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o-NITROSOPHENOL COMPLEXES AND THEIR SYNTHETIC POTENTIAL.

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National Academic Awards in partial
fulfilment of the requirements for the
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by

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o-Nitrosophenol complexes and their synthetic potential.

Abstract.

Interaction of triphenylphosphine with $Ni(XqO)_2$ (XqOH = 2-nitrosophenol, X = 4-chloro, 4-bromo, 4-methyl and 5-methoxy) resulted in deoxygenation to give mainly bis(2-triphenylphosphiniminophenolato) nickel(II). Similarly the interaction of triphenyl phosphine with $Zn(qO)_2$ (qOH = 5-methoxy-2-nitrosophenol) involved deoxygenation and formation of bis(2-triphenylphosphiniminophenolato)zinc(II). Action of dilute hydrochloric acid on these complexes afforded the hydrochlorides of the corresponding N(2-hydroxybenzene)iminotriphenyl phosphoranes. The hydrochlorides on neutralisation with sodium carbonate gave, in most cases, the parent N(2-hydroxybenzene)iminotriphenylphosphorane.

Interaction of triphenylphosphine with $Cu(XqO)_2$ (XqOH = 2-nitrosophenol, X = 4-methyl and 5-methoxy) resulted in deoxygenation of the ligand and reduction of the copper. In both cases the complex $Cu(XqO)(PPh_3)_2$ was formed along with a complex mixture of organic compounds. Some of these organic compounds were characterized e.g. 1,6-dihydroxy-3,8-dimethoxyphenazine. One of the ligands in $Fe(qO)_3$ (qOH = 5-methoxy-2-nitrosophenol) was also deoxygenated and the iron reduced by triphenylphosphine. The complex $Fe(qO)_2 2py$ and 1,6-dihydroxy-3,8-dimethoxyphenazine were isolated.

The free 5-methoxy-2-nitrosophenol was deoxygenated by triphenyl phosphine to give a mixture of organic compounds. 1,6-Dihydroxy-3,8-dimethoxy-dihydrophenazine was identified among the products.

Reaction pathways for the above systems, involving nitrene intermediates, are suggested.

The structure of N-(2-hydroxybenzene)iminotriphenylphosphoranes and of their nickel(II) and zinc(II) complexes has been investigated. The iminophosphoranes have cyclic benzoxazaphosphole structures in the solid state and in solution but the mass spectrometric studies suggest an open structure in the vapour state. The nickel(II) complexes are pseudo-tetrahedral as indicated by magnetic studies and their electronic spectra. A similar structure is suggested for $Zn(5\text{-}MeOqPPh_3)_2$. The structure of the complexes reflects the steric features of the ligands.

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DECLARATION

Whilst registered as a candidate for this degree, the author has not been a registered candidate for any other award.

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CHAPTER 1

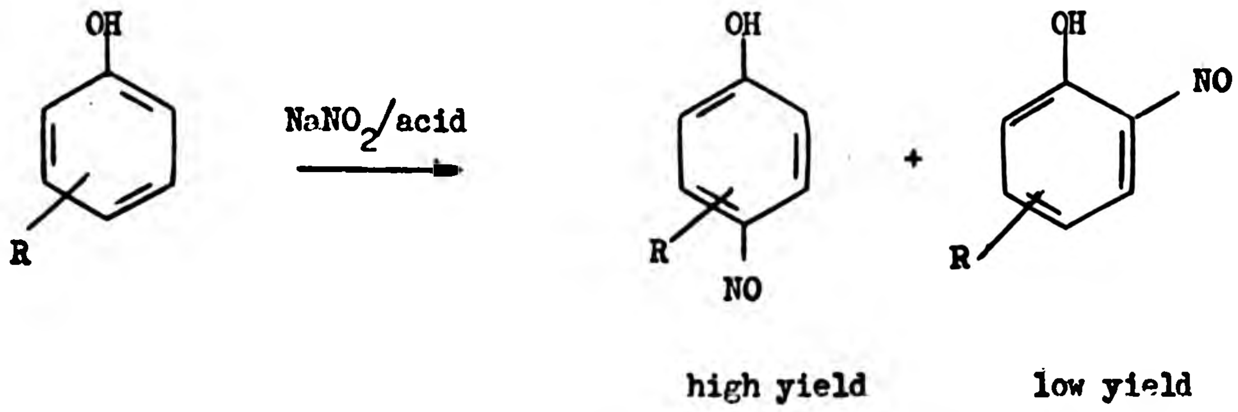
The Nature of some 2-Nitrosophenols and their Metal Complexes.

1.1. Introduction.

In this first chapter, a brief description of the early work on 2-nitrosophenols is presented. This is followed by an account of the present state of knowledge of the structure and bonding in their metal complexes, and the potential of such complexes in synthesis.

1.2. 2-Nitrosophenols.

The nitrosation of phenols using sodium nitrite/acid leads mainly to the 4-substituted products[1] (Reaction 1.1.).



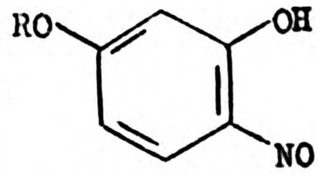
Reaction 1.1.

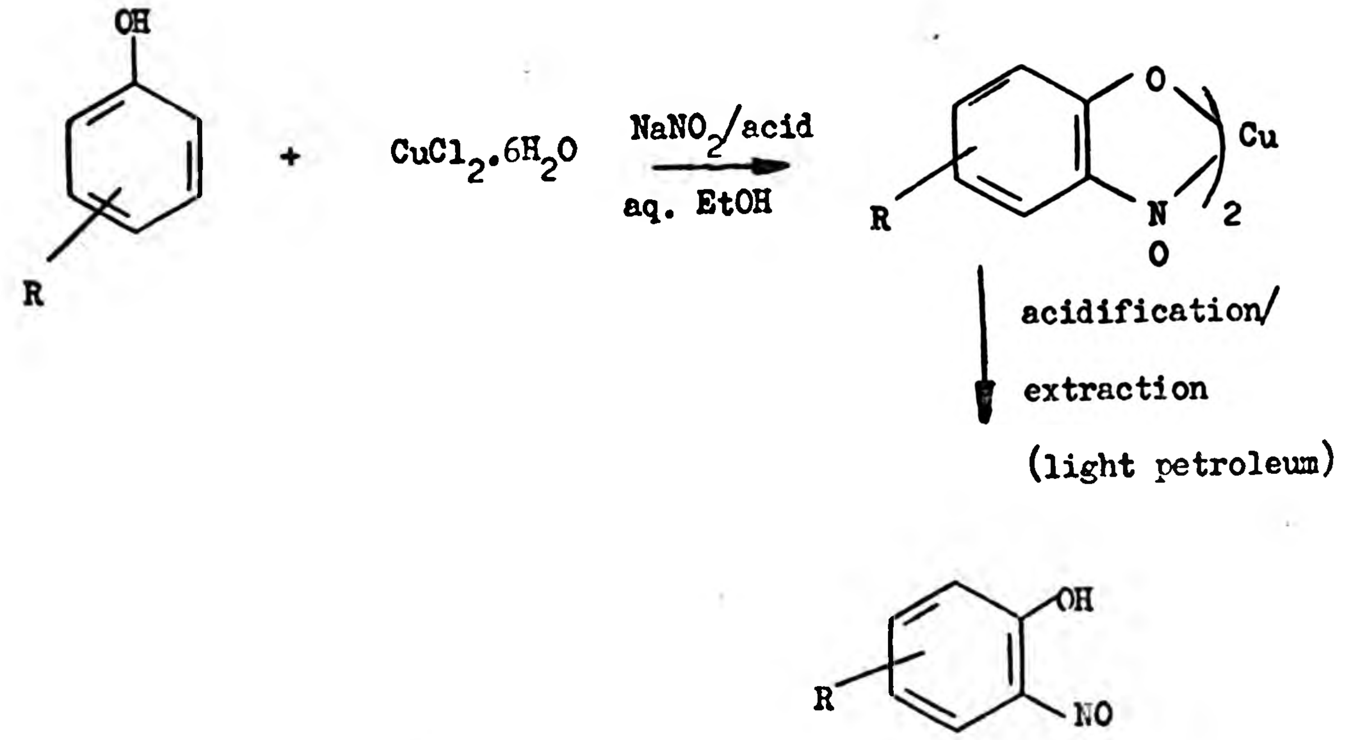
In some cases (e.g. resorcinol and its derivatives) a mixture of the 2- and 4- isomers are formed.[2 - 8] (Table 1.1.)

A number of 2-nitrosophenols have been obtained by acidification of the corresponding copper complex. These complexes were obtained either by the reaction of hydroxylamine hydrochloride, hydrogen peroxide and an aromatic compound in the presence of a copper salt[9], or by the nitrosation of a phenol using sodium nitrite and acetic acid in the presence of a copper salt[10] (Reaction 1.2.). These and other more specific methods have recently been discussed.[11]

Table 1.1.

2-Nitroso Derivatives of Resorcinol.

R in 	Name	Abbreviation
CH_3	5-Methoxy-2-nitrosophenol[3]	5-MeOqOH
C_2H_5	5-Ethoxy-2-nitrosophenol[4]	5-EtOqOH
H	5-Hydroxy-2-nitrosophenol[5]	5-HOqOH
n-C_3H_7	5-n-Propoxy-2-nitrosophenol[6]	5-n-PrOqOH
iso-C_3H_7	5-iso-Propoxy-2-nitrosophenol[7]	5-iso-PrOqOH
n-C_4H_9	5-n-Butoxy-2-nitrosophenol[8]	5-n-BuOqOH

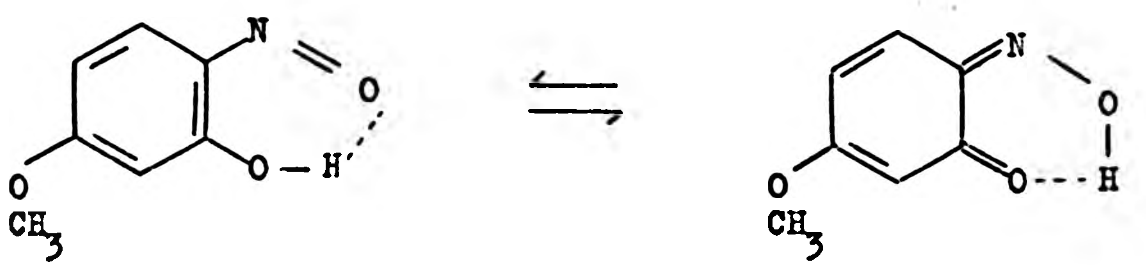


Reaction 1.2.

1.3. Tautomerism of 2-Nitrosophenols.

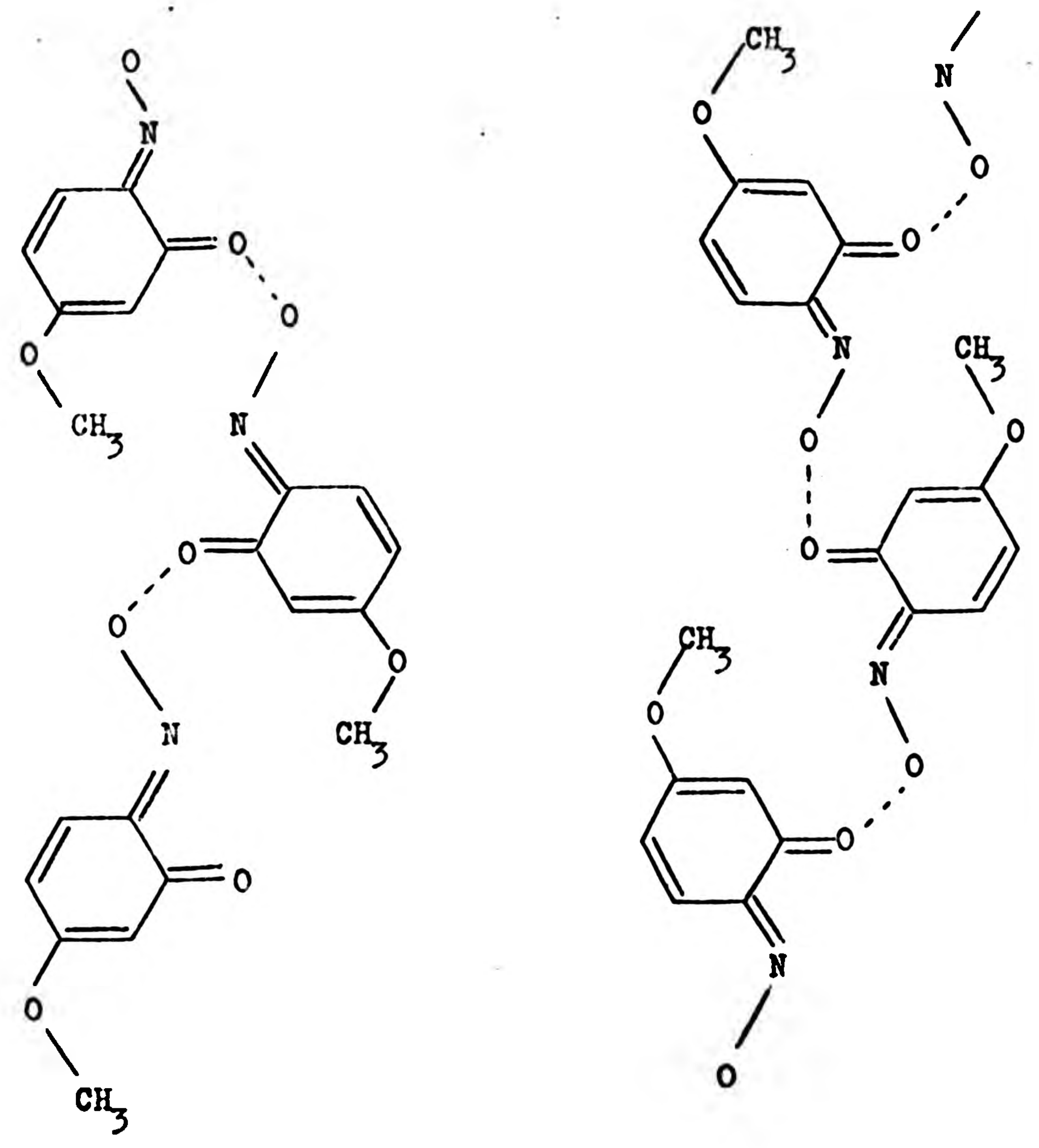
Most of the studies of tautomerism of 2-nitrosophenols have involved the 5-alkoxy-2-nitrosophenols. When Henrich and Eisenach[3] prepared 5-methoxy-2-nitrosophenol, they found that it crystallised in green rectangular plates from benzene and in red needles from ethanol. Furthermore they observed that at 128 - 130°C the green form changed to the red form which then melted at 154°C. They suggested that the two forms were tautomers and proposed that the green form was the nitrosophenol form and the yellow form was the quinoneoxime form.

Although the X-ray powder pattern photographs of the two forms were different, their solution u.v. spectra were identical[12]. Comparison of the spectra with those of 2,4-dimethoxy-1-nitrosobenzene and 3-methoxy-6-methoxyiminocyclohexadienone suggested that in solution a solvent dependent tautomeric equilibrium between the intramolecularly hydrogen bonded species (1.3.) and (1.4.) exists.



(1.3.) (1.4.)

Subsequent crystal structure determinations of the red form of 5-methoxy-2-nitrosophenol[13] (1.5.), the green form of β-5-n-propoxy-1-quinone-2-oxime[14] (1.6) and the red form of 5-(2^1-chloroethoxy)-1-quinone-2-oxime[15] (1.7.) indicated they had the following structures.



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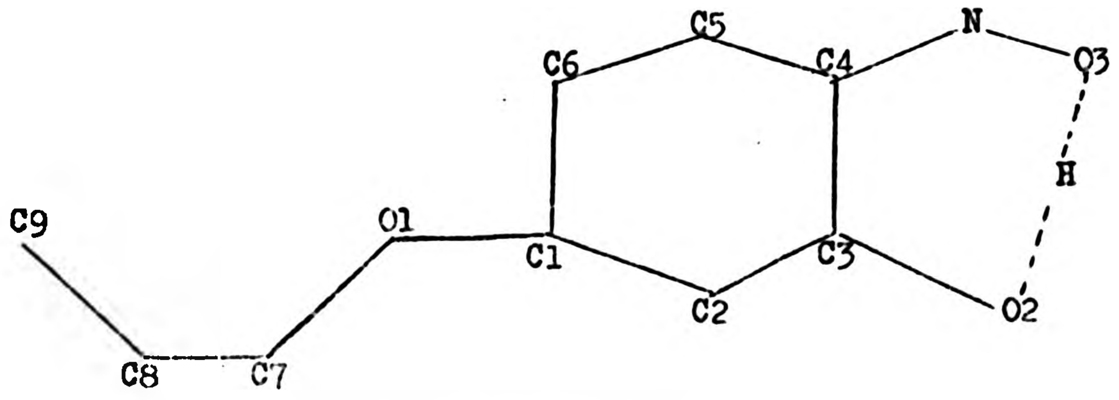
(1.5.)



