THE   CHEMISTRY   OF   SOME   HETEROCYCLIC

DERIVATIVES   OF   PHOSPHORUS

by

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S U M M A R Y

The synthesis of 2,2'-biphenylylenebisdiethylphosphine and its use to form heterocyclic diquaternary dibromides by union with alkylene α,ω-dibromides and o-xylylene dibromide are described. The thermal decomposition reactions of the cyclic salts, and the dimethiodide of the diphosphine, have been studied and found to proceed in a novel manner to give 9-alkyl-9-phosphafluorenes. Similar ring-contraction reactions have been observed in the thermal decomposition of analogous salts derived from 2,2'-biphenylylenebisdiethylarsine. It is suggested that the ring-contraction reactions shown by the above salts on heating, are examples of a general internal nucleophilic displacement mechanism.

The alkaline hydrolysis of quaternary salts of the 9-substituted-9-phosphafluorenes has been studied and found to proceed with opening of the heterocyclic ring. A related reaction leading to ring-expansion is also described. The proton magnetic resonance spectra of certain of the above salts have been examined and the results related to theories concerning the magnitude of coupling constants in organophosphorus compounds.

The 9-alkyl-9-phosphafluorenes have unusual properties as

ligands in that they form a series of five-co-ordinate

tris(phosphine) complexes with cobalt(II), nickel(II),

palladium(II) and platinum(II) halides. The properties and

probable structures of these complexes are discussed.

Some aspects of the co-ordination chemistry of the

diphosphine with palladium(II) and nickel(II) compounds are also

described.

ACKNOWLEDGMENTS

C O N T E N T S

INTRODUCTION

Over the past twenty years, there has been a very great
expansion in the field of organo-phosphorus chemistry. This has been
due both to the increasing application of phosphorus compounds in
industrial processes and to the stimulus provided by the development
of novel synthetic procedures, the most notable of these being the
Wittig olefin synthesis.[1]

In some respects, the chemistry of phosphorus bears a
formal resemblance to that of nitrogen, but in general the similarity
of the two elements is only superficial. The availability of 3d orbitals
to phosphorus affects the mechanisms and products of reactions in ways
which have no parallel in the chemistry of nitrogen.

Much of the earlier work concerning the synthesis and
properties of heterocyclic phosphorus compounds has been systematically
treated by F.G. Mann in two publications.[2,3] More recent work on these
systems and particularly on those containing pentavalent or hexavalent
phosphorus, has been reviewed by Märkl.[4]

In this introduction, it is intended to give an outline of
the synthetic methods which have been used to prepare cyclic phosphines
and the phosphonium salts derived from them, with particular reference
to those involving the formation of phosphorus-carbon bonds, and also
to give a brief outline of the chemical properties of such compounds.

The reaction of di-Grignard reagents with suitable phosphonous

dihalides represents one of the earliest methods of preparing cyclic derivatives of phosphorus. Grüttner and Krause[5] showed that phenylphosphonous dichloride reacts with the di-Grignard reagent obtained from tetramethylene dibromide in cold ether to give 1-phenylcyclotetramethylenephosphine (I). By a similar reaction, Grüttner and Wiernik[6] prepared 1-phenylcyclopentamethylenephosphine (II).
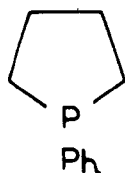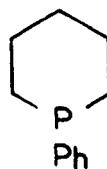
(I)   (II)

The Grignard reaction has been used more recently in another form. Phenylphosphinebis(magnesium bromide), $PhP(MgBr)_2$, represents a special type of reagent which is not strictly a Grignard reagent, but which reacts readily with suitable dihalogenocompounds to form heterocyclic compounds. This reagent is prepared by boiling an ethereal solution of phenylphosphine with phenylmagnesium bromide:-

$$PhPH_2 + 2PhMgBr \longrightarrow PhP(MgBr)_2 + 2C_6H_6$$
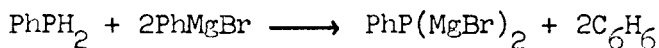
It is used in situ without isolation, the final reaction mixture being hydrolysed to give the cyclic phosphine.

Thus Mann and Millar synthesized hexahydro-1,4-diphenyl-1,4-azaphosphine (III) from the reaction of di(2-bromoethyl)aniline with the above reagent.[7] In a similar manner, Issleib and Häusler[8] have

synthesized the cyclic phosphines (I) and (II) by the reaction of
phenyldilithium phosphide, $PhPLi_2$, with the appropriate
α,ω-dihalogenoalkane, under conditions of high dilution to minimise the
formation of linear polymers.

Ph
N

P
Ph
(III)
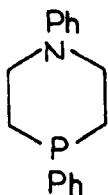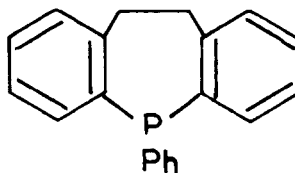
P
Ph
(IV)

In cases where the dihalogeno-compound is not sufficiently reactive to
form a Grignard reagent, the corresponding dilithio-compounds have been
used in a similar way. For example, 2,2'-dibromodibenzyl fails to form
a di-Grignard reagent, but Mann, Millar and Smith[9] by employing an
exchange reaction with n-butyl-lithium, were able to form the dilithio-
compound, which reacted with phenylphosphonous dichloride to yield
1-phenyl-1-phospha-2,3:6,7 dibenzocyclohepta-2,6 diene (IV).

The acid-catalysed nucleophilic addition of secondary phosphines
(or phosphine itself) to alkylene dialdehydes has provided elegant
syntheses of the cyclic α,α'-dihydroxyphosphonium salts (V) and the
spirocyclic phosphonium salt (VI) respectively.[10,11]

(V)

(VI)
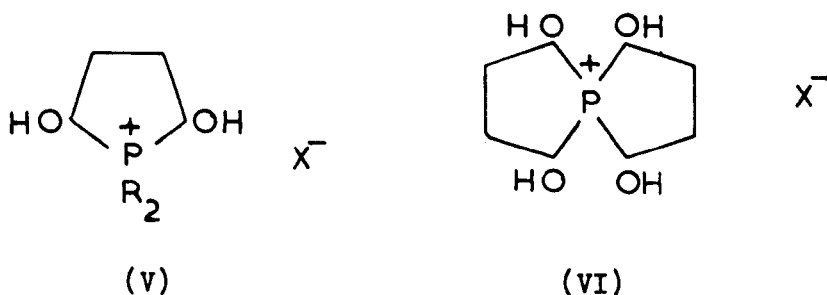
The formation of cyclic quaternary phosphonium salts by the intramolecular quaternisation of w-bromoalkylphosphines has also been used with success, in some cases the free cyclic phosphine being obtained on thermal decomposition of the quaternary salt. Thus Mann and Millar[12] treated the phosphine (VII) with hydrogen bromide in glacial acetic acid to give the intermediate w-bromoalkylphosphine (VIII), which underwent spontaneous intramolecular quaternisation in chloroform solution to give the salt (IX). Thermal decomposition of the latter gave the free cyclic phosphine, 1-ethylphosphindoline (X).

(VII)   (VIII)   (IX)

(X)
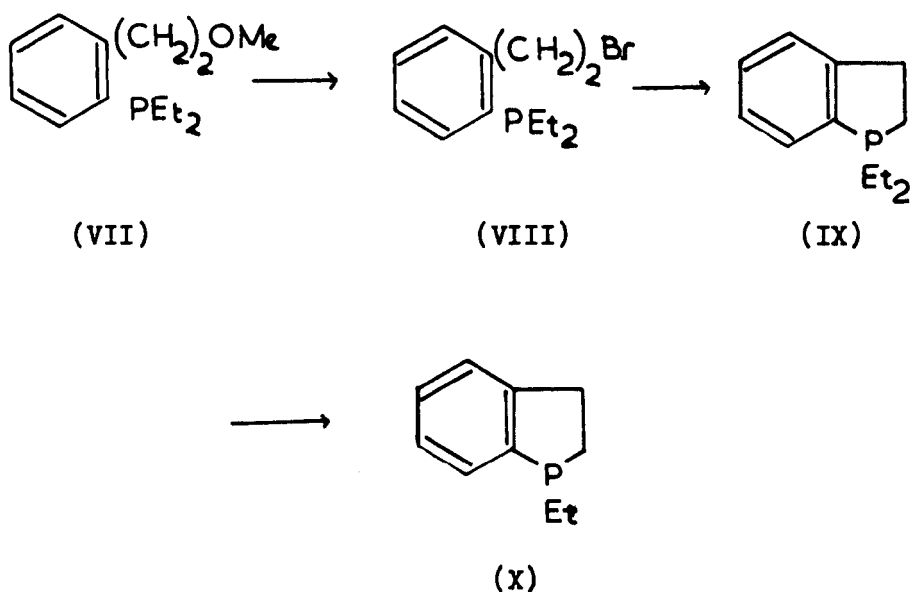
A further type of intramolecular cyclisation reaction has been
described recently by Davies, Downer, and Kirby.[13] Cyclic phosphines
having five-, six-, or seven-membered rings were prepared from
secondary phosphines possessing a terminally unsaturated alkenyl group
by the intramolecular addition of the P-H group to the double bond
under the influence of ultraviolet light. (Fig. 1) (n = 2, 3, or 4.)

$$\underset{\underset{R-P-H}{|}}{(CH_2)_n} \quad \underset{\underset{CH_2}{\|}}{CH} \quad \xrightarrow{\text{u.v.}} \quad \underset{\underset{R-P}{|}}{(CH_2)_n} \quad \underset{\underset{CH_2}{|}}{CH_2}$$
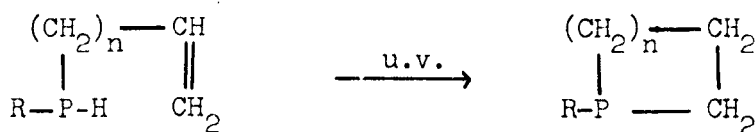
Fig. 1

Intramolecular cyclodehydrohalogenation reactions of suitable
arylphosphonous dihalides and diarylphosphinous halides have also been
used for the synthesis of heterocyclic phosphorus compounds. Thus the
compound (XI), on heating with aluminium powder, undergoes
cyclodehydrohalogenation to yield 10-phenylphenoxaphosphine (XII).[14]
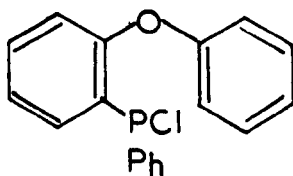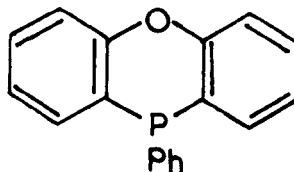
(XI)   (XII)

Until recently, very few cyclic diphosphines have been
investigated. The di-quaternary salts of cyclic diphosphines may
be obtained readily by the intermolecular quaternisation of a
di-tertiary phosphine (in which the phosphorus atoms are suitably
disposed for the formation of a heterocyclic ring) with an alkylene
dihalide.

In this respect, 4-methyl-o-phenylenebisdiethylphosphine (XIII)
undergoes quaternisation with ethylene dibromide to form the salt
(XIV);[15] and 2-diethylphosphino-5-methylbenzyldiethylphosphine (XV)
quaternizes with methylene dibromide to form the salt (XVI), which is
apparently the first phosphorus analogue of the quinazoline system to
be recorded.[16]

(XIII)   (XIV)   (XV)   (XVI)
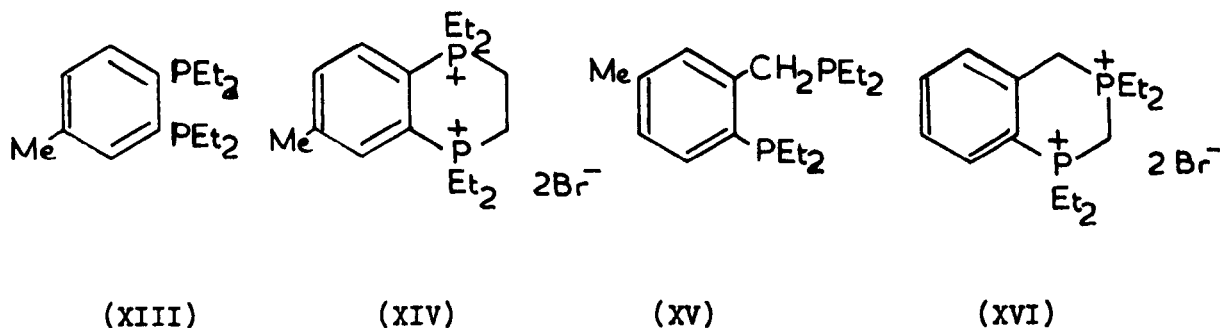
The ethylene ditertiary phosphines (XVII; R = alkyl or aryl)
quaternize readily with ethylene dibromide to form quaternary
derivatives (XVIII) of the 1,4-diphosphacyclohexane system (XIX).[17]
In certain cases it has been possible to obtain the cyclic diphosphines
by reduction of the diquaternary salts with lithium aluminium hydride.[18]

- 6 -
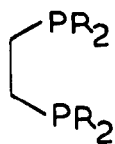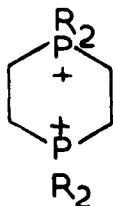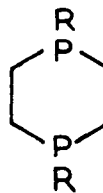
(XVII)   (XVIII)   (XIX)

The availability of secondary bis(phosphino)ethanes (XX) and their lithium derivatives (XXI) enabled Issleib[19] to develop a synthesis of the 1,4-diphosphacyclohexane system (XIX) by the reaction of the lithium derivative with ethylene dichloride, thus avoiding the use of the diquaternary salts (XVIII).
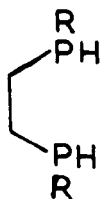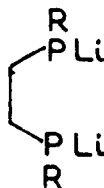
(XX)   (XXI)

The chemical behaviour of ring systems containing trivalent phosphorus is mainly determined by their 'phosphine' character. Such compounds are, in general, easily oxidised to the corresponding (and relatively unreactive) cyclic phosphine oxides by atmospheric oxygen, and therefore they must be handled in an inert atmosphere. On treatment with reactive alkyl halides, quaternisation occurs readily to give the corresponding cyclic phosphonium salts, which are often used as

derivatives for the characterisation of tertiary phosphines. As with acyclic tertiary phosphines, heterocyclic phosphines are able to function as ligands in forming co-ordination complexes with many metallic elements, notably with the transition elements. Indeed, inclusion of the trivalent phosphorus atom in a heterocyclic ring has led in some cases to a ligand having the ability to stabilise unusual co-ordination numbers in complexes of the Group VIII transition elements, similar acyclic phosphines not having these properties, presumably due to unfavourable steric interactions which are modified in the heterocyclic phosphine. Examples of such behaviour are discussed in Part III of this thesis.

Although a great many co-ordination complexes of acyclic ditertiary phosphines are known, little work has been reported on the complexes of heterocyclic ditertiary phosphines, where donor properties may be modified by the stereochemical requirements imposed on the phosphorus atoms by the ring. Hinton and Mann[18] prepared the chelate palladium(II) complexes (XXII) and (XXIII) from the cyclic diphosphine (XIX; R = benzyl). Similar complexes were obtained from the diphosphine, 9,10-diethyl-9,10-dihydrophosphanthrene. (XXIV).[20]
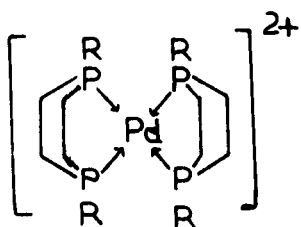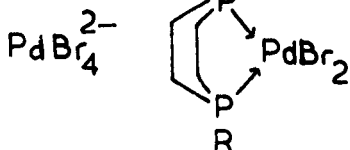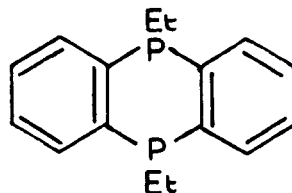
(XXII)   (XXIII)   (XXIV)

This thesis describes the synthesis of a novel ditertiary phosphine from which a series of heterocyclic diphosphonium salts containing seven-, eight-, nine- and ten-membered rings has been obtained by quaternisation with alkylene dihalides. The properties of these salts, and the possible mechanism of certain ring-contraction reactions undergone by them on thermal decomposition are discussed, and compared with those of the cyclic diquaternary salts of the corresponding ditertiary arsine.

The chemistry of a series of heterocyclic phosphines, the 9-substituted-9-phosphafluorenes, has also been investigated. Certain of these phosphines have been found to yield co-ordination complexes with transition elements, in which the central metal ion shows an unusual co-ordination number.

The alkaline hydrolysis of certain heterocyclic phosphonium salts derived from the 9-phosphafluorenes has also been investigated, and found to proceed with cleavage of the heterocyclic ring. A related reaction leading to a ring-expansion is also described.

The nuclear magnetic resonance spectra of certain of the above salts are discussed, and the results related to current theories concerning the magnitude of spin-spin coupling constants in phosphorus compounds.

Finally, some aspects of the co-ordination chemistry of the parent ditertiary phosphine are reported and discussed.

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The synthesis and properties of 2,2'-biphenylylenebisdiethyl-
phosphine and its diquaternary salts.   Novel cyclisation and
ring-contraction reactions.

The ditertiary phosphine, 2,2'-biphenylylenebisdiethylphosphine
(I), appeared to offer possibilities both as a chelating ligand and as
an intermediate for the synthesis of heterocyclic diquaternary
phosphonium salts, from which free cyclic diphosphines might be
obtained on thermal decomposition, by analogy with the comparable
ditertiary arsine, 2,2'-biphenylylenebisdimethylarsine (II).   The
latter on quaternisation with alkylene dihalides has been shown to give
heterocyclic diarsonium salts, some of which on thermal decomposition
give free heterocyclic diarsines.[1,2,3]

Et$_2$P   PEt$_2$ Me$_2$As   AsMe$_2$
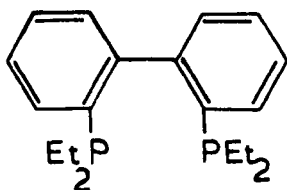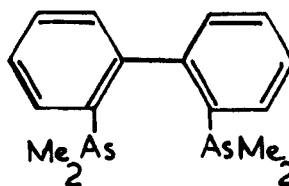
(I)   (II)

The diphosphine (I) was obtained by the following reaction from 2,2'-dilithiobiphenyl in ether:

(I)
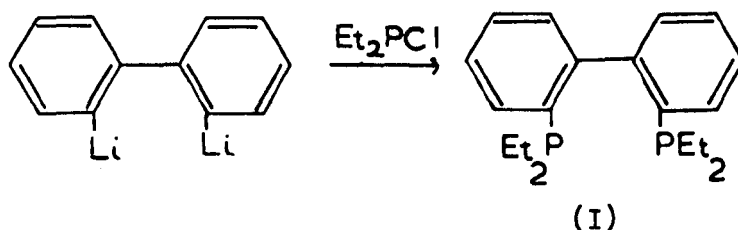
By the Ullmann reaction,[4] o-chloronitrobenzene was converted into 2,2'-dinitrobiphenyl, which was then reduced with metallic iron in aqueous ethanol to 2,2'-diaminobiphenyl. The latter was tetrazotised and converted into the corresponding dibromo compound via the pyrolysis of a stable tetrazonium mercury bromide according to the procedure of Schwechten[5] (the conventional Sandmeyer reaction being reported to give poor yields.[6]) The dibromo compound, on treatment with lithium metal in ether at room temperature, readily underwent conversion to 2,2'-dilithiobiphenyl, which on treatment with diethylphosphinous chloride gave the diphosphine (I) in high yield; the product was purified by distillation to give a viscous liquid, which on standing in the refrigerator slowly crystallised to a low-melting solid. Oxidation of the diphosphine (I) with hydrogen peroxide in acetone solution readily gave the corresponding dioxide (III).

(III)   (IV)   (V)

- 13 -
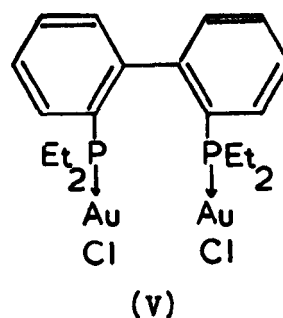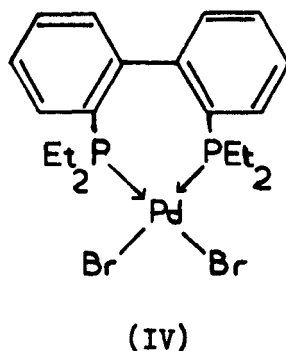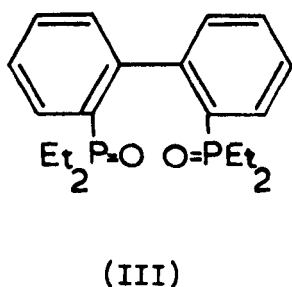
The co-ordinating ability of the diphosphine (I) was
demonstrated by the ready formation of a chelate dibromo-palladium
complex (IV) and a bis(aurous chloride) complex (V), on adding
potassium tetrabromopalladite or sodium chloroaurate, respectively,
to the diphosphine in hot aqueous ethanol. The co-ordination chemistry
of the diphosphine has been investigated further and is discussed in
Part IV of this thesis.

The diphosphine (I) reacted vigorously with methyl iodide
to give the dimethiodide (VI), and on heating with equimolar quantities
of methylene, ethylene, trimethylene, tetramethylene, or o-xylylene
dibromide in a sealed tube at 100° for some hours gave the corresponding
cyclic diphosphonium dibromides (VII; n = 1-4) and (VIII). In these
cases, evidence that cyclisation had occurred and that the products
were not the isomeric mono(bromoalkyl)phosphonium bromides was provided
by the formation of the corresponding dipicrates when a cold, aqueous
solution of the halide was treated with sodium picrate.

(VI)   (VII)
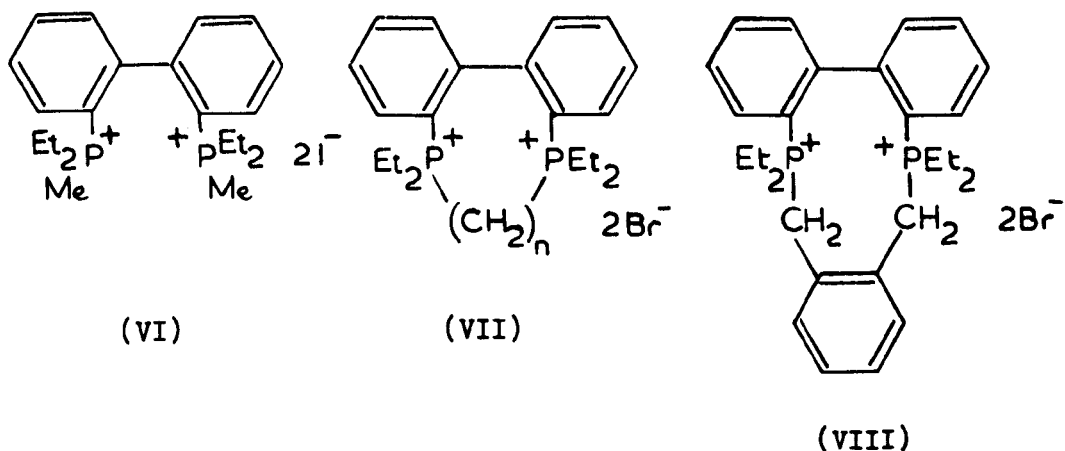
(VIII)

The stereochemistry of the cyclic diphosphonium salts of the types (VII; n = 1-4), and (VIII) is of interest. Construction of models of the cations reveals that the heterocyclic rings are buckled and almost strainless; and that the benzenoid rings of the biphenyl system are not coplanar, and could not become so without great distortion of normal bond angles and lengths. This lack of coplanarity is indicated by the ultraviolet spectra of the cyclic salts, which show no evidence of the typical strong band in the 250 mµ region shown by the unsubstituted biphenyl molecule, although the spectra of several of the cyclic salts (VII) do show a shoulder in the 240 mµ region (ε = 8,000) which may be the displaced biphenyl band. Similar values for this band are shown by 2-methylbiphenyl (237 mµ; ε = 10,500), and 2-ethylbiphenyl (233 mµ; ε = 9,000), but this band is missing in the spectrum of 2,2'-dimethylbiphenyl.[7] Recently, it has been suggested that the presence of such a band in the spectra of 2,2'-disubstituted biphenyls does indicate a small but significant resonance interaction between the two 'perpendicular' π -electron systems of the benzene rings.[8]

A further consequence of this lack of planarity and the twisted heterocyclic ring which it entails, is that the cations are dissymmetric and should therefore be resolvable into optically active forms. Such resolutions are at present under investigation but so far have been unsuccessful. The corresponding cyclic diarsonium salts derived from the diarsine (II) have been resolved and have been shown to be quite stable to racemisation.[9]

In recent years, the application of proton magnetic resonance (p.m.r.) spectroscopy to organophosphorus compounds has been of great value in structural studies, and work describing the salient features of the p.m.r. spectra of various classes of organophosphorus compounds has been reviewed.[10] Recently, there has been considerable interest in the p.m.r. spectra of compounds containing two or more phosphorus atoms, and several papers have appeared describing certain unusual features shown by these spectra, which in certain cases have been described as "deceptively simple".[11,12] The p.m.r. spectra of compounds bearing $P-CH_2CH_3$ groups are, however, extremely complex, due to the coupling interaction of the ^{31}P nucleus (of spin $\frac{1}{2}$) with the protons of the ethyl group. The p.m.r. spectra of the cyclic diphosphonium salts (VII and VIII) are further complicated by the dissymmetry of the salts, thus rendering magnetically non-equivalent groups of protons which are in equivalent chemical environments.

In addition, the resonance signals of the protons of the bridging alkylene chain are often superimposed on those of the $P-CH_2CH_3$ groups. However, the p.m.r. spectra of certain of the cyclic salts do show features of interest which deserve comment.

Due to its situation between two positively charged quaternary phosphorus atoms, it was expected that the methylene resonance of the methylene-bridged salt (VII; n = 1) would occur considerably downfield from the protons of the ethyl groups attached to phosphorus. In the case of the comparable bridged salt $Ph_2(Me)\overset{+}{P}\cdot CH_2\cdot\overset{+}{P}(Me)Ph_2$ $2I^-$, the bridging methylene group resonance occurs as a triplet (due to coupling

between the methylene protons and the two ^{31}P nucleii) centred at

5.55 Υ (J_{P-CH} = 16 cps) for a solution of the salt in trifluoroacetic

acid.[12,13] The p.m.r. spectrum of the cyclic salt (VII; n = 1) in

trifluoroacetic acid solution showed a triplet centred at 5.9 Υ

(J_{P-CH} = 16 cps) due to the bridging methylene group, indicating the

magnetic equivalence of the bridge protons in the dissymmetric salt.

Inspection of a molecular model also showed that the two methylene

protons were in identical magnetic environments. The model also

indicated that the two ethyl groups attached to each phosphorus atom

were in markedly different magnetic environments, one ethyl group being

near to the 'edge' of the benzene ring attached to the phosphorus atom,

and thus experiencing the deshielding effect of the ring current, whereas

the second ethyl group is held above the plane of the other benzene ring

and is thus subject to a net shielding effect.[14] The spectrum of the

salt (VII; n = 1) showed, in addition to the triplet due to the

methylene bridge already referred to, a multiplet centred at 6.85 Υ ,

due to the four methylene protons of the two ethyl groups subject to

deshielding by the aromatic ring current. The remaining set of four

methylene protons was observed as a multiplet centred at 7.8 Υ , which

merged with the very broad signal from 8.0 - 9.4 Υ due to the two sets

of methyl groups.

The dissymmetry of the cyclic salt (VIII) was also apparent

from its p.m.r. spectrum. The signals due to the methylene and methyl

protons of the ethyl groups attached to phosphorus appeared as complex

multiplets extending from 6.9 - 8.3 Υ and 8.3 - 9.3 Υ , respectively.

The benzylic protons, due to their differing magnetic environments, appeared as an ABX multiplet extending from 5.8 - 6.8 τ , of which six broad lines could be distinguished, with the coupling constant $J_{AB} = 16.7$ c/sec.

The stereochemical characteristics of many compounds having a biphenyl nucleus linked across the 2,2'-positions by bridges of various types have been elucidated and some generalisations correlating the nature of the bridge and the conformational stability of the compound, as measured by polarimetry or p.m.r. spectroscopy, have been made.[15] For example, if the bridge consists of 3 or 4 atoms, the compound will have low optical stability unless the biphenyl nucleus has substituents in the 6,6'-positions; also, a biphenyl with a three-membered bridge is less stable than an analogous biphenyl with a four-membered bridge, when both have the same 6,6'-substituents.

The successful resolution of the heterocyclic diarsonium salts derived from the diarsine (II) indicates that, in spite of there being in some cases a three- or four-atom bridge and an absence of substituents in the 6,6'-positions, the dissymmetric cations are conformationally quite stable, since it was demonstrated that racemisation occurs only slowly, even if at all.[9] The complexity of the p.m.r. spectra of the cyclic diphosphonium salts (VII; n = 1) and (VIII) would seem to indicate a similar configurational stability in these salts. If conformational change was rapid, it would lead to a much simpler spectrum in which both ethyl groups attached to phosphorus were equivalent. Furthermore, the benzylic protons of the salt (VIII) would have given rise to a simple

doublet of an A_2X system instead of the observed ABX pattern.

The above generalisations[15] therefore, cannot be applied to the cyclic diarsonium and diphosphonium salts. The inversion of configuration of these compounds must proceed via an intermediate in which both benzenoid rings of the biphenyl system are coplanar, thus bringing the positively charged arsenic or phosphorus atoms into close proximity. The conformational stability of these compounds may therefore be due to the repulsion between the positively charged hetero-atoms inhibiting the attainment of the transition state.

Most quaternary phosphonium halides decompose on heating above 300° with the loss of one alkyl group and the halide anion, to yield tertiary phosphines.[16] In particular, the decomposition of phosphonium halides containing an ethyl group has been used frequently to prepare cyclic phosphines.[17,18,19] In these cases it has been found that the ethyl group is lost as ethylene and tertiary phosphine hydrohalides are formed. (Such observations are in contrast with those of Fenton et al.[20] who reported that they obtained no ethylene on thermal decomposition of an ethyl phosphonium salt but instead observed the formation of an ethyl halide and the free phosphine.) The decomposition of ethyl phosphonium salts normally proceeds to give a single phosphorus-containing product in high yield, but it has been reported[16,21] that mixtures of phosphines are often obtained when benzyl or certain other groups are present. In this respect, a rough order of radical cleavage has been given as ethyl~benzyl > methyl > propyl > iso-pentyl > aryl.[21] Previous attempts[22] to prepare cyclic diphosphines of type (IX) by the

thermal decomposition of cyclic diphosphonium salts of type (X) failed,
due to the elimination of ethylene dibromide with concurrent production
of the original alkylene diphosphine (XI).

$$\text{(IX)} \qquad \text{(X)} \qquad \text{(XI)}$$
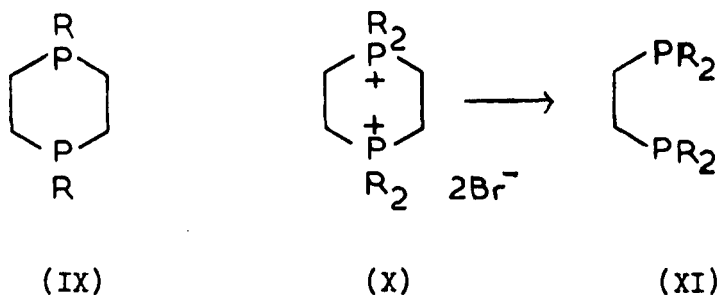
The thermal decomposition of the diphosphonium dihalides (VI)
and (VII; $n = 1 - 4$), and (VIII) reveals features of great interest,
and proceeds in a manner not previously recorded in phosphorus chemistry.
Thus, thermal decomposition of the dimethiodide (VI gave both
9-methyl-9-phosphafluorene (XII; R = Me)), and 9-ethyl-9-phosphafluorene
(XII; R = Et), in the relative proportions of 1:4.8, initially as a
mixture of the free phosphines and their hydriodides. The free
9-alkyl-9-phosphafluorenes (XII) were identified by analytical vapour-
phase chromatography (v.p.c.) by comparison with the authentic phosphines,
prepared by the reaction of the appropriate alkyl phosphinous dichloride
with 2,2'-dilithiobiphenyl in ether.

