution of nickelocene (2g, 0.0106 moles) in tetrahydrofuran (80 mls), at -100°C , this temperature being maintained by a methylene chloride-liquid air mixture in a large Dewar flask. Gilman Colour Test 2 was performed after addition of 25 mls (0.0119 moles), 50 mls (0.0238 moles), and after complete addition of the butyl lithium solution, being negative in each case. The colour of the samples, after withdrawal, changed from green to brown, probably due to thermal decomposition. After stirring for 15 minutes, carbonation was effected by addition of lumps of dry ice, the whole solution being left in the cooling bath overnight to warm up

slowly. Some green solid was then present in the green solution. Withdrawal of a small volume (~ 5 mls) of the solution and extraction with alkali failed to remove the green colour from the organic layer, thus suggesting that little or no reaction had taken place. The bulk of the solution was therefore hydrolysed, made alkaline, and separated, working up of the green organic layer yielding nickelocene (1g, 50%) and inorganic, nickel-containing residue (0.5g). The aqueous layer, on working up, yielded a dark brown, strong smelling oil (3.2g), distilling at 183° - 186° C, to give valeric acid (2.9g, 0.0284 moles), as a colourless liquid.

The negative Gilman Colour Test may be due to rapid attack of the butyl lithium on the nickelocene as the samples were withdrawn, although this is hardly applicable in the case of the last test performed, as excess of butyl lithium was present in any case.

c. Attempted preparation of a nickelocene trimethyl arsonium iodide,



(i) A solution of nickelocene (1g, 0.0053 moles) in tetrahydrofuran (60 mls) was added dropwise, with stirring, to a solution of butyl lithium (0.02 moles) in ether (80 mls) at room temperature, the solution becoming yellow, and then dark brown, as the addition progressed. After stirring for 5 hours, cacodyl iodide, Me_2AsI (2.46g, 0.0106 moles), was added, the flask becoming warm, followed at an interval of 5 minutes, by methyl iodide (1.88g, 0.0133 moles), the dark brown solution being left overnight.

The solution was hydrolysed, filtered from a small amount of dark green solid, and the layers were separated, the red ethereal layer being washed well with water. After drying over magnesium sulphate, removal of the ether gave a tacky, dark, red-brown residue (0.1g), which did not contain nickel. A sample of the pale green aqueous layer was made alkaline, and a few drops of a 1% solution of dimethylglyoxime in ethanol were added, a red precipitate showing presence of the Ni^{2+} ion.

(ii) A solution of nickelocene (3g, 0.0159 moles) in tetrahydrofuran (100 mls) was added to butyl lithium (0.0562 moles) in ether (100 mls) at -78°C , a deep red-brown solution being formed. After stirring for 15 minutes at this temperature, cacodyl iodide (16.7 mls, 0.0955 moles) was added, followed by methyl iodide (6.25 mls, 0.1 moles) and the mixture allowed to warm up slowly in the cooling bath overnight. The dark red-brown reaction mixture was hydrolysed, to give a green aqueous layer with some red-brown solid present, and a red organic layer. After filtration, extraction of the green aqueous layer with ether gave red washings, while the aqueous layer contained the Ni^{2+} ion. The red-brown solid (2g) was dried over phosphorous pentoxide in vacuo, and portions were tested:-

(a) It was slowly soluble in cold water, the resulting solution containing the Ni^{2+} ion, but no As^{3+} (acidified with dilute hydrochloric acid and saturated with hydrogen sulphide).

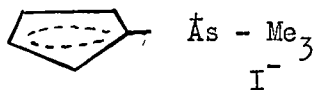
(b) On boiling, a yellow solution was formed, while a smell of arsine was observed, indicating that some decomposition was taking place.

The resultant solution contained Ni^{2+} and I^- , but gave only a faint opalescence when an acidified portion was saturated with hydrogen sulphide.

(c) A sodium fusion was carried out with a small sample of the red-brown solid, the resulting solution giving a strong positive test for As^{3+} .

Repeated attempts at recrystallization of the brown solid were unsuccessful. It dissolved on warming, in methanol, ethanol, acetone, and benzene, to give red or green solutions, always accompanied by the smell of free arsine. A carbon and hydrogen analysis on the original material gave:-

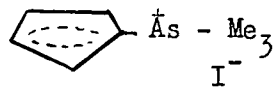
	C	H
Found	19.1%	4.1%
Required for Compound (I)	35.8%	4.15%
Compound (II)	28.2%	3.81%



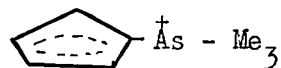
Ni



(I)



Ni



(II)

The material obtained was obviously not the required compound, and probably consisted of a mixture of decomposition products.

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