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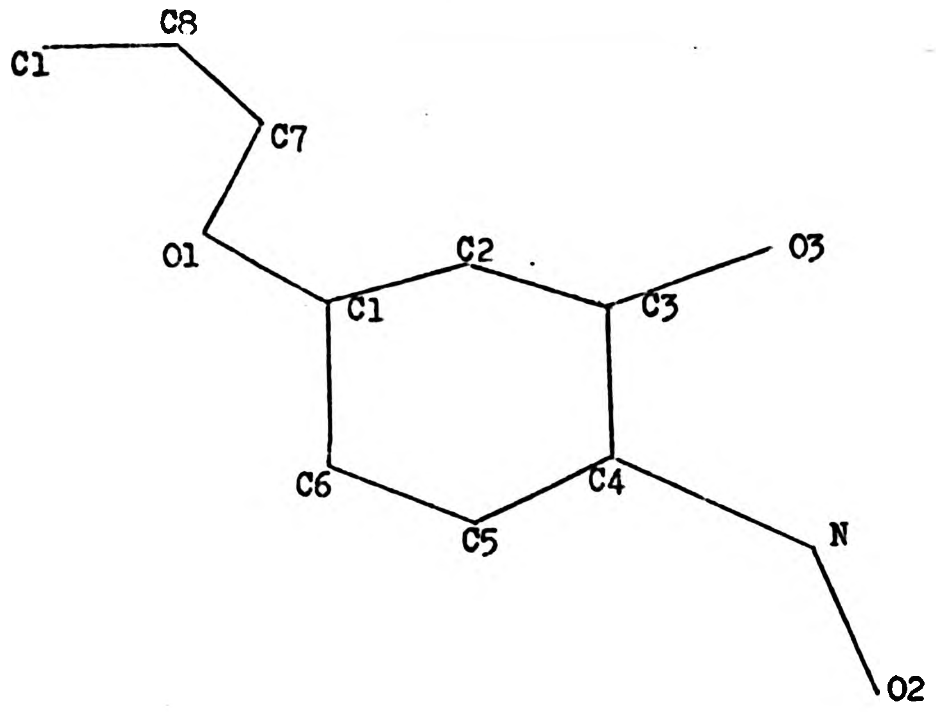
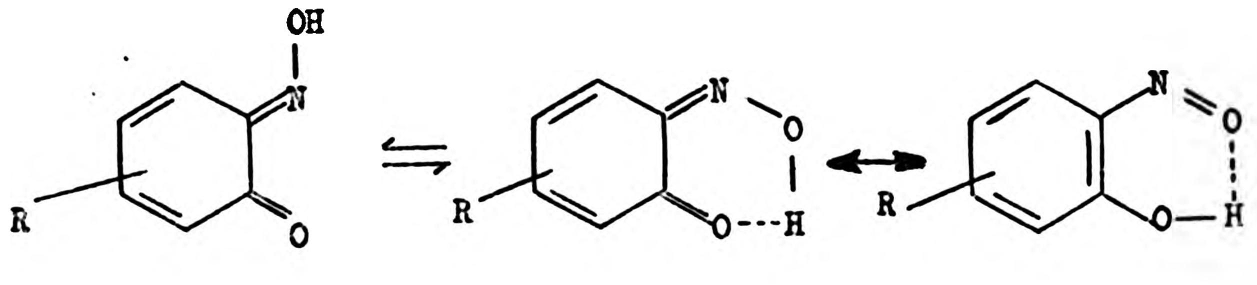
(1.6.)



(1.7.)

All three X-ray determined structures showed predominantly oxime-like structure. The two red forms (1.5. and 1.7.) have the oxime groups anti to the CO groups, while in the green form (1.6.) the oximic oxygen is syn to the CO group.

Consequently, it appears that the 2-nitrosophenol-1-quinone-2-oxime system is best described as shown below (1.8. and 1.9.).



(1.8.) (1.9.a) (1.9.b)

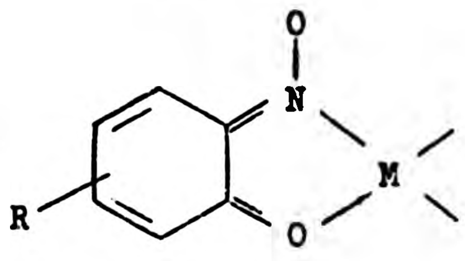
1.4. Structural Features of Metal Complexes Derived from 2-Nitrosophenols.

Although metal chelates[10,11,16-18] of 2-nitrosophenols have been known for a considerable time it is only recently that some have been studied in detail and their structural features elucidated. Most of the complexes studied so far contain the anionic ligand $q\bar{O}$ (qOH = 2-nitrosophenol)[19-23]. However recently complexes containing the neutral qOH ligand have been reported.[11] For example, $(1\text{-nqOH})_2\text{FeCl}_2$(1-nqOH = 1-nitroso-2-naphthol) was prepared by adding ferrous chloride to a suspension of the ligand in chloroform under nitrogen. Compounds containing the protonated ligand qOH_2^+,[19] e.g. $[\text{qOH}_2]_2[\text{CuCl}_4]$ (qOH = 4-chloro-2-nitrosophenol) have also been reported.

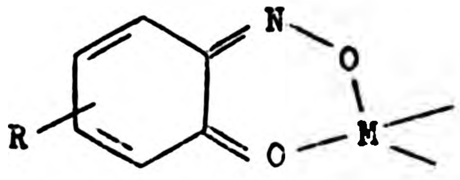
There are two problems of interest in relation to the structure of chelates containing the anionic ligand $q\bar{O}$. One concerns the mode of bonding of the NO group to the metal, and the other, the quinoneoximic-nitrosophenolic character of the coordinated $q\bar{O}$ ligand.

A) The Mode of Bonding of the NO Group.

The NO group may coordinate to the metal through either the nitrogen atom (1.9.) or the oxygen atom (1.10.).



(1.9.)



(1.10)

The presence of peaks corresponding to $[\text{Cu(qO)}_2 - 2\text{xO}]^+$ (i.e. the bis-chelate minus two oxygen atoms) in the mass spectra of the complexes Cu(qO)_2[22] (qOH = 4-chloro-2-nitrosophenol, 4-bromo-2-nitrosophenol, 4-methyl-2-nitrosophenol, and 5-methoxy-2-nitrosophenol), and the presence of peaks due to fragments such as $[\text{Ni}_2(\text{qO})_4 - 4\text{xO}]^+$ and $[\text{Ni(qO)}_2 - 2\text{xO}]^+$ in the spectra of the dimeric complexes $\text{Ni}_2(\text{qO})_4$[22,23] (qOH = 4-chloro-2-

nitrosophenol, 4-methyl-2-nitrosophenol, 4-t-butyl-2-nitrosophenol and 5-methoxy-2-nitrosophenol) were interpreted as indicative of N-M bonding (1.9.).

This mode of bonding has recently been established by X-ray crystallographic studies of a number of complexes (Table 1.2.)

N-M bonding is also indicated for several other complexes by their ready deoxygenation with triphenyl phosphine (see chapters 3 and 4).

B) The Quinoneoximic-Nitrosophenolic Character of the Co-ordinated qO Ligand.

The complexes can be represented in valence-bond terms as involving resonance between structures (1.11.a) and (1.11.b.).

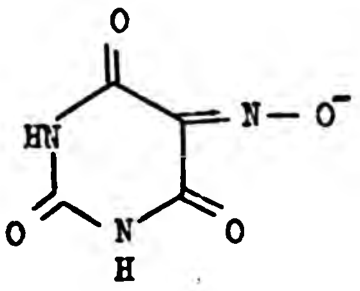
(1.11.a) (1.11.b.)

Several studies[33,34] of the infrared spectra of the chelates have been made in order to ascertain the relative contributions of these structures. These studies consisted of a comparison of the spectra of the chelates with those of the nitrosophenolic and quinoneoximic-forms of the unreacted ligand. Thus it was concluded that in several $Cu(qO)_2$[19] and $Fe(qO)_3$[11] complexes the quinoneoximic structure (1.11.b.) makes a significant contribution. However these conclusions must be viewed with caution, because this comparison involves assignments of bands in the spectra of the complexes and ligands, an operation which is inherently difficult.

As noted earlier the crystal structures of several nitrosophenol complexes are now available. In principle, bond length considerations

Table 1.2.

Nitrosophenol and Nitrosonaphthol Complexes whose Structure has been Determined by X-ray Crystallography.

Complex	qOH Ligand	Reference
$Cu(qO)_2py^a$	4-methyl-2-nitrosophenol	24
$Na[Fe(qO)_3]^b$	4-vinylphenyl ester of 3-nitroso-4-hydroxybenzoic acid.	25
$K[Ni(qO)_3],(CH_3)_2CO$	4-chloro-2-nitrosophenol	26
$Cu(1\text{-}nqO)_2,2(CH_3)_2CO$	1-nitroso-2-naphthol	27
$Cu(2\text{-}nqO)_2,H_2O$	2-nitroso-1-naphthol	28
$Cu(2\text{-}nqOS)(3H_2O),2H_2O$	2-nitroso-1-naphthol 4-sulphonate=$2nqOSH_2$	29
$(NH_4)_2[Zn(H_2O)_2(2\text{-}nqOS)_2]$	" "	30
$Cu(1\text{-}nqO)(PPh_3)_2$	1-nitroso-2-naphthol	31
$[NH_4][FeV_3]\ 4.5H_2O$	V = 	32

a) py = pyridine

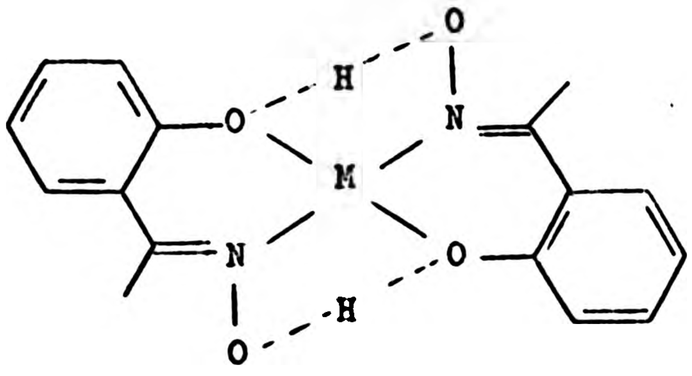
b) ferroverdin

could provide a direct indication of the relative contributions of the nitrosophenolic and quinoneoximic structures.

The M-N, M-O, C-O, C-N, N-O and ring C-C bond lengths of these chelates are presented in Table 1.3. For comparison the corresponding figures for the green oxime form of 5-(2^1-chloroethoxy)-1-quinone-2-oxime are also included.

The hexagonal rings show a pattern of two short (C_3-C_4 and C_5-C_6) and four long (C_1-C_2, C_2-C_3, C_4-C_5 and C_6-C_1) carbon-carbon bond distances which suggests strong quinonoid contributions.

The C-N bond distances (ca 1.35Å) in the complexes are shorter than the C-N bond distances in 1,8-dinitrosonaphthalene[35] (1.44Å) and the C-O bonds are shorter than the C-O bonds in salicyladoximates[36] (1.40Å) (1.12)



(1.12.)

As the C-N in 1,8-dinitrosonaphthalene and the C-O bond in salicyladoximates have essentially single bond character, the above observations provide further evidence for the significance of the quinoneoxime contribution.

C) Bridging in 2-Nitrosophenol Complexes.

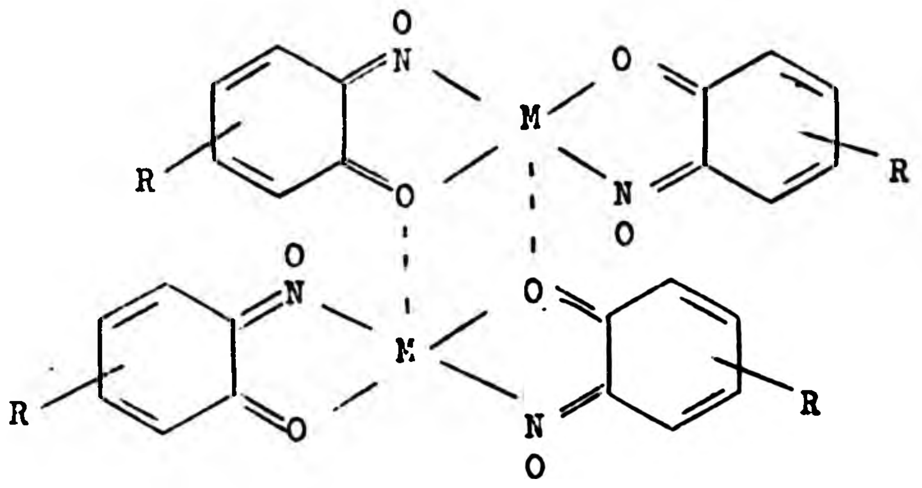
Ligands of the type $q\bar{O}$ have a multidentate character, and may act as bridging ligands (1.16.).

Table 1.3.

Mean Bond Lengths (Å) in the Coordination Planes of Nitrosophenol and Nitrosonaphthol Complexes.

Compound	C–O	C–N	N–O	M–O	M–N	C–C (s)	C–C (l)
Na$[Fe(qO)_3]$	1.30	1.42	1.25	1.95	1.84	-	-
(qOH = 4-vinylphenyl ester of 4-hydroxy-3-nitrosobenzoic acid)							
Cu$(qO)_2$,Py	1.27	1.35	1.25	1.97	2.00	1.37	1.43
(qOH = 4-methyl-2-nitrosophenol)							
K$[Ni(qO)_3]$,$(CH_3)_2CO$	1.25	1.33	1.27	2.06	2.01	1.36	1.43
(qOH = 4-chloro-2-nitrosophenol)							
Cu$(1\text{-}nqO)_2$,$2(CH_3)_2CO$	1.30	1.35	1.26	1.95	1.99	1.39	1.43
(1-nqOH = 1-nitroso-2-naphthol)							
Cu$(1\text{-}nqO)_2$,H_2O	1.28	1.35	1.26	1.97	1.98	-	-
(2-nqOH = 2-nitroso-1-naphthol)							
Cu(2-nqOS)($3H_2O$),$2H_2O$	1.26	1.35	1.25	1.95	1.96	-	-
(2-nqOSH$_2$= 2-nitroso-1-naphthol 4-sulphonate)							
$(NH_4)_2[Zn(H_2O)_2(2\text{-}nqOS)_2]$	1.26	1.35	1.27	2.12	2.16	-	-
α-5-(2^1-chloroethoxy)-1-quinone-2-oxime	1.25	1.31	1.37	-	-	1.35	1.46