(VI)   (VII)   (VIII)

(XII)   (XIII)
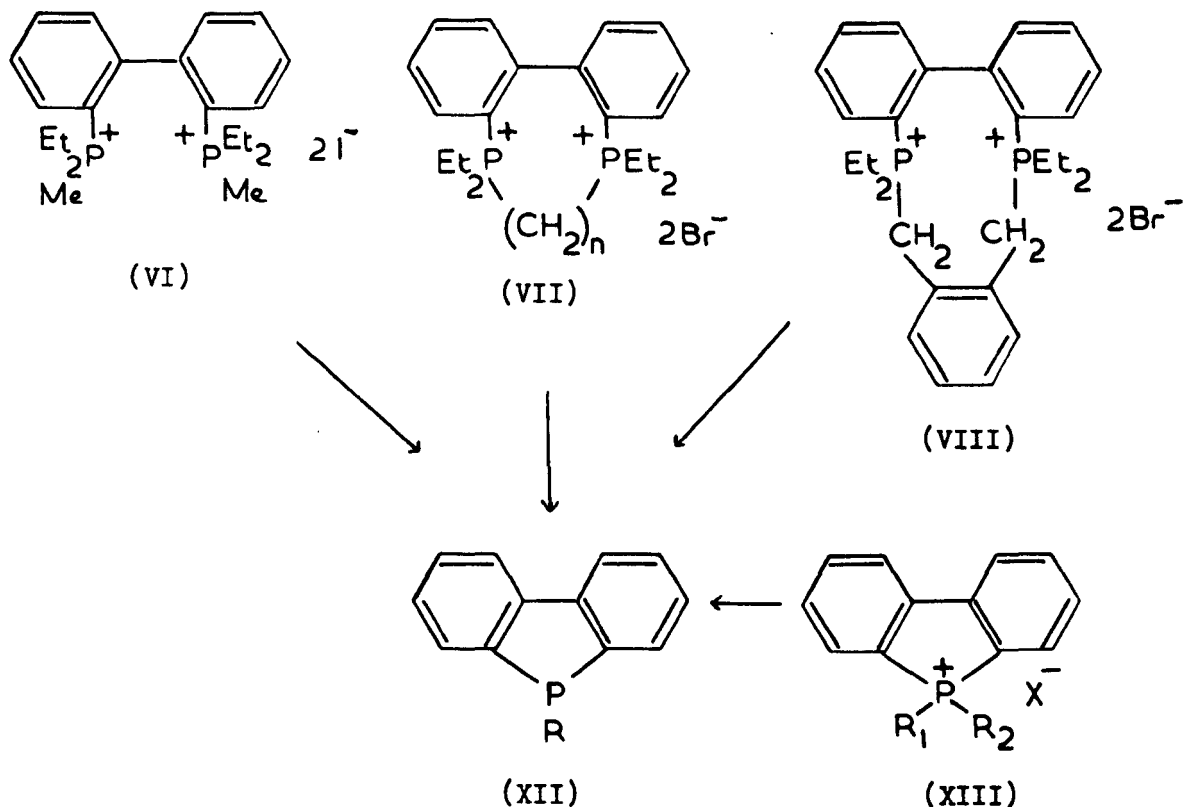
Thermal decomposition of the methylene-bridged salt (VII; n = 1) also gave both 9-methyl- and 9-ethyl-9-phosphafluorenes in the relative proportions of 1:2, again initially as a mixture of the free phosphines and their hydrobromides. The remaining alkylene-bridged salts (VII; n = 2 - 4), on thermal decomposition gave 9-ethyl-9-phosphafluorene (XII; R = Et), as the sole product, again in the first instance as a mixture of the free phosphine and its hydrobromide. In addition to identification of the product by v.p.c., the product was converted into the corresponding methopicrate (XIII; R_1 = Et, R_2 = Me, X = $C_6H_2N_3O_7^-$) which was found to be identical with the corresponding derivative of

authentic 5-ethyl-5-phosphafluorene. The o-xylylene dibromide salt (VIII)

on thermal decomposition gave mainly 5-ethyl-5-phosphafluorene

(XII; R = Et) and a small proportion of the original diphosphine (I).

No traces of any cyclic diphosphines were observed in the
thermal decomposition reactions of the above cyclic diphosphonium salts.
Comparable ring contraction reactions have been observed in arsenic
chemistry,[2,3,25] e.g. in a study of the thermal decomposition reactions
of the diquaternary salts of 2,2'-biphenylylenebisdimethylarsine (II).
Thermal decomposition of the cyclic diarsonium dibromides (XIV: n = 2,3,4)
proceeded with ring contraction to form the arsafluorene (XV). However,
thermal decomposition of the salts (XIV; n = 1) and (XVI) gave the cyclic
diarsines (XVII) and (XVIII) respectively, and the dimethiodide (XIX) gave
the original diarsine, (II), without the formation of arsafluorene (XV)

(XIX)

(XIV)

(XVI)

(II)

(XVII)

(XV)

(XVIII)
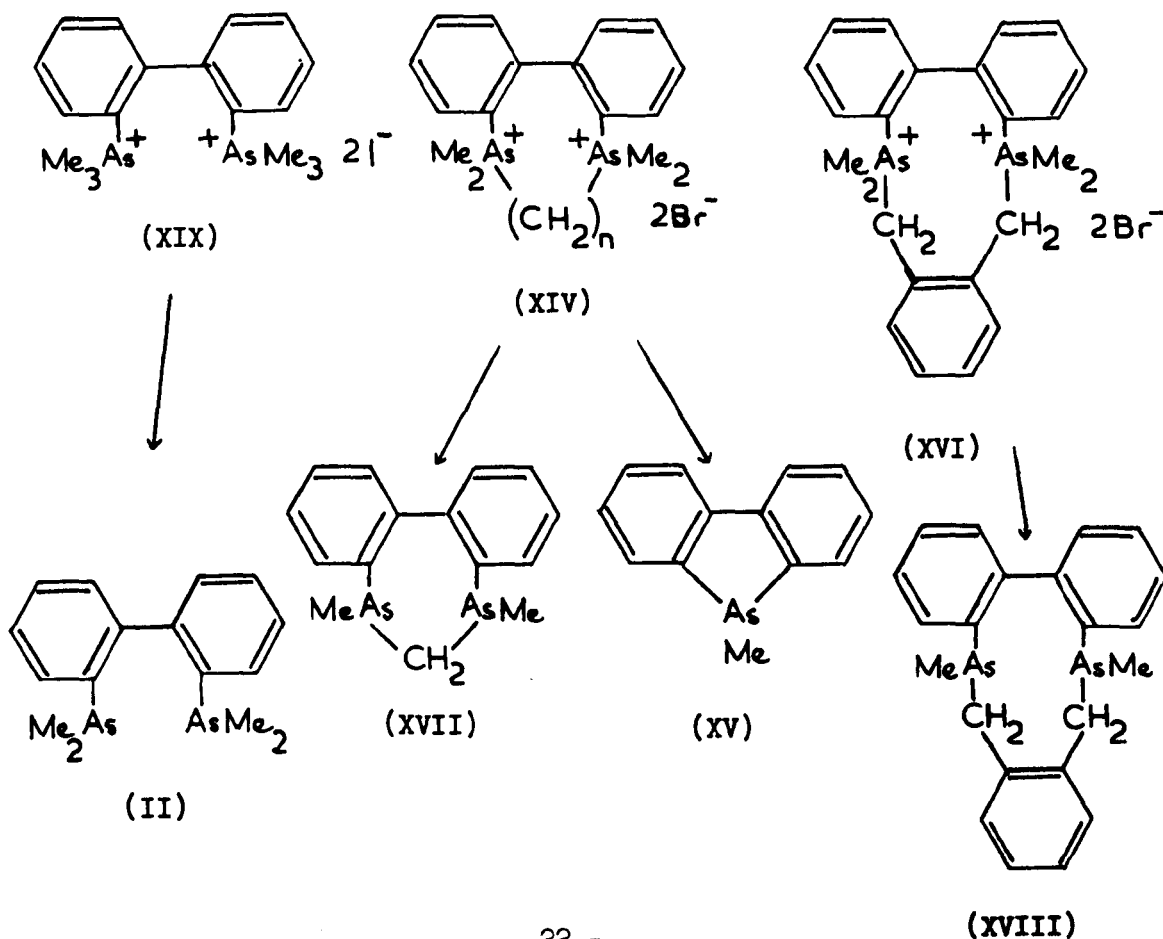
The ease with which five-membered rings containing arsenic are
formed has been discussed, and the prediction made that a similar
tendency would be found in suitable phosphorus compounds.[24] The formation
of the 5-phosphafluorene system on thermal decomposition of the cyclic
diphosphonium salts might therefore have been anticipated, but the
formation of 5-alkyl-5-phosphafluorenes on thermal decomposition of the
dimethiodide (VI) is remarkable. It is of interest that the high
stability of the 5-phosphafluorene system has been demonstrated by recent
thermochemical studies.[25]

Such cyclisation reactions would appear to be further examples
of the general internal nucleophilic displacement ($S_N i$) mechanism outlined
in scheme (1).
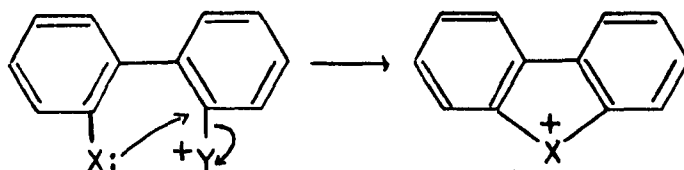
Scheme (1)

This mechanism involves an $S_N i$ displacement of the leaving group Y (as
a neutral species), with the formation of a positively charged cyclic
species, which might then undergo further reaction. Several cyclisation
reactions of this type are known. The decomposition of diazotised
2-amino-2'-halobiphenyls (XX) (X = Cl, Br, I), with displacement of
nitrogen to form the cyclic halonium salts (XXI; X = Cl, Br, I), would
seem to fall into this classification.[26,27]

(XX)   (XXI)
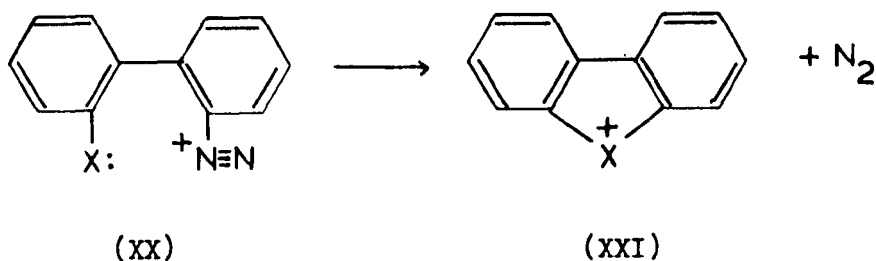
Similarly, the decomposition of diazotised 2-amino-2'-aryloxybiphenyl
(XXII) to form the cyclic oxonium salt (XXIII), and the decomposition
of diazotised 2-amino-2'-diphenylaminobiphenyl (XXIV) to form the cyclic
quaternary ammonium salt (XXV) can also be viewed as $S_N i$ displacements
of this type.[78]

(XXII)   (XXIII)

(XXIV)   (XXV)
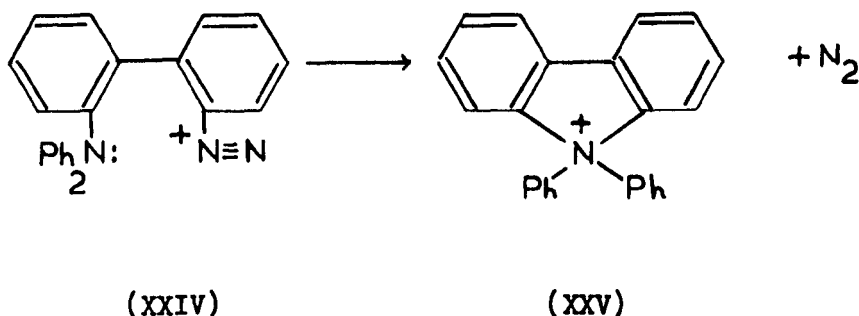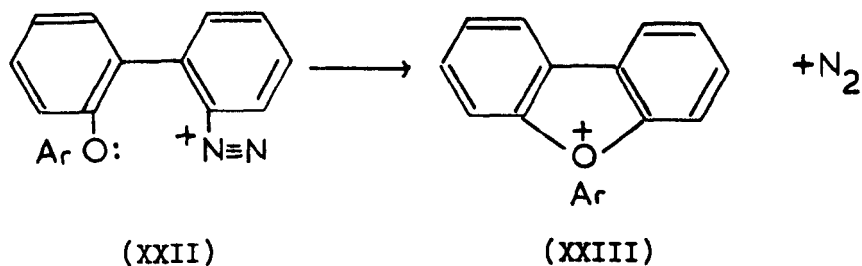
In the case of the thermal decomposition of the dimethiodide (VI) of the
diphosphine (I), it is proposed that initial loss of ethyl (or methyl)
iodide occurs to yield the monophosphonium salts (XXVI) which then undergo
an $S_N i$ displacement of diethylmethylphosphine to form quaternary

derivatives (XXVII) of a 9-alkyl-9-phosphafluorene. These would then
undergo the usual loss of an alkyl group on further heating to yield
the free 9-alkyl-9-phosphafluorenes (XII; R = Me or Et).
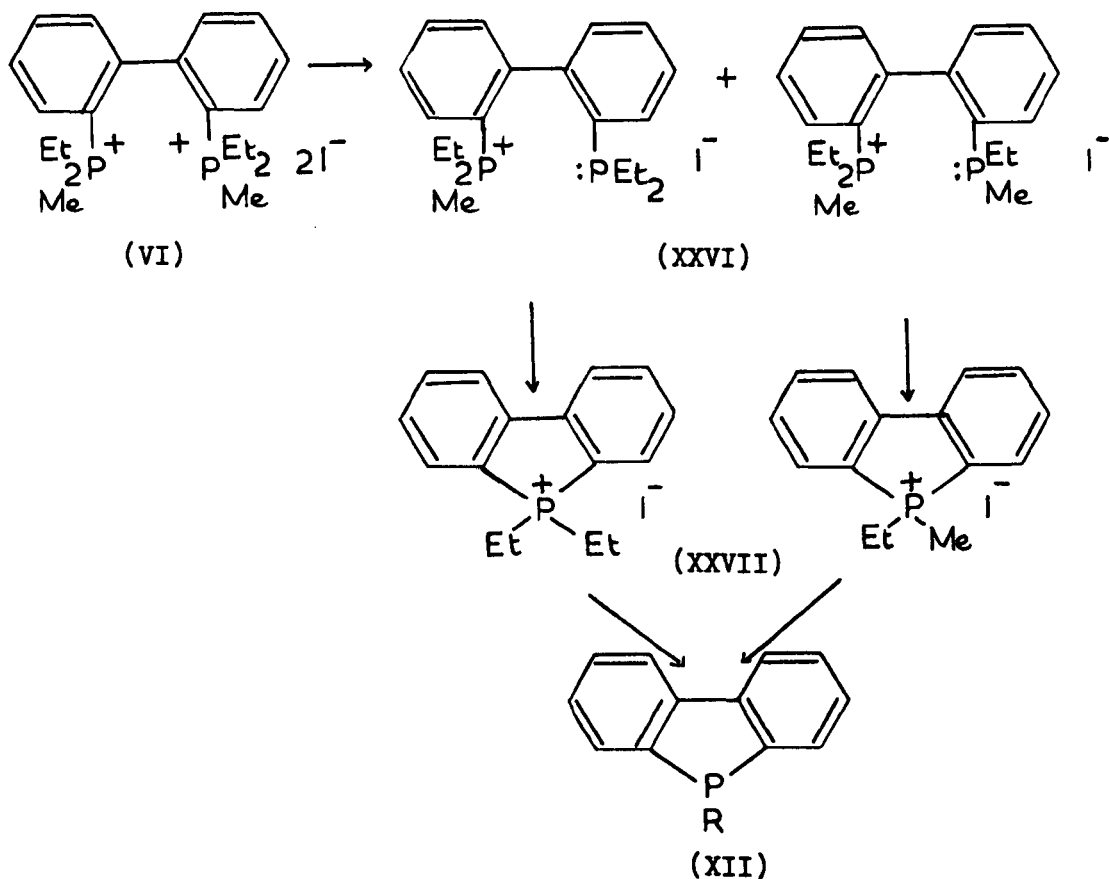
Furthermore, the quaternary salt (XIII; R_1 = Me; R_2 = Et) identical with
one of the intermediates (XXVII) postulated in the mechanism, on thermal
decomposition gives both 9-methyl- and 9-ethyl-9-phosphafluorenes in
approximately equal amounts (1:1.3). This finding is in contrast to the
observations of Meisenheimer et al.[21] who reported a preferential
elimination of ethyl groups over methyl groups in the thermal decomposition
of simple phosphonium salts. In this example, there is a slight preference
for methyl group loss.

A similar mechanism is proposed for the ring contraction reaction observed in the thermal decomposition of the cyclic diphosphonium salts, (VII; n = 1 - 4) and (VIII). It is suggested that the initial step is dealkylation with ring opening at one of the phosphorus atoms, giving a tervalent phosphorus derivative similar to (XXVI) which then would undergo an $S_N i$ displacement of the remaining phosphorus fragment to give the ethobromide of 9-ethyl-9-phosphafluorene. Thermal decomposition of this salt would then give 9-ethyl-9-phosphafluorene (XII; R = Et). For the thermal decomposition of the o-xylylene dibromide salt (VIII), the proposed mechanism would be as shown in Scheme (2).

(VIII)   (XXVIII)
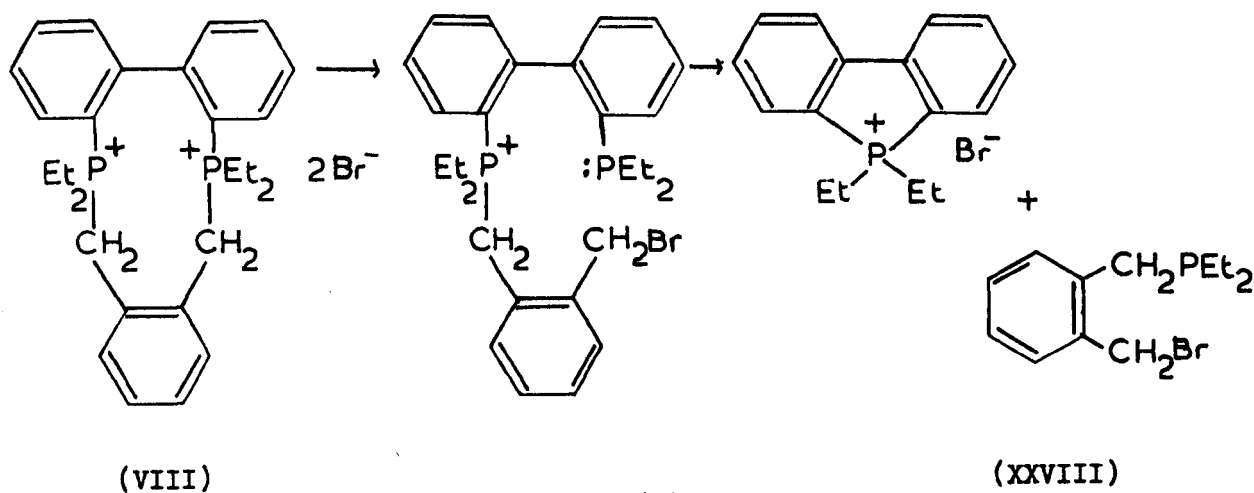
Scheme (2)

Efforts have been made to identify the fragment (XXVIII) in order to provide further support for this scheme. It was anticipated that (XXVIII) would occur in the distillate where it would undergo rapid self-quaternization to form a quaternary salt (XXIX) of the unknown 2-ethyl-isophosphindoline (XXX). It was thought that under the conditions prevailing in the treatment of the distillate, the salt (XXIX) would be

decomposed to a phosphine oxide, probably (XXXI), which could be
isolated and identified.

(XXVIII) (XXIX) (XXX)

(XXXIII) + (XXXI)

Et$_2$PBr
(XXXII)
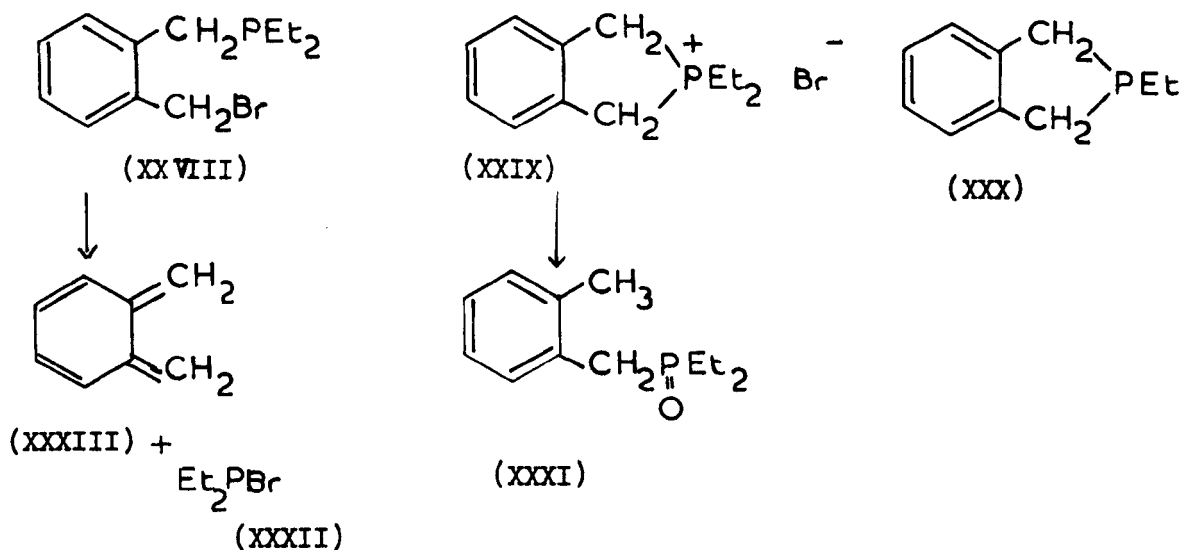
The aqueous solution of sodium bicarbonate used in the extraction of
9-ethyl-9-phosphafluorene from the distillate was made strongly alkaline
and heated on a steam-bath for some time to effect the hydrolysis of
phosphonium salts to phosphine oxides. The resulting solution was
evaporated to dryness and the inorganic residues extracted with chloroform.
The resulting extract on evaporation yielded a negligible quantity of
material, which from examination by thin-layer chromatography appeared to
contain a number of components, each in small traces. In addition, the
phosphines produced on thermal decomposition of (VIII) were as a matter
of routine analysed by v.p.c. No trace of any volatile product which
might correspond to the free 2-ethylisophosphindoline (XXX) arising from
the salt (XXIX) by thermal decomposition, was detected.

The fate of the eliminated fragment therefore remains in doubt,

but a possible mode of decomposition under the conditions of thermal

decomposition to diethylphosphinous bromide (XXXII) and the o-quinodimethane

(XXXIII) by intramolecular attack of tertiary phosphine on benzylic halogen

should be considered. (It is noteworthy that the residue in the bulb-tube

was dark and carbonaceous, and the liquid nitrogen-cooled trap of the

pump used in the distillation had a foul odour typical of halophosphines

and fumed on exposure to the air.) Many instances of attack by tervalent

phosphorus compounds on halogen are known, and have been reviewed

recently.[29] In this connection it is also of interest to consider the

earlier observation of Hitchcock and Mann,[22] on the thermal decomposition

of $Et_3\overset{+}{P}CH_2CH_2Br\ Br^-$, which was reported to lead to general charring.

The above reactions involving nucleophilic displacement of

groups attached to aryl rings are particularly interesting because

established examples of heterolytic aromatic substitution by phosphorus

are rather rare. It has been shown recently that triethylphosphite attacks

o-dinitrobenzene to yield diethyl o-nitrophenylphosphonate and ethyl

nitrite, and it has been claimed that this is evidence of a reaction

involving nucleophilic substitution of groups attached to benzene by

tervalent phosphorus.[30]

Of the cyclic diphosphonium salts, the methylene dibromide salt

(VII; n = 1) was unique in giving both 9-methyl- and 9-ethyl-phosphafluorenes

on thermal decomposition. The formation of a methyl phosphine from a

starting material which does not contain a $P-CH_3$ group may suggest that a

free radical pathway is involved. Collie[16] reported that the thermal

decomposition of tetramethylphosphonium bromide gave ethylene as one of

the products, which may imply (as Collie suggested) that methylene is involved.

It seems reasonable to suggest that similar $S_N i$ mechanisms might be postulated for the ring contraction reactions observed in the thermal decomposition of cyclic diarsonium salts, (XIV; n = 2,3,4). The difference in behaviour of the dimethiodide (XIX) of the diarsine (II) and the cyclic diarsonium salts, (XIV; n = 1) and (XVI), as compared to the corresponding phosphorus compounds, (VI), (VII; n = 1) and (VIII) might be ascribed to steric causes and the less strongly nucleophilic properties of tervalent arsenic under conditions in which the simple loss of methyl halide becomes the favoured process. In order to investigate the effect of the alkyl group present in the original diarsine on the course of such thermal decomposition reactions, a study was made of the mode of thermal decomposition of various salts derived from 2,2'-diphenylylenebisdiethylarsine (XXXIV).

This diarsine has been little investigated. Forbes et al.[3] reported that it failed to form a cyclic diquaternary salt with ethylene dibromide. It has now been found that cyclisation with ethylene dibromide to yield the cyclic diarsonium salt (XXXV) does occur on prolonged heating of equimolecular quantities of the diarsine and ethylene dibromide in a sealed tube containing a trace of ethanol. Similarly, cyclisation occurs with o-xylylene dibromide to give the cyclic diarsonium salt (XXXVI). Evidence that cyclisation had occurred was obtained by either conversion to the corresponding dipicrate or by the determination of ionic bromine.

The ultraviolet and p.m.r. spectra of these salts were similar

to those of the corresponding phosphorus compounds, the p.m.r. spectra
being somewhat easier to interpret as arsenic (nuclear spin $5/2$) has
a large quadrupole moment and proton splittings are not observed. The
dissymmetry of the salts was also apparent from the p.m.r. spectra.
That of the o-xylylene bridged salt (XXXVI) in trifluoroacetic acid
solution showed, in addition to a multiplet centered at 1.9 Υ and a
broad singlet at 2.42 Υ corresponding to the protons of the biphenyl
system and bridging benzene ring respectively, an AB system centered at
5.95 Υ (J_{AB} = 15.4 c/s) corresponding to the magnetically non-equivalent
benzylic protons. The two sets of methylene protons of the ethyl groups
attached to arsenic subject to the anisotropic effect of the benzene rings
of the biphenyl system appeared as partially resolved quartets centered
at 7.0 Υ and 7.9 Υ respectively, (J_{HCCH} = 7.7 c/s). The methyl protons
of the ethyl groups appeared as a multiplet centered at 8.6 Υ. The
spectrum of the ethylene bridged salt (XXXV) in trifluoroacetic acid
solution exhibited a complex multiplet centered at 2.0 Υ due to the
aromatic protons, a partially resolved quartet centered at 7.0 Υ (J_{HCCH} =
7.7 c/s) due to the four deshielded methylene protons of the ethyl groups
attached to arsenic, and a complex multiplet centered at 7.6 Υ due to the
remaining set of four methylene protons and the four methylene protons of
the bridge. The methyl protons of the ethyl groups appeared as a broad
multiplet centered at 8.6 Υ.
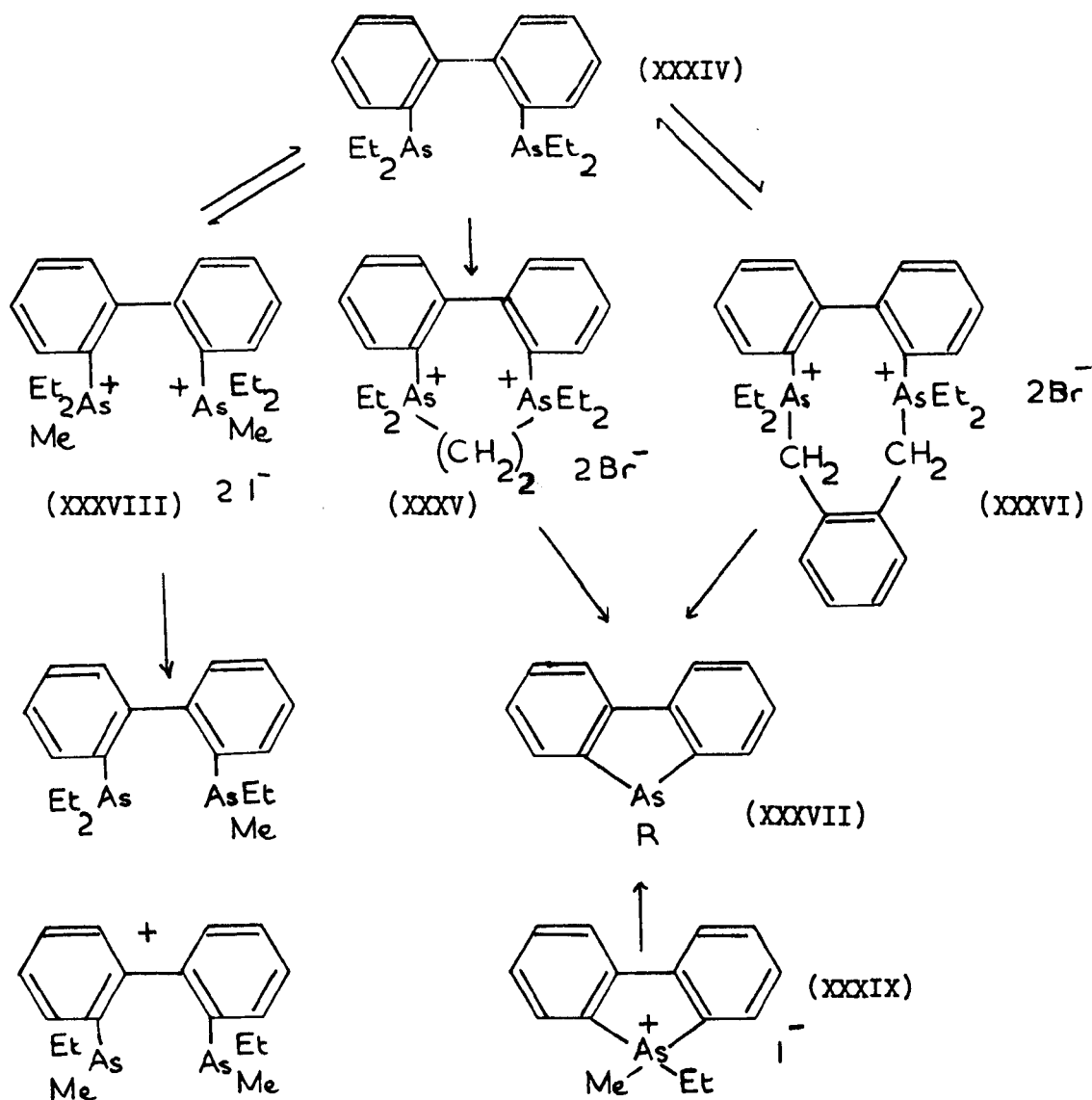
The thermal decomposition reactions of the cyclic salts of 2,2'-biphenylylenebisdiethylarsine have been found to differ from those of the corresponding salts of 2,2'-biphenylylenebisdimethylarsine. Thus, thermal decomposition of the o-xylylene bridged salt (XXXVI) gives a mixture of the ring contraction product, 9-ethyl-9-arsafluorene, (XXXVII; R = Et), and 2,2'-biphenylylenebisdiethylarsine (XXXIV), and none of the cyclic diarsine corresponding to (XVIII).

The ethylene bridged salt (XXXV) decomposed smoothly to yield 9-ethyl-9-arsafluorene (XXXVII; R = Et) as the sole product of the reaction.

The corresponding salt of 2,2'-biphenylylenebisdimethylarsine yielded 9-bromo-9-arsafluorene in addition to 9-methyl-9-arsafluorene on pyrolysis.[2]

The thermal decomposition of dimethiodide (XXXVIII) of the diarsine has also been investigated. On pyrolysis, this salt gave a mixture of arsines of similar boiling point to the parent diarsine (XXXIV) which was also a major product of the reaction. Although the other arsines were not identified, it seems reasonable to assume that they were the products obtained by the loss of ethyl instead of methyl from one or both of the arsonium centres. No arsafluorenes were detected in this reaction.

Thermal decomposition of the methiodide (XXXIX) of 9-ethyl-9-arsafluorene gave a mixture of 9-methyl-arsafluorene (XXXVII; R = Me) and 9-ethyl-9-arsafluorene (XXXVII; R = Et), in the relative proportions of 1:2, again indicating the preferential loss of methyl groups from simple arsonium salts.