s = short   l = long



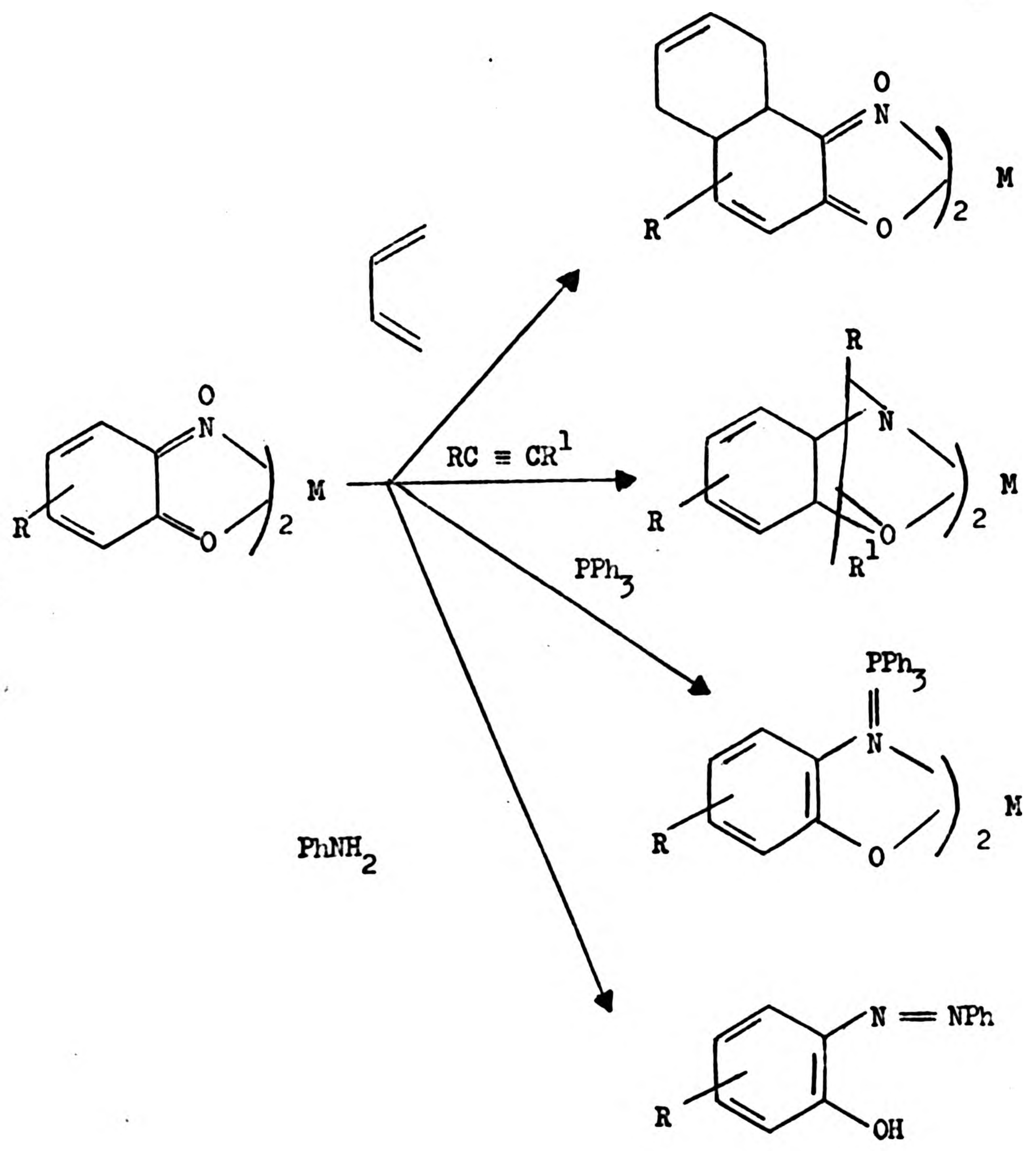
(1.16.)

In a complex of the type $M(qO)_2$ association of the units $M(qO)_2$ may occur with the resultant formation of dimeric or polymeric structures. Polymer formation has been suggested for several $Cu(qO)_2$[19] complexes in the solid state. Dimer formation of type (1.16.) has been suggested for several $Ni(qO)_2$[21,23] complexes on the bases of magnetic, molecular weight measurements and mass spectrometric studies. This chelating/bridging capacity of the ligand leading to association of its complexes is not uncommon. For example, bis(dimethylglyoximato)copper(II)[37] and (N,N^1-disalicylidene-ethylenediamino)copper(II)[38] associate in a similar fashion.

1.5 The Potential of Metal Complexes of 2-Nitrosophenols in Synthesis.

The structure of $M(qO)_n$ suggests diene, dienophile and heterodiene character and indicates the presence of reactive NO and CO groups. This multifunctional character and ready availability of 2-nitrosophenol complexes makes them most promising substrates for the synthesis of a variety of useful or novel types of compounds. Several reactions outlining their synthetic potential are given below (1.17). These reactions are currently under systematic investigation at The Polytechnic of North London.

The quinoneoximic character of 2-nitrosophenol complexes is potentially useful in Schiff base type condensation reactions and in the synthesis of azo compounds. A satisfactory synthesis of an azo compound has recently been achieved.[39] The quinoneoximic character also suggests the potential



(1.17.)

of such complexes in Diels-Alder type reactions. The involvement of the heterodiene system of such complexes in cyclo-addition reactions has recently been demonstrated.[40] Thus dimethyl acetylene dicarboxylate was found to add across the heterodiene system to give 1,4-benzoxazines.

Organic nitroso compounds are readily deoxygenated with tervalent phosphorus compounds.[41-45] The mode of bonding of the NO group in 2-nitrosophenol complexes suggests that such compounds are particularly amenable to deoxygenative reduction. Indeed such reduction can be effected by a variety of reagents e.g. phosphorus (III) compounds[46], amines[47], and olefins[47] leading to a variety of products.

The deoxygenative reduction of 2-nitrosophenol complexes with triphenyl phosphine is the subject of this work and is presented and discussed in the following chapters.

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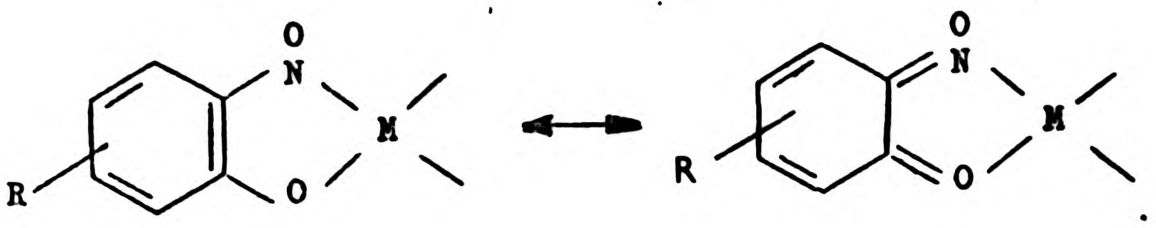
CHAPTER 2

The Interaction of Metal Complexes Derived from 2-Nitrosophenols with Triphenyl Phosphine.

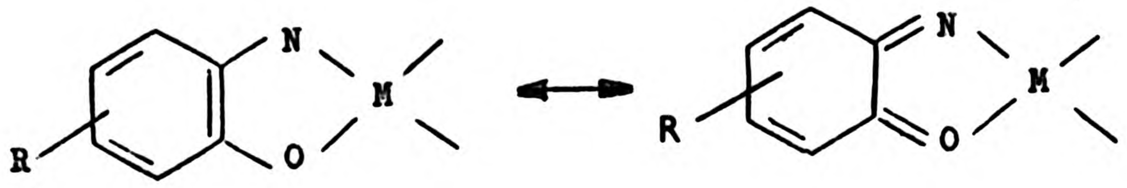
2.1. Introduction

As noted in chapter I there is now a considerable body of evidence to suggest that metal complexes of 2-nitrosophenols are N-bonded 2.1..



2.1.

As a consequence, such compounds would be expected to undergo facile deoxygenation brought about by phosphorus (III) compounds. Phosphorus (III) compounds are known to deoxygenate organic nitroso and nitro-compounds to give a variety of products.[41] It is believed that, in some cases at least, these products arise through nitrene intermediates.[48] It is thus reasonable to expect that deoxygenation of metal complexes of 2-nitrosophenols could lead to the trapping of nitrenes as complexes because of the possibility of stabilization through chelation and resonance (2.2.).



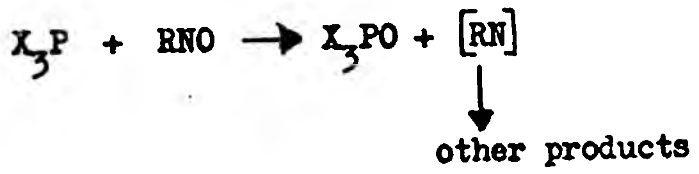
2.2.

Stabilization of nitrenes through complexation has previously been achieved using low-valent transition metal systems, mainly by reactions involving organoazides.[49]

In the next three sections of this chapter an outline of the literature on (a) the deoxygenation of organic nitroso-and nitro-compounds, (b) the trapping of nitrenes as metal complexes and (c) the synthetic potential of the deoxygenation of metal complexes of 2-nitrosophenols are considered. Subsequently the results of the investigations undertaken for this thesis on the deoxygenation of 2-nitrosophenols and their complexes by triphenyl phosphine are presented and discussed.

2.2. Deoxygenation of Organic Nitro- and Nitroso- Compounds by Tervalent Phosphorus Compounds.

The interaction of tervalent phosphorus compounds X_3P, such as triphenyl phosphine, with a wide variety of organic nitro- and nitroso-compounds (RNO) to give the corresponding pentavalent phosphorus oxo derivatives (X_3PO) and deoxygentated organic species ($\boxed{RN}$) is very well documented[41 - 45, 50, 51] (Reaction 2.1.).



$$X_3P + RNO \longrightarrow X_3PO + \underset{\substack{\downarrow \\ \text{other products}}}{\boxed{RN}}$$

Reaction 2.1.

The major driving force for these reactions is the great strength of the P=O bond formed. Typical values for P=O bond dissociation energies in phosphates and phosphine oxides lie in the range of 502 - 628 kJ/mole, which can be compared with values in the range 209 - 293 kJ/mole for the N^{+}— O^{-} bond in amine oxides.

Most of the reported reactions of nitroso-compounds with tervalent phosphorus reagents involve aromatic systems and give a variety of deoxygentated nitrogen compounds (eg: azo- and azoxy- compounds, phenazines, iminophosphoranes , and carbazoles). Bunyan and Cadogen[42] reported, for example, that the interaction of nitroso-arenes (eg. 2-dimethylamino-nitrosobenzene) with triethyl phosphite gives the azoxy compound 4,4'-bisdimethylaminoazoxybenzene, and triethyl N-2-dimethylaminophenyl-phosphorimidate (Reaction 2.2.). This led to the suggestion that such reactions involve the intermediacy of nitrenes (Scheme 2.1.). Tervalent

$$ArNO + (EtO)_3P \rightarrow Ar\overset{O}{N}{=}NAr + (EtO)_3PO + (EtO)_3P = NAr$$

Reaction 2.2.

$$(Ar = 2\text{-}(CH_3)_2N{\cdot}C_6H_4)$$

phosphorus compounds X_3P and organic nitro-compounds RNO_2 behave similarly but the reaction is slower [41] (reaction 2.3.)

$$\begin{array}{lllll} ArNO & + & X_3P & \rightarrow & X_3P\underset{O}{O} + \boxed{ArN} \\ \boxed{ArN} & + & ArNO & \rightarrow & ArN{=}NAr \\ \boxed{ArN} & + & X_3P & \rightarrow & ArN{=}PX_3 \end{array}$$

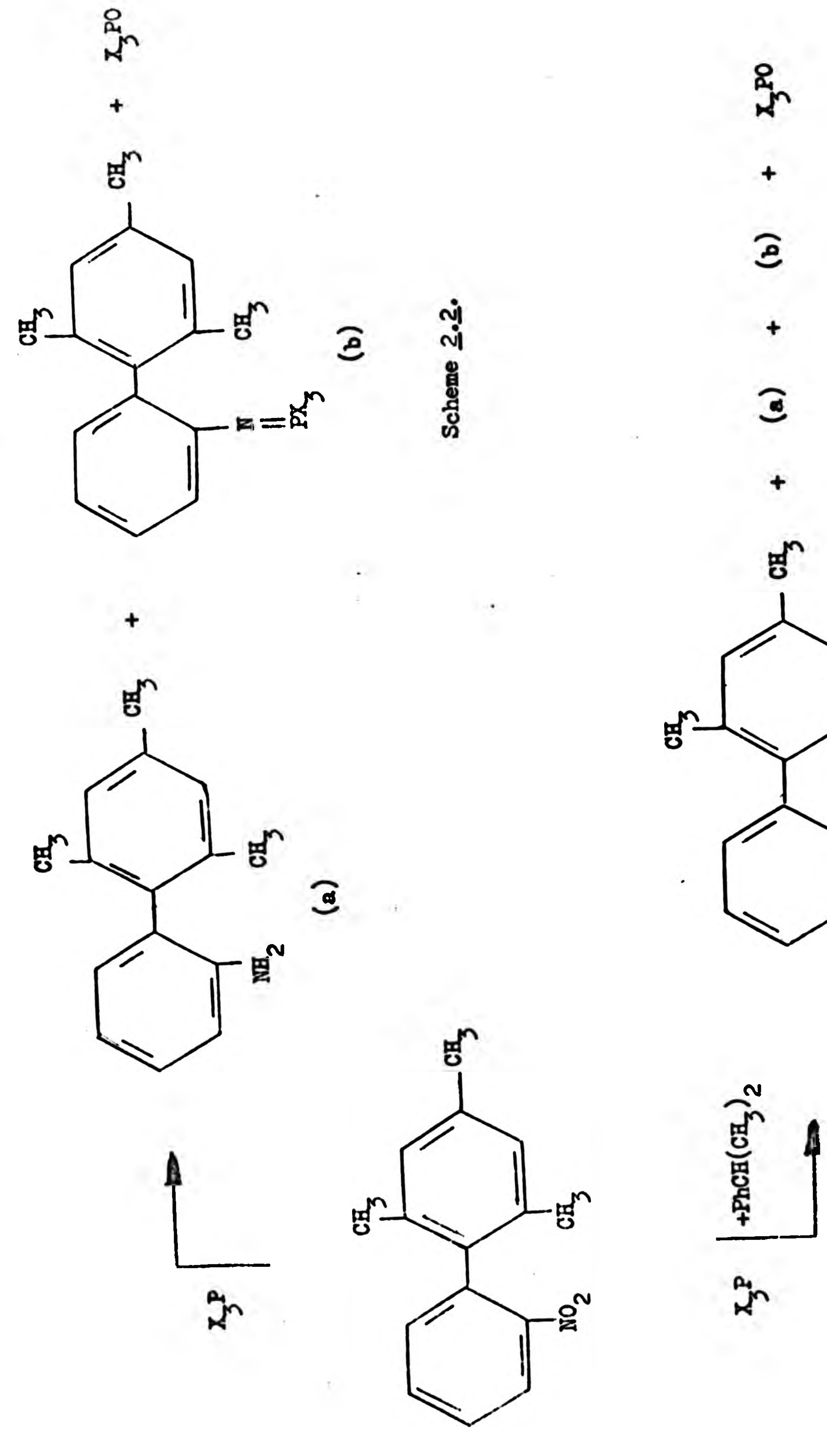
Scheme 2.1.

$$\begin{tikzcd} RNO_2 \arrow[r, "X_3P"] & RNO \arrow[r, "X_3P"] & \boxed{RN} \arrow[d] \\ & & \text{products} \end{tikzcd}$$

Reaction 2.3.

Convincing evidence for the intermediacy of nitrenes has been obtained from the interaction of 2'-nitro-2,4,6-trimethyl biphenyl with triethyl phosphite [52] (Scheme 2.2.). The isolation of 2'-amino-2,4,6-trimethyl-biphenyl (a in Scheme 2.2.) the product of hydrogen abstraction by an electron-deficient nitrogen species, and triethyl N-(2',4',6-trimethylbiphenyl-2-yl) phosphorimidate (b) the product of coupling with the tervalent phosphorus reagent are both typical reactions of nitrenes. Also when the reaction is carried out using iso-propyl benzene as the solvent, in addition to (a) and (b), the insertion product 8,10-dimethylphenanthridine (c) is isolated. Furthermore bi-α-cumyl is formed which can only arise by the dimerisation of α-cumyl radicals produced by intermolecular hydrogen abstraction by a nitrene.

Further support for nitrene intermediacy in the deoxygenation of the nitroso group has been obtained from the thermal decomposition of organo



Scheme 2.2.

azides[53, 54]. The thermal decomposition of organo azides which on kinetic evidence goes via nitrene intermediates[55] leads to products similar to those obtained by deoxygenation of analogous nitroso-compounds[43].

However, it is clear from reports in the literature that several aspects of the mechanism of deoxygenation of nitroso-compounds cannot be accounted for by nitrene intermediates alone. Deoxygenation of nitroso-compounds has also been accounted for (a) by assuming electrophilic attack by tervalent phosphorus on the nitroso oxygen[51] and (b) in terms of the concept of a cyclic or Zwitterionic intermediate which dissociates into the products[56].

2.3. Nitrenes Trapped as Metal Complexes.

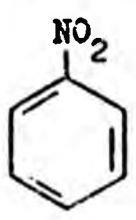
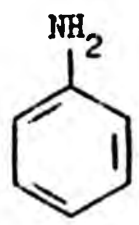
There are not many examples of nitrenes stably coordinated in metal complexes Table 2.1. Most of those that have been reported were trapped by low-valent transition metal systems, mainly by reactions involving organoazides.

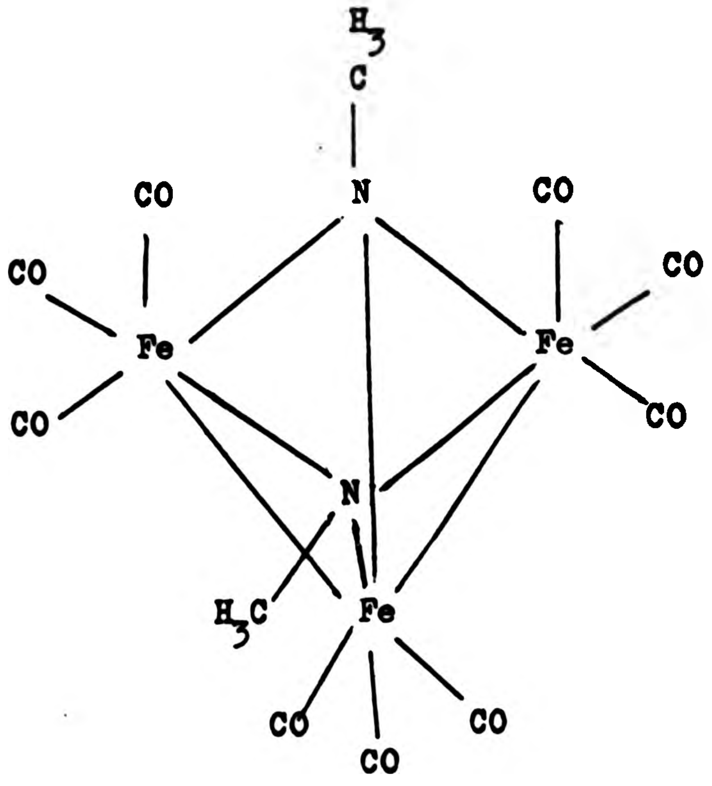
The decomposition of azides in the presence of nonacarbonyldiiron(0) gives products which may be regarded as containing nitrenes as ligands. Dekker and Knox[57] isolated di-μ_3-methylimido-tris(tricarbonyliron), $(CH_3N)_2Fe_3(CO)_9$ from the interaction of methyl azide, and $(C_6H_5N)_2Fe_2(CO)_6$ from the interaction of azidobenzene with nonacarbonyldiiron, respectively. An X-ray crystallographic study by Doedens[58] confirmed the structure of $(CH_3N)_2Fe_3(CO)_9$ (2.3). Iron[59], ruthenium, cobalt, rhodium[49] and nickel[60] nitrene complexes have been isolated from the decomposition trimethylsilyl azide in the presence of the respective metal carbonyls. Recently Sappa and Milone[61] reported an analogous complex μ_3-phenylimido (decacarbonyl-triruthenium), formed by reacting nitrobenzene or aniline with $Ru_3(CO)_{12}$.

The nitrene complexes derived from trimethylsilyl azide gave remarkably stable crystalline solids having decomposition temperatures in the range 110-250°C. Mass spectrometric studies on these complexes indicated retention of structure even in the vapour state.

TABLE 2.1.

Nitrene Complexes

Complex	Synthesis	Ref.
μ_3-trimethylsilylimido- (decacarbonyltriruthenium) $(CH_3)_3SiN[Ru_3(CO)_{10}]$	$Ru_3(CO)_{12} + (CH_3)_3SiN_3$	49
μ_3-trimethylsilylimido-μ_3 carbonyl tris(cyclopentadienylcobalt) $[(CH_3)_3SiN]CO[\pi\text{-}C_5H_5Co]_3$	$\pi\text{-}C_5H_5Co(CO)_2$ + $(CH_3)_3SiN_3$	49
μ_3-trimethylsilylimido-μ_3 carbonyl tris(cyclopentadienylrhodium) $[(CH_3)_3SiN]CO[\pi\text{-}C_5H_5Rh]_3$	$(RhC_5H_5)_3(CO)_2$ + $(CH_3)_3SiN_3$	49
μ_3-trimethylsilylimido- (decacarbonyltriiron) $(CH_3)_3SiN[Fe_3(CO)_{10}]$	$Fe_2(CO)_9$ + $(CH_3)_3SiN_3$	59
μ_3-tertbutylimido- tris(cyclopentadienylnickel) $t\text{-}C_4H_9N(\pi\text{-}C_5H_5Ni)_3$	$(\pi\text{-}C_5H_5)_2Ni$ + $(t\text{-}C_4H_9N)_2S$	60
Di-μ_3-methylimido- tris(tricarbonyliron) $(CH_3N)_2Fe_3(CO)_9$	$Fe_2(CO)_9$ + CH_3N_3	57
Bis(1,2-diphenylphosphine-ethane) dichloroimido molybdenum $[Mo(NH)Cl_2(dpe)_2]$ (dpe = $Ph_2\text{-}PCH_2CH_2P\text{-}Ph_2$) (TMSA = $(CH_3)_3SiN_3$)	$[Mo(N_2)_2(dpe)_2]$ $\downarrow$ TMSA $[MoN(N)_3(dpe)_2]$ $\downarrow$ 2HCl $[MoCl_2(NH)(dpe)_2]$	62
μ_3-phenylimido (decacarbonyltriruthenium) $Ru_3(CO)_{10}NPh$	$Ru_3(CO)_{12}$ +  NO_2 or  NH_2	61



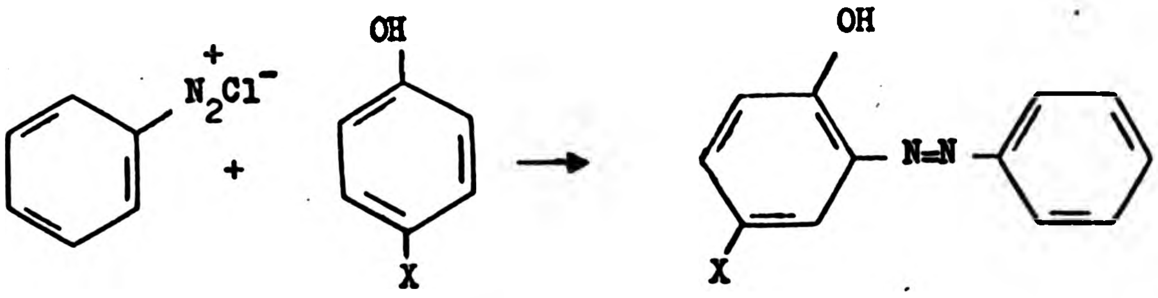
Di-μ_3-methylimido-tris(tricarbonyliron)

2.3.

2.4. The Interaction of Bis(benzoquinone-2-oximato)Nickel(II) complexes with excess Triphenyl Phosphine.

By analogy to the deoxygenating behaviour of nitro and nitroso compounds, outlined in the previous section, it is reasonable to expect that 2-nitrosophenol complexes and triphenyl phosphine could also afford a variety of products (Scheme 2.3.). Furthermore it is quite conceivable that such reactions could lead to isolable nitrene complexes, stabilized through chelation and resonance.

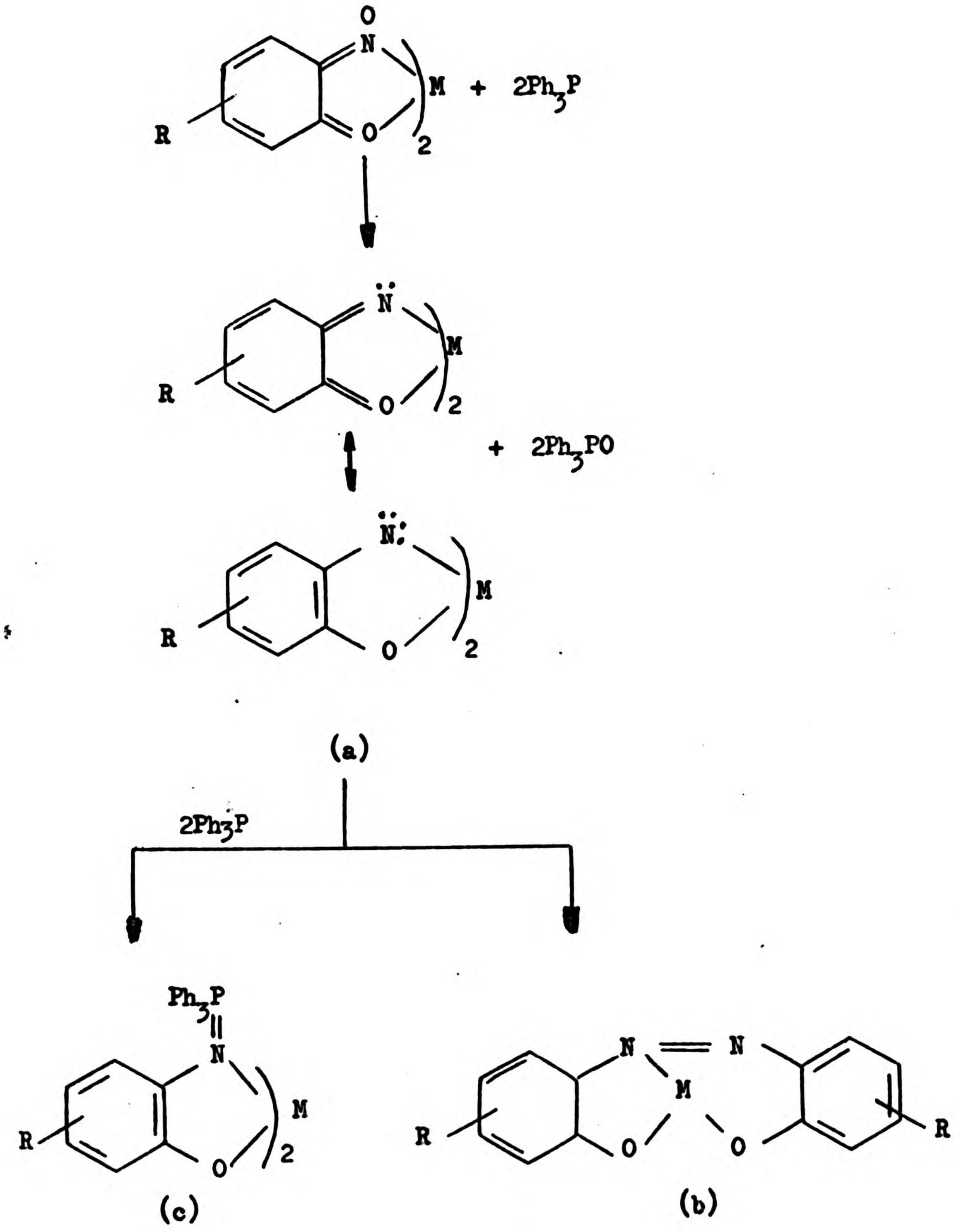
The synthetic potential of the deoxygenation of 2-nitrosophenol complexes is outlined in Scheme 2.3.. The quinoneimine/nitrene species ('a' Scheme 2.3.) could give the 2,2'-dihydroxyazo complex ('b' Scheme 2.3.). This may be a convenient method for making unsubstituted 2,2'-dihydroxyazo compounds, as diazonium salts usually undergo coupling in the 2-position only when the 4-position is substituted[1] (Reaction 2.4.)



Reaction 2.4.

If, however, an excess of triphenyl phosphine is present, the quinoneimine/nitrene species 'a' could react further to form an iminophosphorane complex ('c' Scheme 2.3.).

The reaction of triphenyl phosphine (5 mol. equiv.) and $Ni(qO)_2$ (qOH = 5-methyl-2-nitrosophenol, 4-bromo-2-nitrosophenol, 4-chloro-2-nitrosophenol and 4-methyl-2-nitrosophenol) (1 mol. equiv.) proceeded readily at room temperature to give a mixture of products. The presence of triphenyl phosphine oxide, indicated by thin layer chromatography, in each of the mixtures arising from the above reactions suggested that deoxygenation had taken place. The separation of the components of these



Scheme 2.3.

mixtures presented considerable difficulties. Attempts to purify the mixtures by recrystallization were unsuccessful. However, partial separation was achieved by using a combination of extraction and column chromatographic techniques.

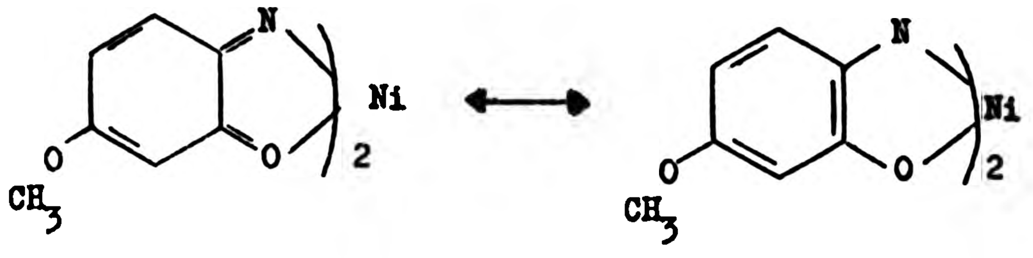
Using these techniques, it was shown that the interaction of bis(5-methoxybenzoquinone-2-oximato) nickel (II) (1 mol. equiv.) and triphenyl phosphine (5 mol. equiv.) afforded triphenyl phosphine oxide (1.5 mol. equiv.) and a pale brown nickel-containing solid. Unreacted triphenyl phosphine (1.8 mol. equiv.) was also obtained from the mixture.

The elemental analysis of the pale brown solid and the formation of triphenyl phosphine oxide indicated that its composition corresponded closely to '$Ni(5\text{-}MeOq)_2(L)_2$' where L = triphenyl phosphine and/or triphenyl phosphine oxide. Three formulations are in accord with the composition '$Ni(5\text{-}MeOq)_2(L)_2$':

(a) the triphenyl phosphine or triphenyl phosphine oxide adduct of the nitrene/quinone imine complex (2.4.) arising by deoxygenation of the complex $Ni(qO)_2$;

(b) the iminophosphorane complex (2.5.) which formally arises by coupling the nitrene function of the complex (2.4.) with triphenyl phosphine:

(c) the triphenyl phosphine or triphenyl phosphine oxide adduct of the azo/complex (2.6.) which formally arises by coupling of the nitrene functions of the complex (2.4.)



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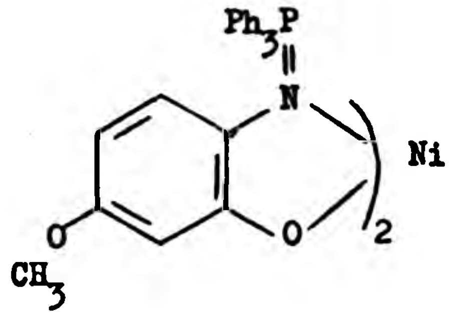
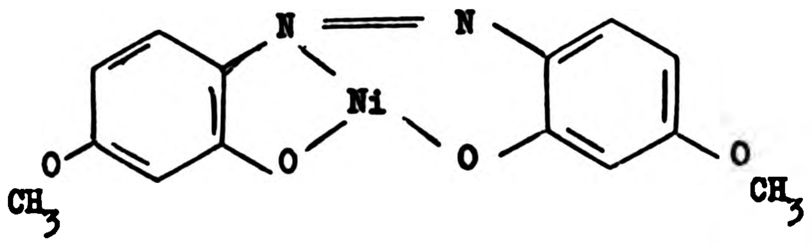


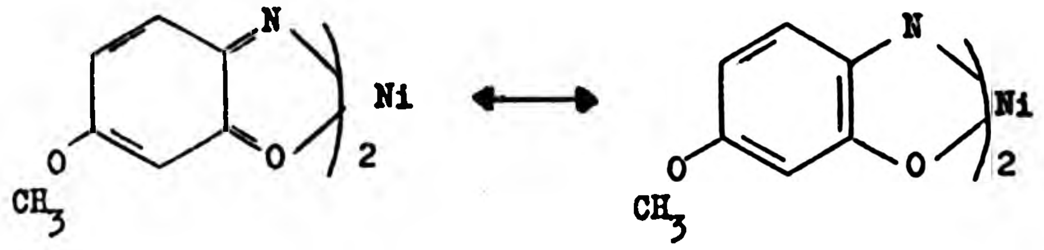
2.5.



2.6.