The thermal decomposition reactions of the cyclic salts derived from 2,2'-biphenylylenebisdiethylarsine therefore resemble those of the corresponding salts of 2,2'-biphenylylenebisdiethylphosphine, rather than those of the salts of 2,2'-biphenylylenebisdimethylarsine. The nature of the alkyl group present in the original diarsine clearly is of importance in determining the course of the thermal decomposition. A study of the thermal decomposition reactions of the corresponding salts of 2,2'-biphenylylenebisdimethylphosphine (XL) would be of interest.
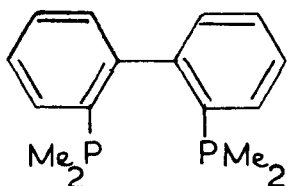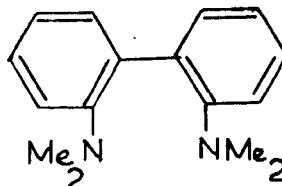
$$(XL) \qquad (XLI)$$

In view of the cyclisation reaction undergone by the dimethiodide of 2,2'-biphenylylenebisdiethylphosphine, it was of interest to investigate the thermal decomposition reactions of simple quaternary salts of 2,2'-biphenylylenebisdimethylamine (XLI). This diamine was first prepared by Shaw & Turner[31] who found that it formed a monohydriodide, (XLII) m.p. 256-7° and a monomethiodide, (XLIII) m.p. 191-2°, and established the non-planarity of the biphenyl system in the latter salt by resolving it. Forbes et al.[3] reinvestigated the diamine and attempted to form both a dimethiodide and cyclic diquaternary salts with alkylene dihalides, but without success. The failure to form diquaternary salts was attributed to steric overcrowding in the molecule resulting from the relatively small size of the nitrogen atom. This effect is less marked in the analogous diarsine (and 2,2'-biphenylylenebisdiethylphosphine) since the larger arsenic (or phosphorus atom) holds the attached groups at greater distances and overcrowding is reduced. When the diamine was heated with an excess of methyl iodide in the presence of methanol or nitromethane (both powerful promoters of quaternisation) for a prolonged period, Forbes et al.[3] reported the isolation of a compound m.p. 250°-1°, whose analytical data suggested that it was the monomethiodide, in spite of the marked difference in melting-point from that of the monomethiodide described by Shaw & Turner.[31] This reaction has now been repeated. The diamine was heated under reflux

with an excess of methyl iodide in nitromethane for several days. After

removal of the solvent, the residue was crystallised from ethanol. The

first fraction which crystallised had m.p. 240 - 50°, which on further

crystallisation from water or ethanol was raised to 257 - 8°, and was

identical with the authentic monohydriodide of the diamine. The p.m.r.

spectrum of this salt in trifluoroacetic acid solution confirmed its

identity, showing an eight-proton multiplet centered at 2.1Υ due to

the aromatic protons, and a broad singlet at 6.48Υ due to the twelve

methyl protons.

Partial evaporation of the mother liquors from the recrystallisation

gave a much larger crop of crystals, m.p. 184°, which on further

crystallisation from water had m.p. 190-1°. The infrared spectrum of

this product was quite different from that of the monohydriodide, and its

identity as the authentic monomethiodide was confirmed by its p.m.r.

spectrum in deuterochloroform solution, which exhibited a multiplet

centered at 2.6Υ due to the eight aromatic protons, a sharp singlet at

6.09Υ due to the nine protons of the $\overset{+}{N}(CH_3)_3$ group, and a sharp singlet

at 7.51Υ due to the neutral $N(CH_3)_2$ group.

The p.m.r. spectrum of the monomethiodide (XLIII) in

trifluoroacetic acid solution was of some interest. The nine methyl

protons of the $\overset{+}{N}(CH_3)_3$ group appeared as a sharp singlet at 7.0Υ,

whereas the methyl protons of the dimethylamino group appeared as a

triplet centered at 7.30Υ (J = 4.5 cps). The appearance of the triplet

was interpreted as indicating protonation of the dimethylamino group in

the strongly acidic solvent, free rotation of the $(CH_3)_2\overset{+}{N}H$ group about

the ring-nitrogen bond being restricted by ion-pairing and hydrogen-bonded interactions with the solvent, thus leading to the magnetic non-equivalence of the methyl groups. Free rotation would have given rise to a simple doublet as both methyl groups would have been magnetically equivalent. The observed triplet must arise from the superimposition of the two doublets due to the coupling interaction of the two non-equivalent methyl groups with the proton on the nitrogen.
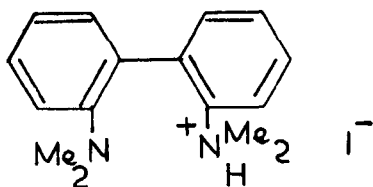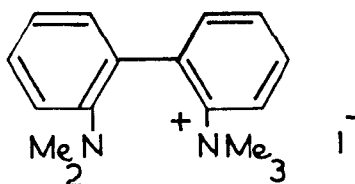
(XLII)   (XLIII)

The thermal decomposition of these salts has been investigated. On heating, the monomethiodide (XLIII) simply lost methyl iodide to give the original diamine (XLI), as the sole product. Thermal decomposition of the monohydriodide (XLII) gave two products, one of which was shown to be 2,2'-biphenylylenebisdimethylamine (XLI) by v.p.c. analysis. The other product, which predominated, had a very similar retention time to N-methyl-carbazole (XLIV), but the ultraviolet spectrum of the reaction products showed the absence of the carbazole chromophore, suggesting the compound might be 2-dimethylamino-2'-methylaminobiphenyl (XLV), arising from simple loss of methyl iodide from the salt.

(XLI)

(XLV)

(XLII)

(XLIV)
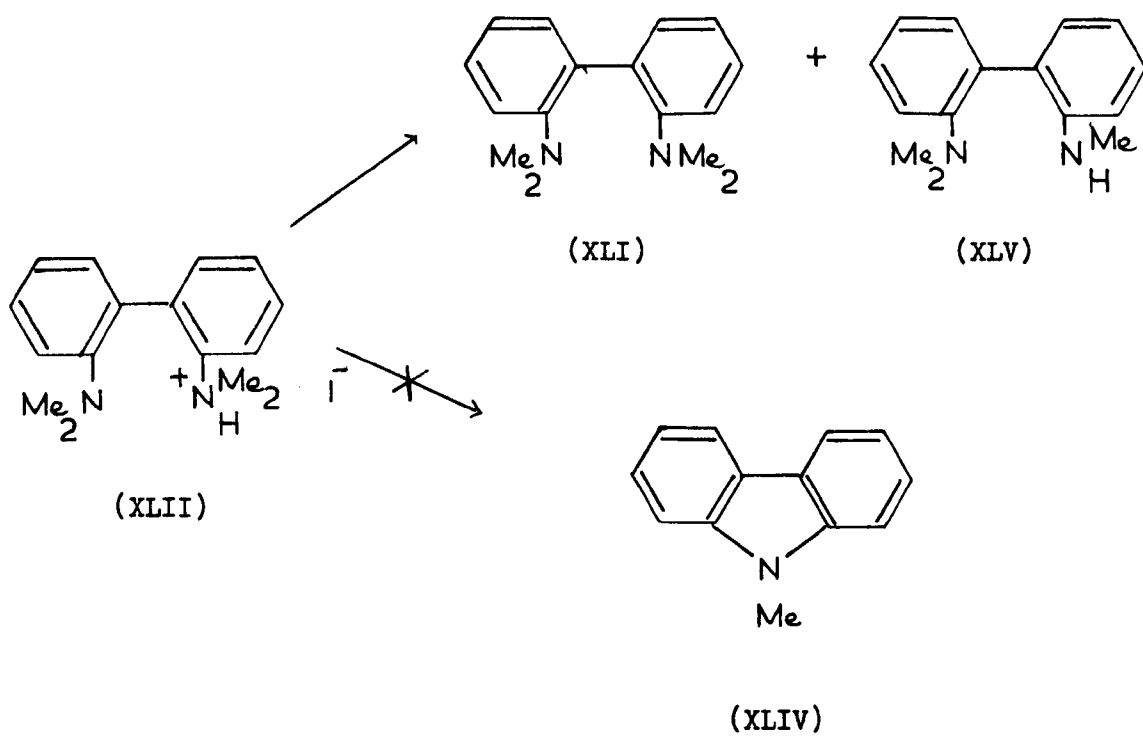
EXPERIMENTAL

Compounds are colourless unless otherwise described.
Operations involving phosphines or arsines were performed under nitrogen.

Melting points were determined on a Kofler hot stage, except
as otherwise stated.

V.p.c. analyses were carried out using a 10' spiral glass
column packed with Gaschrome P coated with 1% S.E.30 silicone oil. An
argon ionization detector was used.

Infrared absorption spectra were obtained using a Perkin Elmer 257
grating spectrophotometer.

Ultraviolet absorption spectra were obtained using a Unicam
S.P. 700 or S.P. 800 spectrophotometer.

Proton magnetic resonance (p.m.r.) spectra were recorded on a
Perkin Elmer 60 megacycle instrument.

Microanalyses were carried out by Mr. J. Boulton in the Department
of Chemistry, University of Keele. For some compounds, the name
corresponding to that used previously in the Journal of the Chemical
Society in cognate work is given first, followed by the name of the same
compound using the Revised Ring Index system.

2,2'-Dinitrobiphenyl.

This was prepared by the Ullmann reaction from o-chloronitrobenzene
in 60% yield, as described by Fuson and Cleveland.[4]

<u>2,2'-Diaminobiphenyl</u>. (prepared by a modification of the general procedure due to West.[32])

To a hot solution of 2,2'-dinitrobiphenyl (100 g.) in 95% ethanol (1 1.) containing concentrated hydrochloric acid (10 ml.) was added 'reduced' iron (150 g.), in portions over 1 hr, the reaction mixture being stirred vigorously during the addition.

The mixture was then heated under reflux with vigorous stirring for four hours, when examination of the reaction mixture by thin layer chromatography (T.L.C.) indicated that reduction was complete. Sodium hydroxide (10 g.) and Hyflo "Super Cel" (40 g.) were then added, and the mixture filtered hot. The filtrate was then evaporated to low bulk, when the product crystallised. The crystals were filtered, and washed with ethanol (95%), and dried, to give the diamine, m.p. 78-9°. (lit.,[33] 81°), (54 g., 72%).

<u>2,2'-Dibromobiphenyl</u>. This was prepared by the method described by Schwechten.[5]

2,2'-Diaminobiphenyl (9.2 g.) dissolved in water (50 ml.) and sulphuric acid (7 ml.) was diazotised by the addition of sodium nitrite (6.9 g.) in water (15 ml.), the reaction mixture being cooled in ice.

Addition of a solution of mercuric nitrate (25 g.) and potassium bromide (40 g.) in water (150 ml.) gave a pale yellow precipitate of a complex salt, which was filtered off, washed with water (400 ml.) and acetone (250 ml.), and dried in vacuo. (The complex salt is light-sensitive and should be stored in the dark.) The dried complex salt was

mixed intimately with twice its weight of crushed potassium bromide and packed into a tube, 1 metre long and 3 cm. wide, sealed at one end and fitted with an air condenser. The tube containing the mixture was clamped with the open end a few inches higher than the closed end. The material in the tube was spread so that it did not fill more than about half the diameter of the tube.

The tube was heated with a Bunsen burner starting at the open end, when the complex salt decomposed smoothly with evolution of nitrogen; the heating was gradually extended down the tube until the whole of the salt had decomposed. The cooled contents of the tube were extracted with water (1 l.) and ether (500 ml.). The dried ether extract was percolated through a 3" x 3" column of activated alumina (Spence, grade O); evaporation of the ether after elution gave 2,2'-dibromobiphenyl (10 g., 58%), which after crystallisation from ethanol (95%) had m.p. 80° (lit.,[5] m.p. 81°).

2,2'-Biphenylylenebisdiethylphosphine (I)

A solution of 2,2'-dibromobiphenyl (12 g.) in ether (150 cc.) was added dropwise to thin lithium foil (1.08 g.) during $1\frac{1}{2}$ - 2 hr., the complete mixture being stirred at room temperature for a further 2 hr. Diethylphosphinous chloride (9.1 g.) in benzene (50 cc.) was added dropwise over 30 min. and the resulting mixture was then refluxed for 1 hr. before cooling and hydrolysing with cold, air-free water. The organic layer was separated, dried (Na_2SO_4), the solvents evaporated, and the residue distilled under reduced pressure in nitrogen to give

2,2'-biphenylylenebisdiethylphosphine, b.p. 152°/0.25 mm. (8.07 g., 70%)

(Found: C, 72.95; H, 8.7. $C_{20}H_{28}P_2$ requires C, 72.7; H, 8.5%). When

set aside in the refrigerator, the diphosphine slowly crystallised, and

then had m.p. 28 - 30°. A sample of the diphosphine (200 mg.) in

acetone (5 cc.) was treated with hydrogen peroxide solution (100 vol., 1 cc.)

and the solution allowed to stand for 24 hr. Evaporation of the solvents

gave an oil which was dissolved in chloroform (10 cc.), and shaken with

aqueous sodium hydrogen sulphite. The chloroform solution was then

dried (Na_2SO_4), and evaporated to give crystals of 2,2'-biphenylylenebis-

-diethylphosphine dioxide (III) m.p. 193 - 195° (sealed, evacuated tube

(S.E.T.)) (Found: C, 65.9; H, 7.75. $C_{20}H_{28}O_2P_2$ requires C, 66.3;

H, 7.75%); i.r. (mull) 1180 cm.$^{-1}$, (P = 0).

Quaternary salts of 2,2'-biphenylylenebisdiethylphosphine -

a)   2,2'-Biphenylylenebisdiethylmethylphosphonium di-iodide (VI).

        To the diphosphine (0.1 g.) was added an excess of methyl iodide;

a vigorous reaction ensued. Removal of the excess of methyl iodide and

recrystallisation of the residue from ethanol gave the crystalline

dimethiodide, m.p.255 - 256°. (Found: C, 42.7; H, 5.4 $C_{22}H_{34}I_2P_2$

requires C, 43.05; H, 5.6%). The corresponding dipicrate formed yellow

crystals, m.p. 137 - 138°, from aqueous ethanol (Found: C, 50.0;

H, 4.85; N, 9.7. $C_{34}H_{38}N_6O_{14}P_2$ requires C, 50.0; H, 4.65; N, 10.2%).

b)   5,5:7,7-Tetraethyl-5,7-diphosphonia-1,2:3,4-dibenzocycloheptadiene

dibromide (i.e. 6,7-dihydro-5,5,7,7-tetraethyl-5H-dibenzo[d,f][1,3]

diphosphepinium dibromide) (VII; n = 1).

The diphosphine (1.0 g., was heated with dibromomethane
(0.53 g.) in a sealed tube at 100° for 15 hr. The product when washed
with dry ether gave the extremely hygroscopic dibromide, m.p. 228 - 230°.
Satisfactory analytical data could not be obtained for this salt, but
the corresponding <u>dipicrate</u> formed yellow crystals, m.p. 221 - 222°, from
aqueous ethanol (Found: C, 49.3; H, 4.55; N, 11.0 $C_{33}H_{34}N_6O_{14}P_2$
requires C, 49.5; H, 4.25; N, 10.5%).

The dibromide gave the following spectroscopic data:-

λ_{max} (95% ethanol): 208 mµ ($\epsilon = 30,470$); 240 mµ (sh)

($\epsilon = 7185$); 280 mµ ($\epsilon = 4590$)

p.m.r. (trifluoroacetic acid): 1.85Υ (multiplet, 8 aromatic

protons);

5.9Υ (triplet, J = 16 cps, 3 methylene protons); 6.85Υ (multiplet

4 methylene protons); 7.8Υ (multiplet, 4 methylene protons);

8.0 - 9.4Υ (multiplet, 12 methyl protons).

c) <u>5,5:8,8-Tetraethyl-5,8-diphosphonia-1,2:3,4-dibenzocyclo-</u>
<u>octadiene dibromide</u> (i.e. 5,6,7,8-tetrahydro-5,5,8,8-tetraethyldibenzo[e.g.]
[1,4]diphosphocinium dibromide) (VII; n = 2).

The diphosphine (1.35 g.) was heated with 1,2-dibromoethane
(0.77 g., 1 mol.) in a sealed tube containing a trace of methanol at 100°
for 12 hr. The product was washed with dry ether and purified by
precipitation from a chloroform solution by the addition of acetone, giving
the hygroscopic <u>dibromide</u>, m.p. 268 - 272° (Found: C, 51.7; H, 6.15
$C_{22}H_{32}Br_2P_2$ requires C, 51.0; H, 6.2%).

λ_{max} (95% ethanol): 206 mμ (ϵ = 31,950); 244 mμ (sh),

(ϵ = 8,484); 275 mμ (ϵ = 4,492)

p.m.r. (trifluoroacetic acid): 2.0 Υ (multiplet, 8 aromatic

protons); 6.6 - 8.0 Υ (multiplet, 12 methylene protons);

8.1 - 9.4 Υ (multiplet, 12 methyl protons)

The corresponding dipicrate monoethanolate formed yellow crystals on

recrystallisation from aqueous ethanol, m.p. 142°, followed by

solidification and remelting at 164 - 165°. (Found: C, 50.3; H, 4.6;

N, 10.25 $C_{34}H_{36}N_6O_{14}P_2$, C_2H_5OH requires, C, 50.2; H, 4.9; N, 9.8%).

d)   5,5:9,9-Tetraethyl-5,9-diphosphonia-1,2:3,4-dibenzocyclononadiene

dibromide (i.e. 6,7,8,9-tetrahydro-5,5,9,9-tetraethyl-5H-dibenzo$[f,k][1,5]$

diphosphoninium dibromide) (VII; n = 3).

The diphosphine (1.65 g.) was heated with 1,3-dibromopropane

(1.01 g., 1 mol.) and methanol (1 ml.) in a sealed tube at 100° for 16 hr.

The methanol was evaporated, and the product washed with dry ether, and

recrystallised from ethanol to form the dibromide sesquihydrate,

m.p. 335 - 336° (decomp.) (Found: C, 49.1; H, 6.7. $C_{23}H_{34}Br_2P_2$, 1.5 H_2O

requires C, 49.4; H, 6.6%).

λ_{max} (95% ethanol): 208 mμ (ϵ = 27,390); 271 mμ (ϵ = 4,117);
278 mμ (ϵ = 3,959).

p.m.r. (trifluoroacetic acid): 2.0 Υ (multiplet, 8 aromatic

protons); 6.6 - 9.2 Υ (complex multiplet, 26 protons).

The corresponding dipicrate on crystallisation from aqueous ethanol gave

yellow crystals, m.p. 185 - 186° (Found: C, 50.8; H, 4.45; N, 9.8.

$C_{35}H_{38}N_6O_{14}P_2$ requires C, 50.7; H, 4.6; N, 10.15%).

e)   5,5:10,10-Tetraethyl-5,10-diphosphonia-1,2:3,4-dibenzocyclodecadiene dibromide (i.e. 5,5,10,10-tetraethyl-5,6,7,8,9,10-hexahydrodibenzo[b,d][1,6] diphosphacinium dibromide) (VII; n = 4).

The diphosphine (1.65 g.) was heated with 1,4-dibromobutane (1.08 g. 1 mol.) and methanol (1 ml.) in a sealed tube at 100° for 20 hr. The product was triturated with ether to give the dibromide tetrahydrate, m.p. 152 - 155° (Found: C, 46.45; H, 7.6. $C_{24}H_{36}Br_2P_2$, 4 H_2O requires C, 46.6; H, 7.1%).

λ_{max} (95% ethanol): 210 mμ (ε = 26,650); 241 mμ (sh) (ε = 7,812); 273 mμ (ε = 3,767); 280 mμ (ε = 4,255).

p.m.r. (trifluoroacetic acid): 1.9 ᴛ (multiplet, 8 aromatic protons); 6.7 - 9.2 ᴛ (multiplet, 28 protons).

On treatment with aqueous sodium picrate, the salt gave the corresponding picrate, which resisted crystallisation.

f)   5,5:10,10-Tetraethyl-5,10-diphosphonia-1,2:3,4:7,8-tribenzo-decatriene dibromide (i.e. 9,10,15,16-tetrahydro-9,9,16,16-tetraethyl-tribenzo[b,d,h][1,6]diphosphecinium dibromide) (VIII).

The diphosphine (1.51 g.) was heated with o-xylylene dibromide (1.32 g., 1 mol.) and methanol (1 ml.) in a sealed tube at 100° for 20 hr. The product was triturated with ether and purified by boiling in ethanol, to give a white solid, m.p. 360° (decomp.). The salt was too insoluble in organic solvents for satisfactory recrystallisation (Found: C, 57.2;

H, 6.45. $C_{28}H_{36}Br_2P_2$ requires C, 56.5; H, 6.05%).

λ_{max} (95% ethanol): 207 mµ ($\varepsilon = 37,800$); 273 mµ ($\varepsilon = 4,276$);

280 mµ ($\varepsilon = 3,824$).

p.m.r. (trifluoroacetic acid): 2.0 Υ (multiplet, 8 aromatic

protons); 2.4 Υ (broad singlet, 4 aromatic protons);

5.8 - 6.8 Υ (multiplet, 6 broad lines, $J_{AB} = 16.7$ c/sec, 4

benzylic protons); 7.0 - 8.2 Υ (multiplet, 8 methylene protons);

8.35 - 9.2 Υ (multiplet, 12 methyl protons).

The corresponding dipicrate on crystallisation from water formed yellow

crystals, m.p. 77 - 78° (Found: C, 54.4; H, 4.55; N, 9.4. $C_{40}H_{40}N_6O_{14}P_2$

requires C, 53.95; H, 4.5; N, 9.45%).

9-Ethyl-9-phosphafluorene (i.e., 5-ethyl-5H-dibenzophosphole) (XII;

R = Et).

A solution of 2,2'-dibromobiphenyl (10 g.) in ether (150 cc.)

was added dropwise to fine lithium foil (0.9 g.) during 1.5 - 2 hr.,

the complete mixture being stirred at room temperature for a further 2 hr.

Ethylphosphonous dichloride (3.77 g.) in benzene (50 cc.) was added dropwise

over 30 min. and the resulting mixture was then refluxed for 1 hr. before

cooling and hydrolysing with cold, air-free water. The organic layer was

separated, dried (Na_2SO_4), the solvents evaporated, and the residue was

distilled giving 9-ethyl-9-phosphafluorene, b.p. 106°/0.15 mm. (3.91 g.,

58%) (Found C, 79.1; H, 6.4. $C_{14}H_{13}P$ requires C, 79.25; H, 6.15%).

The phosphine slowly crystallised in the refrigerator and then had m.p.

42 - 44°.

9-Ethyl-9-methyl-9-phosphafluorenonium iodide (XIII; R_1 = Me, R_2 = Et:
X = I).

      9-Ethyl-9-phosphafluorene (0.1 g.) was dissolved in an excess
of methyl iodide and the mixture allowed to stand overnight. The excess
of methyl iodide was then distilled under reduced pressure. The residue was
triturated with ether and purified by crystallisation from acetone with
the addition of ethanol to yield crystals, m.p. 195°. (Found: C, 51.0;
H, 4.7. $C_{15}H_{16}IP$ requires C, 50.8; H, 4.5%).

      p.m.r. (trifluoroacetic acid): 1.9 Υ (multiplet, 8 aromatic
protons); 7.1 Υ (multiplet, J_{HCCH} = 7.3 c/sec), 7.55 Υ (doublet,
J_{PCH} = 14.7 c/sec, 3 methyl protons); 8.78 Υ (sextet, J_{HCCH} = 7.3
c/sec, 3 methyl protons). J_{PCCH} = 22.3 c/sec.
The corresponding picrate, after crystallisation from aqueous ethanol
formed yellow crystals, m.p. 190 - 191° (Found: C, 54.9; H, 4.0;
N, 9.45. $C_{21}H_{18}N_3O_7P$ requires C, 55.3; H, 3.95; N, 9.25%).

9-Methyl-9-phosphafluorene (i.e., 5-methyl-5H-dibenzophosphole) (XII;
R = Me).

      A solution of 2,2'-dibromobiphenyl (10 g.) in ether (150 cc.) was
added dropwise to fine lithium foil (0.9 g.) during 1.5 - 2 hr. The
complete mixture was stirred at room temperature for a further 2 hr.
Methylphosphonous dichloride (3.75 g.) in benzene (50 cc.) was added
dropwise over 30 min., and the resulting mixture was then refluxed for 1 hr.,
and cooled and hydrolysed with cold, air-free water. The organic layer was

separated, dried (Na_2SO_4), the solvents evaporated, and the residue was distilled giving 9-methyl-9-phosphafluorene, b.p. $103^{o}/0.2$ mm. (2.37 g., 37%) (Found: C, 78.2; H, 5.8. $C_{13}H_{11}P$ requires C, 78.8; H, 5.5%).

9,9'-Dimethyl-9-phosphafluorenonium iodide (XIII; $R_1 = R_2 = Me$; $X = I$).

9-Methyl-9-phosphafluorene (0.1 g.) was dissolved in an excess of methyl iodide and the mixture set aside overnight. The excess of methyl iodide was then evaporated. The residue was triturated with ether and purified by crystallisation from ethanol, to yield crystals, m.p. 280 – 280.5^{o} (Found: C, 49.9; H, 4.25; $C_{14}H_{14}IP$ requires C, 49.4; H, 4.15%).

p.m.r. (trifluoroacetic acid): 1.97 Υ (multiplet, 8 aromatic protons); 7.55 Υ (doublet, $J_{PCH} = 15.0$ c/sec, 6 methyl protons).

The corresponding picrate after recrystallisation from aqueous ethanol formed yellow crystals, m.p. 217° (Found: C, 54.9; H, 3.65; N, 9.4 $C_{20}H_{16}N_3O_7P$ requires C, 54.45; H, 3.7; N, 9.5%).

Thermal Decompositions

(A) 2,2'-Biphenylylenebisdiethylmethylphosphonium di-iodide (VI)

The di-iodide (0.5 g.) in a bulb-tube distillation apparatus evacuated to 0.15 mm. was heated to 250° to give a viscous semi-crystalline distillate, which was treated with aqueous sodium hydrogen carbonate solution, and the liberated phosphines extracted with ether. The dried extract was

examined by vapour-phase chromatography (v.p.c.) at 130°, which showed it to be 9-methyl-9-phosphafluorene (XII, R = Me), Rt 10.0 min., and 9-ethyl-9-phosphafluorene (XII, R = Et), Rt 14.4 min., in the proportions of 1:4.8. V.p.c. examination of the dried ether extract at 176° indicated the absence of any diphosphines, which might have arisen from pyrolysis of the salt with simple loss of alkyl halide. At this temperature, authentic 2,2'-biphenylylenebisdiethylphosphine had Rt = 11.4 min.

(B) 9-Ethyl-9-methyl-9-phosphafluorenonium iodide (VI; R_1 = Me, R_2 = Et; X = I).

The iodide (1.0 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described above. V.p.c. examination of the dried ether extract at 130° showed the products of pyrolysis to be 9-methyl--9-phosphafluorene (XII, R = Me) Rt = 10.0 min., and 9-ethyl-9-phosphafluorene (XII, R = Et), Rt = 14.4 min., in the proportions of 1:1.3.

(C) 5,5:7,7-Tetraethyl-5,7-diphosphonia-1,2:3,4-dibenzocycloheptadiene dibromide (VII; n = 1).

The dibromide (1.0 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described above. V.p.c. examination of the dried ether extract at 130° showed it to contain 9-methyl-9-phosphafluorene (XII, R = Me) Rt = 10.0 min., and 9-ethyl-9-phosphafluorene (XII, R = Et) Rt = 14.4 min., in the proportions of 1:2. V.p.c. examination of the dried ether extract at 170° indicated the absence of diphosphines.

(D) 5,5:8,8-Tetraethyl-5,8-diphosphonia-1,2:3,4-dibenzocyclo-octadiene dibromide (VII; n = 2).

The dibromide (0.5 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described above. V.p.c. examination of the dried ether extract at 130° showed it to be 9-ethyl-9-phosphafluorene (XII, R = Et) Rt = 14.4 min.

V.p.c. examination of the dried ether extract at 180° indicated the absence of diphosphines. The ether extract was evaporated in a stream of nitrogen, and the oily residue treated with methyl iodide. The mixture was refluxed for 30 min., and the excess of methyl iodide removed by distillation. The resulting crude methiodide resisted crystallisation and was converted into the corresponding methopicrate of 9-ethyl-9-phospha-fluorene, m.p. 188 - 190° from aqueous ethanol.

(E) 5,5:9,9-Tetraethyl-5,9-diphosphonia-1,2:3,4-dibenzocyclononadiene dibromide (VII; n = 3).

The dibromide (1.0 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described above. The dried ether extract was examined by v.p.c. at 130°, which showed the product of pyrolysis to be 9-ethyl-9-phosphafluorene (XII, R = Et), Rt = 14.4 min. V.p.c. examination of the dried ether extract at 180° indicated the absence of diphosphines. The ether extract was evaporated and the oily residue converted into the corresponding methopicrate of 9-ethyl-9-phosphafluorene, m.p. and mixed m.p. 189 - 190° (from aqueous ethanol).

(F) <u>5,5:10,10-Tetraethyl-5,10-diphosphonia-1,2:3,4-dibenzocyclodecadiene</u>

<u>dibromide</u> (VII; n = 4).

The dibromide (0.7 g.) was decomposed in a bulb-tube apparatus

and the distillate treated as described above. The product of pyrolysis

was shown to be 9-ethyl-9-phosphafluorene by v.p.c. and by conversion into

the corresponding methopicrate (m.p. 189 - 190° after crystallisation

from aqueous ethanol), identical with the methopicrate of authentic

9-ethyl-9-phosphafluorene. As in the above cases, v.p.c. indicated the

absence of diphosphines.

(G) <u>5,5:10,10-Tetraethyl-5,10-diphosphonia-1,2:3,4:7,8-tribenzocyclo-</u>

<u>decatriene dibromide</u> (VIII).

The dibromide (2.0 g.) in a bulb-tube distillation apparatus

evacuated to 0.15 mm. was heated to 300° to give a viscous, semi-

crystalline distillate, which was treated with aqueous sodium hydrogen

carbonate solution and the liberated phosphines extracted with ether. The

dried extract was examined by v.p.c. at 130° and also at 182°, which

showed it to contain 9-ethyl-9-phosphafluorene (XII, R = Et) Rt = 14.4 min.

at 130°, together with a very small quantity of 2,2'-biphenylylenebisdiethyl-

phosphine (I) Rt = 8.8 min. at 182°. The ether extract was evaporated and

the oily residue (0.7 g.) converted into the corresponding methiodides by

treatment with excess of methyl iodide. Attempted recrystallisation of the

crude methiodides from ethanolic acetone yielded a small crop of crystals,

m.p. 254 - 256°, identical with the dimethiodide of 2,2-biphenylylenebis-

diethylphosphine (m.p. 255 - 256°). The supernatant liquid was then poured

into water and the resulting aqueous solution treated with a saturated solution of sodium picrate. The resulting picrate could not be purified by crystallisation due to the presence of traces of the dimethopicrate of the diphosphine. The aqueous phase from the ether extraction of the distillation products was made alkaline and heated on a steam bath for 1 hr. to decompose any phosphonium salts to phosphine oxides, and the resulting solution evaporated to dryness. The inorganic residue was then extracted with hot chloroform and the chloroform extract evaporated to yield a gum (33 mg.). Examination of the gum by thin-layer chromatography (silica-gel, 95% ethanol as solvent) showed it to consist of a number of components, which were incompletely separated. The cold-traps of the oil-pump used for the distillation contained little material, but on exposure to the air, a foul smell was noticeable, and considerable fuming occurred.

Quaternary salts of 2,2'-Biphenylylenebisdiethylarsine - The diarsine (XXXIV; was prepared as described[3] in 61% yield (Found: C, 57.3; H, 6.45. Calc. for $C_{20}H_{28}As_2$; C, 57.45; H, 6.7%).

(A) 2,2'-Biphenylylenebis(diethylmethylarsonium) di-iodide (XXXVIII).

To a solution of the diarsine (0.1 g.), in benzene was added an excess of methyl iodide and the mixture heated to boiling and set aside for 24 hr. Removal of the solvent and crystallisation of the residue from absolute ethanol gave the crystalline dimethiodide, m.p. 199 - 200° (Found: C, 37.15; H, 4.55. $C_{22}H_{34}As_2I_2$ requires C, 37.6; H, 4.8%).

(B) 5,5:8,8-Tetraethyl-5,8-diarsonia-1,2:3,4-dibenzo-cyclo-octadiene

dibromide (i.e., 5,6,7,8-tetrahydro-5,5,8,8-tetraethyldibenzo[e,g][1,4]

diarsocinium dibromide) (XXXV).

    The diarsine (1.97 g.) was heated with 1,2-dibromoethane

(0.87 g. 1 mol.) in a sealed tube containing a trace of ethanol at 100°

for 300 hr. The product was washed several times with dry ether to give

the extremely hygroscopic dibromide, which resisted purification by

crystallisation or precipitation.

    p.m.r. (trifluoroacetic acid): 2.0Υ (multiplet, 8 aromatic

protons); 7.0Υ (quartet, J_{HCCH} = 7.7 c/sec, 4 methylene protons);

7.6Υ (multiplet, 8 methylene protons); 8.15 - 9.2Υ (multiplet,

12 methyl protons).

    The dibromide was characterised by conversion into the

corresponding dipicrate, which after several crystallisations from aqueous

ethanol formed yellow crystals, m.p. 153 - 155°. (Found: C, 45.3; H, 3.95;

N, 9.0. $C_{34}H_{36}As_2N_6O_{14}$ requires C, 45.25; H, 4.0; N, 9.3%).

(C) 5,5:10,10-Tetraethyl-5,10-diarsonia-1,2:3,4:7,8-tribenzo-cyclodecatriene

dibromide (i.e. 9,10,15,16-tetrahydro-9,9,16,16-tetraethyltribenzo[b,d,h]

[1,6] diarsecinium dibromide) (XXXVI).

    The diarsine (1.89 g.) was heated with o-xylylene dibromide

(1.18 g., 1 mol.) and methanol (1 ml.) in a sealed tube at 100° for 8 hr.

The product was triturated with dry ether and purified by boiling in

ethanol, to give a solid, m.p. 267 - 270° (decomp.). (Found: C, 49.4;

H, 5.15; ionic Br, 23.0. $C_{28}H_{36}As_2Br_2$ requires C, 49.3; H, 5.3;

ionic Br, 23.4%).

λ_{max} (95% ethanol): 210 mμ (ϵ = 39,520);

269 mμ (ϵ = 3,383); 276 mμ (ϵ = 2,977).

p.m.r. (trifluoroacetic acid): 1.9 Υ (multiplet, 8 aromatic

protons); 2.42 Υ (broad singlet, 4 aromatic protons);

5.95 Υ (quartet, J_{AB} = 15.4 c/sec, 4 benzylic protons);

7.0 Υ (quartet, J_{HCCH} = 7.7 c/sec, 4 methylene protons);

7.9 Υ (quartet, J_{HCCH} = 7.7 c/sec, 4 methylene protons);

8.6 Υ (multiplet, 12 methyl protons).

9-Ethyl-9-arsafluorene (i.e. 5-ethyl-5H-dibenzoarsole) (XXXVII; R = Et).

A solution of 2,2'-dibromobiphenyl (6.2 g.) in ether (100 ml.)
was added dropwise to fine lithium foil (0.54 g.) during 1.5 - 2 hr., the
complete mixture being stirred at room temperature for a further 2 hr.
Ethylarsonous di-iodide (7 g.) in benzene (50 ml.) was added dropwise over
30 min. and the resulting mixture was then refluxed for 1 hr. before cooling
and hydrolysing with cold, air-free water. The organic layer was separated,
dried (Na$_2$SO$_4$), the solvents evaporated, and the residue was distilled,
(under reduced pressure in nitrogen) giving 9-ethyl-9-arsafluorene,
b.p. 120°/0.07 mm. (3.18 g., 64%) (Found: C, 65.5; H, 4.6. C$_{14}$H$_{13}$As
requires C, 65.65; H, 5.05%).

9-Ethyl-9-arsafluorene (0.1 g.) was dissolved in an excess of
methyl iodide and the mixture heated under reflux for 2 hr. The excess
of methyl iodide was distilled, and the residue recrystallised from light
petroleum (b.p. 60 - 80°) with the addition of acetone to give crystals
of 9-ethyl-9-methyl-9-arsafluorenonium iodide, (XXXIX) m.p. 156.5° - 157°

(decomp.) (Found: C, 45.1; H, 3.6. $C_{15}H_{16}AsI$ requires C, 45.25; H, 4.0%).

The corresponding picrate formed yellow crystals, m.p. 182 - 183°, from aqueous ethanol (Found: C, 50.5; H, 3.6; N, 8.2. $C_{21}H_{18}AsN_3O_7$ requires C, 50.5; H, 3.6; N, 8.4%).

Thermal decompositions

(A) 2,2'-Biphenylylenebisdiethylmethylarsonium di-iodide. (XXXVIII)

The di-iodide (100 mg.) in a bulb-tube distillation apparatus evacuated to 0.1 mm., was heated gently until decomposition occurred, to give a mobile, colourless distillate. The distillate was dissolved in ether (1 c.c.) and examined by v.p.c. at 160°, which showed it to contain 2,2'-biphenylylenebisdiethylarsine (Rt, 20.0 min.) together with similar quantities of other products (unidentified) having retention times of 14.4 min., 12.5 min., and 10.1 min. respectively. 9-Ethyl-9-arsafluorene was not detected as a product of the thermal decomposition of the di-iodide.

(B) 9-Ethyl-9-methyl-9-arsafluorenonium iodide. (XXXIX)

The iodide (100 mg.) was decomposed in a bulb-tube apparatus to give a mobile, colourless distillate. The distillate was dissolved in ether (1 c.c.) and the ether solution examined by v.p.c. at 134°, which showed it to contain 9-methyl-9-arsafluorene (XXXVII, R = Me) (Rt 7.8 min.), identified using authentic material,[34] and 9-ethyl-9-arsafluorene (XXXVII; R = Et) (Rt 10.8 min.), in the proportions of 1:2.

(C) 5,5:8,8-Tetraethyl-5,8-diarsonia-1,2:3,4-dibenzocyclo-octadiene

dibromide (XXXV).

        The dibromide (0.8 g.) in a bulb-tube distillation apparatus

evacuated to 0.05 mm. was heated gently until decomposition occurred to

give a viscous distillate, which was treated with ether and aqueous

sodium hydrogen carbonate solution as in the case of the corresponding

phosphonium salt. The dried ether extract was examined by v.p.c. at 134°

and 180°, which showed it to contain 9-ethyl-9-arsafluorene, (Rt 10.8 min.

at 134°). The ether extract was evaporated and the oily residue was

mixed with methyl iodide, refluxed for 2 hr. and the excess of methyl

iodide removed by distillation. The resulting crude methiodide resisted

crystallisation and was converted into the corresponding methopicrate,

which after crystallisation from aqueous ethanol had m.p. 181 - 183°,

identical with the methopicrate of 9-ethyl-9-arsafluorene.

(D) 5,5:10,10-Tetraethyl-5,10-diarsonia-1,2:3,4:7,8-tribenzocyclo-

decatriene dibromide (XXXVI).

        The dibromide (1.0 g.), in a bulb-tube distillation apparatus

evacuated to 0.05 mm., was heated gently when the solid decomposed with

considerable decrepitation to give a viscous distillate, which was treated

with aqueous sodium hydrogen carbonate and ether as in the above case. The

ether extract was dried (Na_2SO_4) and examined by v.p.c. at 180° and 134°,

which showed it to contain 9-ethyl-9-arsafluorene (Rt, 10.8 min. at 134°)

and 2,2'-biphenylylenebisdiethylarsine (Rt 9.8 min. at 180°).

2,2'-Biphenylylenebisdimethylamine. (XLI)

The diamine was prepared from 2,2'-diaminobiphenyl by the method due to Shaw and Turner,[31] and had m.p. 69°, after two crystallisations from 40 - 60° petrol. (lit.,[31] m.p. 72-3°).

Quaternary salts

a) The monohydriodide (XLII)

The monohydriodide was prepared from the diamine according to the procedure of Shaw and Turner[31] and after several crystallisations from water had m.p. 257 - 258° (lit.[31] m.p. 256 - 257°).

p.m.r. (trifluoroacetic acid): 2.1 Υ (multiplet, 8 aromatic

protons); 6.4 Υ (broad singlet, 12 methyl protons).

b) The monomethiodide (XLIII)

2,2'-Biphenylylenebisdimethylamine (0.5 g.) was dissolved in nitromethane (5 ml.) and methyl iodide (3 ml., excess), and the resulting solution heated under reflux for several days. The solvents were then removed by distillation under reduced pressure, and the residue recrystallised from ethanol to yield a solid, m.p. 240 - 250°d. Further recrystallisation from water gave needles, m.p. 257 - 258°. (Found: C, 52.3; H, 5.45; N, 7.3; Calc. for $C_{16}H_{21}IN_2$: C, 52.2; H, 5.7; N, 7.6%). The infrared and p.m.r. spectra of this product were identical with those of the authentic monohydriodide.

Partial evaporation of the mother-liquors from the initial crystallisation of the reaction products gave a much larger crop of crystals,

which after a further recrystallisation from water had m.p. 200 - 201° (Kofler block); 190 - 191° (cap. tube inserted in heating block at 180°). The infrared spectrum of this product was different from that of the hydriodide.

p.m.r. a) (CDCl$_3$): 2.6 Υ (multiplet, 8 aromatic protons); 6.09 Υ (singlet, 9 methyl protons); 7.51 Υ (singlet, 6 methyl protons).

b) (trifluoroacetic acid): 3.0 Υ (multiplet, 8 protons); 7.0 Υ (singlet, 9 protons); 7.30 Υ (triplet, J = 4.5 c/sec, 6 protons), which was in keeping with the identification of the compound as the authentic monomethiodide. (XLIII)

(Found: C, 53.8; H, 5.85; N, 7.1; Calc. for C$_{17}$H$_{23}$IN$_2$, C, 53.4; H, 6.0; N, 7.3%).

(Shaw and Turner[31] report that the melting point of this salt is markedly dependent on the rate of heating, their m.p. of 190 - 192° being obtained after immersion of the sample in a bath preheated to 180°).

Thermal decompositions

a) The monomethiodide (XLIII)

The salt (20 mg.) was heated at atmospheric pressure in a bulb-tube distillation apparatus. The decomposition products were extracted with ether (1 ml.). Examination of the ether extract by v.p.c. at 134° showed the sole product of pyrolysis to be 2,2'-biphenylylenebisdimethylamine. (Rt = 7.6 min.).

b) <u>The monohydriodide</u> (XLII)

        The salt (20 mg.) was decomposed at atmospheric pressure in a small bulb-tube. The decomposition products were extracted with ether (1 ml.) Examination of the ether extract by v.p.c. at 134° showed the presence of two compounds, of Rt = 7.6 min. (identified as 2,2'-biphenylylenebisdimethyl-amine) and Rt = 9.6 min. Incorporation of authentic 9-methyl carbazole (XLIV) into the sample caused a shoulder to appear on the latter peak, and examination of the ultra-violet spectrum of the thermal decomposition products showed the absence of the carbazole system. It was concluded that the component of Rt = 9.6 min. was probably 2-dimethylamino-2'-methyl-aminobiphenyl (XLV).

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P A R T   I I

a) The alkaline hydrolysis of quaternary salts of
9-substituted-9-phosphafluorenes; ring opening and
ring expansion reactions.

The alkaline hydrolysis of simple quaternary phosphonium salts
has been investigated by several workers, and in general it has been
found that the reaction of hydroxyl ions with alkyl- or aryl-phosphonium
salts gives phosphine oxides and hydrocarbons as the major products:

$$R_3 \overset{+}{P} R^1 \; X^- \xrightarrow{\;\;OH^-\;\;} R_3 P = O \; + \; R^1 H$$
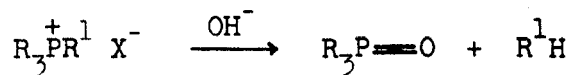
Generally the group eliminated as the hydrocarbon is that which is able
to form the most stable anion, and the following order of preference for
group cleavage has been established:[1-7]

p-nitrobenzyl > benzyl > aryl > phenylethyl > alkyl

Depending on the stability of the negatively charged leaving group, such
hydrolysis reactions are known to obey third order[1-7] or second order[5]
kinetics, and two mechanistic pathways have been proposed. (Fig. 1).

- 61 -

a) $R_3\overset{+}{P}\text{-}CH_2R \xrightarrow[]{OH^-} \underset{\overset{|}{R}}{\overset{\overset{R}{\diagdown}\overset{R}{\diagup}}{HO\text{-}P\text{-}CH_2R}} \xrightarrow[]{OH^-} \underset{\overset{|}{R}}{\overset{\overset{R}{\diagdown}\overset{R}{\diagup}}{\bar{O}\text{-}P\text{-}CH_2R}} \longrightarrow R_3PO + \bar{C}H_2R$

(I)

b) $R_3P\text{-}CH_2R \xrightarrow[]{OH^-} \underset{\overset{|}{R}}{\overset{\overset{R}{\diagdown}\overset{R}{\diagup}}{HO\text{-}P\text{-}CH_2R}} \longrightarrow H\text{-}O\text{-}\overset{+}{P}R_3 + \bar{C}H_2R \longrightarrow R_3PO + RCH_3$

(II)
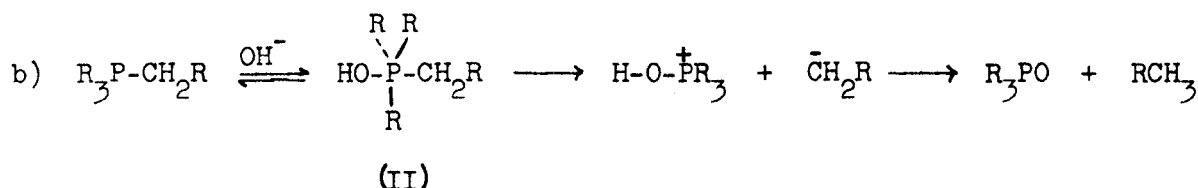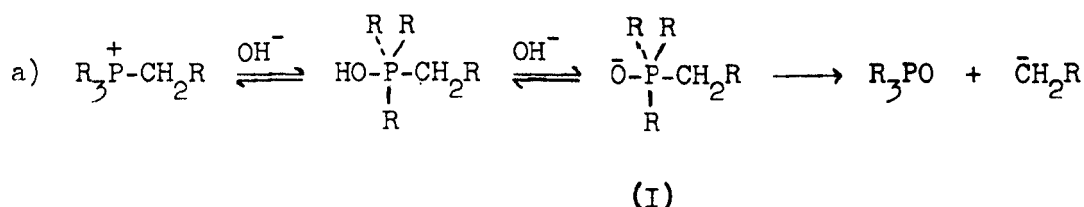
Fig. (1)

In path (a) two hydroxyl ions are involved in the rapid, reversible formation of the pentacovalent intermediate (I), which undergoes slow, rate-determining collapse to the reaction products, and reactions proceding by this path show third order kinetics. In path (b) only one hydroxyl ion is involved in the rapid, reversible formation of the intermediate (II), which undergoes slow, rate-determining collapse to the products, and reactions proceding by this path show second order kinetics.

Relatively little work has been reported on the hydrolysis of quaternary salts of heterocyclic phosphines in which the phosphorus forms part of a ring system having possible aromatic character. Thermo-chemical studies have indicated that both pentaphenylphosphole (III), and 9-phenyl-9-phosphafluorene (IV; R = Ph) have significant resonance

energies.[8,9] However, both phosphines readily undergo oxidation or

quaternisation,[10,11] indicating that the lone-pair on phosphorus is

accessible, in marked contrast to the behaviour of the corresponding

nitrogen heterocycles.
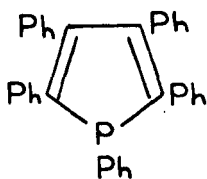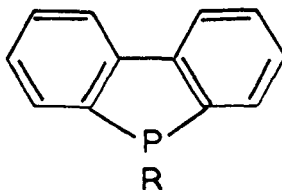
(III)   (IV)

The alkaline hydrolyses of the methiodides of 1,2,5-triphenylphosphole

(V; R = H) and 1,2,3,4,5-pentaphenylphosphole (V; R = Ph) have been

studied by Bergeson,[12] who found that ring-opening occurred exclusively

to give the phenyl substituted butadienylphosphine oxides (VI; R = H, Ph)

respectively. The reactions were found to have second-order kinetics

and the following mechanism was proposed:

(V)   (VIII)   (VII)   (VI)
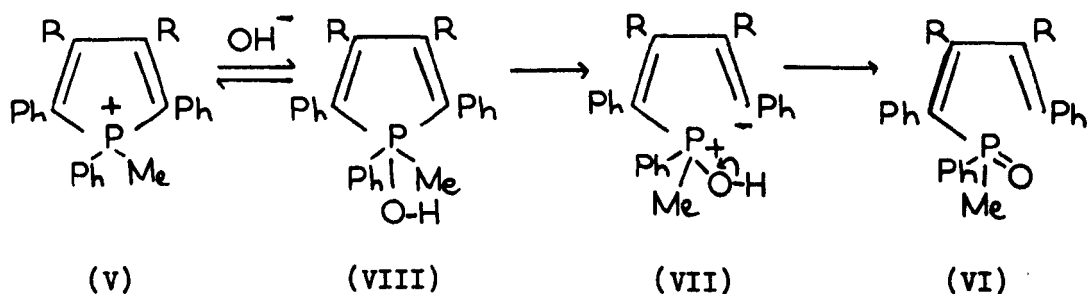
The observed direction of cleavage resulting in ring-opening was attributed to the stability of the intermediate (VII) in which the negative charge occurs on one of the carbon atoms of the diene system as opposed to the stability of a phenyl carbanion produced by P-phenyl cleavage. The kinetic studies of Bergeson also indicated a very low activation energy of 11-12 Kcal/mole for the ring-opening, compared with 35 Kcal/mole for hydrolysis reactions in which a phenyl carbanion is the leaving group.

However, the possibility of conjugative stabilisation of the intermediate (VII) (as suggested by Bergeson) seems unlikely considering the various resonance forms. An alternative explanation of the observed exclusive ring-opening could be the relief of strain in the intermediate (VIII) which contains a pentacovalent phosphorus atom in a five-membered unsaturated ring.

The alkaline hydrolysis of similar quaternary salts of the 9-substituted-9-phosphafluorenes has also been found to proceed with exclusive ring-opening. Hydrolysis of the methiodide (IX; R = Ph) of 9-phenyl-9-phosphafluorene gave 2-biphenylylphenylmethylphosphine oxide (X; R = Ph), and that of the methiodide (IX; R = Me) of 9-methyl-9-phosphafluorene gave 2-biphenylyldimethylphosphine oxide (X; R = Me). No ring-preserved products were detected. In the case of the methiodide (IX; R = Me), this is not surprising in view of the established preference for $\overset{+}{P}$-aryl cleavage under alkaline conditions. In the case of the methiodide (IX; R = Ph), the absence of $\overset{+}{P}$-phenyl cleavage to give a ring-preserved product may indicate the preferential formation of an intermediate

of the type (XI) in which a negative charge is developed at the

2'- position of the biphenyl system, a situation paralleling that in

the phosphole series (VII).
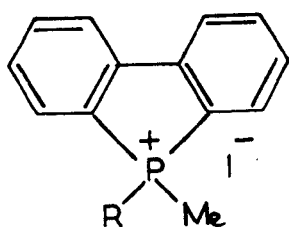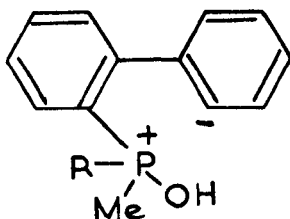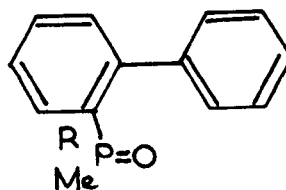
(IX)   (XI)   (X)

The structures of the phosphine oxides (X; R = Me or Ph) were determined

by a) analytical data b) their infrared spectra which exhibited strong

peaks at 1160 and 1175 cm^{-1} respectively, in accord with the presence of

a P=O group; c) their ultraviolet spectra which were typical of hindered

biphenyl systems, and very different from the characteristic spectra of

9-phosphafluorene derivatives (Fig. 2); and d) their proton magnetic

resonance spectra. The p.m.r. spectrum of the oxide (X; R = Ph), in

deuterochloroform solution, showed a multiplet centered at 2.6 Υ due to

the 14 aromatic protons and a doublet at 8.35 Υ (J_{PCH} = 14 c/sec) due to

the 3 methyl protons. The p.m.r. spectrum of the oxide (X; R = Me), also

in deuterochloroform solution, showed a multiplet centered at 1.75 Υ due to

one aromatic proton, a multiplet centered at 2.5 Υ due to 8 aromatic

protons, and a doublet at 8.5 Υ (J_{PCH} = 14 c/sec) due to the 6 methyl

protons.

Ultraviolet Spectra of Phosphine Oxides
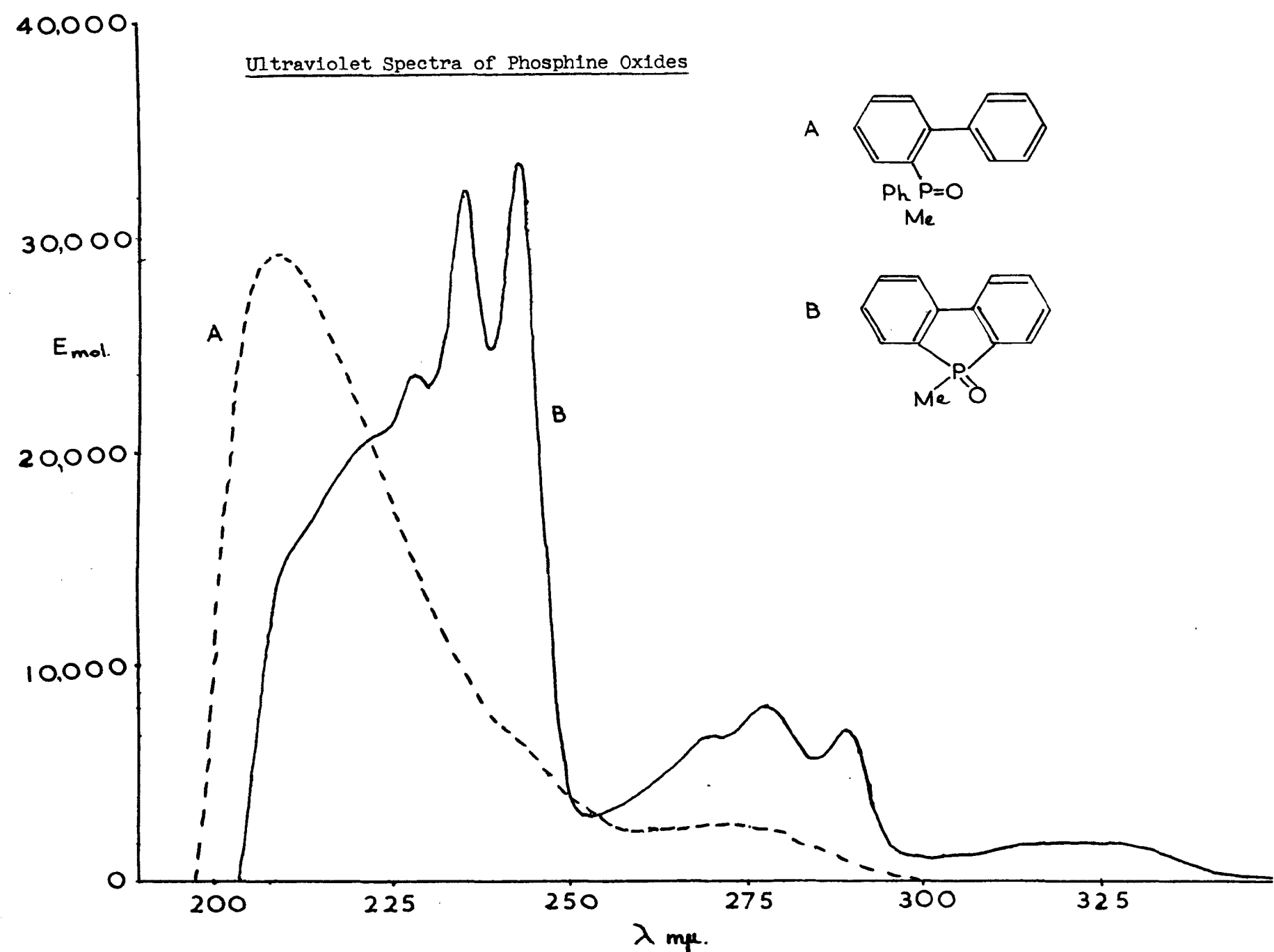
Fig. (2)

Similar ring-opening reactions of 9-phosphafluorenonium salts

bearing dimethylamino substituents in the benzene rings have been reported.[11]

It was also of interest to investigate the alkaline hydrolysis

of the methiodide (XII) of 9-diethylamino-9-phosphafluorene (XIII).

Aminophosphines react with alkyl halides to give quaternary phosphonium

and not quaternary ammonium salts, owing to the greater nucleophilicity

of the phosphorus atom:

$$R_2P - NR_2 + R^1X \longrightarrow R_2\overset{+}{\underset{\underset{R^1}{|}}{P}} - NR_2 \; X^-$$
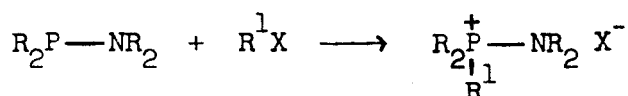
Such aminophosphonium salts are readily hydrolysed in hydroxylic solvents:[13]

$$R_3\overset{+}{P} - NR_2 \xrightarrow{OH^-} R_3P = O + R_2NH$$
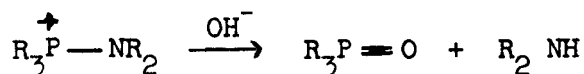
The phosphafluorene (XIII) was synthesised in 23% yield by the addition

of a solution of 2,2'-dilithiobiphenyl to a solution of diethylaminophos-

phonous dichloride in ether, the reaction mixture being kept cool to

minimise attack by the organolithium reagent at the P-N bond.

(XIII)
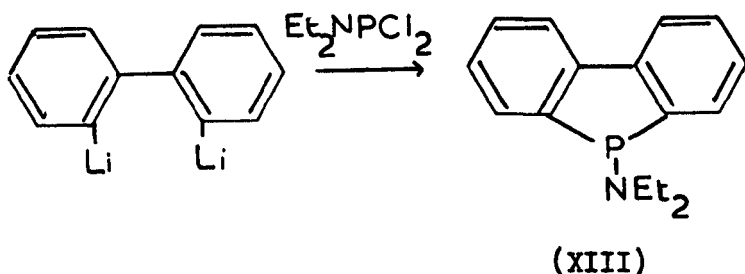
On treatment with methyl iodide, the phosphafluorene was converted into

the corresponding monomethiodide (XII); the p.m.r. spectrum and mode of

alkaline hydrolysis of this compound demonstrated that quaternisation had occurred at phosphorus. The p.m.r. spectrum of the salt (XII), in deuterochloroform solution, exhibited a complex multiplet centered at 1.90 Υ due to the aromatic protons, a multiplet centered at 6.77 Υ due to the methylene protons of the ethyl groups attached to nitrogen, a doublet centered at 7.03 Υ (J_{PCH} = 12 c/sec) due to the $\overset{+}{P}$-Me group, and a multiplet centered at 8.78 Υ due to the methyl protons of the $N(CH_2CH_3)_2$ group. The alkaline hydrolysis of the salt (XII) proceded quite differently from the hydrolyses of the methiodides (IX; R = Me or Ph) in giving the ring-preserved product, 9-methyl-9-phosphafluorene-9-oxide (XIV). The salt (XII) therefore resembles other aminophosphonium salts in undergoing cleavage of the P-N bond on alkaline hydrolysis. The structure of the hydrolysis product (XIV) was proved by comparison with a sample of the authentic material obtained from the oxidation of 9-methyl-9-phosphafluorene with hydrogen peroxide.

(XII)   (XIV)
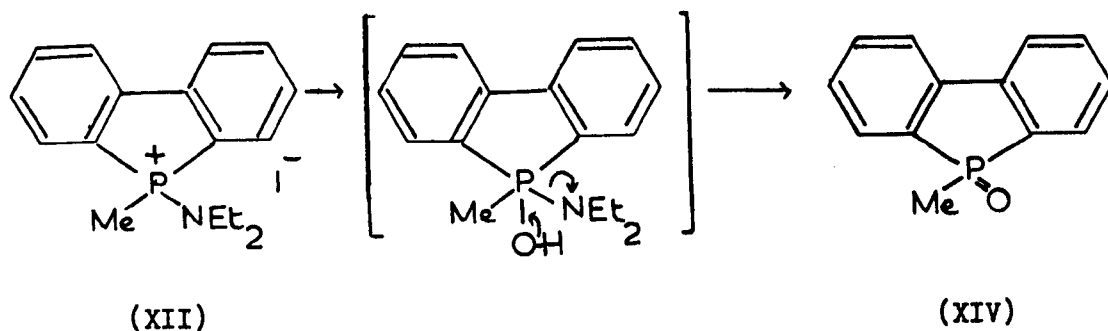
In a study of the alkaline hydrolysis of phosphonium salts containing substituted methyl groups, Schlosser[14] found that a phenyl group is lost in preference to a $-CH_2OCH_3$ group, whereas chloromethyl and

bromomethyl groups are released together with phenyl groups. In

addition, it was found that on hydrolysis of bromomethyltriphenylphosphonium

bromide (XV), an unusual migration of an aryl group occurs, giving

benzyldiphenylphosphine oxide (XVI).

$$Ph_3\overset{+}{P}CH_2Br \quad Br^- \quad \xrightarrow{OH^-} \quad Ph_2\overset{\overset{\displaystyle O}{\|}}{P}-CH_2Ph$$

(XV)   (XVI)
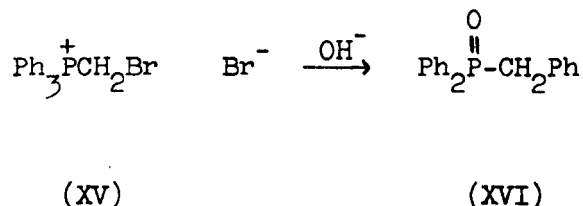
In view of Schlosser's findings on the hydrolysis of the salt (XV), it

was of interest to investigate the hydrolysis of similar salts of the

9-substituted -9-phosphafluorenes (XVII; R = Me, Ph; X = leaving group)

in the hope that migration of one of the ring C-P bonds would occur via

an intermediate of type (XVIII) to give a 9-substituted-9,10-dihydro-9-

phosphaphenanthrene-9-oxide (XIX), thus achieving a novel ring-expansion

reaction, and yielding an otherwise elusive cyclic system.

(XVII)   (XVIII)   (XIX)
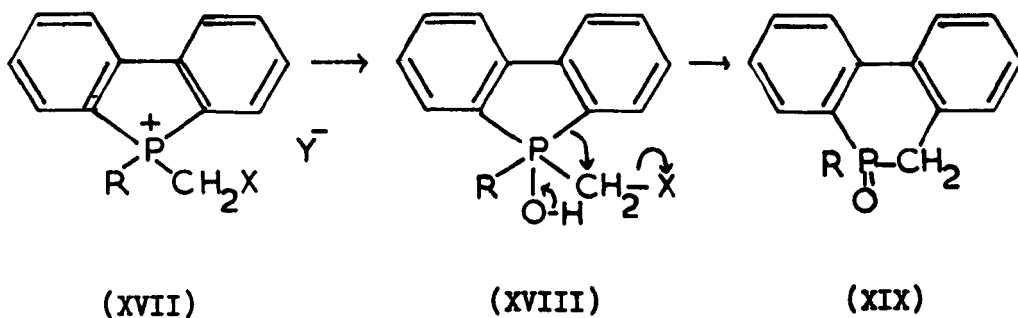
Treatment of 9-methyl-9-phosphafluorene (IV; R = Me) with chloromethyl

methyl ether gave the salt (XVII; R = Me, X = OMe, Y = Cl$^-$). Attempts to

convert this salt into the corresponding bromomethyl salt (XVII; R = Me,

X = Br, Y = Br-) by heating under reflux with constant-boiling hydrobromic

acid gave only the hydroxymethyl salt (XVII; R = Me, X = OH, Y = Br⁻).
The iodomethyl salts (XVII; R = Me or Ph; X = I, Y = I⁻) were obtained
directly in high yield from the phosphines (IV; R = Me or Ph) by heating
with an excess of di-iodomethane in benzene.

Alkaline hydrolysis of the salt (XVII; R = Me, X = OMe, Y = Cl⁻)
proceded exclusively with ring-opening to furnish 2-biphenylylmethoxymethyl-
methylphosphine oxide (X; R = MeOCH$_2$-), ring expansion not having occurred
presumably because the methoxide ion is a poor leaving group. The structure
of the oxide (X; R = MeOCH$_2$) was proved by a) analytical data; b) the
infrared spectrum which exhibited strong bands at 1178 cm⁻¹ (P = O) and
1110 cm⁻¹ (C - O); c) its ultraviolet spectrum (Fig. 3) which is
typical of a hindered biphenyl system; and d) its proton magnetic resonance
spectrum, in deuterochloroform solution, which exhibited a multiplet at
1.85 Υ , due to one aromatic proton, a broad singlet at 2.45 Υ due to 8
aromatic protons, a two proton doublet at 6.41 Υ (J = 5.3 c/sec,
P-CH$_2$-OCH$_3$), a three proton singlet at 6.66 Υ (O-CH$_3$), and a three proton
doublet at 8.55 Υ (J = 13.4 c/sec, P(O)CH$_3$).