The pale brown solid on treatment with aqueous acid afforded a white solid which was formulated, on the basis of elemental analysis and mass spectrometry as the hydrochloride of N(5-methoxy-2-hydroxybenzene)-iminotriphenylphosphorane. This observation indicates that the brown product of the reaction between bis(5-methoxy-benzoquinone-2-oximato) nickel (II) (1 mol.equiv.) and triphenyl phosphine (5 mol. equiv.) is bis (5-methoxy-2-triphenylphosphinimino-phenolato) nickel (II)(formulation 2.5.). Further evidence for this is provided by the magnetic behaviour and diffuse reflectance spectrum of the complex which indicate, that in the solid state, the nickel atom is in a tetrahedral environment (see also Chapter 3).

Similar behaviour towards triphenyl phosphine (5 mol. equiv.) was also observed in the case of the complexes $Ni(qO)_2$ (1 mol equiv.)



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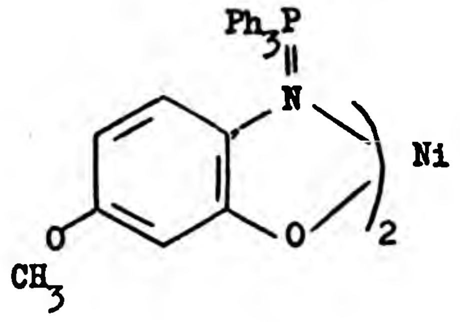
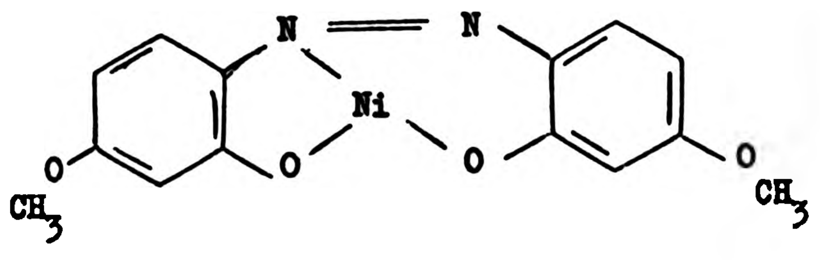


2.5.



2.6.

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Similar behaviour towards triphenyl phosphine (5 mol. equiv.) was also observed in the case of the complexes $Ni(qO)_2$ (1 mol equiv.)

(qOH = 4-methyl-2-nitrosophenol, 4-chloro-2-nitrosophenol, and 4-bromo-2-nitrosophenol) and of the zinc complex bis(5-methoxybenzoquinone-2-oximato) zinc (II). Again in each case the formulation was fully supported by analysis, isolation and characterisation of the ligand hydrochloride, (formed by the action of aqueous acid) and physicochemical studies. Thus the iminophosphorane complexes: bis(4-methyl-2-triphenylphosphinimino-phenolato) nickel (II); bis(4-chloro-2-triphenyl phosphiniminophenolato) nickel (II): bis(4-bromo-2-triphenylphosphiniminophenolato) nickel (II) and bis(5-methoxy-2-triphenyl phosphiniminophenolato) zinc (II) were obtained in reasonable yields (Table 2.2.) indicating the wide applicability of this synthetic route.

The formation of $>$P=N– linkage in the deoxygenation reaction of nitro- and nitroso- compounds with tervalent phosphorous compounds is generally accepted as indicative of nitrene intermediacy. As a consequence and with the aim of isolating either nitrene or azo complexes of the type 2.4. and 2.6. a study of the reaction $Ni(qO)_2$ (1 mol. equiv.) with triphenyl phosphine (2 mol. equiv.) was carried out.

2.5. The Interaction of Bis(benzoquinone-2-oximato)Nickel(II) Complexes (1 mol equiv.) with Triphenyl Phosphine (2 mol. equiv.).

The reaction of triphenyl phosphine (2 mol. equiv.) and bis(4-methylbenzoquinone-2-oximato) nickel (II) as in the case of excess triphenyl phosphine, proceeded at room temperature in chloroform and acetone, but molar ratio control could not be achieved because of the insolubility of the complex in these solvents. Molar ratio control is important as at all times the complex must be in excess with regards to triphenyl phosphine otherwise the iminophosphorane complex will be formed. Thus pyridine was used as the solvent for the 1:2 molar ratio reactions. However, even in pyridine the 1:2 molar ratio reaction between triphenyl phosphine and bis(4-methyl-benzoquinone-2-oximato) nickel (II) gave bis(4-methyl-2-triphenyl phosphiniminophenolato) nickel (II) and unreacted bis(4-methylbenzoquinone-

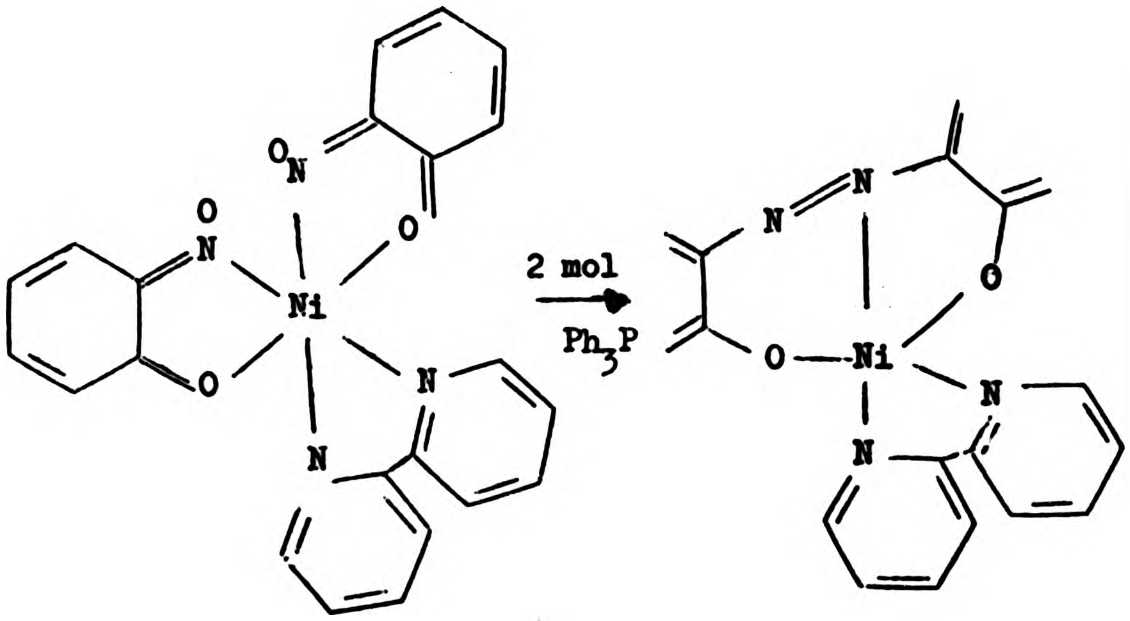
TABLE 2.2.

Iminophosphorane Complexes

$M(qO)_n$ (1 mol.)			$P(C_6H_5)_3$	Solvent	Yield %
M	n	qOH	x mol. equiv.		
Zn	2	5-MeOqOH	5	Chloroform	24
			2	Pyridine	19
			5	"	33
Ni	2	4-MeqOH	2	Pyridine	
		"	5	Chloroform	33
		5-MeOqOH	5	"	38
		4-ClqOH	5	"	32
		4-BrqOH	5	"	51

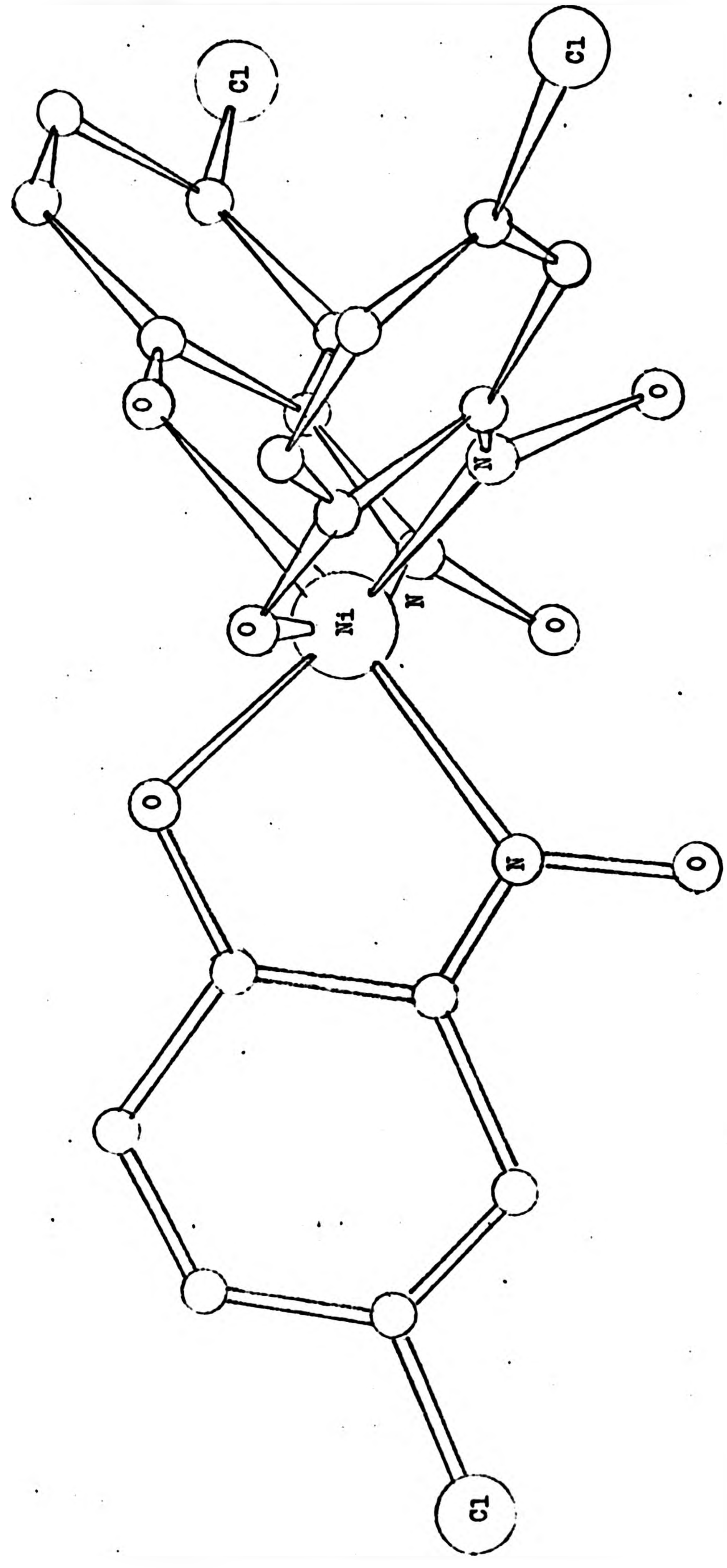
2-oximato) nickel (II).

To induce an azo-linkage as in (2.6.), the 2,2'- dipyridyl adduct of $Ni(qO)_2$ (qOH = 5-methoxy-2-nitrosophenol) was prepared. In this adduct the benzoquinone-2-oximato ligands are in a cis configuration and therefore might react as in Reaction 2.5.. However, no reaction with triphenyl phosphine was observed.



Reaction 2.5.

Recently we have shown by X-ray structural analysis that in the complex potassium tris(4-chlorobenzoquinone-2-oximato) nickelate (II) (2.7.), the anion has three benzoquinone-2-oximato ligands bonded to the nickel (II) atom.[26] These are in a distorted octahedral arrangement with a cis conformation i.e. all the NO- groups adjacent. This complex reacted readily with triphenyl phosphine but instead of the anticipated azo-compound, the reaction led to the pale brown bis(4-chloro-2-triphenyl-phosphiniminophenolato) nickel (II).



2.7.

2.6. The Interaction of Bis(benzoquinone-2-oximato)Copper(II) Complexes with Triphenyl Phosphine.

A. Introduction.

When the copper complex $Cu(qO)_2$ derived from 4-methyl-2-nitrosophenol was treated with triphenyl phosphine a mixture of products results. The separation of one of the main products was simple. This metal-containing product (A) was separated by filtration. Subsequent chromatography of the filtrate offered unreacted triphenylphosphine, triphenylphosphine oxide, a purple organic product and traces of five other products. Reaction of the copper complex $Cu(qO)_2$ derived from 5-methoxy-2-nitrosophenol with triphenylphosphine also afforded a metal-containing product (B), triphenylphosphine, triphenylphosphine oxide, a red organic product and traces of five other products. In this case separation of the metal-containing product was achieved by extraction (Soxhlet) with diethyl ether.

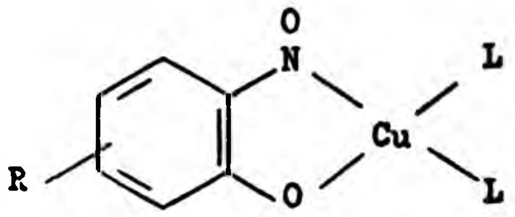
B. The Characterization and Structure of the Metal-containing Products.

The formulation of the metal-containing products arising from the reactions of triphenyl phosphine with $Cu(4\text{-}MeqO)_2$ and $Cu(5\text{-}MeOqO)_2$ presented considerable difficulties. The elemental analysis of each of these products obtained in the early experiments indicated a Cu : N ratio of ca 1 : 1 and the presence of approximately two Ph_3P or Ph_3PO units per metal atom. On the basis of these results and in view of the established (c.f. section 2.4.) deoxygenating action of triphenyl phosphine towards analogous nickel and zinc complexes, formulations 2.8. - 2.10. were considered most likely. As shown in Table 2.3. the elemental composition

TABLE 2.3.

Elemental Composition of Formulations

Formulation	$L = Ph_3P$						$L = Ph_3PO$						Found					
	C	H	N	O	Cu	P	C	H	N	O	Cu	P	P	H	N	O	Cu	P
$R = CH_3$																		
2.8.	71.3,	5.0,	1.9,	4.4,	8.8,	8.6	68.3,	4.8,	1.9,	8.5,	8.4,	8.2						
2.9.	72.9,	5.1,	2.0,	2.3,	9.0,	8.8	69.8,	4.9,	1.9,	6.5,	8.6,	8.4	72.8,	5.2,	1.9,	- ,	9.3,	8.5
2.10.	72.9,	5.1,	2.0,	2.3,	9.0,	8.8	71.3,	5.0,	1.9,	4.4,	8.8,	8.6						
$R = CH_3O$																		
2.8.	69.8,	4.9,	1.9,	6.5,	8.6,	8.4	66.9,	4.7,	1.8,	10.4,	8.2,	8.0						
2.9.	71.3,	5.0,	1.9,	4.4,	8.8,	8.5	68.3,	4.8,	1.9,	8.5,	8.4,	8.2	69.8,	4.9,	1.9,	- ,	9.0,	8.1
2.10.	71.3,	5.0,	1.9,	4.4,	8.8,	8.5	69.8,	4.9,	1.9,	6.5,	8.6,	8.4						



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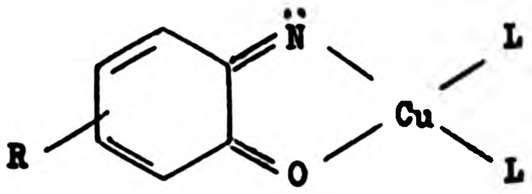

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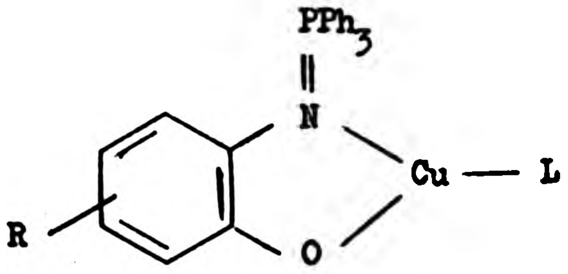

2.10.

(L = Ph_3P or Ph_3PO)

of all formulations chosen for consideration corresponds closely to those found for the reactions products (A) and (B). Furthermore, molecular weight measurements in chloroform, for both of the products, were found to be in accord with the formulations 2.8. - 2.10.

Magnetic susceptibility measurements indicated that both products were diamagnetic in the solid state. This supports formulations 2.8. - 2.10. which involve copper (I).

Further support for the involvement of copper (I) and in particular for formulations 2.8. and 2.9. is provided by the well-established reduction of a variety of copper (II) compounds by R_3P [63] (Table 2.4.)

Table 2.4.

Complexes of the Type $Cu(chel)(R_3P)_2$ Arising from the Interaction of $Cu(chel)_2$ with R_3P.

Complex	Ref.
$Cu(NO_3)(Ph_3P)_2$	64
$Cu(NO_3)(Hex_3P)_2$	65
$Cu(\beta\text{-diket})(Ph_3P)_2$	65
$Cu(RCO_2)(Ph_3P)_2$	66
$Cu(R_2CNS_2)(Ph_3P)_2$	67

Hex = cyclohexyl

$\beta\text{-diket}^- = CF_3COCHCOCH_3$ and $CF_3COCHCOCF_3$

R in $RCO_2^- = H, CH_3$ and C_6H_5

R in $R_2CNS_2^- = CH_3, C_2H_5$

This type of reaction leads to complexes of the type $Cu(chel)(Ph_3P)_2$,

$$Cu(chel)_2 + Ph_3P \longrightarrow Cu(chel)(Ph_3P)_2$$

+

unidentified
organic
products

Reaction 2.6.

where $chel^-$ is a chelating ligand.

The n.m.r. spectra of solids (A) and (B) were recorded. Both products gave complex spectra but sharp resonance lines, suggesting that they are diamagnetic in solution also.

Having established the oxidation state of the metal in the product, several reactions were carried out. The aim of these reactions were to establish the nature of the anionic and/or the neutral ligands and thus determine which of the formulations 2.8. to 2.10. corresponds to (A) and (B). The reagents used, the reasons and the expected products are summarized in Table 2.5.

There was no reaction between the metal-containing product (A) and 2,2' dipyridyl in benzene or hexane, even when heated under reflux. However (A) and 2,2' dipyridyl reacted readily in chloroform at room temperature to give a green solid and as shown by t.l.c. a complicated mixture of soluble products. Elemental analysis suggested the green solid was a dipyridyl adduct of copper (II) chloride i.e. $CuCl_2$, dipy. This suggestion was further supported by a comparison of the infrared spectrum with that of an authentic sample. This, rather unexpected result, which involves formation of a product with Cu-Cl bonds, could arise through carbene formation[68], the latter being produced by the presence of a base (dipyridyl) in the solvent (chloroform). Conversely it could arise via the Michaelis-Arbusov[69] reaction which involves the interaction of a triaryl phosphine with a halogenated hydrocarbon. (Scheme 2.4.)

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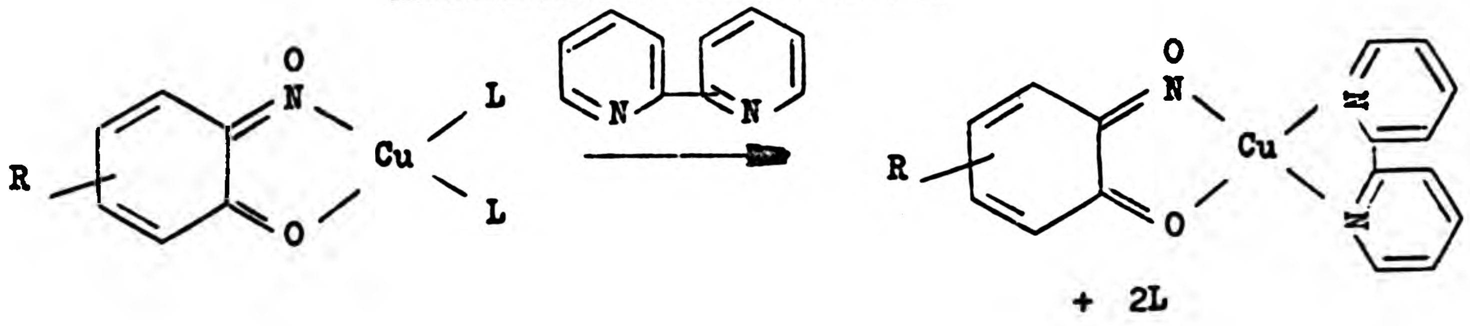
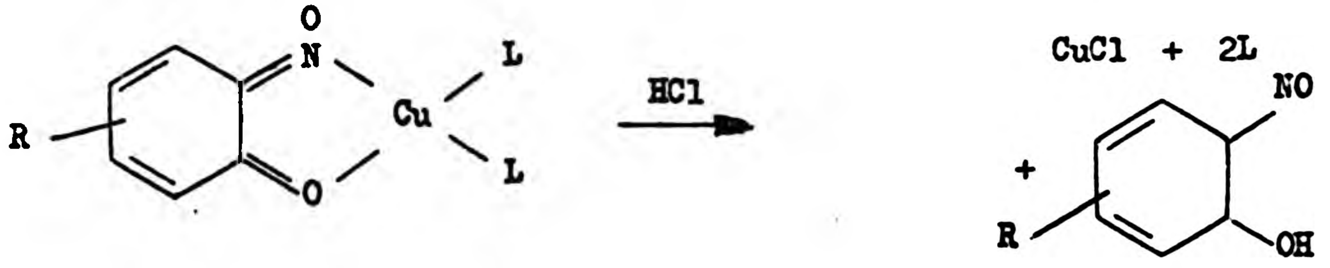
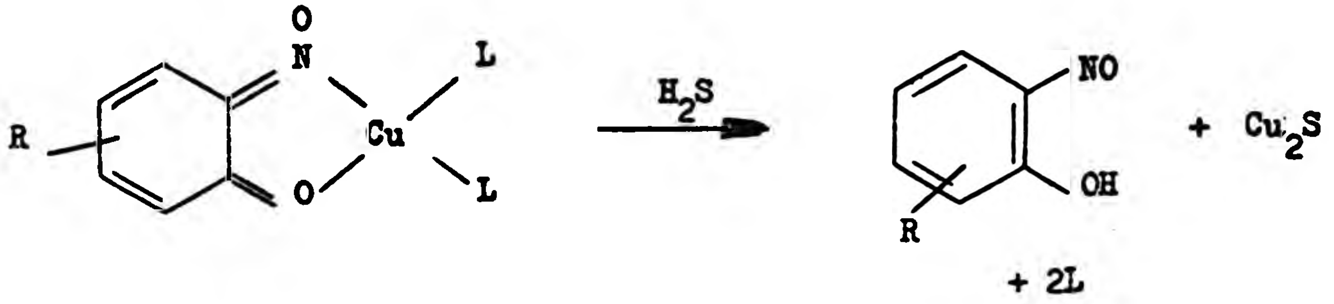
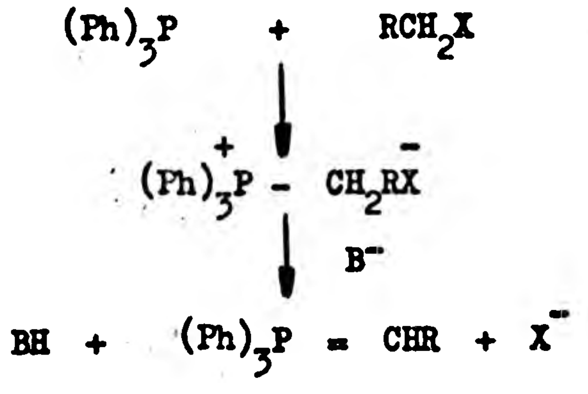
TABLE 2.5.

Examples of Expected Reactions

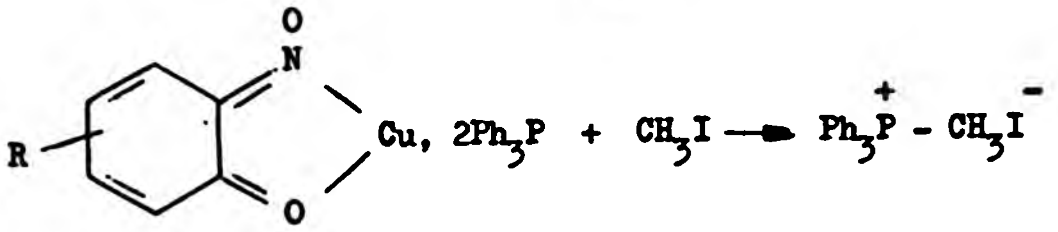
Reagents		Comments
2,2'-dipyridyl		To liberate the neutral ligand L.
Hydrochloric acid		To liberate both the neutral and anionic ligands.
Methyl iodide		To establish the nature of L and methylate the chelating ligand.
Hydrogen sulphide		To liberate both the neutral and anionic ligands.



$$(Ph)_3P + RCH_2X \longrightarrow (Ph)_3\overset{+}{P}-CH_2R\overset{-}{X} \xrightarrow{B^-} BH + (Ph)_3P=CHR + X^-$$

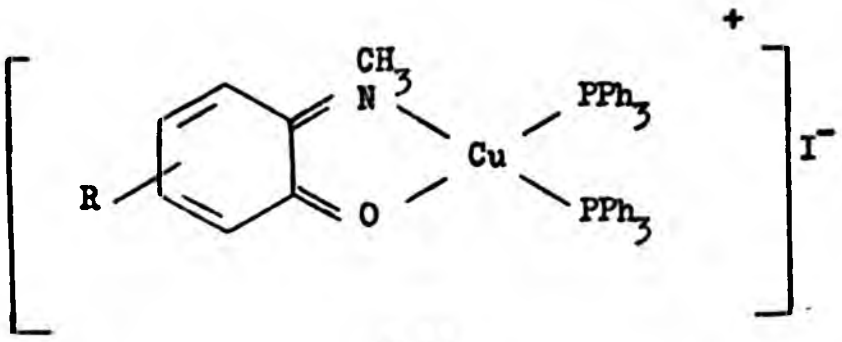
Scheme 2.4.

In view of the above observations the interaction of the metal-containing products (A) and (B) with methyl iodide was carried out. The reaction of triaryl phosphines with alkyl halides, the Michaelis-Arbusov reaction, involves nucleophilic attack by phosphorus to form a quasiphosphonium salt (scheme 2.4.) which is relatively stable. This quasiphosphonium salt can then react readily with a base to give phosphorus ylides. If the compounds (A) or (B) have formulations 2.8., 2.9. or 2.10. where L is a triphenyl phosphine, interaction between methyl iodide could occur to give a quasiphosphonium salt (Reaction 2.7.).



Reaction 2.7.

However, if L is triphenyl phosphine oxide no quasiphosphonium salt is expected to be formed. There is also the possibility of alkylation of the imine or nitroso group to form a compound such as 2.11.



2.11.

Both solids (A) and (B) reacted readily with excess methyl iodide under reflux. In both cases the reaction mixtures on cooling afforded the quasiphosphonium salt (Reaction 2.7.) which was characterized (a) by elemental analysis after recrystallisation from acetone and (b) by comparison of its infrared spectrum with that of an authentic sample. The filtrates obtained after the removal of the quasiphosphonium salt were shown by t.l.c. to be very complex mixtures. Attempts to separate these mixtures by chromatography were unsuccessful because of extensive decomposition on the column.

The formation of the quasiphosphonium salt from the reaction of (A) or (B) with methyl iodide clearly indicates that the neutral ligand L in these complexes is triphenyl phosphine and not triphenyl phosphine oxide.

Several attempts were made to liberate the anionic ligand in (A), by the action of aqueous acids, isolate it in its protonated form and identify it. However, all attempts proved unproductive. As a consequence an alternative method involving the action of hydrogen sulphide on (A) was tried.

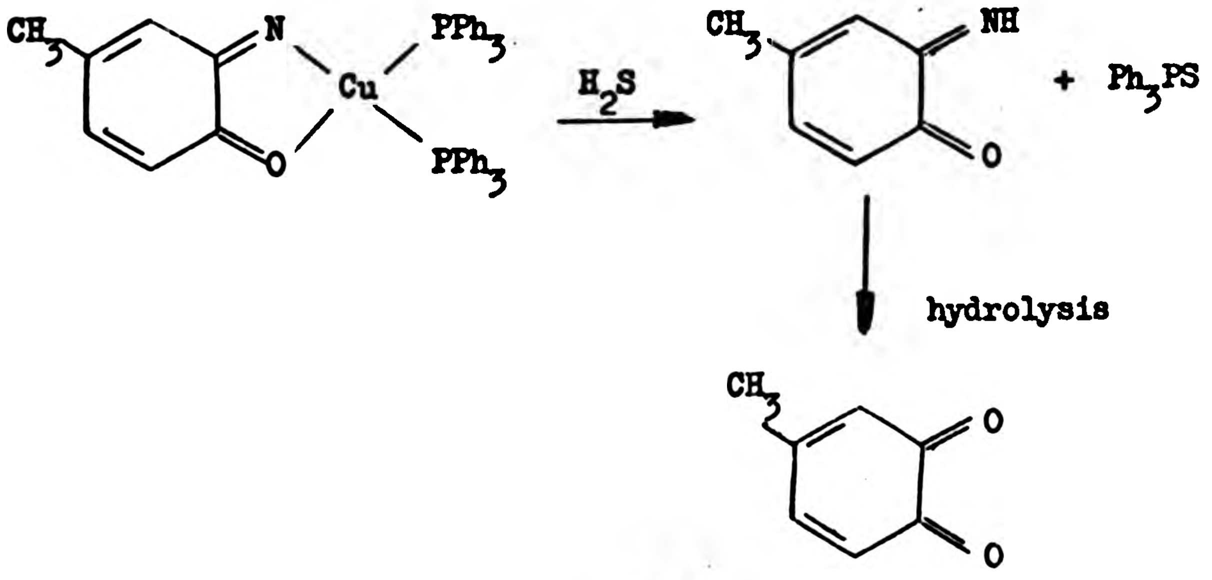
When hydrogen sulphide was passed through a suspension of solid (A) in benzene a black solid and several soluble products resulted. The solid consisted of copper sulphide and unreacted (A). The filtrate obtained after removal of the black solid was shaken with aqueous alkali and the organic and aqueous phases were separated.

The organic phase on concentration afforded a crystalline white solid and a mother liquor which contained several components as indicated by t.l.c.. Elemental analysis and the Lassaigne test[70] suggested the white solid was triphenyl phosphine sulphide. This formulation was supported by the mass spectrum which had a molecular ion corresponding to m/e 294 and fragments arising from loss of a sulphur atom and of phenyl radicals from the molecular ion. The isolation of triphenyl phosphine sulphide as a product of the reaction between (A) and hydrogen sulphide provides further support for the formulation of the neutral ligand L in (A) as triphenyl phosphine.

The aqueous alkali layer on acidification and extraction with diethyl ether afforded a yellow etherial extract. Removal of the solvent from the extract followed by sublimation of the residue afforded a small quantity of a yellow solid, whose elemental analysis indicated the absence of nitrogen. Mass spectrometry indicated that the yellow solid was 4-methyl-1,2-benzoquinone.

The mass spectrum of the yellow solid (Table 2.6.) is similar to the spectra of other 2-benzoquinones recorded in the literature.[71-73] The fragmentation pattern (Fig. 2.1.) involves loss of the ring substituent and carbon monoxide, such as the sequence P → B → G → J which is a typical pathway in all spectra reported.

It is known that benzoquinones can be readily obtained by hydrolysis of quinoneimines.[69] As a consequence at first glance it may be concluded that the anionic ligand in (A) is the 4-methylbenzoquinone-2-iminato anion and (A) has formulation 2.9. (R = 4-Me) rather than formulations 2.8. or 2.10.. However, the presence of the 4-methylbenzoquinone-2-oximato anion in complex (A) i.e. formulation 2.8. cannot be precluded. This is because of the reducing character of hydrogen sulphide which could reduce (deoxygenate) the oximato ligand to the corresponding iminato ligand (Scheme 2.6.)



Scheme 2.5.