Alkaline hydrolysis of the salt (XVII; R = Me, X = OH, Y = Br⁻)
gave mainly 9-methyl-9-phosphafluorene, the established mode of decomposition
of a hydroxymethylphosphonium salt having occurred.[15]

The alkaline hydrolysis of the salt (XVII; R = Me, X = I, Y = I⁻)
proceded readily to give the ring-expanded product (XIX; R = Me), in high
yield. The structure of the oxide (XIX; R = Me) was proved by a)
analytical data; b) its infrared spectrum which exhibited strong absorption
in the region 1150-1200 cm⁻¹ (P = O); c) its characteristic ultraviolet
spectrum (Fig. 3) which is seen to be quite different from that of the

Ultraviolet Spectra of Phosphine Oxides
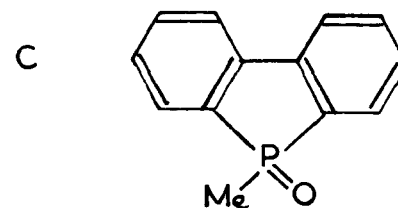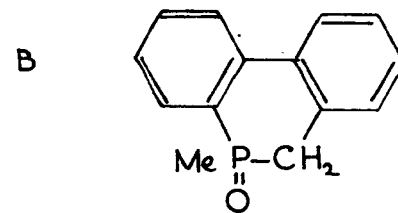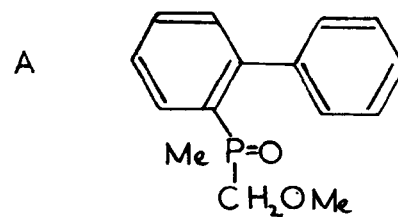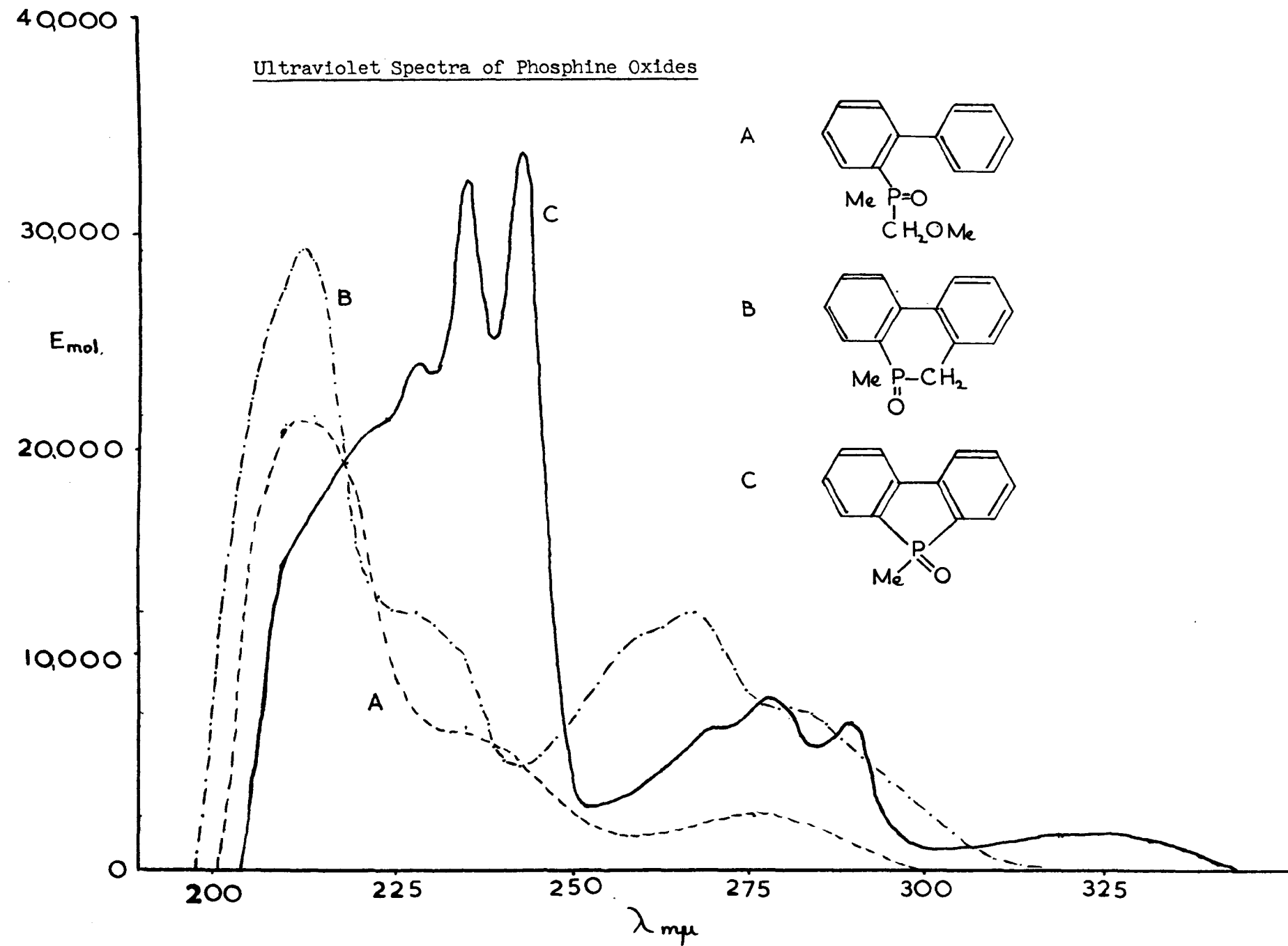
Fig. (3)

ring-opened product (X; R = MeOCH$_2$) and that of 9-methyl-9-phosphafluorene

oxide (XIV); but it is very similar to the u.v. spectra of the structurally

similar salts (XX)[16] and (XXI)[17] and to that of the cyclic phosphinic acid

(XXII)[18]. Also, d) its p.m.r. spectrum (Fig. 4) confirmed this

identification (see below).
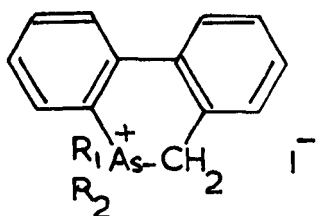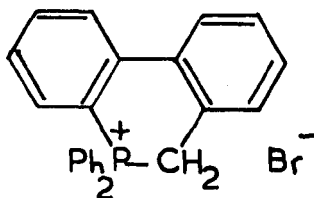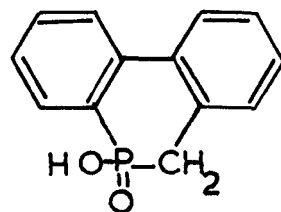
(XX)   (XXI)   (XXII)

It has been pointed out that in the salts (XX), due to the

tetrahedral disposition of the central atoms of the bridging group, the

two benzene rings of the biphenyl system cannot become coplanar, and such

a molecule must therefore possess molecular dissymmetry. In addition,

such a molecule having two dissimilar groups (R$_1$, R$_2$) attached to the

arsenic atom would also have an asymmetric arsenic atom, and should

therefore be capable of existing in two distinct racemic forms.[16] A

similar situation prevails in the ring-expanded product (XIX; R = Me).

The general asymmetry of the molecule was revealed by the p.m.r. spectrum

in which the two magnetically non-equivalent benzylic protons (H$_A$ and H$_B$)

appeared as an ABX multiplet centered at 6.5 Υ (J$_{AB}$ = 16.3 c/sec) for a

solution in deuterochloroform. The spectrum also included a multiplet

P.M.R. Spectrum of 9-Methyl-9,10-dihydro-9-phosphaphenanthrene-9-oxide (in CDCl₃)
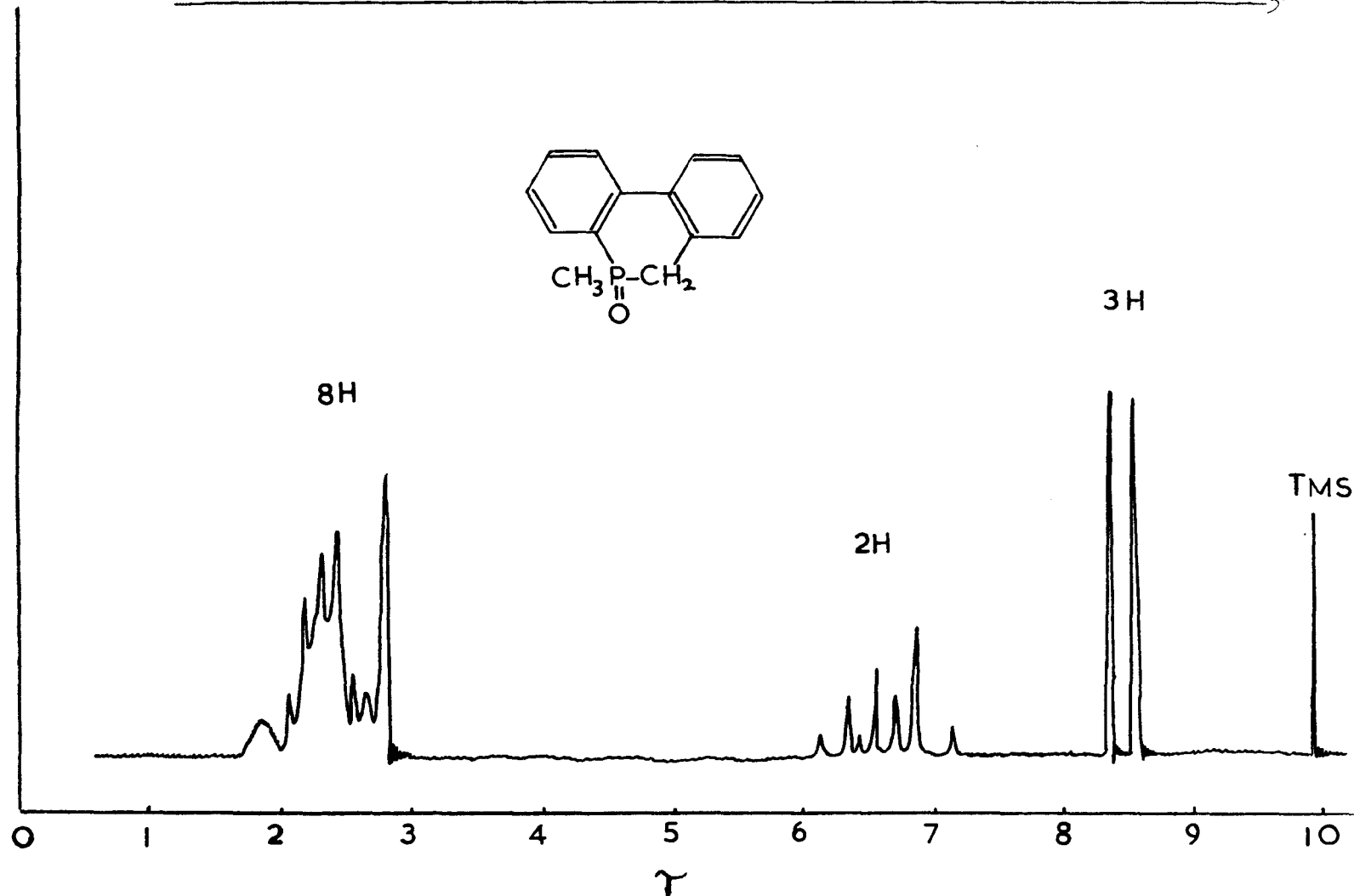
Fig. (4)

centered at 2.2 Υ due to the eight aromatic protons, and a doublet
centered at 8.53 Υ (J_{PCH} = 13.5 c/sec) due to the P(O)-CH$_3$ group.

The p.m.r. spectrum of the cyclic phosphinic acid (XXII) in
trifluoroacetic acid solution[18] and that of the cyclic salt (XXI) in
deuterochloroform solution[19] are of interest in that the benzylic protons
of both compounds appear as simple doublets and not as ABX multiplets.
The appearance of the simple doublet of an A$_2$X spectrum must indicate
rapid conformational inversion in these compounds, which results in the
"time-averaged" equivalence of the benzylic protons. Such equivalence
cannot occur in the ring-expanded product (XIX; R = Me) due to the
presence of the asymmetric phosphorus atom whose stability to inversion
of configuration is to be expected to be considerable, in view of the
resolution of a number of tervalent and tetravalent phosphorus compounds,
accomplished in recent years.[20]

In the case of the salt (XVII; R = Ph, X = I, Y = I$^-$), it was
anticipated that on hydrolysis, migration of the phenyl group to the
adjacent methylene to give 9-benzyl-9-phosphafluorene-9-oxide (XXIII;
R = Bz) might compete with the ring-expansion reaction. However, alkaline
hydrolysis of the salt (XVII; R = Ph, X = I, Y = I$^-$) gave the ring-expanded
product (XIX; R = Ph) in high yield, with traces of 9-phenyl-9-phosphafluoren
(IV; R = Ph) and 9-phenyl-9-phosphafluorene-9-oxide (XXIII; R = Ph).
The last two products may be accounted for on the basis of 1) competitive
attack by OH$^-$ on the -CH$_2$I group to give a hydroxymethyl phosphonium salt,
this then rapidly losing formaldehyde to give the free phosphafluorene;
and 2) loss of the -CH$_2$I fragment (as CH$_3$I) from the intermediate (XVIII);

9-benzyl-9-phosphafluorene oxide was not detected, again indicating

the preferred cleavage of the ring C - P bond. The structure of

(XIX; R = Ph) was deduced as for the corresponding methyl compound

(XIX; R = Me), the p.m.r. spectrum of the compound in deuterochloroform

again exhibiting an ABX multiplet for the benzylic protons centered at

6.3 Υ (J_{AB} = 16.3 c/sec).
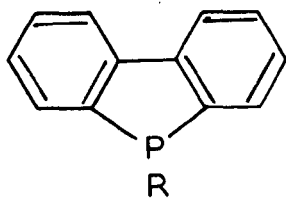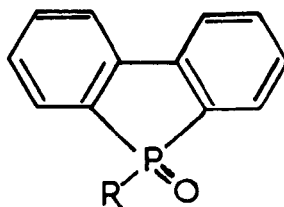
(IV)   (XXIII)

The alkaline hydrolysis of the fairly readily available

iodomethyl salts of heterocyclic tertiary phosphines in which an aryl-P

bond is incorporated in the ring system, appears to offer a route to

some previously elusive heterocyclic phosphorus systems by use of a ring

expansion reaction of the type now described.

Another reaction involving a 1,2-aryl migration from phosphorus

to carbon has been applied recently to achieve a ring expansion reaction

of a 9-phosphafluorene to a 9,10-disubstituted-9,10-dihydro-9-phospha-

phenanthrene-9-oxide. Triaryl phosphines react with phenylacetylene and

water in boiling diethyleneglycol to give the compound (XXIV; R = Ph),

aryl migration from P→C having occurred.[21] A similar reaction using

methyl propiolate was found to occur under much milder conditions to give

the compound (XXIV; R = COOMe), and this reaction has been applied to

9-methyl-9-phosphafluorene to yield the ring-expanded product (XXV).[22]

$$Ar_2\overset{\overset{O}{\|}}{P}\underset{Ar}{-}CH-CH_2R$$
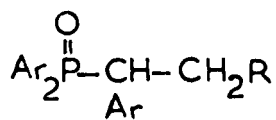
(XXIV)
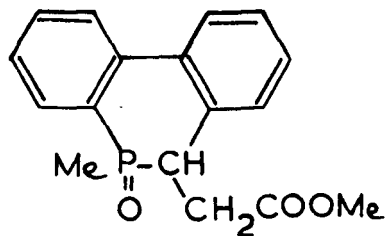
(XXV)

b) Unusually low PCH coupling constants in the proton
   magnetic resonance spectra of phosphonium salts and
   phosphine oxides.

The observed PCH geminal coupling constants of the p.m.r.

spectra of quaternary phosphonium salts lie in the range 11-16 c/sec.[23]

However, there are a few examples of unusually low values.

Hendrickson et al.[24] observed one such example for the phosphonium

salt (XXVI) in which J_{PCH} = 4 c/sec., and put forward a tentative

suggestion that fitted in with their general hypothesis that the s

character of the phosphorus bonding orbitals was the major factor in

determining the size of J_{PCH}. From a study of the p.m.r. spectra of a

range of organophosphorus compounds, these workers considered that an

electronegative group attached to phosphorus increases the s character of

the phosphorus orbitals which point to alkyl carbon atoms and this in

turn increases J_{PCH}. In order to explain the low coupling constant of

the salt (XXVI), it was suggested that the phosphorane form (XXVII) made

a significant contribution to the structure of the salt, thus reducing the

positive nature of the phosphorus atom and hence reducing the value of

J_{PCH}. It is to be assumed that apart from reducing the positive charge

on the phosphorus, this contribution was expected to decrease the s

character of the phosphorus bonding orbitals directed towards the methylene

carbon and thus reduce the coupling constant accordingly.

$$Ph_3\overset{+}{P}-\underset{}{CH_2} \quad Cl^- \qquad Ph_3P\overset{\overset{+}{O}-Me}{\diagup}CH_2 \quad Cl^- \qquad Z=\overset{X}{\underset{X}{P}}-CH_2Cl$$

$$\overset{O-Me}{|}$$
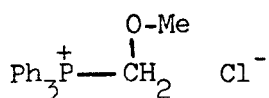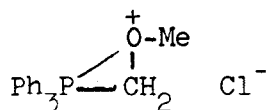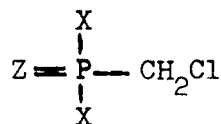
(XXVI) (XXVII) (XXVIII)

Nixon and Schmutzler[25] studied the p.m.r. spectra of a number of compounds of the type (XXVIII; X = Cl, F, OC_3H_7; Z = O,S) and observed a range of values of J_{PCH} from 3.9 to 11.5 c/sec. Applying Hendrickson's ideas, these workers expected the electronegative groups to divert a large amount of s character into the orbital of phosphorus directed toward the $-CH_2Cl$ group, and thus to increase J_{PCH}, but their data showed that this is not so.

Manatt, Juvinall, Wagner, and Elleman[26] have determined the relative signs of the PH, PCH, and HCPH couplings for methyl-, dimethyl-, and trimethylphosphine and found them all to be positive. The PCH coupling constants for triethylphosphine and the methylphosphines (which all have low s character in the bonding orbitals of phosphorus) were close to zero and J_{PCH} was found to become more negative as the phosphorus bonding orbitals gain s character. The large PCH coupling constants of phosphonium salts (e.g. 14.4 c/sec for tetramethylphosphonium iodide)[23] which should have phosphorus bonding orbitals possessing $\sim$ 25% s character are therefore most certainly negative. From the large positive shift of J_{PCH} for trivinylphosphine (having an sp^2 hybridised carbon atom attached

to phosphorus), it was deduced that the effect of the electronegative methoxyl group in the salt (XXVI) is to increase the $\underline{s}$ character of the bonding orbitals of carbon to phosphorus and cause a positive shift for J_{PCH}, leading to a numerically smaller coupling constant.

The p.m.r. spectra of a series of compounds of type $Ph_3\overset{+}{P}CH_2X\ Y^-$ (X = electronegative atom or group; Y^- = halide), in which the electronegativity of the substituent X is varied, have been examined. The details of the spectra are given in Table 1.

Table 1.

Coupling Constants and Chemical Shifts for the Aliphatic
Protons of the Triphenylphosphonium Salts.

Salt	Solvent	Υ_{PCH_2X} ppm.	J_{PCH} c/sec.	Remarks
$Ph_3\overset{+}{P}CH_2OH\ Cl^-$	$CDCl_3$	4.49	0	Singlet.
	CF_3COOH	4.37	1.5	
$Ph_3\overset{+}{P}CH_2OMe\ Cl^-$	$CDCl_3$	4.18	4.0	See Hendrickson et al.[24]
	CF_3COOH	4.81	4.0	
$Ph_3\overset{+}{P}CH_2Cl\ Cl^-$	$CDCl_3$	3.68	6.0	
	CF_3COOH	4.93	6.3	
$Ph_3\overset{+}{P}CH_2Br\ Br^-$	$CDCl_3$	3.78	6.0	See Driscoll et al.[27]
	CF_3COOH	5.20	6.3	
$Ph_3\overset{+}{P}CH_2I\ I^-$	CF_3COOH	5.45	7.8	Insoluble in $CDCl_3$

It has been reported that the nature of the anion in methyltriphenylphosphonium salts does not affect the P-methyl coupling constant.[23] The marked changes in the coupling constant J_{PCH} shown in Table 1 for the salts $Ph_3\overset{+}{P}CH_2X\ Y^-$ must therefore be due to the substituent X. It is seen that the geminal coupling constant increases in the order:

$$J_{PCH_2OH} < J_{PCH_2OCH_3} < J_{PCH_2Cl} = J_{PCH_2Br} < J_{PCH_2I}$$
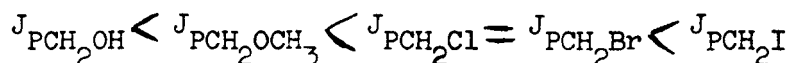
Furthermore, it is clear that the coupling constant increases as the electronegativity of X decreases, and it will be shown later that these coupling constants are negative. The effect of the substituent X is most marked in the case of the hydroxymethylphosphonium salt (X = OH). In deuterochloroform solution, the methylene resonance appears as a singlet, the coupling constant being too small for resolution. In trifluoroacetic acid solution, however, the methylene resonance appears as a closely spaced doublet with J_{PCH} = 1.5 c/sec.
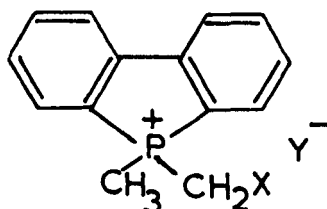
(XXIX)

The spectra of several phosphonium salts of the general structure (XXIX), in which the phosphorus atom bears a methyl group as well as a substituted methyl group, have also been examined. Hybridization changes

at the methyl carbon in the methylphosphine series have been shown to be small,[26] and it was expected, therefore, that any changes in the P-Me coupling constant would reflect changes in the hybridization of the phosphorus atom. The details of the spectra are given in Table 2.

Table 2.

Coupling Constants and Chemical Shifts for the Aliphatic Protons of the 9-Phosphafluorenonium Salts (XXIX)

Salt	Solvent	τ_{PCH_2X} ppm.	J_{PCH_2X} c/sec.	τ_{PCH_3}	J_{PCH_3} c/sec.
X = OH; Y = Br⁻	$CDCl_3$	4.74	0	7.15	15.4
	CF_3COOH	4.82	1.1	7.50	15.0
X = OMe; Y = Cl⁻	$CDCl_3$	4.40	4.4	7.05	15.6
	CF_3COOH	5.31	4.8	7.57	15.0
X = Cl; Y = Cl⁻	$CDCl_3$	4.07	8.0	6.81	15.6
	CF_3COOH	5.44	7.4	7.41	14.9
X = I; Y = I⁻	CF_3COOH	5.94	8.4	7.32	14.8
X = CH₃; Y = I⁻	CF_3COOH			7.55	14.7
X = H; Y = I⁻	CF_3COOH			7.55	15.0

As for the corresponding triphenylphosphonium salts (Table 1), the size of the methylene coupling constant J_{PCH_2X} increases as the electronegativity of the substituent X decreases. In contrast, the P-Methyl coupling constant J_{PCH_3} does not change appreciably, and in trifluoroacetic

acid the values of J_{PCH_3} for the salts (XXIX; X = OH, OMe, Cl, I) are, within experimental error, the same as those shown by the salts (XXIX; X = H, Y = I^-) and (XXIX; X = CH_3, Y = I^-). These results would seem to indicate that there is little or no increase in the s character of the bonding orbitals of the phosphorus atom. Although one would accept that the phosphorus bonding orbital to the methyl carbon will not experience exactly the same change as the phosphorus bonding orbital to the methylene carbon atom, the absence of any change for the former would imply that changes in the latter are quite small and that the low PCH coupling constants are due mainly to rehybridization at the methylene carbon atom.

Several workers[28,29] have indicated that the s orbital of an atom tends to concentrate in the hybrid orbitals that are directed to the less electronegative atoms, and it has been found[30] that halogen and oxygen atoms bonded to a methyl group cause the geminal coupling constant to decrease (which is, in fact, a positive shift of a negative coupling constant). It is to be expected that when two electronegative groups are bonded to a methylene group, an even larger proportion of s character would be directed into the bonding orbitals of carbon which point to hydrogen, resulting in a correspondingly larger decrease in the geminal coupling constant. A positively charged phosphorus atom (when bonded to the methylene group) will act as an electronegative group as well as a probe for detecting hybridisation changes on the carbon atom. Thus for the grouping $\overset{+}{P}$-CH_2-X, one would predict that so long as there are no hybridisation changes for the phosphorus atom, then both J_{HCH} and J_{PCH} will

show fairly large positive shifts. The above results (Tables 1 and 2) confirm this prediction for J_{PCH}.

Such parallel changes in J_{HCH} and J_{PCH} give further confirmation that the sign of the geminal coupling constant, J_{PCH}, is negative in phosphonium salts. Furthermore, the trend for the low coupling constant, J_{PCH}, for the methylene protons of the salts $Ph_3\overset{+}{P}CH_2$-X Y^- and (XXIX) to decrease with increasing electronegativity of the substituent X indicates that these coupling constants also have a negative sign.

Similar effects on the size of the coupling constant would be expected to occur for phosphine oxides and phosphine sulphides.[25] The spectra of the phosphine oxides (XXX) and (XXXI)[31] (see Table 3) confirm this; the oxides exhibit high P-methyl geminal coupling and low P-CH$_2$X coupling.
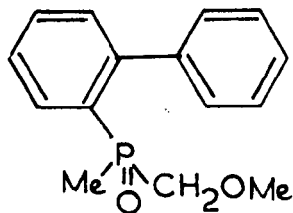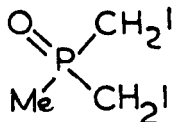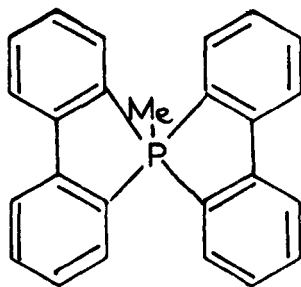
(XXX)   (XXXI)   (XXXII)

Table 3.

Coupling Constants and Chemical Shifts for the Aliphatic
Protons of the Phosphine Oxides

Oxide	Solvent	τ_{PCH_2X}	J_{PCH_2X} c/sec.	τ_{PCH_3}	J_{PCH_3} c/sec.
(XXX)	$CDCl_3$	6.4	5.3	8.55	13.4
(XXXI)	$CDCl_3$	6.59	7	8.08	13

It is also apparent that the above phosphine oxides are most unlikely to have contributing phosphorane forms as a cause for the low coupling constants.[24] Furthermore, in the phosphorane (XXXII), the coupling constant J_{PCH_3} = 11 c/sec.,[32] a value not greatly lower than some geminal coupling constants reported for phosphonium salts,[23] in spite of the decrease in s character of the phosphorus bonding orbitals in passing from a phosphonium salt (sp^3 hybridised phosphorus) to the phosphorane (sp^3d hybridised phosphorus).

Proton magnetic resonance spectra were recorded on a Perkin-Elmer 60 megacycle instrument using tetramethylsilane as internal standard. Coupling constants were determined from spectra expanded to 1 c/sec per unit.

Preparation of phosphines and phosphonium salts

9-Phenyl-9-phosphafluorene. (IV; R = Ph)

A solution of phenylphosphonous dichloride (4.3 ml; 5.6 g.) in benzene (50 ml.) was added dropwise to a solution of 2,2'-dilithiobiphenyl (prepared from 2,2'-dibromobiphenyl (10 g.) and lithium foil (0.9 g.) in ether (150 ml.)) and the resulting solution heated under reflux for 30 min. before cooling and hydrolysing with cold, boiled-out distilled water. The organic layer was separated, dried over anhydrous sodium sulphate, and the solvents evaporated. Distillation of the residue under reduced pressure in nitrogen gave 9-phenyl-9-phosphafluorene (IV, R = Ph), (3.7 g., 45%), b.p. 152-6° (0.05 mm). The crude phosphine was recrystallised from absolute ethanol to yield crystals, m.p. 92-3° (lit.[11] 92-4°). (Found: C, 82.7; H, 5.3; Calc. for $C_{18}H_{13}P$: C, 83.05; H, 5.05%).

A small sample of the phosphine, when treated with a solution of hydrogen peroxide (100 vol.) in acetone and allowed to stand overnight gave 9-phenyl-9-phosphafluorene-9-oxide (XXIII, R = Ph), m.p. 163-4° (from aqueous ethanol (lit.[33] 162-164.5°). (Found: C, 78.7; H, 4.0; Calc. for $C_{18}H_{13}OP$: C, 78.25; H, 4.6%). i.r. (mull): 1195 cm^{-1} (s) (P=O).

<u>9-Methyl-9-phenyl-9-phosphafluorenonium iodide.</u> (IX; R = Ph)

9-Phenyl-9-phosphafluorene was allowed to stand at room temperature with an excess of methyl iodide for some hours. Evaporation of the excess of reagent gave a residue which after trituration with dry ether and recrystallisation from ethanol-light petroleum (b.p. 60-80°) gave crystals of the salt, m.p. 204-5° (lit.,[11] m.p. 204-6°). (Found: C, 57.4; H, 4.15. Calc. for $C_{19}H_{16}IP$: C, 57.4; H, 4.0%).

<u>9-Iodomethyl-9-phenyl-9-phosphafluorenonium iodide.</u> (XVII; R = Ph, X = I, Y = I^{-})

9-Phenyl-9-phosphafluorene (0.2 g.) was dissolved in benzene (5 ml.) and methylene di-iodide (4 ml.) and the resulting solution heated on a steam-bath for 1 hr. The solvents were then removed by distillation under reduced pressure, and the residue triturated with absolute ethanol to give the salt (XVII; R = Ph, X = I, Y = I^{-}) (0.306 g. 75%). A small sample, on recrystallisation from absolute ethanol had m.p. 219-20°. (Found: C, 43.2; H, 2.70; $C_{19}H_{15}I_{2}P$ requires C, 43.2; H, 2.85%). p.m.r. (CF$_{3}$COOH) p.p.m.: 1.9 Υ (multiplet, 13 aromatic protons), 5.54 Υ (doublet, $J_{PCH} = 8.1$ c/sec, 2 protons).

<u>9-Methyl-9-phosphafluorene-9-oxide.</u> (XIV)

9-Methyl-9-phosphafluorene (0.1 g.) (prepared as described in Part I of this thesis) was dissolved in aqueous acetone (50%, 5 ml.); hydrogen peroxide solution (100 vol, 1 ml.) was added and the mixture allowed to stand overnight. Evaporation of the solvents gave a gum which was dissolved in chloroform (10 ml.) and shaken with an aqueous solution

of sodium bisulphite. The chloroform solution was then dried over anhydrous sodium sulphate and evaporated to give a colourless residue which on recrystallisation from petrol (b.p. 80-100°) - benzene gave crystals of the oxide (XIV), m.p. 149-50°. (Found: C, 73.2; H, 5.05; $C_{13}H_{11}OP$ requires: C, 72.9; H, 5.15%).

i.r. (mull): 1190 cm^{-1}(s) (P=O).

u.v. (95% ethanol): λ_{max} 229 mμ (ϵ = 23,890); 235 mμ (ϵ = 31,800); 243 mμ (ϵ = 32,800); 278 mμ (ϵ = 8093); 289 (ϵ = 7065); 323 mμ (ϵ = 1850).

p.m.r. (CDCl$_3$) p.p.m.: 2.2 Υ (multiplet, 8 aromatic protons); 8.08 Υ (doublet, J_{PCH} = 13.7 c/sec., 3 protons).

9-Hydroxymethyl-9-methyl-9-phosphafluorenonium chloride. (XVII; R = Me, X = OH, Y = Cl$^-$)

9-Methyl-9-phosphafluorene (0.5 g.), formaldehyde (37% aq.sol., 0.35 ml.) and concentrated hydrochloric acid (0.4 ml.) were shaken together for 15 min., when the mixture solidified to a white crystalline mass. The supernatant liquid was decanted and the residue triturated several times with dry ether and then recrystallised from isopropanol to give the salt (XVII; R = Me, X = OH, Y = Cl$^-$), m.p. 151-2°d. (Found: C, 63.3; H, 5.2; $C_{14}H_{14}ClOP$ requires C, 63.5; H, 5.35%).

p.m.r. (CF$_3$COOH) p.p.m.: 2.0Υ (multiplet, 8 aromatic protons); 4.91Υ (doublet, J_{PCH} = 1.1 c/sec, 2 methylene protons); 7.52 Υ (doublet, J_{PCH} = 15.0 c/sec, 3 methyl protons).

9-Chloromethyl-9-methyl-9-phosphafluorenonium chloride.

The hydroxymethyl salt (XVII; R = Me, X = OH, Y = Cl⁻) was dissolved in an excess of thionyl chloride and the solution heated under reflux for 1 hr. The excess of reagent was then removed and the residue triturated with dry ether to give the hygroscopic phosphonium chloride (XVII; R = Me, X = Cl, Y = Cl⁻).

p.m.r. (CDCl₃) p.p.m.: 0.9 � (multiplet, 2 aromatic protons);

4.07 Υ (doublet, J_{PCH} = 8.0 c/sec, 2 methylene protons);

6.81 Υ (doublet, J_{PCH} = 15.6 c/sec, 3 methyl protons).

(CF₃COOH) p.p.m.: 1.95 Υ (multiplet, 8 aromatic protons);

5.44 Υ (doublet, J_{PCH} = 7.4 c/sec, 2 methylene protons);

7.41 Υ (doublet, J_{PCH} = 14.9 c/sec, 3 methyl protons).

Satisfactory analytical values could not be obtained for the above salt (XVII; R = Me, X = Cl, Y = Cl⁻) and for characterization it was converted into the corresponding picrate, which after crystallisation from ethanol had m.p. 214°. (Found: C, 50.5; H, 3.05; N, 8.8; $C_{20}H_{15}ClN_3O_7P$ requires C, 50.5; H, 3.20; N, 8.85%).

9-Methoxymethyl-9-methyl-9-phosphafluorenonium chloride. (XVII; R = Me, X = OMe, Y = Cl⁻)

9-Methyl-9-phosphafluorene (0.5 g.) was dissolved in chloromethyl-methylether (5 ml.) and the mixture heated on a steam-bath for 1 hr. The solvents were evaporated and the residue triturated with dry ether to yield the salt (XVII; R = Me, X = OMe, Y = Cl⁻), m.p. 167-8° (0.63 g.; 90%). (Found: C, 63.9; H, 6.0; $C_{15}H_{16}ClOP$ requires C, 64.6; H, 5.7%).

p.m.r. (CDCl₃) p.p.m.: 1.0 Υ (multiplet, 2 aromatic protons);

2.0 Υ (multiplet, 6 aromatic protons); 4.40 Υ (doublet, J_{PCH} = 4.4 c/sec, 2 methylene protons); 6.44 Υ (singlet, 3 methyl protons); 7.05 Υ (doublet, J_{PCH} = 15.6 c/sec, 3 methyl protons).

(CF_3COOH) p.p.m.: 1.95 Υ (multiplet, 8 aromatic protons); 5.31 Υ (doublet, J_{PCH} = 4.8 c/sec, 2 methylene protons); 7.57 Υ (doublet, J_{PCH} = 15.0 c/sec, 3 methyl protons).

9-Hydroxymethyl-9-methyl-9-phosphafluorenonium bromide. (XVII; R = Me, X = OH, Y = Br^-)

The above salt (XVII, R = Me, X = OMe, Y = Cl^-) (0.26 g.) was dissolved in hydrobromic acid (50% aq. soln., 10 ml.) and the solution heated under reflux for 1 hr. After standing overnight, the excess of acid was removed by distillation under reduced pressure to give a glassy solid, purified by precipitation from chloroform solution by the addition of ethyl acetate to yield the salt (XVII, R = Me, X = OH, Y = Br^-), m.p. 170-3°. (Found: C, 54.3; H, 4.45; $C_{14}H_{14}BrOP$ requires C, 54.4; H, 4.55%).

p.m.r. ($CDCl_3$) p.p.m.: 1.3 Υ (multiplet, 2 aromatic protons); 2.1 Υ (multiplet, 6 aromatic protons); 4.74 Υ (singlet; 2 methylene protons); 7.15 Υ (doublet, J_{PCH} = 15.4 c/sec, 3 methyl protons).

CF_3COOH (ppm): 1.95 Υ (multiplet, 8 aromatic protons); 4.82 Υ (doublet, J_{PCH} = 1.1 c/sec, 2 methylene protons); 7.50 Υ (doublet, J_{PCH} = 15.0 c/sec, 3 methyl protons).

9-Iodomethyl-9-methyl-9-phosphafluorenonium iodide.   (XVII; R = Me,
X = I, Y = I$^-$)

    9-Methyl-9-phosphafluorene (0.5 g.) was dissolved in benzene (10 ml.
and methylene di-iodide (6 ml.), and the resulting solution heated on a
steam-bath for 1 hr. The solution was then cooled, and the crystals of the
crude salt filtered off. Evaporation of the mother-liquor gave a further
crop of crystals, which was combined with the initial crop and heated
with absolute ethanol (5 ml.) for 5 min. to remove soluble impurities and
give the salt (XVII, R = Me, X = I, Y = I$^-$), m.p. 234-5° (0.98 g., 83%).
A sample recrystallised several times from absolute ethanol had m.p. 235-6°.
(Found: C, 37.4; H, 3.1; $C_{14}H_{13}I_2P$ requires C, 37.7; H, 2.95%).

        p.m.r. (CF_3COOH) p.p.m.: 1.85 Υ (multiplet, 8 aromatic protons);

        5.94 Υ (doublet, J_{PCH} = 8.4 c/sec, 2 methylene protons);

        7.32 Υ (doublet, J_{PCH} = 14.8 c/sec, 3 methyl protons).

Salts of the type $Ph_3\overset{+}{P}CH_2X$ Y$^-$ derived from triphenylphosphine.

    The salts $Ph_3\overset{+}{P}CH_2OH$ Cl$^-$,[15] $Ph_3\overset{+}{P}CH_2OCH_3$ Cl$^-$,[24] $Ph_3\overset{+}{P}CH_2Cl$ Cl$^-$,[15]
$Ph_3\overset{+}{P}CH_2Br$ Br$^-$,[27] and $Ph_3\overset{+}{P}CH_2I$ I$^-$[34] were prepared and purified as described
in the literature. Melting points and infrared spectroscopic data were
identical with published values. Details of the p.m.r. spectra of the above
salts, for solutions in both $CDCl_3$ and CF_3COOH where possible, are recorded
in Table 1 in the Discussion (p. 76). In each case, the phenyl protons
occurred as complex multiplets in the region of 2 Υ and were not analysed
further.

Hydroxymethyltriphenylphosphonium bromide.

Methoxymethyltriphenylphosphonium chloride[24] (0.5 g.) was
heated under reflux for 90 min. with hydrobromic acid (50% aqueous soln.,
10 ml.). After standing overnight, the excess of acid was removed by
distillation under reduced pressure to yield a pale orange gum, which was
purified by precipitation from a chloroform solution by the addition of
ether to give hydroxymethyltriphenylphosphonium bromide, m.p. 193-5°
(cap. tube) (lit.[35] 203-5°). (Found: C, 60.9; H, 4.80; Calc. for
$C_{19}H_{18}BrOP$: C, 61.15; H, 4.85%). The i.r. and p.m.r. spectra were
identical with those for $Ph_3\overset{+}{P}CH_2OH$ Cl^-.[15]

Diethylaminophosphonous dichloride.

This was prepared in 67% yield from diethylamine and phosphorus
trichloride, as described by Issleib et. al.[36] (b.pt. 67°/12 mm.; lit.,[36]
b.p. 73-74°/13 mm.)

9-Diethylamino-9-phosphafluorene. (XIII)

A solution of 2,2'-dilithiobiphenyl (prepared from 2,2'-dibromo-
biphenyl (11.03 g.) and lithium foil (0.98 g.) in ether (150 ml.) was
added dropwise over 1 hr. to a solution of diethylaminophosphonous
dichloride (5.8 g., 0.95 mol.) in dry ether (50 ml.) at -10°, the reaction
mixture being stirred vigorously during the addition. The solution was
then allowed to warm to room temperature and was then heated under reflux
for 45 min. The solution was then cooled, filtered under nitrogen, and
evaporated to yield a viscous residue which on distillation under reduced
pressure in nitrogen gave 9-diethylamino-9-phosphafluorene (XIII), (2.05 g.,

23%), b.p. 130°/0.1 mm. (Found: C, 75.5; H, 7.05; N, 5.3; $C_{16}H_{18}NP$ requires C, 75.3; H, 7.05; N, 5.5%).

9-Diethylamino-9-methyl-9-phosphafluorenonium iodide (XII)

The aminophosphine (XIII) (0.14 g.) was allowed to stand at room temperature with an excess of methyl iodide for 3 hr. The excess of methyl iodide was then evaporated and the residue triturated with dry ether to give a hygroscopic solid, which resisted crystallisation from a variety of solvents.

> p.m.r. ($CDCl_3$) p.p.m.: 1.90 Υ (multiplet, 8 aromatic protons); 6.0 - 7.18 Υ (multiplet, 7 protons including a sharp doublet centered at 7.03 Υ (J_{PCH} = 12 c/sec) due to the methyl group attached to phosphorus); 8.78 Υ (multiplet, 6 protons).

Treatment of an aqueous solution of the salt (XII) with a cold, saturated aqueous solution of sodium picrate gave the corresponding picrate, which after recrystallisation from aqueous ethanol formed yellow crystals, m.p. 115°. (Found: C, 55.8; H, 4.25; N, 10.8; $C_{23}H_{23}N_4O_7P$ requires C, 55.4; H, 4.6; N, 11.2%). An aqueous solution of the salt (XII) rapidly became cloudy on standing, indicating that hydrolysis was occurring.

Alkaline hydrolyses of phosphonium salts.

(A) 9-Methyl-9-phenyl-9-phosphafluorenonium iodide (IX; R = Ph)

To a solution of the iodide (250 mg.) in 50% aqueous acetone (10 ml.) was added sodium hydroxide solution (30%, 1 ml.), and the resulting solution allowed to stand at room temperature for 24 hr. The

solution was then heated on a steam-bath for 5 min. and the excess of
alkali was then neutralised by dropwise addition of concentrated
hydrochloric acid. The resulting solution was then poured into water
(15 ml.) and extracted with chloroform (2 x 10 ml.). The dried chloroform
extract was then evaporated to yield a colourless, viscous residue (163 mg.).
Examination of the residue by t.l.c. showed it to contain one major
component: it gave the following spectroscopic data:

i.r. (mull), 1175 cm.$^{-1}$ (P = O);

u.v. (95% EtOH), λ_{max} 208 mμ (ϵ = 29,550), 274 mμ (ϵ = 2496);

p.m.r. (CDCl$_3$) p.p.m. 2.6Υ (multiplet, 14 protons); 8.35Υ

(doublet, J_{PCH} = 14 c/sec. 3 protons), in accord with
identification of the product as 2-biphenylylmethylphenylphosphine oxide
(X; R = Ph). The residue resisted crystallisation from a variety of
solvents, and could not be purified satisfactorily by sublimation, or by
column chromatography. It was therefore converted into the cobalt(II)
chloride complex by the procedure due to Pickard and Kenyon.[37] The complex
was purified by precipitation from a benzene solution by the addition of
light petroleum (b.p. 60 - 80°) to yield a blue solid, dichlorobis(2-biphenyl-
ylmethylphenylphosphine oxide) cobalt, m.p. 68 - 70°. (Found: C, 63.5;
H, 4.5. C$_{38}$H$_{34}$O$_2$Cl$_2$P$_2$Co requires C, 63.9; H, 4.75%).

(B) 9,9'-Dimethyl-9-phosphafluorenonium iodide (IX; R = Me)

The iodide (250 mg.), prepared as described in Part I of this
thesis, was hydrolysed and the product extracted with chloroform as described
above. Evaporation of the dried chloroform extract gave a colourless oil,

which crystallised on standing to give the hygroscopic <u>2-biphenylyldi-</u>
<u>methylphosphine oxide</u> m.p. 92 - 93° (156 mg.). (Found: C, 72.7; H, 6.0.
$C_{14}H_{15}OP$ requires: C, 73.05; H, 6.5%).

Examination of the product by t.l.c. showed it to be a pure
compound. It gave the following spectroscopic data:

i.r. (mull), 1160 cm.$^{-1}$ (P = O);

u.v. (95% ethanol), λ_{max} 210 mµ (ε = 22,320), 235 mµ (shoulder)

(ε = 5860), 275 mµ (ε = 1862);

p.m.r. (CDCl$_3$) p.p.m., 1.75 Υ (multiplet, 1 proton); 2.5 Υ

(multiplet, 8 protons) 8.58 Υ (doublet, J_{PCH} = 14 c.p.s., 6 protons).

(C) <u>9-Hydroxymethyl-9-methyl-9-phosphafluorenonium bromide</u> (XVII; R = CH$_3$,
X = OH, Y = Br$^-$)

The salt (0.167 g.) was dissolved in aqueous acetone (50%),
(10 ml.) containing potassium hydroxide solution (30% aq., 0.15 ml.), and
the resulting mixture heated under reflux for 2 hr. The acetone was then
removed by distillation and the residual solution neutralised and extracted
with chloroform (2 x 10 ml.). The chloroform extract was dried over
soxium sulphate and evaporated to give an oil (0.135 g.). Examination of
the extract by t.l.c. (Silica-gel, ethyl acetate) showed it to contain
two components, which were separated by column chromatography on silica-gel
(6 g.). Elution with ethyl acetate gave 9-methyl-9-phosphafluorene
(IV; R = Me) (60 mgs.), characterized by conversion to the methiodide
(m.p. and mixed m.p. 280°) and methopicrate (m.p. and mixed m.p. 218°).
Elution with absolute ethanol then gave <u>9-methyl-9-phosphafluorene-9-oxide</u>
(XIV; R = Me) (20 mgs.), identical with authentic material obtained by

direct oxidation of 9-methyl-9-phosphafluorene with hydrogen peroxide in acetone.

(D) 9-Methoxymethyl-9-methyl-9-phosphafluorenonium chloride. (XVII; R = Me, X = OMe, Y = Cl$^-$)

The salt (250 mg.) was hydrolysed and the product extracted with chloroform as described above. Evaporation of the dried chloroform extract gave a colourless oil, which crystallised on standing to give 2-biphenylylmethoxymethylmethylphosphine oxide (X; R = MeOCH$_2$), m.p. 84-5° (230 mg.). (Found: C, 69.4; H, 6.55; C$_{15}$H$_{17}$O$_2$P requires C, 69.25; H, 6.55%).

i.r. (thin film): 1178 cm^{-1} (s) (P = O); 1110 cm^{-1} (s) (C - O).

u.v. (95% ethanol) λ_{max}: 213 mμ (ε = 21,410); 240 mμ (ε = 6,661) (sh.); 277 mμ (ε = 2,379).

p.m.r. (CDCl$_3$) p.p.m.: 1.8 Υ (multiplet, 1 proton); 2.46 Υ (multiplet, 8 aromatic protons); 6.4 Υ (doublet, J$_{PCH}$ = 5.3 c/sec, 2 methylene protons); 6.62 Υ (singlet, 3 methyl protons); 8.55 Υ (doublet, J$_{PCH}$ = 13.4 c/sec, 3 methyl protons).

(E) 9-Iodomethyl-9-methyl-9-phosphafluorenonium iodide (XVII; R = Me, X = I, Y = I$^-$)

The salt (0.7 g.) was hydrolysed and the products extracted with chloroform as described above. Examination of the dried chloroform extract by t.l.c. (silica-gel, ethyl acetate) showed it to contain one major and several minor components. Column chromatography on silica-gel (10 g.) gave,

on elution with ethyl acetate - ethanol (70:30), 9-methyl-9,10-dihydro-9-phosphaphenanthrene-9-oxide (XIX; R = Me) (0.24 g. 71%) as a viscous gum, which resisted crystallisation from a variety of solvents. It was purified further by preparative scale t.l.c. (Kieselgel P.F. 254, 1.5 mm. thickness, ethyl acetate x 6) to give the oxide (XIX; R = Me) as a hygroscopic gum. (Found: C, 73.2; H, 5.7. $C_{14}H_{13}OP$ requires C, 73.7; H, 5.7%).

i.r. (thin film): 1190 cm^{-1} (s) (P=O).

u.v. (95% ethanol), λ_{max}: 215 mμ (ϵ = 28,950); 228 mμ (ϵ = 11,990) (sh); 267 mμ (ϵ = 11,980); 281 mμ (ϵ = 7,236) (sh).

p.m.r. ($CDCl_3$) p.p.m.: 2.2 Υ (multiplet, 8 aromatic protons); 6.5 Υ (multiplet, J_{AB} = 16.3 c/sec, 2 benzylic protons); 8.53 Υ (doublet, J_{PCH} = 13.5 c/sec, 3 methyl protons).

(F) 9-Iodomethyl-9-phenyl-9-phosphafluorenonium iodide (XVII; R = Ph, X = I, Y = I^-)

The iodide (0.28 g.) was hydrolysed and the product extracted with chloroform as described above. Examination of the dried extract by t.l.c. (silica-gel, ethyl acetate) showed it to contain several components. Initial separation of polar and non-polar products was achieved by column-chromatography on silica-gel (7 g.). Elution with ethyl acetate gave 9-phenyl-9-phosphafluorene (IV; R = Ph) (27 mgs.). Elution with ethyl acetate - ethanol (80:20) gave a viscous gum (130 mg.) which by t.l.c. was shown to contain one major and one minor component. Preparative scale t.l.c. (Kieselgel P.F. 254, 1.5 mm., ethyl acetate x 4) gave 9-phenyl-9-phosphafluorene-9-oxide (XXIII; R = Ph) (10 mg.), identical with authentic

material, and 9-phenyl-9,10-dihydro-9-phosphaphenanthrene-9-oxide (XIX; R = Ph), m.p. 127-30° (89 mg., 58%). (Found: C, 78.6; H, 5.15; $C_{19}H_{15}OP$ requires C, 78.65; H, 5.15%).

i.r. (thin film): 1197 cm^{-1} (s) (P=O)

u.v. (95% ethanol) λ_{max}: 213 mµ (ϵ = 34,580); 271 mµ (ϵ = 11,600); 286 mµ (ϵ = 6,960).

p.m.r. (CDCl$_3$) p.p.m.: 2.3Υ (multiplet, 13 aromatic protons); 6.3Υ (multiplet, J_{AB} = 16.3 c/sec, 2 benzylic protons).

(G) 9-Di ethylamino-9-methyl-9-phosphafluorenonium iodide (XII)

The iodide (XII) (0.4 g.) was hydrolysed and the product extracted with chloroform as described above. Column chromatography of the dried chloroform extract on silica-gel gave, on elution with ethanol, 9-methyl-9-phosphafluorene-9-oxide (XIV) (100 mg.) which on recrystallisation from petroleum (b.p. 100-120°) - benzene mixture gave crystals, m.p. 148-50°, undepressed on mixing with authentic material obtained by direct oxidation of 9-methyl-9-phosphafluorene.

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Five-co-ordinate Complexes of 9-Substituted-9-
phosphafluorenes with some Group VIII Transition
Metal Halides.

The ability of tertiary phosphines to form four-co-ordinate
complexes of the type $(R_3P)_2MX_2$ with the halides of the d^8 divalent
transition metals nickel, palladium and platinum is well known.[1] Two
distinct classes of four-co-ordinate nickel(II) complexes of the above
type have been recognised. Trialkylphosphines generally form red-brown,
diamagnetic complexes which have been shown to have a square-planar
structure with the phosphine ligands trans to each other, resulting in a
zero dipole moment for the complex.[2,3,4] Triarylphosphines form a series
of complexes $(Ar_3P)_2MX_2$ which are generally blue-green to dark brown in
colour and which are paramagnetic with a magnetic moment which corresponds
to two unpaired electrons. Such complexes have been shown to possess a
distorted tetrahedral structure.[5,6] Certain diphenylalkylphosphines form
complexes $(Ar_2PAlk)_2MX_2$ which exist in both square-planar (diamagnetic) and
tetrahedral (paramagnetic) forms.[7,8,9]

Tertiary phosphines with palladium(II) halides form the diamagnetic
trans square-planar complexes, $(R_3P)_2PdX_2$, which are yellow in colour and
are readily crystallised, having a well-defined melting-point. In the
presence of an excess of the palladium salt, more deeply coloured planar

bridged complexes of type I (X = halogen) are formed. Of the several geometrical isomers, the form below predominates in solution.[1]

$$
\begin{array}{c}
R_3P \diagdown \qquad \diagup X \diagdown \qquad \diagup X \\
\mathrm{Pd} \qquad \mathrm{Pd} \\
X \diagup \qquad \diagdown X \diagup \qquad \diagdown PR_3
\end{array}
$$
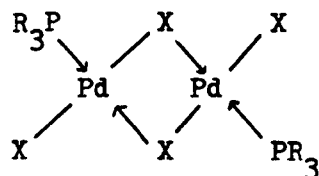
(I)

With platinum(II) halides, tertiary phosphines form diamagnetic square-planar complexes of the type $(R_3P)_2PtX_2$; mixtures of the <u>cis</u> and <u>trans</u> isomers are usually produced. Bridged binuclear platinum complexes similar to those of palladium are also known.[1]

Cobalt(II) halides with tertiary phosphines form a series of blue complexes of the type $(R_3P)_2CoX_2$ which have a high dipole moment and are paramagnetic, with a magnetic moment corresponding to the three unpaired electrons of a tetrahedral d^7 metal complex. (A square-planar d^7 complex would have only one unpaired electron.)

The 9-alkyl-9-phosphafluorenes (II, R = Me, Et), however, have been found to behave abnormally with the above transition metal halides in giving a series of apparently five-co-ordinate tris(phosphine) derivatives of type (III) under conditions where the normal four-co-ordinate complexes might be expected to be formed. Similar behaviour has been observed previously in the formation of complexes of type (III) from the heterocyclic phosphine, 2-phenylisophosphindoline (IV).[10,11]
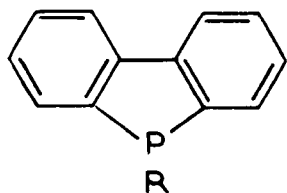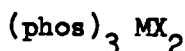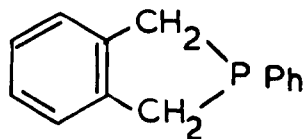
(II)   (III)   (IV)

At the present time, considerable interest is displayed in the preparation and characterization of stable, five-co-ordinate complexes of the d^7 and d^8 transition elements. Many such complexes are now known and the subject of penta-co-ordination has been reviewed.[12] In recent years, numerous stable five-co-ordinate complexes of cobalt(II), nickel(II), palladium(II) and platinum(II) have been prepared using 'umbrella-type' polydentate ligands such as $P(\underline{o}\text{-}C_6H_4PPh_2)_3$,[13] $As(\underline{o}\text{-}C_6H_4AsPh_2)_3$,[14,15] $P(\underline{o}\text{-}C_6H_4SCH_3)_3$,[16] and $P(\underline{o}\text{-}C_6H_4SeCH_3)_3$.[17]

However, apart from 2-phenylisophosphindoline (IV) relatively few simple monodentate ligands capable of stabilising the five-co-ordinate state in complexes of type (III) are known. It has been reported[18,19] that diphenylphosphine forms a series of complexes of type (III) (phos = Ph_2PH; M = Co(II), Ni(II) and Pd(II); X = halogen). Recent X-ray work[20] has confirmed that these complexes are five-co-ordinate in the solid state. In solution, however, they undergo dissociation to the ionic species $\left[(Ph_2PH)_3MX \right]^+ X^-$.

Recently, systematic studies have been made of the tendency of four-co-ordinate complexes of the type $(R_3P)_2MX_2$ (M = Co(II), Ni(II);

X = halogen, NCO, NCS, CN) to add a third molecule of a tertiary phosphine to give a complex of type (III). It has been shown that the tris(phosphine) complexes $(R_3P)_3 CoX_2$ (R = alkyl or aryl) are thermodynamically unstable when X = Cl, Br, or NCO, but are easily formed in solution by the addition of the phosphine, R_3P, to the four-co-ordinated complex $(R_3P)_2 CoX_2$ when X = NCS. In two cases, $(Pr_3P)_3Co(NCS)_2$ and $(PhPEt_2)_3 Co(NCS)_2$, the five-co-ordinate complexes were isolated in the solid state.[21] Similarly, the reaction of the complexes <u>trans</u> $(R_3P)_2Ni(CN)_2$ with the corresponding phosphine gives in solution the stable five-co-ordinate complexes as shown by the visible spectra. In addition, the complex $(PhPEt_2)_3Ni(CN)_2$ has been obtained in the solid state.[22]

A few other isolated examples of complexes of type (III) have been described; they include $(PhPEt_2)_3Ni(C\equiv C.Ph)_2$,[23] $(Ph_3P)_3Ni(CN)_2$,[24] $(PhP(OEt)_2)_3Ni(CN)_2$,[25] $(Ph_2PMe)_3PdBr_2$,[18] and $(PhPEt_2)_3PdCl_2$.[1] The heterocyclic tertiary phosphines, 2-phenylisophosphindoline (IV) and the 9-alkyl-9-phosphafluorenes (II, R = Me, Et), therefore seem to be remarkable in their capacity to form a series of complexes of type (III) which are stable in the solid state.

There are two idealised configurations that can be adopted by five-co-ordinate complexes; the trigonal bipyramid and the tetragonal or square pyramid, (Fig. 1). It has also been pointed out that when all five ligands are not the same, the complex can exist in several isomeric forms, each form based on either of the two idealised geometries.[12] For example, for a five-co-ordinate complex of the type L_3MX_2 there are three possible isomers in trigonal bipyramidal geometry, and for each of these there is a

closely related isomer in square pyramidal geometry.

and other geometrical isomers

Fig. (1)

Although the crystal structures of a number of five-co-ordinate transition metal complexes are known, the factors responsible for the preferred adoption of either a trigonal bipyramidal or a square pyramidal geometry are not fully understood. The following factors have been suggested by various authors: (a) repulsions between bonding electron pairs,[26] (b) π-bonding requirements of the ligands,[27] (c) ligand-field stabilisation effects,[27] (d) the steric requirements of the ligands,[28] and (e) the packing requirements in the crystal.[29] The relative importance of these factors in determining geometry is difficult to estimate, but for d^7 and d^8 transition elements it has been pointed out that all the above factors may be important.[29] Blundell and Powell[29] have recently suggested that for the five-co-ordinate complexes of the d^8 transition elements, a square pyramidal structure will be preferred to a trigonal bipyramidal structure in the absence of special steric requirements of the ligands or very strongly π-bonding ligands, due to the importance of the ligand-field

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stabilisation energy for the d^8 configuration where it is greater for the square pyramidal geometry.[27]

Thus the complexes (triars)$NiBr_2$ (where triars = methylbis(3-dimethylarsinopropyl)arsine)[30] and the red form of the 2-phenylisophosphindolin complex of palladium bromide of type (III)[10] both have a distorted square pyramidal structure, with all three arsenic or phosphorus atoms in the basal plane, which also contains the metal atom. One bromine atom is slightly depressed from the plane of the metal and the arsenic or phosphorus atoms, the other bromine occupying the apical position. (Fig. 2) In each case, the apical metal-bromine distance is significantly longer than the basal metal-bromine distance. A distortion of the geometry so that the metal atom is above the plane of the four ligand atoms, as has been demonstrated for many square pyramidal complexes,[12] would decrease electron-pair repulsions at the expense of the ligand-field stabilisation energy. In the case of the above d^8 complexes, it would therefore appear that the electron-pair repulsions are less important and that the ligand-field stabilisation energy is more important in determining the stereochemistry. Steric repulsions between the ligands may be responsible for the slight distortion of the bromine atoms from the basal plane in the above complexes.
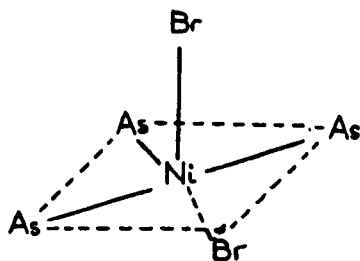
Structure of (Triars)$NiBr_2$.

Fig. (2)

Due to their steric requirements, tripod-like polydentate ligands of the type $As(\underline{o}\text{-}C_6H_4AsPh_2)_3$, ($\equiv$ QAS) result in the formation of trigonal bipyramidal complexes.[13-17] Thus the complex ion $\left[QASPtI\right]^+$ has been shown to have a trigonal bipyramidal structure with the iodine atom occupying one apical position.[28] (Fig. 3)
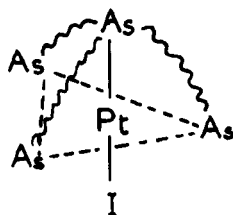
Structure of $\left[(QAS)Pt\ I\right]^+$

Fig. (3)

It has also been suggested[29] that the strong π-bonding present in the Pt-Sn bonds in the complex ion $Pt(SnCl_3)_5^{3-}$, together with the bulkiness of the ligands, is responsible for the observed trigonal bipyramidal structure of the ion, due to increased repulsions between the various bonds and the ligands.

The preference for square pyramidal co-ordination in d^8 complexes has been demonstrated further in a recent structure determination.[29] The tetradentate ligand $\underline{o}$-phenylenebis($\underline{o}$-dimethylarsinophenylmethylarsine) ($\equiv$ TPAS), which could co-ordinate to give either a trigonal bipyramidal or square pyramidal complex, gives the complex ion $\left[TPAS\ Pd\ Cl\right]^+$ which was shown to have a square pyramidal structure, the palladium, chlorine, and three arsenic atoms lying in the basal plane, with the remaining arsenic

atom in the apical position.

Addition of a hot, ethanolic, solution of the metal halide (1 mol.) to a hot ethanolic solution of the 9-alkyl-9-phosphafluorene (II, R = Me or Et) (3 mols.), under nitrogen, results in the immediate formation of an intensely coloured solution which rapidly deposits deeply coloured crystals of the appropriate complex. The nickel complexes of type (III) (M = Ni(II); X = Cl, Br, I, NCS; phos = 9-methyl- or 9-ethyl-9-phosphafluorene) are olive-green or almost black solids, soluble in organic solvents to yield dark green solutions, some of which on heating in the absence of air and water become red-brown, indicating probable dissociation to a four-co-ordinate species. On cooling, the colour changes are reversed. Molecular weight determinations in solution in methylene dichloride at 30° indicate that the complexes are dissociated to some extent in solution, presumably into either the ionic species $\left[(\text{phos})_3 \text{NiX}\right]^+ \text{X}^-$, or into $(\text{phos})_2 \text{NiX}_2$ and free phosphine. Solutions of the complexes in nitrobenzene show only a negligible conductivity, thus excluding the former mode of dissociation in this solvent. Addition of the complexes to hot benzene gives a deep red solution from which, in certain cases, crystals of the "normal" four-co-ordinate complex of the type $(\text{phos})_2 \text{NiX}_2$ may be obtained on dilution with light petroleum. Attempts to synthesise the "normal" four-co-ordinate complexes by addition of the phosphine (2 mols.) to the nickel halide (1 mol.) in ethanol produces the olive-green tris(phosphine) complexes. The complexes of type (III), in solution, are rapidly destroyed on addition of water.

The spectroscopic and magnetic properties of the nickel(II) complexes of type (III) are of interest in that they are somewhat different

from those of other five-co-ordinate nickel(II) complexes. These properties,
however, do not resemble those of the nickel(II) complexes with the more
common co-ordination numbers of four and six. The ligand-field splitting
diagrams for the d orbitals of a transition metal ion in both square
pyramidal and trigonal bipyramidal complexes are shown in figure (4). The
eight d electrons of a nickel(II) ion may be distributed among the d levels
as shown, indicating that for each configuration both diamagnetic (spin-
paired) and paramagnetic (spin-free, high spin) complexes could occur,
depending on the strength of the ligand-field (i.e. the capacity of the ·
ligands to promote spin-pairing).

Both paramagnetic and diamagnetic five-co-ordinate complexes of
nickel(II) of both configurations have been observed. The majority of
five-co-ordinate nickel(II) complexes are diamagnetic, and usually contain
ligand atoms such as phosphorus, arsenic, sulphur and selenium, which are
polarizable and capable of forming strong covalent bonds with the metal
ion. Such atoms also possess vacant d orbitals of favourable energy
which may be involved in π-bonding with the metal, thus helping to promote
spin-pairing in the complex.[13-17] Recently, however, a few high-spin
five-co-ordinate complexes of nickel(II) have been reported, in which the
ligand donor atoms are the electronegative oxygen or nitrogen, which show
little tendency to be involved in π-bonding with the metal. Thus polydentate
ligands such as the N-substituted salicylaldimines[31] and aliphatic polyamines
with bulky terminal groups,[32] and the monodentate ligand diphenylmethylarsine
oxide[33] have given examples of high-spin five-co-ordinate nickel(II)
complexes of both stereochemistries. Furthermore, the tridentate ligand
di(2-pyridyl-β-ethyl)sulphide (in which the donor atoms have the ability to

Ligand-field Splitting Diagram for Five-co-ordinate d^8 Complexes
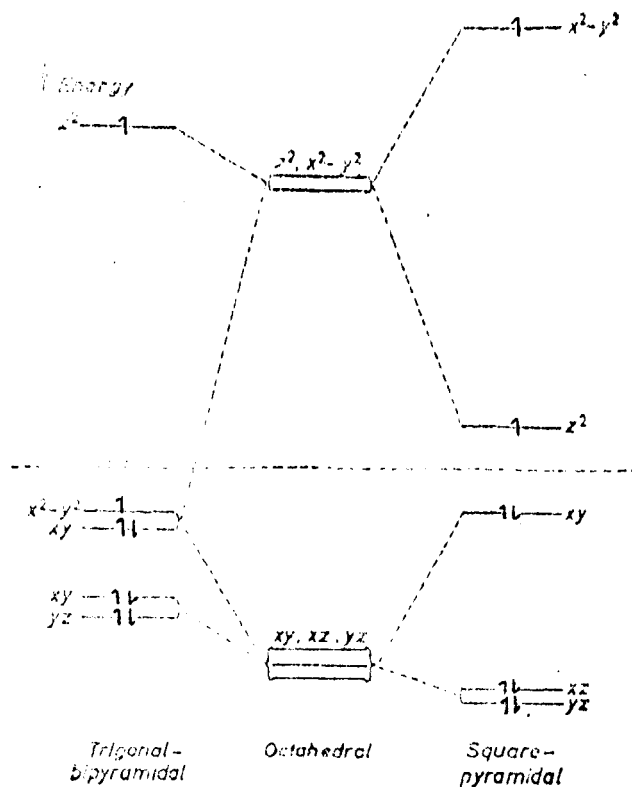
High Spin (low ligand-field)
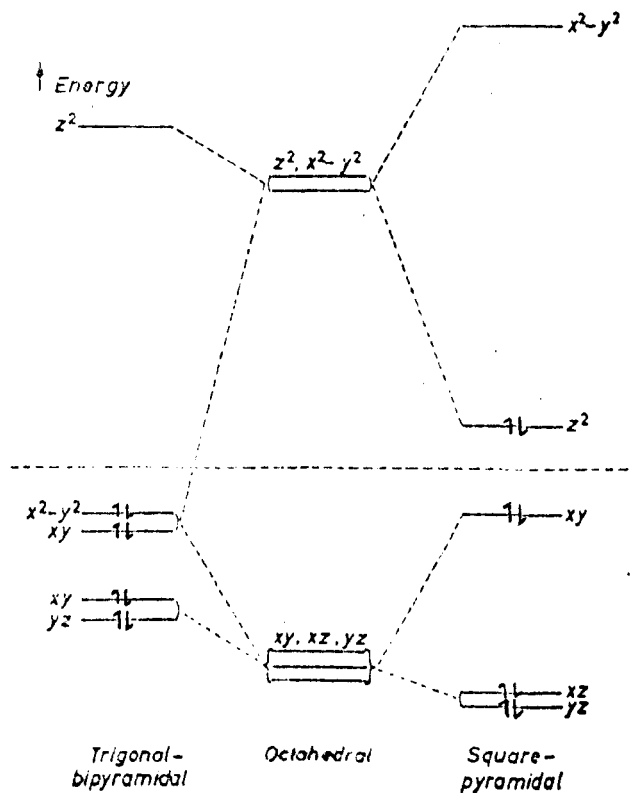
Low Spin (high ligand-field)

Fig. 4

participate in π-bonding with the metal) has given a high-spin five-co-ordinate nickel(II) complex.[34] Such complexes have magnetic moments in the range 3.1 - 3.4 B.M., corresponding to the two unpaired electrons of high-spin nickel(II).