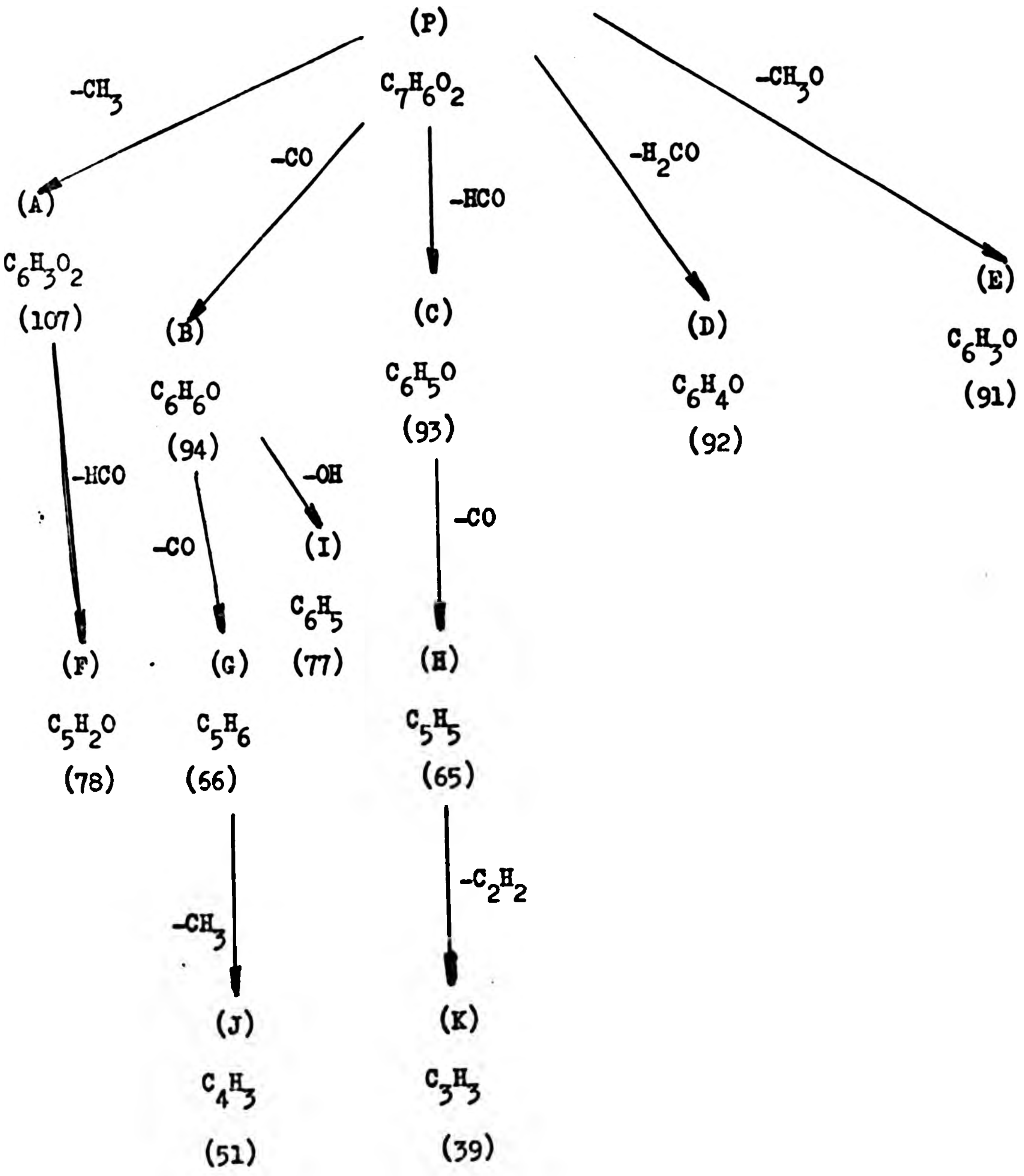
TABLE 2.6.

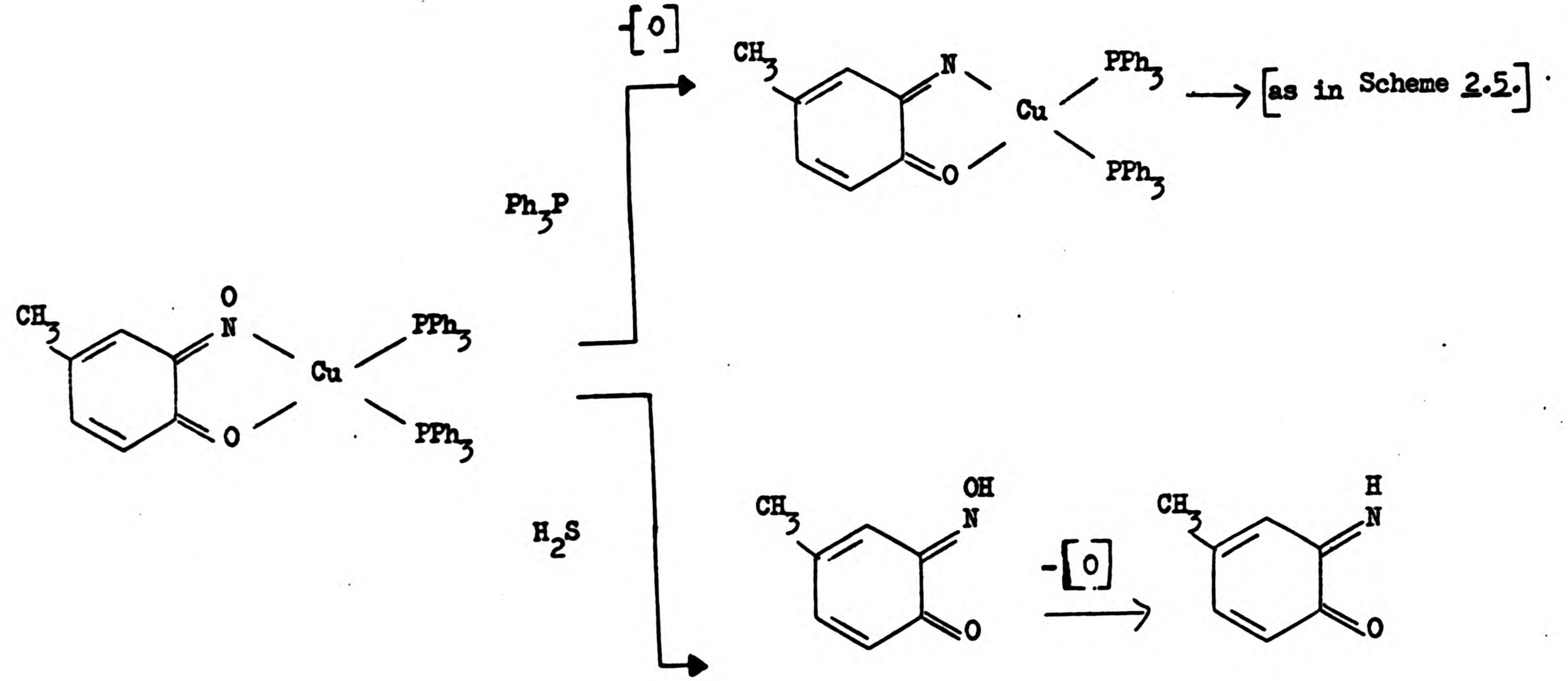
Ion Abundances for 2-Methyl-2-benzoquinone.

Ion	m/e	%	Assignment
P	122	100	$C_7H_6O_2$
[P-15]=A	107	12.0	$C_6H_3O_2$
[P-28]=B	94	11.6	C_6H_6O
[P-29]=C	93	8.3	C_6H_5O
[P-30]=D	92	9.9	C_6H_4O
[P-31]=E	91	9.9	C_6H_3O
[P-44]=F	78	7.6	C_5H_2O
[P-45]=I	77	14.6	C_6H_5
[P-56]=G	66	20.6	C_5H_6
[P-57]=H	65	23.2	C_5H_5
[P-71]=J	51	11.8	C_4H_3
[P-83]=K	39	18.8	C_3H_3

Fig. 2.1.

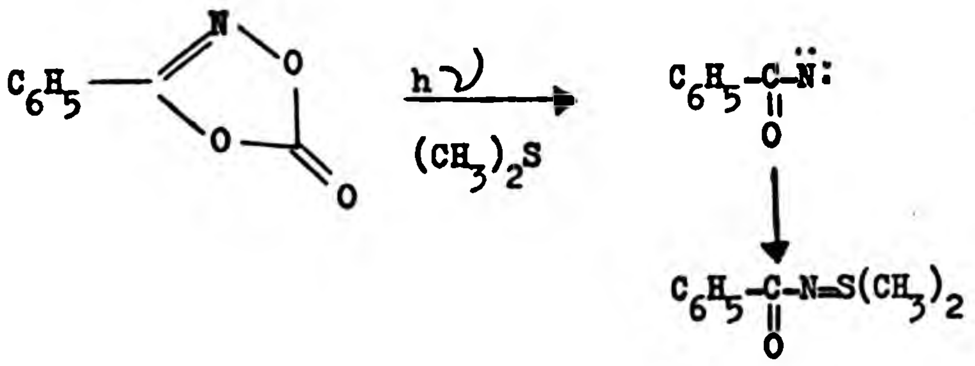
Fragmentation Scheme for 2-Methyl-2-benzoquinone





Scheme 2.6.

As electrophilic intermediates, nitrenes are expected to react readily with nucleophiles such as tertiary phosphines and sulphides.[74] Thus nitrenes can be trapped by dimethyl sulphide or by dimethyl sulphoxide in solution as for example in Scheme 2.7.



Scheme 2.7

The copper-containing compound (A) did not react with dimethyl sulphide even under reflux suggesting that the nitrene/imine group as in formulation 2.9. was not present.

The inconclusive evidence for the formulation of the anionic ligands in (A) and (B) prompted a comparison of their infrared spectra with those of the corresponding bis(benzoquinone-2-oximato)copper (II) complexes from which they have been obtained. The sets of infrared spectra in the region 1700-1499 cm^{-1} (Table 2.7) i.e. the region of νCO, νCN and νNO are similar. On the basis of the above, it may be concluded that the anionic ligand in (A) and (B) is the quinone-2-oximato anion and their formulation is 2.8. . The non-availability of spectra of complexes containing the quinone-2-iminato anion as the ligand restricts the validity of the above conclusion. However, support for this conclusion is provided by the results of a recent X-ray crystallographic study in these laboratories.[31] This study concerns the product of the reaction between bis(1-naphthoquinone-2-oximato) copper (II) and triphenyl phosphine which has a composition analogous to the composition of (A) and (B). This product has been shown

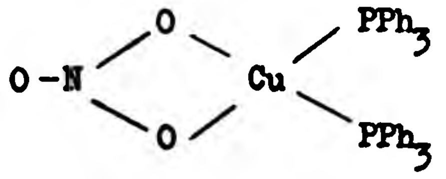
TABLE 2.7.

Bands Observed in the Infrared Spectra of Bis(benzoquinone-2-oximato)copper(II) Complexes and their Triphenyl Phosphine Derivatives in the Region 1700 - 1400 cm^{-1}.

	X = 4-Me	X = 5MeO
	$\nu\,cm^{-1}$	$\nu\,cm^{-1}$
$Cu(XqO)_2$	1625	1600 B
	1530	1580 Sh
	1515	1570 Sh
		1530
	1450	1510 Sh
	1410	1505
		1465 Sh
		1450
		1435
	Compound (A)	Compound (B)
$Cu(XqO),(Ph_3P)_2$	1625	1605
	1525	1600 Sh
	1510	1590
	1450 Sh	1570 Sh
	1430	1540
		1515
		1510 Sh
		1470 Sh
		1455 Sh
		1420

B = broad

by X-ray crystallography to have formulation 2.8. with isolated copper atoms within a tetrahedral environment. Therefore it is reasonable to assume that the copper (I) complexes (A) and (B) prepared during this study are also pseudo-tetrahedral. Indeed complexes of the type (chel)Cu$(Ph_3P)_2$ are well documented (Table 2.4.) and in several cases[75-79] e.g. 2.12, X-ray studies have indicated tetrahedral or pseudo-tetrahedral structures for them.



2.12.

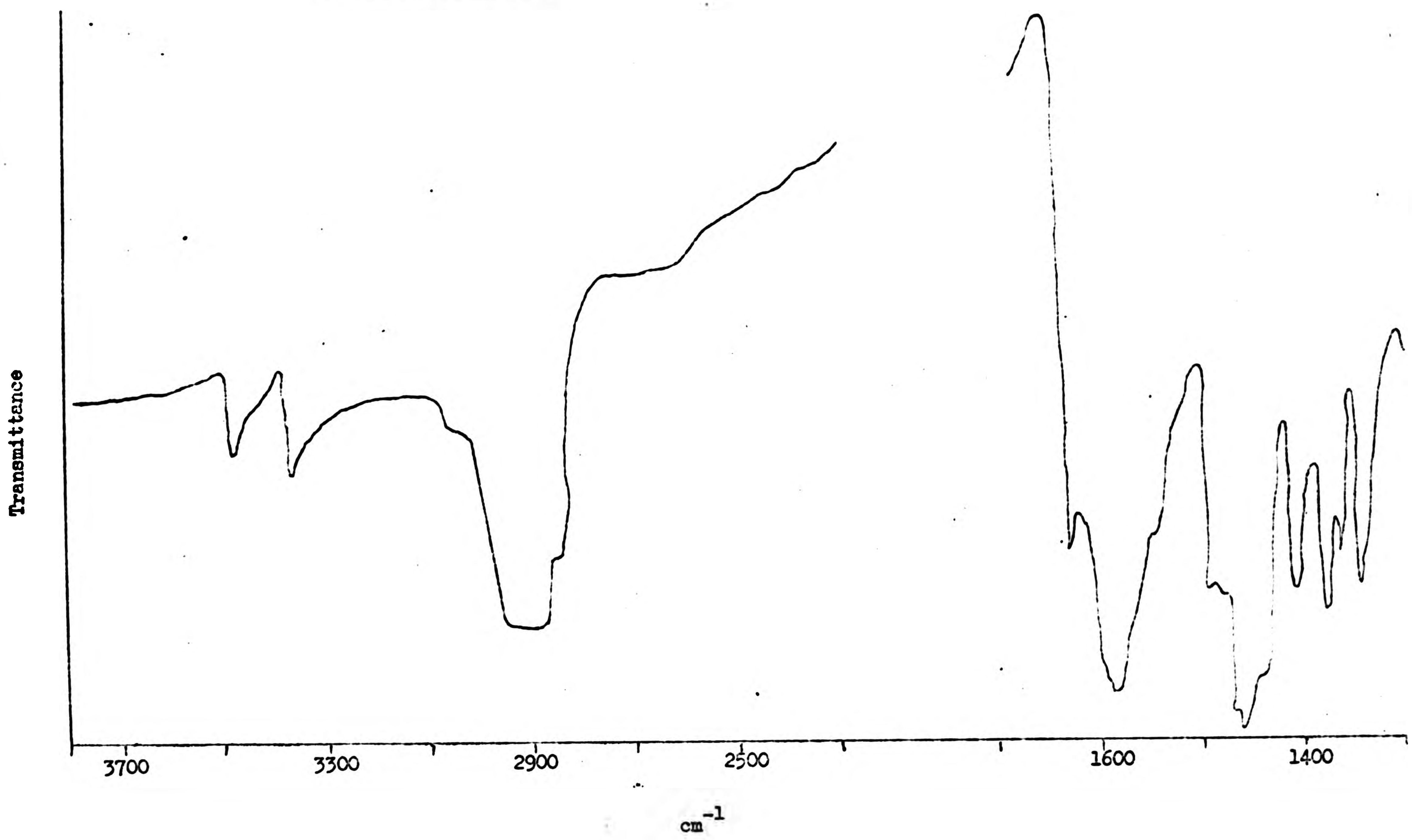
C. The Nature of the Organic Products.

Although reduction of copper(II) complexes by triphenyl phosphine has been reported, the fate of the deposed ligand has not.[65, 66] In the case of the reduction of bis(5-methoxybenzoquinone-2-oximato)copper(II) by triphenyl phosphine a compound formed from the deposed ligand radical has been isolated and identified. As noted in Section 2.6.A. the reaction between bis(5-methoxybenzoquinone-2-oximato)copper(II) and triphenyl phosphine gave a metal-containing product, and several other products, the separation of which was achieved by a combination of chromatographic and extraction techniques. The metal-containing product di(triphenyl phosphine)(5-methoxybenzoquinone-2-oximato)copper(I) was extracted (Soxhlet) from the mixture with diethyl ether, together with triphenyl phosphine and triphenyl phosphine oxide. Separation of these compounds was accomplished by chromatography.

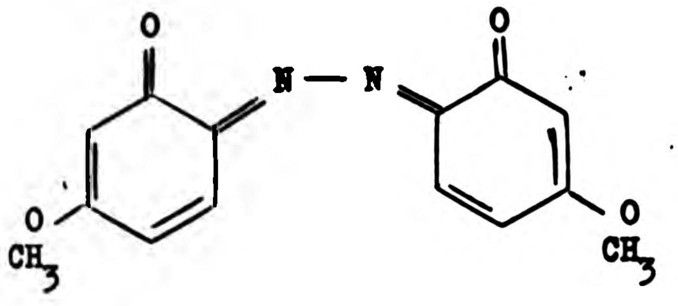
The residue remaining after the diethyl ether extraction was further extracted with ethyl acetate, methanol, and finally with a methanol-hydrochloric acid mixture. The ethyl acetate extract offered a red solid.