The nickel complexes of type (III)(M = Ni(II); X = Cl, Br, I, NCS; phos = 9-methyl- or 9-ethyl-9-phosphafluorene) are unusual in that they possess magnetic moments in the range from 0.65 - 1.50 B.M., (Table 1), values which are intermediate between those of the low-spin and high-spin complexes discussed above. (During the determination of the magnetic susceptibilities by the Faraday method, it was noted[35] that the complexes appeared to lose weight, suggesting gradual loss of phosphine. However, this appears unlikely since these nickel complexes are unchanged after heating for several hours at 80° under high vacuum. In view of the known instability of the complexes to water, the apparent weight loss may be due to displacement of phosphine by atmospheric water vapour). A comparable magnetic moment has also been reported for the complex $(Ph_2PH)_3NiI_2$ for which μ_{eff} = 1.48 B.M. but no suggestion as to the origin of the observed moment was offered.[18]

Table 1.

Magnetic Moments of the Five-co-ordinate Complexes of the
9-Alkyl-9-phosphafluorenes with Nickel(II) Salts.
(9-Me. P.F. = 9-methyl-9-phosphafluorene; 9-Et.P.F. =
9-ethyl-9-phosphafluorene).

Complex	Magnetic Moment, $\mu_{eff.}$,B.M.
$(9\text{-Me.P.F.})_3NiCl_2$	0.88
$(9\text{-Me.P.F.})_3NiBr_2$	0.98
$(9\text{-Me.P.F.})_3NiI_2$	1.50
$(9\text{-Me.P.F.})_3Ni(NCS)_2$	1.20
$(9\text{-Et.P.F.})_3NiCl_2$	0.90
$(9\text{-Et.P.F.})_3NiBr_2$	0.75
$(9\text{-Et.P.F.})_3NiI_2$	0.65
$(9\text{-Et.P.F.})_3Ni(NCS)_2$	0.95
$(9\text{-Me.P.F.})_3Ni(CN)_2$	0.46
$(9\text{-Et.P.F.})_3Ni(CN)_2$	0.42

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Recently, Ciampolini has calculated the splitting of the free ion terms of nickel(II) for five equivalent point dipoles situated 2.0 Å from the metal ion in both square pyramidal and trigonal bipyramidal fields.[36] It was shown that the high-spin form predominates over the low-spin form for the ground states of both geometries for donor dipole strengths from zero to 8D, the "cross-over point" (from high- to low-spin form) therefore occurring only for much higher ligand field strengths. It has been suggested by Ciampolini that the formation of the diamagnetic five-co-ordinate nickel(II) complexes from polydentate ligands containing phosphorus or arsenic donor atoms must be due to the promotion of spin-pairing by extensive π-bonding between the ligand atoms and the metal, since the ligand field of such donors cannot be reasonably expected to be very much greater than for the Schiffs-base ligands which give high-spin complexes. However, Livingstone[37] has pointed out that the effective dipole moments of polarizable ligand atoms can be increased considerably above the permanent dipole value because of an additional induced dipole moment, which is directly proportional to the polarizability. Other factors have also been shown to be of importance in determining the energy separation between the high-spin and low-spin states.[36] Spin-pairing in a trigonal bipyramidal complex is favoured by an increase in the axial field strength, whereas the converse is true for a square pyramidal complex. Furthermore, in the latter, spin-pairing is made less favourable by structural distortions due to ligand repulsions which lead to an increase in the angle between the axial ligand, the metal atom and the ligand atoms in the basal plane.

The 'intermediate' magnetic moments of the nickel(II) halide and thiocyanate complexes of the 9-alkyl-9-phosphafluorenes appear to indicate that the energy gap between the high- and low-spin states is quite small, thus making possible a thermal equilibrium between the two states. This situation could be due to the ligand-field strength of the 9-alkyl-phosphafluorenes being intermediate between that of the polydentate phosphines or arsines and the polydentate nitrogen donors, so that the resulting complexes are at the 'cross-over point' between high- and low-spin forms. Alternatively, if as suggested by Blundell and Powell[29] the square pyramidal structure is favoured on ligand-field stabilisation grounds for such complexes, then distortions from this state due to repulsions between the bulky ligands around the relatively small nickel atom would lower the energy gap between the two spin states, as shown by Ciampolini,[36] and give rise to the thermal equilibrium in the electronic distribution.

In this connection it is of interest to recall the properties of the complexes $(Ph_2PH)_3 NiX_2$ (X = Cl, Br, I).[18] In this series, the chloro and bromo complexes are essentially diamagnetic whereas the iodo complex has μ_{eff} = 1.48 B.M. These complexes have recently been reinvestigated by Bertrand and Plymale[20] whose X-ray studies on the bromo and iodo complexes showed them to have a structure which is intermediate between a trigonal bipyramid and a square pyramid, indicating considerable distortion from the ideal states. The intermediate value of the magnetic moment of the iodo complex was also accounted for on the basis of a thermal equilibrium between the two close-lying spin states. The diamagnetism of the chloro and bromo complexes was attributed to the greater ligand-field of chlorine

and bromine as opposed to that of iodine, the ligand-field of the halogens increasing in the order I<Br<Cl.[38] The paramagnetism of all of the nickel(II) halide and thiocyanate complexes of the 9-alkyl-9-phosphafluorenes would seem to indicate that the ligand-fields of the latter are less than that of diphenylphosphine.

The existence of such a thermal equilibrium in the electronic distribution in complexes of the above type should be revealed by a study of the temperature-dependence of the magnetic susceptibility, which for these compounds would not be expected to follow the Curie-Weiss law,[39] and which would yield values of the magnetic moment, μ_{eff}, tending toward those of high-spin complexes as the temperature is raised or towards those of low-spin complexes as the temperature is lowered. Such a study has been carried out on the complex of 9-methyl-9-phosphafluorene with nickel(II) iodide. At 300°K, the complex has μ_{eff} = 1.50 B.M. On lowering the temperature to 293°K, the moment drops to 0.70 B.M.; further lowering of the temperature to 93°K reduces the moment to 0.66 B.M. The magnetic properties of this complex are therefore unusual and support the above suggestion of a thermal equilibrium between the two spin states.

The importance of ligand-field effects on the electron distribution in the above type of five-co-ordinate complex is further revealed by the properties of the complexes of the 9-alkyl-9-phosphafluorenes with nickel(II) cyanide. These complexes (of type III; phos = 9-methyl or 9-ethyl-9-phosphafluorene; M = Ni(II); X = CN) are prepared by heating a suspension of freshly prepared hydrated nickel(II) cyanide in an ethanolic solution of the phosphine (3 mols.), the nickel cyanide dissolving to yield

a deep red solution from which red-purple crystals of the cyanide complexes separate on standing. Determination of the molecular weights of the cyanide complexes in solution in methylene dichloride indicates that the 9-methyl-9-phosphafluorene complex does not dissociate to any noticeable extent whereas the corresponding complex of 9-ethyl-9-phosphafluorene is slightly dissociated. Both cyanide complexes are essentially diamagnetic, the spin-paired state being stabilised by the greater ligand-field of the cyanide ligands.[38] These complexes therefore resemble other tris(phosphine) complexes of nickel cyanide, all of which have been reported to be diamagnetic and more stable than the corresponding halide complexes.[22,24,25].

The spectroscopic properties of the five-co-ordinate nickel(II) complexes have also been examined. All of the paramagnetic complexes in the solid state have very similar visible and near-infrared absorption spectra, which exhibit bands in the regions of 12,000 - 14,000; 23,000; 30,500 and 35,000 cm^{-1}, more intense absorption occurring at higher energies. In the position and relative intensity of the low-energy bands, the spectra of the above complexes resemble that of the high-spin five-co-ordinate nickel(II) complex of di(2-pyridyl-β-ethyl)sulphide, reported recently.[34] The complexes of diphenylphosphine with nickel(II) also show an absorption band in the 13,000 cm^{-1} region. The spectra differ markedly from those of the trigonal bipyramidal low-spin complexes of polydentate phosphines and arsines which have a characteristic absorption band in the 16,000 cm^{-1} region.[13-17] The positions of the low-energy bands in the mull spectra of

the nickel(II) halide complexes of 9-ethyl-9-phosphafluorene are shown in table 2, the position of the band in the 23,000 cm^{-1} region being sensitive to the nature of the halogen and moving to lower frequencies in the order Cl→Br→I.

Table 2.

Mull Spectra of the Nickel(II) Halide Complexes of
9-Ethyl-9-phosphafluorene, $(9-Et.P.F)_3NiX_2$

Complex	$\lambda_{max.}$, cm^{-1}
$(9-Et.P.F.)_3NiCl_2$	11,800; 24,250
$(9-Et.P.F.)_3NiBr_2$	11,800; 23,050
$(9-Et.P.F.)_3NiI_2$	12,500; 19,000

Solution spectra of the five-co-ordinate nickel(II) halide complexes have been found to be dependent upon the nature of the solvent, the concentration, and the temperature.[35] At high concentrations of the 9-ethyl-9-phosphafluorene - nickel halide complexes in methylene dichloride, three absorption bands are observed in the near infrared at ˜12,500; 14,000; and ˜15,000 cm^{-1}, the position of the bands being slightly sensitive to the nature of the halogen and moving to lower frequencies from chlorine to bromine to iodine. In addition there is also a two-band system in the visible at about 18,000 - 20,000 cm^{-1}, and a very intense band in the near ultraviolet at about 24,000 - 25,000 cm^{-1}. As the concentration is lowered,

the middle band of the three near infrared bands reduces considerably in intensity compared with the other two which move to slightly higher frequencies. The two-band structure in the visible does not appear to alter appreciably on dilution. On the other hand, on lowering the temperature similar behaviour is seen for the near infrared bands although the two outer bands also increase considerably in intensity, but the pattern in the visible is considerably altered as the two-band system disappears and a new band appears at about $15,000 - 15,600 \text{ cm}^{-1}$ depending upon the nature of the halogen. At the same time, the colour of the solution changes from red to green, and the above pattern can be reversed by raising the temperature. The spectra in benzene closely resemble the low temperature spectra in methylene chloride. The above spectra do not compare well with the solid state mull spectra, which suggests that the structure of the complexes in the solid state must be somewhat different from that in solution. Furthermore, the complexity of the solution spectra would seem to indicate the existence of a rather complex equilibrium, which probably involves a square planar complex, a five-co-ordinate complex, and a tetrahedral complex. It seems that at low concentrations in methylene dichloride, there is considerable dissociation, the predominant species being square planar, but with smaller amounts of the tetrahedral and five-co-ordinate species. On lowering the temperature, the five-co-ordinate species becomes more predominant and very little of the tetrahedral and square planar species is present. The dissociation observed in solution in the molecular weight determinations is thus confirmed by the above spectroscopic data.

The spectra of the diamagnetic nickel(II) cyanide complexes differ considerably from those of the halide and thiocyanate complexes described above. The complex of 9-methyl-9-phosphafluorene with nickel(II) cyanide in the solid state exhibits absorption bands at 18,750 (shoulder); 27,000; 31,200; and 35,500 cm^{-1}, whereas the corresponding complex of 9-ethyl-9-phosphafluorene exhibits bands at 23,000; 30,500; and 35,000 cm^{-1}. The spectrum of the latter resembles the spectrum of the complex $(PhPEt_2)_3Ni(CN)_2$.[22] However, in solution in methylene dichloride, both of the 9-alkyl-9-phosphafluorene complexes of nickel(II) cyanide are identical in having an absorption band at ~24,000 cm^{-1} (ε ~3,200) the intensity of which increases on addition of the appropriate phosphine to the solution, thus indicating some degree of dissociation at the low concentrations employed for the determination of the spectra. The spectra of the two complexes in the solid state suggests a different structure for each, the two probably becoming very similar in solution when restrictions imposed by the lattice are removed. The infrared spectra of the solid complexes have given further support to this view. The infrared spectrum of the complex of 9-methyl-9-phosphafluorene in the C≡N stretching region is complex, consisting of three sharp absorptions of unequal intensity at 2118, 2108, and 2102 cm^{-1}, whereas that of the corresponding complex of 9-ethyl-9-phosphafluorene consists of one sharp absorption at 2118 cm^{-1}. Assuming a basic square pyramidal geometry on the grounds of a greater ligand-field stabilisation energy for this structure, the two complexes could have the structures shown below. (Fig. 5) It is suggested that in the case of the complex of 9-methyl-9-phosphafluorene, one cyanide ligand

occupies the apical position and one is in the basal plane, whereas in the 9-ethyl-9-phosphafluorene complex both cyanide ligands are in the basal plane and probably trans to each other. The crystal structures of the two nickel cyanide complexes are being studied by X-ray diffraction methods by Dr. H.M. Powell (Oxford).
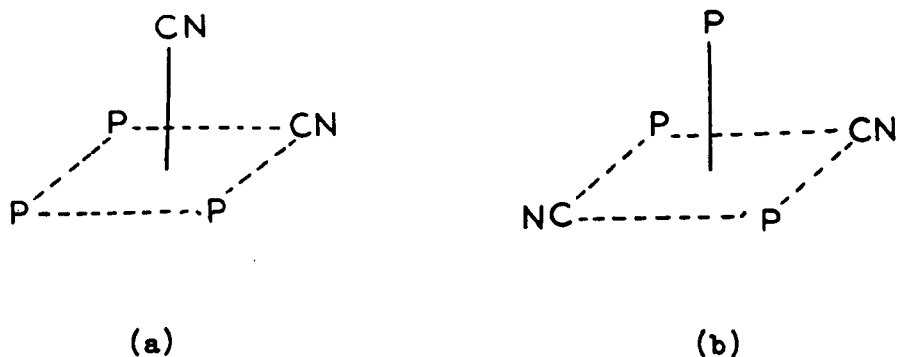
Proposed structures of the complexes of the 9-alkyl-9-
phosphafluorenes with nickel(II) cyanide

(a) The 9-methyl-9-phosphafluorene complex
(b) The 9-ethyl-9-phosphafluorene complex

Fig. (5)

Similar complexity occurs in the infrared spectra of the complexes of the 9-alkyl-9-phosphafluorenes with nickel thiocyanate. The mull spectrum of the 9-methyl-9-phosphafluorene complex shows a complex

absorption in the C≡N stretching region at 2110, 2090 and 2033 cm^{-1}, whereas that of the corresponding complex of 9-ethyl-9-phosphafluorene shows two sharp bands of equal intensity at 2099 and 2090 cm^{-1}. These observations can best be accommodated on the basis of the complexes having structures similar to those of the corresponding cyanide complexes and in which the thiocyanate ligands are bonded to the nickel via the nitrogen atom. The mode of bonding of thiocyanate ligands in transition metal complexes has been shown to depend markedly on both steric and electronic factors. Thiocyanate complexes containing other π-bonding ligands, e.g. Ph_3P and Ph_3As, have been shown to favour bonding via the nitrogen.[40] In crowded structures, bonding via the nitrogen is also favoured on steric grounds as the M-NCS grouping is linear (or nearly so) whereas the grouping M-SCN is bent about the sulphur atom as, for example, in a thioether. Generally, for a nitrogen bonded (isothiocyanate) ligand, the C≡N stretching frequency occurs at or slightly below 2100 cm^{-1}, whereas for the sulphur bonded (thiocyanate) ligand, it occurs slightly above 2100 cm^{-1}.[41] In the case of bridging thiocyanate groups, the C≡N absorption occurs in the region 2120 - 2170 cm^{-1}.[41] Other regions of the infrared spectrum are useful in establishing the mode of co-ordination of the thiocyanate ligand. The C-S stretching frequency falls into two clear-cut ranges, 880 - 760 cm^{-1} for M-NCS and 750 - 690 cm^{-1} for M-SCN. However, these bands are of low intensity and are easily masked by other ligand vibrations. It has been suggested that a more reliable distinction between the two types of bonding can be made in the SCN or NCS bending region. The nitrogen bonded ligand absorbs near 475 cm^{-1} whereas the corresponding sulphur bonded ligand absorbs near 420 cm^{-1}.[41] In the case of the 9-alkyl-9-phosphafluorene

complexes, ligand vibrations obscure the region 400 - 500 cm^{-1}, but the spectrum of the 9-methyl-9-phosphafluorene complex exhibits a weak band at 820 cm^{-1}, assigned to the C-S stretching frequency of a nitrogen bonded isothiocyanate group. This band is not present in the spectrum of the related nickel cyanide complex.

Both high- and low-spin five-co-ordinate complexes of the d^7 cobalt(II) ion have also been characterised. As in the case of the complexes of nickel(II), bulky ligands which contain electronegative donor atoms give rise to high-spin complexes having magnetic moments ~4.5 B.M., corresponding to three unpaired electrons.[31-33] Polydentate donors of the polarizable atoms P, As, S, and Se, on the other hand have given low-spin five-co-ordinate complexes having magnetic moments of 2.0 - 2.5 B.M., corresponding to one unpaired electron with considerable orbital contribution.[13,14,42] The above values of the magnetic moments of such complexes should be compared with a range of 1.8 - 2.0 B.M. for low-spin, octahedral cobalt(II) complexes and 2.3 - 2.9 B.M. for low-spin, planar cobalt(II) complexes.[43]

The cobalt(II) bromide complexes of type (III) of the 9-alkyl-9-phosphafluorenes are olive-green to black solids, stable in the solid state, and which are soluble in organic solvents to give deeply coloured solutions. Molecular weight determinations in solution in methylene dichloride at 30° indicate some dissociation, and conductivity data in nitrobenzene solution show that ionization is not occurring. The complexes were found to have magnetic moments in the range 1.95 - 2.0 B.M., and thus resemble other low-spin five-co-ordinate complexes of cobalt(II) with phosphine donors. It is of interest that the cobalt(II) bromide complexes of type (III) are of the

low-spin type whereas the corresponding complexes of the nickel(II) halides have the unusual magnetic properties discussed above. Similarly, the five-co-ordinate cobalt(II) complexes of diphenylphosphine are of the low-spin type, whereas the corresponding nickel(II) iodide complex has an intermediate magnetic moment.[18-20] It has been suggested that these differences in magnetic properties of related complexes of cobalt(II) and nickel(II) indicate that, assuming similar ligand-field splittings for the cobalt and nickel ions, the "cross-over point" for cobalt(II) occurs at a lower ligand-field strength than that for nickel(II).[20]

The palladium(II) complexes of type (III) (phos=9-methyl- or 9-ethyl-9-phosphafluorene; M = Pd(II); X = Br) are scarlet crystalline solids, soluble in organic solvents with dissociation, as indicated by molecular weight determinations. Conductivity data for nitrobenzene solutions indicates that the complexes are not ionised, unlike the corresponding complexes of 2-phenylisophosphindoline (IV).[10] The visible absorption spectra of the complexes in the solid state exhibit bands at ~40,000; 36,000; 27,000; and 19,000 cm^{-1}, and solution spectra again confirm the dissociation into four-co-ordinate species shown by the molecular weight values. Prolonged heating of the tris(phosphine) complexes under high vacuum leads to the formation of the yellow, four-co-ordinate complexes of the type $(phos)_2PdBr_2$, which may also be obtained indirectly from the appropriate phosphine (2 mols.) and potassium tetrabromopalladate(II) (1 mole), via the Magnus salts $(phos)_4Pd^{++} PdBr_4^{=}$.

The platinum(II) complexes of type (III), (phos = 9-methyl- or

9-ethyl-9-phosphafluorene; M = Pt(II); X = Br, SCN) are yellow-orange crystalline solids, which like the corresponding nickel(II) and palladium(II) complexes are soluble in organic solvents with some dissociation. Conductivity data for the platinum(II) bromide complexes in nitrobenzene solution indicates some degree of ionization, and it has been shown that the conductivity depends markedly on concentration, approaching that of a 1:1 electrolyte at infinite dilution. The platinum(II) complexes of the 9-alkyl-9-phosphafluorenes therefore resemble those of 2-phenylisophosphindoline (IV) in tending to form species of the type $\left[(phos)_3 PtX\right]^+ X^-$ in solution in ionising solvents.[10]

All of the platinum(II) complexes have very similar visible absorption spectra in the solid state, exhibiting bands at 23-25,000; 30,500; and 34-36,000 cm^{-1}, suggesting that all of the complexes are similar in structure. The infrared spectra of the thiocyanate complexes are similar to each other and to the nickel(II) thiocyanate complex of 9-methyl-9-phosphafluorene in having a complex absorption in the C≡N stretching region. The spectrum of the 9-methyl-9-phosphafluorene complex in this region exhibits a sharp doublet at 2115 cm^{-1}, and sharp peaks at 2087 and 2078 cm^{-1}. The corresponding complex of 9-ethyl-9-phosphafluorene exhibits sharp peaks at 2115, 2073 and 2058 cm^{-1}. Although the position of the above absorption bands suggests that the thiocyanate ligands are bonded at the nitrogen atom, the absence of a band between 780 and 860 cm^{-1} in the spectrum of the 9-methyl-9-phosphafluorene complex implies that sulphur bonded thiocyanate ligands are present. In the absence of further evidence, this point must therefore remain uncertain.

It is likely that the five-co-ordinate complexes of the 9-alkyl-9-phosphafluorenes with palladium(II) and platinum(II) salts have a distorted square pyramidal structure resembling that of the palladium(II) complex of 2-phenylisophosphindoline,[10] in view of the expected greater ligand-field stabilisation energy for this structure.[29]

Normal four-co-ordinate derivatives of the type $(phos)_2 PtCl_2$ can also be obtained from the 9-alkyl-9-phosphafluorenes via the Magnus salts which undergo rearrangement on heating in dimethylformamide to give the highly crystalline colourless complexes.

In view of the difference in properties of the halide and cyanide complexes in the nickel(II) complexes of the 9-alkyl-9-phosphafluorenes, it was of interest to examine the complexes of these phosphines with palladium(II) and platinum(II) cyanides. Numerous ammine complexes of palladium(II) cyanide are known but few phosphine complexes have been described, and the chemistry of platinum(II) cyanide has been little investigated.[44] When an alcoholic suspension of palladium(II) cyanide is heated with a solution of either 9-methyl- or 9-ethyl-9-phosphafluorene, a pale yellow solution is obtained, which rapidly deposits an off-white crystalline solid, of composition $(phos)_2Pd(CN)_2$. Although the complex of 9-methyl-9-phospha-fluorene is insufficiently soluble in methylene dichloride for molecular weight determination, the corresponding complex of 9-ethyl-9-phosphafluorene has a molecular weight corresponding to the monomeric, four-co-ordinate complex. The infrared spectra of the complexes show only one sharp C≡N band in the region 2130 - 2136 cm^{-1}, indicating the absence of bridging cyanide groups. These complexes therefore resemble the normal,

four-co-ordinate complexes of tertiary phosphines with palladium(II) halides apart from their rather pale colour. Complexes of the type (phos)$_2$PdX$_2$ (X = halogen) are usually yellow-orange in colour, and have the <u>trans</u> square-planar configuration as indicated by their zero dipole moments. Complexes of palladium(II) with chelating diphosphines (which of necessity have the <u>cis</u> configuration) are paler in colour and of high dipole moment.[1]

Recently, proton magnetic resonance (p.m.r.) studies on the complexes of dimethylphenylphosphine with palladium(II) and platinum(II) halides have been used to determine their stereochemistry.[45] It has been shown that for <u>trans</u> complexes of this ligand, the P-CH$_3$ resonance occurs as a triplet (J = 3.8 c/sec) due to "virtual" coupling through the metal atom, whereas for <u>cis</u> complexes, the P-CH$_3$ resonance occurs as a simple doublet (J = 7 c/sec). Application of this technique to the palladium(II) cyanide complex of 9-methyl-9-phosphafluorene in solution in trifluoroacetic acid shows the methyl resonance to consist of a distorted triplet (J = 3.8 c/sec), indicating that even in this highly polar solvent the complex exists largely in the <u>trans</u> form.

The 9-alkyl-9-phosphafluorene complexes of platinum(II) cyanide are similarly obtained on heating an alcoholic suspension of platinum(II) cyanide with the phosphine (3 mols.) to give colourless, insoluble complexes of composition (phos)$_2$Pt(CN)$_2$. The complex of 9-methyl-9-phosphafluorene proved to be too insoluble for ebullioscopic molecular weight determination, but the corresponding complex of 9-ethyl-9-phosphafluorene is monomeric, in accord with its formulation as a simple, four-co-ordinate complex. The

infrared spectra of the complexes in the solid state show only one C≡N band in the region 2136 - 2140 cm^{-1} indicating the absence of bridging cyanide groups.

Both _cis_ and _trans_ forms of complexes of the type (phos)$_2$PtX$_2$ (X = halogen) have been isolated and in general it has been found that the _cis_ isomers are colourless and of low solubility whereas the _trans_ isomers are pale yellow and more soluble in organic solvents.[1] Application of these simple criteria to the 9-alkyl-phosphafluorene complexes of platinum(II) cyanide suggests that they have the _cis_ configuration. However, the p.m.r. spectrum of the 9-methyl-9-phosphafluorene complex in solution in trifluoroacetic acid exhibits a sharp, symmetrical triplet centered at 7.8τ (J = 4.2 c/sec), with two satellite triplets at 7.52 and 8.07τ, due to the spin of the Pt^{195} isotope (33% natural abundance), indicating that even in this highly polar solvent, the complex has the _trans_ configuration. In contrast, the p.m.r. spectrum of the colourless complex of 9-methyl-9-phospha-fluorene with platinum(II) chloride, of the type (phos)$_2$PtCl$_2$, in trifluoroacetic acid solution exhibits a doublet centered at 8.11τ (J = 9.1 c/sec), with satellite doublets at 7.83 and 8.37τ, showing this complex to have the _cis_ configuration.

The inability of palladium(II) and platinum(II) cyanides to add three molecules of a 9-alkyl-9-phosphafluorene to give a five-co-ordinate species must be related to the well-known π-bonding ability of the cyanide ligand in stabilising the square-planar state (which is well established in the chemistry of these elements) and demonstrates the decreasing tendency to assume the five-co-ordinate state in a given group of elements with

increasing atomic weight.

In general, the properties of the five-co-ordinate complexes of type (III) of the 9-alkyl-9-phosphafluorenes are similar to those of the heterocyclic phosphine 2-phenylisophosphindoline (IV),[10,11] and diphenylphosphine.[18-20] Certain of the latter complexes also undergo partial dissociation in dichloromethane, but many of them undergo ionisation in polar solvents to give the species $\left[(phos)_3 \ MX \right]^+ X^-$. This is shown by their conductivities in nitrobenzene and by their reaction with cold ethanolic sodium tetraphenylborate or sodium picrate to give the corresponding tetraphenylborate or picrate. The 9-alkyl-9-phosphafluorene complexes do not appear to show this reaction, in accord with their observed low conductivities in nitrobenzene solution.

In view of the unusual co-ordinating ability of the 9-alkyl-9-phosphafluorenes (II; R = Me or Et), it was of interest to examine the complexes of the related 9-phenyl-9-phosphafluorene (II; R = Ph) with nickel(II), palladium(II) and platinum(II) halides. Unlike the 9-alkyl-9-phosphafluorenes, 9-phenyl-9-phosphafluorene has been found to resemble triphenylphosphine in forming four-co-ordinate complexes with the above metal halides. The nickel(II) halide complexes are of the type $(phos)_2 NiX_2$ (X = Cl, Br, I), and are obtained on addition of a solution of the appropriate nickel(II) salt in absolute ethanol to an ethanolic solution of the phosphine. Like the corresponding complexes of triphenylphosphine,[5] the nickel halide complexes are paramagnetic, having a magnetic moment equivalent to two unpaired electrons, and are assumed to have tetrahedral structures. The corresponding thiocyanate complex, also prepared in

absolute ethanol, is diamagnetic, again resembling the corresponding complex of triphenylphosphine in having a square-planar structure.

Similarly, with potassium tetrabromopalladate(II) and tetrabromoplatinate(II), 9-phenyl-9-phosphafluorene gives complexes of the type $(phos)_2 MX_2$ (M = Pd(II), Pt(II); X = Br). The palladium complex is yellow in colour and is thus presumed to have the _trans_ configuration, whereas the platinum complex is colourless suggesting that it has the _cis_ configuration. Complexes of type (III) could not be obtained from 9-phenyl-9-phosphafluorene and the above metal halides.

The conditions which favour the formation of five-co-ordinate d^7 and d^8 complexes have been discussed by Nyholm.[46] The ability of a mono-dentate tertiary phosphine ligand to stabilise the five-co-ordinate state in complexes of type (III) appears to depend on there being a favourable balance between its steric and electronic (donor-acceptor) properties. The formation of complexes of type (III) from the 9-alkyl-9-phosphafluorenes (II; R = Me or Et), and from the isophosphindoline (IV) may depend on the fact that in both phosphines, the two ring P-C bonds are being pulled together, and the steric freedom and consequent reactivity of the phosphorus atom are thus enhanced. It is noteworthy that compounds of type (III) (X = halogen) formed by diethylphenylphosphine[10] and methyldiphenylphosphine[18] are much less stable than the corresponding complexes of the above heterocyclic phosphines. The steric requirement at phosphorus must be critical, as the cyclic phosphine, 1-ethylphosphindoline (V) has been reported not to form trisphosphine palladium(II) halide complexes.[47]
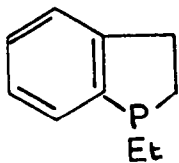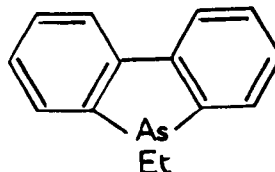
(V)   (VI)

       The importance of electronic factors is indicated by the
inability of 9-phenyl-9-phosphafluorene (II; R = Ph) to form five-co-
ordinate complexes of type (III). In this phosphine, the phosphorus is
too electronegative and phosphorus-metal σ-bonding is restricted. In
the trialkylphosphines, in addition to an unfavourable steric effect,
the lack of electronegative substituents on the phosphorus atom allows
insufficient π- character in the phosphorus-metal bond, the metal atom
experiencing too great a build-up of charge from the polarizable ligands
for the formation of a tris(phosphine) complex. It is noteworthy that
in the monodentate tertiary phosphine ligands capable of giving
tris(phosphine) complexes, the phosphorus atom carries groups which
provide a favourable balance between σ- and π-bonding character. In the
case of the above heterocyclic phosphines, the above steric effects are
also doubtless of consequence in the stabilization of the complexes.
In addition, it is of interest that the presence of ligands such as
-C≡N and -C≡C.Ph, which have a high ligand-field strength, is also of
importance with regard to the stability of complexes of type (III).

It has been suggested recently[22] that the reason for the stability of the complexes of type (III) derived from diphenylphosphine, (apart from the less severe steric interactions), can be attributed to the lower basicity of the secondary phosphine, which results in a smaller net transfer of charge to the metal atom than would occur with a tertiary phosphine, which have been shown to be considerably more basic.[48] It would be of interest to determine the basicities of the heterocyclic tertiary phosphines discussed in the above study and to compare them with that of diphenylphosphine, and those of other related tertiary phosphines.

Five-co-ordinate complexes similar to those of type (III) could not be obtained from the related arsenic heterocycle, 9-ethyl-9-arsafluorene (VI). This ligand does not appear to form complexes with nickel(II) halides in any of the usual solvents, and with palladium(II) bromide gives only the yellow-orange four-co-ordinate complex of the type $(arsine)_2PdBr_2$, even in the presence of an excess of the ligand.

EXPERIMENTAL

The 9-substituted-9-phosphafluorenes (II; R = Me, Et, Ph) were prepared as described in Parts I and II of this thesis.

Molecular weights were determined in methylene dichloride solution by the vapour-pressure thermistor technique, at 30°. Molar conductivities were determined in nitrobenzene solution.

Magnetic susceptibilities were determined by Mrs. R.M. Canadine, Petrochemical and Polymer Laboratory, I.C.I. Ltd. A Faraday balance was used, and the data are corrected for the diamagnetism of the ligands. A temperature of 27° was maintained during the determinations.

Preparation of the complexes

(A) The 9-alkyl-9-phosphafluorene complexes with nickel(II) halides

These were prepared under nitrogen by the addition of a hot, ethanolic solution of the 9-alkyl-9-phosphafluorene (slightly more than 3 mols.) to a hot solution of the nickel(II) salt in absolute ethanol, the complexes (III; phos = 9-methyl- or 9-ethyl-9-phosphafluorene; M = Ni(II); X = Cl,Br,I,SCN) separating on cooling. In the preparation of the chloro- and bromo- complexes, the appropriate 'A.R.' nickel(II) salt was used. The solution of nickel(II) iodide (or thiocyanate) was

prepared by dissolving 'A.R.' nickel(II) nitrate in absolute ethanol, and heating with an excess of crushed sodium iodide (or potassium thiocyanate); the resulting solution was cooled and filtered before use.

The complexes prepared were as follows:-

Dichlorotris(9-methyl-9-phosphafluorene)nickel(II), olive-green crystals, m.p. 169-71°. (Found: C, 64.0; H, 4.15%; $\underline{M}$, 511. $C_{39}H_{33}P_3NiCl_2$ requires C, 64.4; H, 4.55%; $\underline{M}$, 723.7). Λ_m 0.52; μ_{eff} 0.88 B.M.

Dibromotris(9-methyl-9-phosphafluorene)nickel(II), dark-green crystals, m.p. 185-6°. (Found: C, 58.0; H, 4.1%; $\underline{M}$, 780; $C_{39}H_{33}P_3NiBr_2$ requires C, 57.6; H, 4.05%; $\underline{M}$, 812.5). Λ_m 0.47; μ_{eff} 0.98 B.M.

Di-iodotris(9-methyl-9-phosphafluorene)nickel(II), green-black crystals, m.p. 173-4°. (Found: C, 52.0; H, 3.65%; $\underline{M}$, 875; $C_{39}H_{33}P_3NiI_2$ requires C, 51.6; H, 3.65%; $\underline{M}$, 906.5). Λ_m 0.76; μ_{eff} 1.50 B.M.

Di-isothiocyanatotris(9-methyl-9-phosphafluorene)nickel(II), dark green-brown crystals, m.p. 142-4°. (Found: C, 64.4; H, 4.4; N, 3.5%; $\underline{M}$, 485; $C_{41}H_{33}P_3NiN_2S_2$ requires C, 64.0; H, 4.3; N, 3.65%; $\underline{M}$, 769.5). Λ_m 0.26; μ_{eff} 1.20 B.M. i.r.(mull): 2,110; 2,090; 2033 cm^{-1} (ν C≡N); 820 cm^{-1}(w) (ν C-S).

Dichlorotris(9-ethyl-9-phosphafluorene)nickel(II), olive-green crystals, m.p. 139-41°. (Found: C, 65.7; H, 5.2%; $\underline{M}$, 476; $C_{42}H_{39}P_3NiCl_2$ requires C, 65.8; H, 5.1%; $\underline{M}$, 765.7). Λ_m 0.18; μ_{eff} 0.90 B.M.

Dibromotris(9-ethyl-9-phosphafluorene)nickel(II), olive-green crystals, m.p. 155-6°. (Found: C, 59.4; H, 4.6%; $\underline{M}$, 830; $C_{42}H_{39}P_3NiBr_2$ requires C, 58.95; H, 4.55%, $\underline{M}$, 854.5). Λ_m 0.26; μ_{eff} 0.75 B.M.

Di-iodotris(9-ethyl-9-phosphafluorene)nickel(II), green-black crystals, m.p. 143-7°. (Found: C, 52.8; H, 3.9%; $\underline{M}$, 657; $C_{42}H_{39}P_3NiI_2$ requires C, 53.15; H, 4.1%; $\underline{M}$, 948.5). Λ_m 1.93; μ_{eff} 0.65.

Di-isothiocyanatotris(9-ethyl-9-phosphafluorene)nickel(II), dark brown-black crystals, m.p. 128-30°. (Found: C, 65.1; H, 4.8; N, 3.4%; $\underline{M}$, 465; $C_{44}H_{39}P_3NiN_2S_2$ requires C, 65.1; H, 4.85; N, 3.45%; $\underline{M}$, 811.6). Λ_m 0.13; μ_{eff} 0.95 B.M.
i.r.(mull): 2099; 2090 cm^{-1} ($\nu C\equiv N$). Other diagnostic regions were obscured by ligand vibrations.

Dichlorobis(9-methyl-9-phosphafluorene)nickel(II)

The complex, dichlorotris(9-methyl-9-phosphafluorene)nickel(II) (50 mg) in benzene (10 ml.) was heated under reflux, the colour of the solution changing from dark green to red, and a red-brown solid being deposited. The solid was filtered off and washed with petrol (60-80°) to

give the complex, red-brown crystals m.p. >230°d. (Found: C, 59.3; H, 4.25. $C_{26}H_{22}P_2NiCl_2$ requires C, 59.35; H, 4.2%). The above solid was soluble in chloroform to give an olive-green solution.

(B) The 9-alkyl-9-phosphafluorene complexes of nickel(II) cyanide.

To a solution of nickel nitrate hexahydrate (30 mg) in water (2 ml) was added sodium cyanide (10 mg, >2 mols) and the resulting precipitate of hydrated nickel(II) cyanide was centrifuged. The supernatant liquid was removed and the precipitate resuspended in absolute ethanol and then recentrifuged. The nickel(II) cyanide was then immediately resuspended in absolute ethanol and added to a hot ethanolic solution of the 9-alkyl-9-phosphafluorene, (>3 mols). On heating, the nickel cyanide dissolved to give a deep red solution which was centrifuged and the clear supernatant liquid allowed to crystallise to give:-

Dicyanotris(9-methyl-9-phosphafluorene)nickel(II), purple crystals, m.p. >300°d. (Found: C, 69.8; H, 4.75; N, 3.95%; $\underline{M}$, 700; $C_{41}H_{33}P_3NiN_2$ requires C, 69.8; H, 4.7; N, 3.95%; $\underline{M}$, 705.4). Λ_m 0; μ_{eff} 0.46 B.M.

i.r.(mull): 2118; 2108; 2102(sh) cm^{-1} (ν C≡N).

u.v. - visible - near i.r.(mull): λ_{max} 18,750(sh); 27,000; 31,200; 35,500 cm^{-1}.

(solution, CH_2Cl_2): λ_{max} 24,000 cm^{-1} (ϵ; 2710).

The intensity of the latter increased on addition of the free ligand to the solution.

<u>Dicyanotris(9-ethyl-9-phosphafluorene)nickel(II)</u>, red-purple
crystals, m.p. 212-14°d. (Found: C, 70.8; H, 5.35; N, 3.8%; $\underline{M}$, 667;
$C_{44}H_{39}P_3NiN_2$ requires C, 70.7; H, 5.25; N, 3.75%; $\underline{M}$, 747). Λ_m 0.01;
μ_{eff} 0.42 B.M.

i.r.(mull): 2118 cm^{-1} (ν C≡N).

u.v. – visible – near i.r.(mull): λ_{max} 23,000; 30,500; 35,000 cm^{-1}.

(solution, CH_2Cl_2): λ_{max} 24,000 cm^{-1} (ε; 3698).

The intensity of the latter increased on addition of the free ligand to
the solution.

(C) <u>The 9-alkyl-9-phosphafluorene complexes of palladium(II) compounds.</u>

(i) <u>The palladium(II) bromide complexes</u>

To a hot solution of the 9-alkyl-9-phosphafluorene (3 mols) in
ethanol was added a hot, aqueous ethanolic solution of potassium tetrabromo-
palladate(II), resulting in the formation of a deep red solution from which
crystals of the respective complex separated on cooling.

The complexes prepared were:-

<u>Dibromotris(9-methyl-9-phosphafluorene)palladium(II)</u>, scarlet crystals,
m.p. 320-2°d. (Found: C, 53.85; H, 4.25%; $\underline{M}$, 753. $C_{39}H_{33}P_3PdBr_2$
requires C, 54.3; H, 3.85%; $\underline{M}$, 951). Λ_m 0.96.

Dibromotris(9-ethyl-9-phosphafluorene)palladium(II), scarlet crystals,
m.p. 268-70°. (Found: C, 55.65; H, 4.75%; $\underline{M}$, 902. $C_{42}H_{39}P_3PdBr_2$
requires C, 55.8; H, 4.3%; $\underline{M}$, 925). Λ_o 0.84.

u.v. - visible - near i.r.(mull): λ_{max} 19,000; 27,000; 36,000; 40,000
cm^{-1}.

Dibromobis(9-methyl-9-phosphafluorene)palladium(II).

To a solution of potassium tetrabromopalladate(II) (50 mg) in
water (1.5 ml) was added a solution of 9-methyl-9-phosphafluorene (45 mg,
~2 mols) in ethanol (2 ml), the solution being shaken continuously during
the addition, to give a russet-red compound which was filtered off, washed
with water, and digested in hot dimethylformamide to give the insoluble
yellow complex, which after washing with ethanol had m.p. 300°d. (Found:
C, 47.8; H, 3.4. $C_{26}H_{22}P_2PdBr_2$ requires C, 47.1; H, 3.35%). The same
compound could be obtained on prolonged heating of dibromotris(9-methyl-9-
phosphafluorene)palladium(II) at 100°/0.1 mm.

(ii) The palladium(II) cyanide complexes

Palladium(II) cyanide was prepared according to the procedure
of Bailey and Lamb.[49] To a solution of mercuric cyanide (25 mg) in water
was added an aqueous solution of potassium tetrabromopalladate(II), and
the resulting gelatinous yellow precipitate digested hot for a few minutes,
before centrifuging. The supernatant liquid was discarded and the solid
resuspended in absolute ethanol and recentrifuged. The palladium(II)

cyanide was then resuspended in ethanol (1 ml) and added to a hot solution of the 9-alkyl-9-phosphafluorene (3 mols) in ethanol, and the resulting pale yellow solution heated for a few minutes. On standing, colourless crystals of the complexes separated.

The complexes prepared were:-

Dicyanobis(9-methyl-9-phosphafluorene)palladium(II), colourless crystals, m.p. >300°d. (Found: C, 60.3; H, 3.95; N, 4.8%. $C_{28}H_{22}P_2PdN_2$ requires C, 60.55; H, 4.0; N, 5.05%). The complex was too insoluble in CH_2Cl_2 for molecular weight determination.

i.r.(mull): 2136 cm^{-1} ($\nu C\equiv N$)

p.m.r. (CF_3COOH): unsymmetrical triplet centered at 8.08τ (J = 3.8 c/sec).

Dicyanobis(9-ethyl-9-phosphafluorene)palladium(II), colourless crystals, m.p. 272-5°d. (Found: C, 62.2; H, 4.45; N, 5.1%; $\underline{M}$, 570; $C_{30}H_{26}P_2PdN_2$ requires C, 61.8; H, 4.5; N, 4.8%; $\underline{M}$, 583.2).

(D) The 9-alkyl-9-phosphafluorene complexes of platinum(II) compounds.

(i) The platinum(II) halide and thiocyanate complexes

To a hot solution of the 9-alkyl-9-phosphafluorene (3 mols) in ethanol was added a cold, aqueous solution of potassium tetrabromoplatinate(II (containing in the case of the corresponding thiocyanate complexes an excess

of potassium thiocyanate (4 mols)), resulting in the formation of a
bright yellow solution from which crystals of the respective complexes
separated.

The complexes prepared were:-

Dibromotris(9-methyl-9-phosphafluorene)platinum(II), yellow-orange
crystals, m.p. 175-77°d. (Found: C, 49.4; H, 3.95%; $\underline{M}$, 781;
$C_{39}H_{33}P_3PtBr_2$ requires C, 49.3; H, 3.5%; $\underline{M}$, 949). Λ_o 5.34, increasing
with dilution and approaching that of a 1:1 electrolyte at infinite
dilution.
u.v. - visible - near i.r.(mull): λ_{max} 25,000; 30,400; 36,000 cm^{-1}.

Dibromotris(9-ethyl-9-phosphafluorene)platinum(II), yellow crystals,
m.p. 209-11°. (Found: C, 50.7; H, 4.2%; $\underline{M}$, 900; $C_{42}H_{39}P_3PtBr_2$ requires
C, 50.85; H, 3.95%; $\underline{M}$, 991). Λ_m, 8.28, increasing on dilution and
approaching that of a 1:1 electrolyte at infinite dilution.
u.v. - visible - near i.r.(mull); λ_{max} 24,500; 30,300; 35,700 cm^{-1}.

Dithiocyanatotris(9-methyl-9-phosphafluorene)platinum(II), orange crystals,
m.p. 182-4°d. (Found: C, 54.1; H, 3.55; N, 3.0%; $\underline{M}$, 810.
$C_{41}H_{33}P_3PtN_2S_2$ requires C, 54.4; H, 3.65; N, 3.1%; $\underline{M}$, 905.8). Λ_m 10.09.
i.r.(mull): 2,112; 2,085; 2078 cm^{-1} (ν C≡N). Other useful regions of
the spectrum were obscured by ligand vibrations.
u.v. - visible - near i.r.(mull): λ_{max} 23,200; 31,000; 34,300 cm^{-1}.

<u>Dithiocyanatotris(9-ethyl-9-phosphafluorene)platinum(II)</u>, yellow crystals,

m.p. 201-3°. (Found: C, 55.5; H, 4.05; N, 3.1%; $\underline{M}$, 590;

$C_{44}H_{39}P_3PtN_2S_2$ requires C, 55.75; H, 4.15; N, 2.95%; $\underline{M}$, 947.9). Λ_m 7.02.

i.r.(mull): 2,115; 2,070; 2055 cm^{-1}. (ν C$\equiv$N). Other useful regions

of the spectrum were obscured by ligand vibrations.

u.v. - visible - near i.r.(mull): λ_{max} 25,000; 30,200; 34,000 cm^{-1}.

<u>Dichlorobis(9-methyl-9-phosphafluorene)platinum(II)</u>.

To a cold aqueous solution of potassium tetrachloroplatinate(II)

(41 mg) was added dropwise, with shaking, a solution of 9-methyl-9-phospha-

fluorene (40 mg, 2 mols) in absolute ethanol (2 ml), resulting in the

precipitation of a pale pink solid. The salt was filtered off, washed with

water, and digested in hot dimethylformamide (2 ml) until a fairly clear

solution was obtained. The solution was filtered hot, and then was diluted

gradually with hot water until a white crystalline solid deposited. After

cooling, the complex was filtered off and washed with ethanol to give a

white, crystalline solid, m.p. 295-8° decomp. (Found: C, 46.25; H, 3.35%;

$\underline{M}$, 659; $C_{26}H_{22}P_2PtCl_2$ requires C, 46.45; H, 3.3%; $\underline{M}$, 672.4).

p.m.r. (CF$_3$COOH): Distorted doublet centered at 8.11τ (J = 9.1 c/sec), with

satellite doublets centered at 7.83τ and 8.37τ.

(ii) <u>The platinum(II) cyanide complexes</u>.

Platinum(II) cyanide was prepared from the reaction of potassium

tetrachloroplatinate(II) and sodium cyanide,[44] and also from the reaction

of potassium tetrachloroplatinate(II) with mercuric cyanide.

Solutions of potassium tetrachloroplatinate(II) (40 mg) and

mercuric cyanide (25 mg) in water were heated together for 1 hr. to give

a gelatinous precipitate which was centrifuged, resuspended in absolute

ethanol and recentrifuged. The platinum(II) cyanide was then resuspended

in absolute ethanol and added to a hot ethanolic solution of the 9-alkyl-

9-phosphafluorene (3 moles), to give a yellow solution from which white

crystals of the complex separated.

The complexes prepared were:-

Dicyanobis(9-methyl-9-phosphafluorene)platinum(II), white crystals,

m.p. >300°d. (Found: C, 51.9; H, 3.55; N, 4.4%. $C_{28}H_{22}P_2PtN_2$ requires

C, 52.25; H, 3.45; N, 4.35%).

i.r.(mull): 2136 cm^{-1} (ν C≡N)

p.m.r. (CF$_3$COOH): 7.8τ (triplet, J = 4.2 c/sec);

satellite triplets at 7.52 and 8.07τ.

The complex was insufficiently soluble in CH_2Cl_2 for the determination of

molecular weight in this solvent.

Dicyanobis(9-ethyl-9-phosphafluorene)platinum(II), white crystals,

m.p. >295°d. (Found: C, 52.9; H, 3.8; N, 4.1%; M, 706. $C_{30}H_{26}P_2PtN_2$

requires C, 53.65; H, 3.9; N, 4.15%; M, 671.6).

i.r.(mull): 2140 cm^{-1} (ν C≡N).

(E) <u>The 9-alkyl-9-phosphafluorene complexes of cobalt(II) bromide</u>.

These were prepared by the addition of a hot ethanolic solution of cobalt(II) bromide to a hot ethanolic solution of the 9-alkyl-9-phosphafluorene (3 mols), giving an intensely coloured solution from which crystals of the complex separated on cooling.

The complexes prepared were:-

<u>Dibromotris(9-methyl-9-phosphafluorene)cobalt(II)</u>, black crystals, m.p. 184°. (Found: C, 57.9; H, 4.05%; $\underline{M}$, 756. $C_{39}H_{33}P_3CoBr_2$ requires C, 57.6; H, 4.05%; $\underline{M}$, 812.7). Λ_m 1.33; μ_{eff} 1.95 B.M.

<u>Dibromotris(9-ethyl-9-phosphafluorene)cobalt(II)</u>, intense olive-green crystals, m.p. 155-6°. (Found: C, 58.7; H, 4.35%; $\underline{M}$, 610. $C_{42}H_{39}P_3CoBr_2$ requires C, 58.95; H, 4.55%; $\underline{M}$, 854.7). Λ_m, 1.03; μ_{eff} 2.03 B.M.

(F) <u>The complexes of 9-phenyl-9-phosphafluorene with nickel(II),
palladium(II) and platinum(II) halides</u>.

The complexes were prepared as described above for the 9-alkyl-9-phosphafluorene complexes.

The complexes prepared were:-

<u>Dichlorobis(9-phenyl-9-phosphafluorene)nickel(II)</u>, red-brown crystals, m.p. 209-10°. (Found: C, 66.7; H, 3.9%. $C_{36}H_{26}P_2NiCl_2$ requires C, 66.5; H, 4.0%). μ_{eff} 3.3 B.M.

<u>Dibromobis(9-phenyl-9-phosphafluorene)nickel(II)</u>, yellow-brown crystals,
m.p. 205-7°. (Found: C, 58.2; H, 3.45%. $C_{36}H_{26}P_2NiBr_2$ requires C, 58.75;
H, 3.5%). μ_{eff} 3.4 B.M.

<u>Di-iodobis(9-phenyl-9-phosphafluorene)nickel(II)</u>, red-brown crystals,
m.p. 187-8°. (Found: C, 51.9; H, 3.1%. $C_{36}H_{26}P_2NiI_2$ requires C, 51.9;
H, 3.1%). μ_{eff} 3.8 B.M.

<u>Di-thiocyanatobis(9-phenyl-9-phosphafluorene)nickel(II)</u>, red-brown crystals,
m.p. 188-90°d. (Found: C, 65.9; H, 3.6; N, 3.7%. $C_{38}H_{26}P_2NiN_2S_2$ requires
C, 65.65; H, 3.75; N, 4.0%). Diamagnetic.

<u>Dibromobis(9-phenyl-9-phosphafluorene)palladium(II)</u>, yellow crystals,
m.p. >300°d. (Found: C, 54.9; H, 3.40%. $C_{36}H_{26}P_2PdBr_2$ requires
C, 54.9; H, 3.3%).

<u>Dibromobis(9-phenyl-9-phosphafluorene)platinum(II)</u>, white crystals,
m.p. >330°d. (Found: C, 49.3; H, 3.0%. $C_{36}H_{26}P_2PtBr_2$ requires C, 49.4;
H, 2.95%).

Tris(phosphine) derivatives could not be isolated from the reaction
of 9-phenyl-9-phosphafluorene with the above metal halides.

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The Preparation and Properties of Some Nickel(II) and
Palladium(II) Complexes of 2,2'-Biphenylylenebisdiethylphosphine

At the present time, there is much interest in the
preparation and characterization of complexes of the d^8 transition
metal halides with chelating ditertiary phosphines; but compared with
the large number of monodentate tertiary phosphine ligands known,
relatively few suitable ditertiary phosphines have been prepared.
Furthermore, relatively few of the complexes of ditertiary phosphines
have been fully examined by spectroscopic and magnetic susceptibility
methods.

Complexes of the type $(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2$ $NiBr_2$
($\underline{n}$ = 3,4,5) have been described by Issleib and Holfield.[1] Chatt and
Hart[2] prepared the complexes $Et_2P(CH_2)_2PEt_2$ $NiCl_2$, $\underline{o}-C_6H_4(PEt_2)_2$ NiX_2,
(X = Cl, Br, I), and $\underline{o}-C_6H_4(PEt_2)_{2\ 2}NiBr_2$ by halogenation of the
corresponding nickel(0) complexes. Wymore and Bailar[3] reported
$Et_2P(CH_2)_2PEt_2$ NiX_2, (X = halogen; ClO_4), and $Et_2P(CH_2)_2PEt_2$ $NiBr_3$.
Booth and Chatt[4] reported the nickel(II) complexes of the diphosphines
$R_2P(CH_2)_2PR_2$ (R = Me, Et, Ph) and $Ph_2PCH_2PPh_2$ and Van Hecke and Horrocks[5]
have prepared complexes of the diphosphines $Ph_2P(CH_2)_nPPH_2$ ($\underline{n}$ = 1,2,3).

The latter workers also reported extensively on the optical spectra, magnetic properties and the proton magnetic resonance (p.m.r.) spectra of these complexes. It was found that complexes of the type $Ph_2P(CH_2)_3PPh_2$ NiX_2 (X = halogen), which are square-planar and diamagnetic in the solid state, when in solution show an equilibrium between the square-planar (diamagnetic) and the tetrahedral (paramagnetic) forms, whereas the corresponding complexes of $Ph_2P(CH_2)_n PPh_2$ ($\underline{n}$ = 1,2) remain square-planar in solution. In an extension of this work, Sandhu and Gupta[6] reported that the nickel(II) halide complexes of $Ph_2P(CH_2)_4PPh_2$ are tetrahedral in the solid state. Recently, Ramaswamy et al.[7] described the complexes ($\underline{cis}$- $Ph_2PCH = CHPPh_2)_2NiX_2$ (X = NO_3^-, ClO_4^-). Both complexes have magnetic moments which are intermediate between those expected from diamagnetic and paramagnetic species, and the nickel nitrate complex has an anomalous temperature-dependence of the magnetic moment which suggests the existence of a low spin $\rightleftarrows$ high spin equilibrium in this complex due to peturbations produced along the Z axis by the nitrate ion.

In view of the dependence of the bonding and stereochemistry of the complexes on the structure of the bidentate phosphine ligand, revealed in the above studies, it was of interest to study the complexes of the novel ditertiary phosphine, 2,2'-biphenylylenebisdiethylphosphine(I), in which the phosphorus atoms are suitably disposed for the formation of a seven-membered ring by co-ordination with a metal.

The co-ordinating ability of the diphosphine(I) is demonstrated by the ready formation of a chelate dibromopalladium(II) complex (II), and a bis(aurous chloride) complex (III) on mixing hot alcoholic solutions of the diphosphine with aqueous alcoholic solutions of potassium
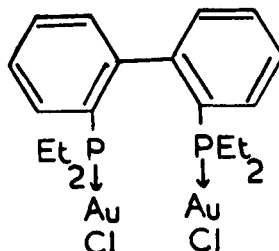
tetrabromopalladate(II) and sodium chloroaurate respectively. The diphosphine readily forms complexes with nickel(II) halides, and the nickel(II) chloride complex appears to provide an interesting example of square-planar ⇄ tetrahedral isomerism.
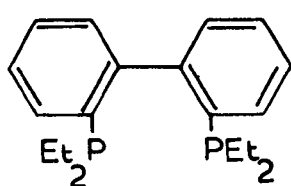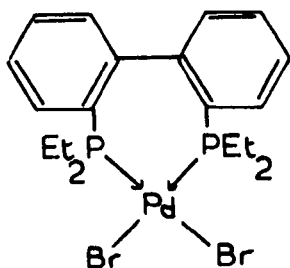
(I)   (II)   (III)

Addition of the diphosphine(I) to an excess of the nickel(II) salt, both in hot absolute ethanol, gives deeply coloured solutions from which crystals of the appropriate complex (IV; X = Cl, Br, I, NCS) separate on cooling. The nickel(II) halide complexes (IV; X = Cl, Br, I) are purple, dark blue, and dark brown in colour respectively, whereas the nickel(II) thiocyanate complex (IV; X = NCS) has the familiar red-brown colour of a square-planar nickel(II) complex. The infrared spectrum of the latter exhibits absorption bands at 2135 and 2100 cm^{-1} (ν C≡N) and a weak band at 825 cm^{-1} (ν C-S) which are absent from the spectrum of the corresponding nickel(II) bromide complex, suggesting the presence of two cis isothiocyanato ligands in which the bonding to the metal is through nitrogen.[8]
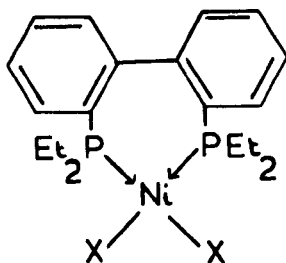
(IV)

Molecular weight values determined ebulliometrically in methylene dichloride indicate that the complexes of type (IV) are monomeric in solution. However, molecular weight determination by the vapour pressure-thermistor method for solutions of the complexes in methylene dichloride at 30° give values some 10-20% greater than the theoretical value for a monomeric form, which would seem to indicate either weak association with the solvent or some association of molecules of the complex at the lower temperature.

Inspection of molecular models suggests that the geometry of the ligand (I; = diphos) is such that both square-planar and tetrahedral forms of the complexes of type (IV) could exist without unfavourable non-bonded interactions, but that octahedral complexes of the type $(diphos)_2NiX_2$, similar to those obtained from other chelating diphosphines, could not be formed on steric grounds.[4,5]

Magnetic susceptibility data for the complexes of type (IV), as determined by the Faraday method, shows that in the solid state both the chloro- and the isothiocyanato- complexes (IV; X = Cl, NCS respectively)

are essentially diamagnetic, implying a square-planar structure. The bromo- and iodo- complexes, however, are paramagnetic in the solid state, having magnetic moments of 2.5 and 2.8 B.M. respectively, suggesting that the complexes have a tetrahedral structure in the solid state. The magnetic susceptibilities of the bromo- and iodo- complexes obey the Curie-Weiss law and the magnetic moments are temperature-independent.[9] A marked change in structure in the solid state therefore occurs in passing from the chloro- complex (IV; X = Cl) to the bromo- complex (IV; X = Br).

In solution in organic solvents, the nickel(II) halide complexes appear to have structures similar to one another as indicated by their electronic absorption spectra[9] and also by their proton magnetic resonance (p.m.r.) spectra which exhibit marked proton shifts due to the paramagnetism of the complexes in solution.[10] Furthermore, the dipole moments of the chloro- and iodo- complexes in solution in benzene are 9.3 and 9.4D respectively, again implying that their structure in solution is similar. The nickel(II) chloride complex of the diphosphine would therefore appear to provide an interesting example of square-planar (solid state) ⇌ tetrahedral (solution) isomerism, whereas the corresponding nickel(II) bromide and iodide complexes are tetrahedral in the crystal and in solution. The isothiocyanato- complex remains square-planar in solution as indicated by its p.m.r. and electronic spectra. Studies on the electronic spectra and the high resolution p.m.r. spectra of the above complexes are continuing.
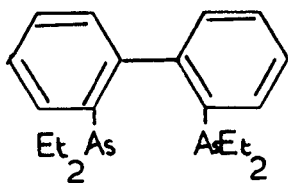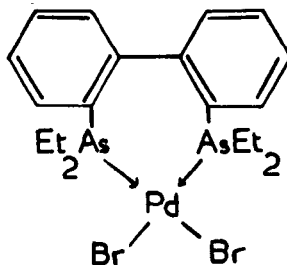
(V)   (VI)

It was also of interest to examine the complexes of the
analogous diarsine, 2,2'-biphenylylenebisdiethylarsine (V) with
palladium(II) and nickel(II) halides. The diarsine (V) readily forms
a chelate palladobromide (VI) on mixing hot ethanolic solutions of the
diarsine and potassium tetrabromopalladate(II). However, attempts to
form the corresponding nickel(II) complexes using ethanol, n-butanol or
glacial acetic acid as solvent failed to give stable complexes. The
donor properties of the diarsine (V) appear therefore to be much inferior
to those of the diphosphine (I).

EXPERIMENTAL

The ditertiary phosphine, 2,2'-biphenylylenebisdiethyl-phosphine was prepared as described in Part I of this thesis. The analogous diarsine, 2,2'-biphenylylenebisdiethylarsine was prepared as described by Forbes et al.[11]

Magnetic susceptibility measurements were made using a Faraday Balance.

Dipole moments were determined by dielectric constant measurements for solutions in benzene and are accurate to ±15%.

Molecular weights were determined ebulliometrically in methylene dichloride at 40°, and also by the vapour pressure–thermistor method in methylene dichloride at 30°.

The complexes prepared were:-

Dibromo(2,2'-biphenylylenebisdiethylphosphine)palladium(II).

A solution of the diphosphine(I) (0.330 g) in absolute ethanol (5 ml) was mixed with an aqueous–ethanolic solution of potassium tetrabromopalladate(II) (0.504 g, 1 mol) and the resulting solution heated to boiling; yellow crystals of the complex (II) separated which after recrystallisation from ethanol had m.p. 246 – 247°. (Found: C, 40.3; H, 4.8. $C_{20}H_{28}P_2PdBr_2$ requires C, 40.1; H, 4.75%).

<u>Dichloro(2,2'-biphenylylenebisdiethylphosphine)digold(I) dihydrate (III)</u>.

A solution of the diphosphine(I) in ethanol when boiled with an aqueous-ethanolic solution of sodium chloroaurate gave pale yellow crystals of the complex, m.p. 292 - 293° after washing with dry ether. (Found: C, 28.25; H, 4.3. $C_{20}H_{28}P_2 \cdot 2AuCl \cdot 2H_2O$ requires C, 28.85; H, 4.0%).

The Nickel(II) Complexes

These were prepared under nitrogen by the addition of a hot ethanolic solution of the diphosphine (slightly less than 1 equivalent) to a hot solution of the nickel salt in absolute ethanol, the complexes (IV; X = Cl, Br, I, NCS) separating on cooling. In the preparation of the chloro- and bromo- complexes, the appropriate 'A.R' nickel(II) salt was used. The solution of nickel(II) iodide (or thiocyanate) was prepared by dissolving 'A.R.' nickel(II) nitrate in absolute ethanol, and heating with an excess of crushed sodium iodide (or potassium thiocyanate); the resulting solution was cooled and filtered before use.

The complexes prepared were as follows:

<u>Dichloro(2,2'-biphenylylenebisdiethylphosphine)nickel(II)</u>, purple crystals from ethanol m.p. 167-8°. (Found: C, 51.8; H, 6.05%; <u>M</u>, 458.9

(ebulliometric); 522 (vapour-pressure method); $C_{20}H_{28}P_2NiCl_2$ requires

C, 52.2; H, 6.1%; $\underline{M}$, 459.8). Diamagnetic. μ, 9.3D.

Dibromo(2,2'-biphenylylenebisdiethylphosphine)nickel(II), deep blue

crystals from ethanol, m.p. 148-50°. (Found: C, 43.85; H, 5.35%;

$\underline{M}$, 578.6 (ebulliometric), 619 (vapour-pressure method). $C_{20}H_{28}P_2NiBr_2$

requires C, 43.75; H, 5.1%; $\underline{M}$, 548.7). μ_{eff}, 2.5 B.M.

Di-iodo(2,2'-biphenylylenebisdiethylphosphine)nickel(II), dark brown

crystals from ethanol, m.p. 175 - 178°d. (Found: C, 37.3; H, 4.3;

$\underline{M}$, 660.8 (ebulliometric), 888 (vapour-pressure method); $C_{20}H_{28}P_2NiI_2$

requires C, 37.35; H, 4.35%; $\underline{M}$, 642.7). μ, 9.4D; μ_{eff}, 2.8 B.M.

Di-isothiocyanato(2,2'-biphenylylenebisdiethylphosphine)nickel(II), red-

brown crystals from ethanol, m.p. 182 - 185°d. (Found: C, 52.2; H, 5.25;

N, 5.5%; $\underline{M}$, 491.5 (ebulliometric), 576 (vapour-pressure method);

$C_{20}H_{28}P_2Ni(NCS)_2$ requires C, 52.3; H, 5.55; N, 5.55%; $\underline{M}$, 504.9);

diamagnetic.

i.r. (mull): 2135, 2100 cm^{-1} (ν C≡N); 825 cm^{-1} (ν C–S). These bands

were absent from the spectrum of the corresponding nickel(II) bromide

complex.

Dibromo(2,2'-biphenylylenebisdiethylarsine)palladium(II).

A solution of potassium tetrabromopalladate(II) (50 mg) in

aqueous ethanol (2 ml) was added to a solution of the diarsine (V)

(60 mg) in ethanol (2 ml). The resulting solution when boiled

deposited yellow crystals of the complex, m.p. 247-50°d. (Found: C, 35.3;

H, 3.8. $C_{20}H_{28}As_2PdBr_2$ requires C, 35.05; H, 4.1%).

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