Elemental analysis of the red compound suggested an empirical formula of $C_7H_6NO_2$. Its infrared spectrum (Fig. 2.2.) showed bands at 3480, 3360 and 1630 cm^{-1} assignable to ν OH and ν CN vibrations. On the basis of the

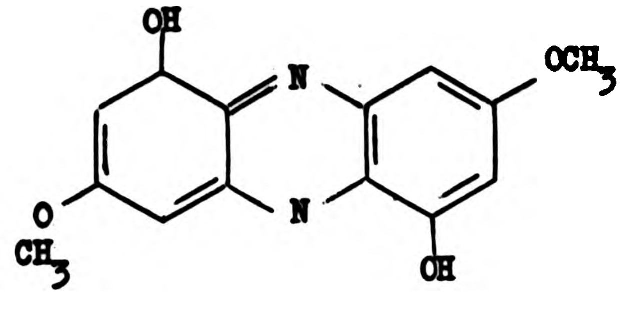
Fig. 2.2. The Infrared Spectrum of 1.6-Dihydroxy-3.8-dimethoxyphenazine.



above and in view of the deoxygenative nature of the reaction, three formulations for the red compound were considered, 2.13., 2.14. and 2.15.



2.13.



2.14.

Due to the insolubility of this compound in most solvents no further information about its formulation could be obtained from n.m.r. or other solution studies. Mass spectrometric studies of this compound were complicated because of the presence of trace amounts of triphenyl phosphine oxide and triphenyl phosphine in it. However, by varying the insertion temperature and residence time of the sample in the mass spectrometer a spectrum (Table 2.8.) of the compound was obtained.

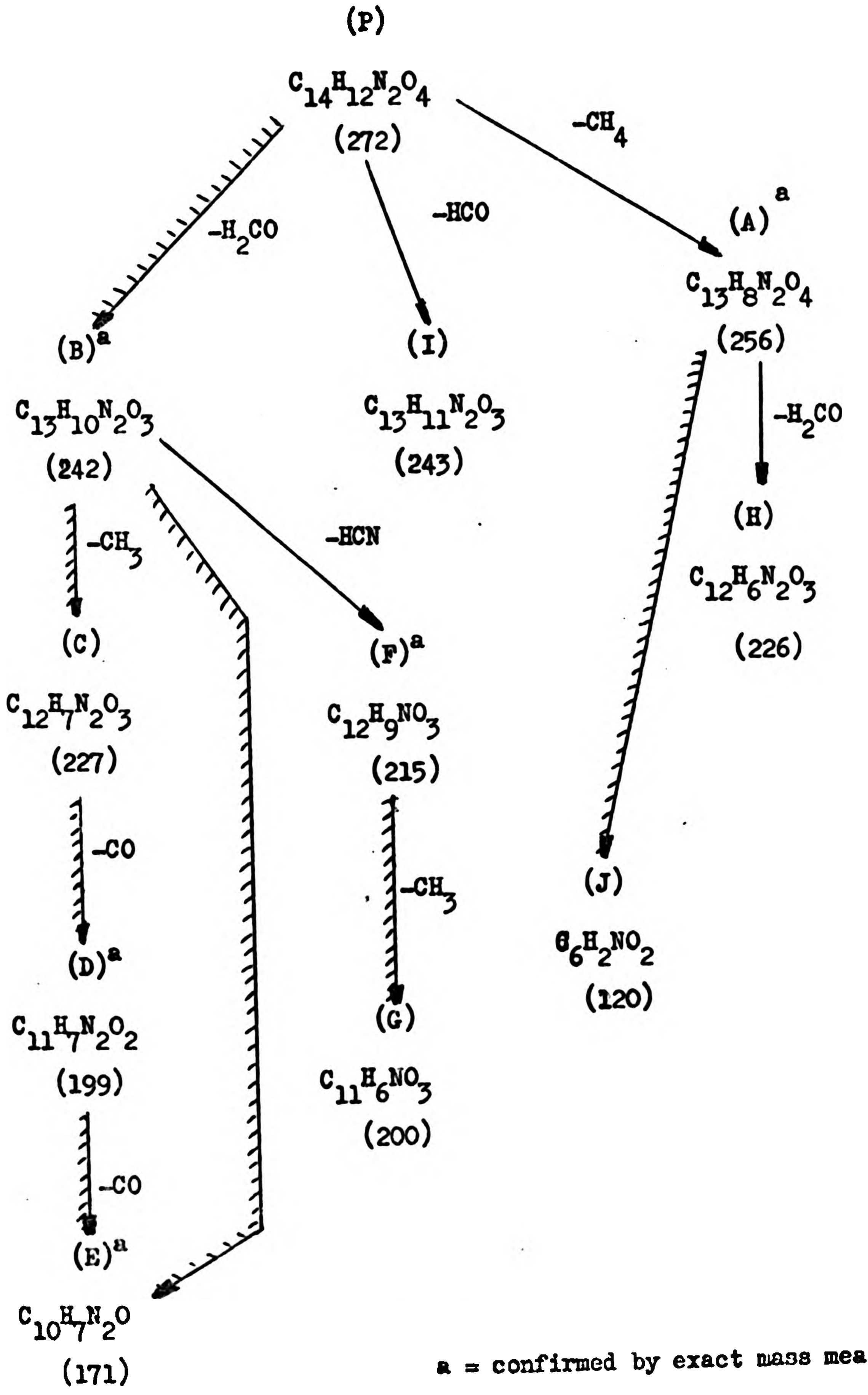
The ion with the highest m/e value appears at 256 a.m.u. This peak does not correspond to the molecular ion (P)$^+$ but to the ion (P-CH$_4$)$^+$ identified by exact mass measurements (Table 2.12.). However, at lower ionising voltage the molecular ion (P)$^+$ m/e value 272 a.m.u. appears.

The fragmentation pattern (Fig. 2.3.), which is compatible with fragmentation patterns of phenazines already reported[80-82], indicated formula 2.14., the phenazine-type compound rather than an azine-type or azo-type compound. The preference for the retention of the nitrogen ring rather than halving of the molecule as in the sequence P → B → C → D → E (Fig. 2.3.) (metastable supported) is typical of a phenazine compound. Further support for the phenazine-structure is the presence in the spectrum of a doubly charged molecular ion peak. Furthermore, the fragmentation behaviour is different from that reported for azine-type compounds[83]. Azine compounds like other compounds of the type

Fig. 2.3.

Fragmentation Scheme for

1.6-Dihydroxy-3.8-dimethoxyphenazine.



a = confirmed by exact mass measurement

ıııı = pathway confirmed by metastable transition.

TABLE 2.8.

Ion Abundance for 1.6-Dihydroxy-3.8-dimethoxy phenazine.

Ion	m/e	%^{b}	Assignment
P^a	272	0.1	$C_{14}H_{12}N_2O_4$
[P-16]=A	256	0.5	$C_{13}H_8N_2O_4$
[P-29]=I	243	5.5	$C_{13}H_{11}N_2O_3$
[P-30]=B	242	29.8	$C_{13}H_{10}N_2O_3$
[P-45]=C	227	19.4	$C_{12}H_7N_2O_3$
[P-46]=H	226	3.9	$C_{12}H_6N_2O_3$
[P-57]=F	215	2.9	$C_{12}H_9NO_3$
[P-72]=G	200	3.8	$C_{11}H_6NO_3$
[P-73]=D	199	11.5	$C_{11}H_7N_2O_2$
[P-101]=E	171	3.2	$C_{10}H_7N_2O$
[P-152]=J	120	10.9	$C_6H_2NO_2$
	106	3.6	
	105	34.2	
	80	7.8	
	79	100.0	
	52	63.4	

a = symbols used in fragmentation schemes

b = % relative abundance.

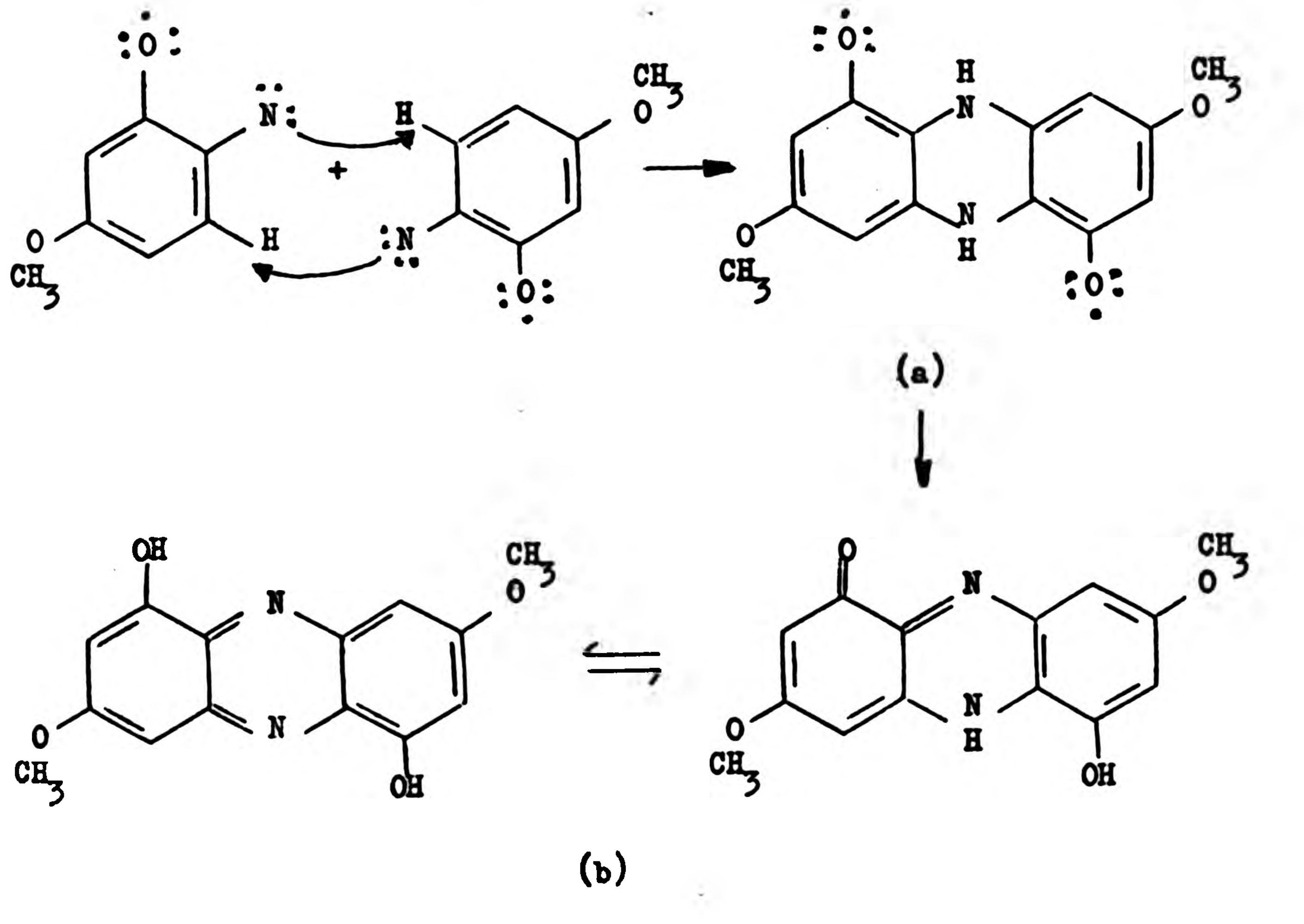
TABLE 2.9.

Metastable Peaks and Transitions for 1,6-Dihydroxy-3,8-dimethoxyphenazine.

Transition	m/e values for the transition	m^* obs.	m^* calc.
P → B	272 → 242	215.0	215.3
A → J	256 → 120	56.3	56.3
B → C	242 → 227	213.0	212.9
C → D	227 → 199	174.2	174.5
B → E	242 → 171	120.3	120.8
F → G	215 → 200	186.0	186.0
D → E	199 → 171	147.0	146.9

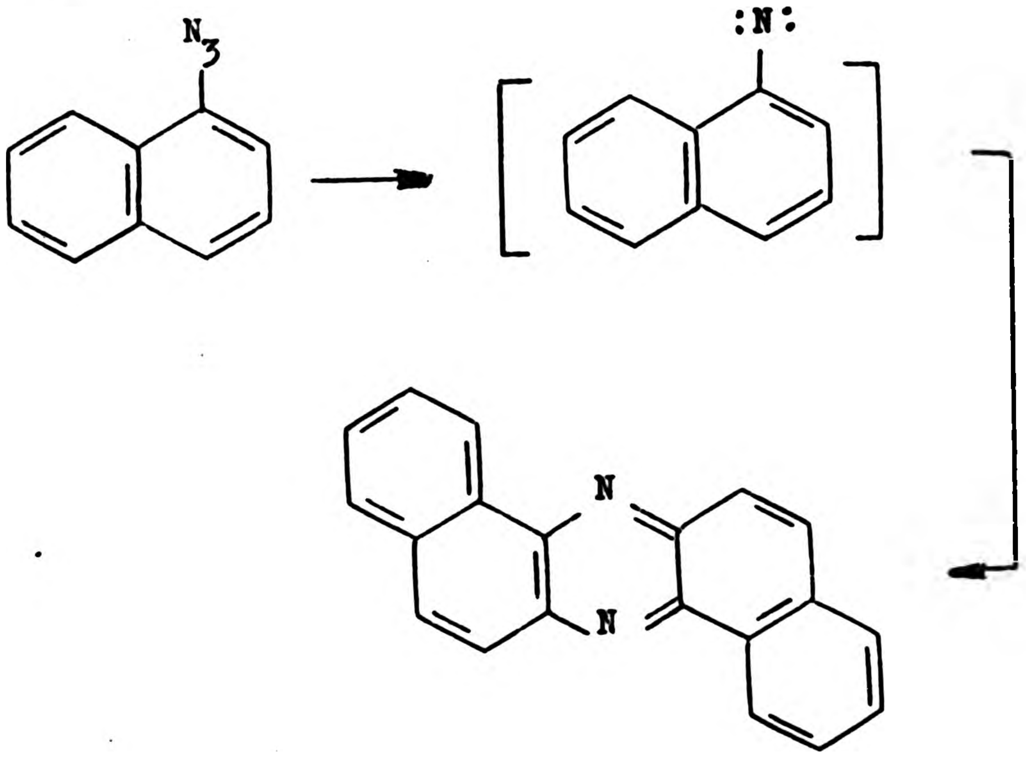
Ar-X-Ar (where Ar = aromatic groups) upon electron impact undergo rearrangement with the loss of the whole or part of the bridging group X. Thus in the fragmentation patterns of azines cleavage of N-N bond takes place with elimination of such even electron molecules as HCN from the molecular ion. However, in the mass spectrum of the red organic compound (1,6-dihydroxy-3,8-dimethoxyphenazine) (Table 2.8.) there was no elimination of HCN from the molecular ion and exact mass measurements (Table 2.12.) also showed retention of the C-N bonds was favoured.

The formation of 1,6-dihydroxy-3,8-dimethoxyphenazine can be rationalized in terms of Scheme 2.8.. Dimerization of the nitrene species or interaction with its precursor by insertion of the nitrene function into aromatic C-H bonds gives species 2.8.a which then rearranges to give the product. This



Scheme 2.8.

type of reaction where nitrenes insert into C-H bonds has been reported in the literature.[84] However, these are usually intramolecular insertion reaction such as the reductive cyclisation of 2-nitrosobiaryls to carbazoles.[42] The proposed involvement of nitrene intermediates in the formation of 1,6-dihydroxy-3,8-dimethoxyphenazine scheme 2.8.b parallels recent suggestions by Hilton et al[85] regarding the formation of phenazines by thermal and photolytic decomposition of naphthyl azides (Scheme 2.9.).



Scheme 2.9.

This involves intermolecular nitrene insertion. It has also been postulated by Breslow et al[86] for the decomposition of phosphonyl azides (Reaction 2.8.)

$$(C_2H_5O)_2PON_3 \quad + \quad C_6H_{12} \longrightarrow$$

Reaction 2.8.

$$(C_2H_5O)_2PONHC_6H_{11} \quad + \quad (C_2H_5O)_2PONH_2$$

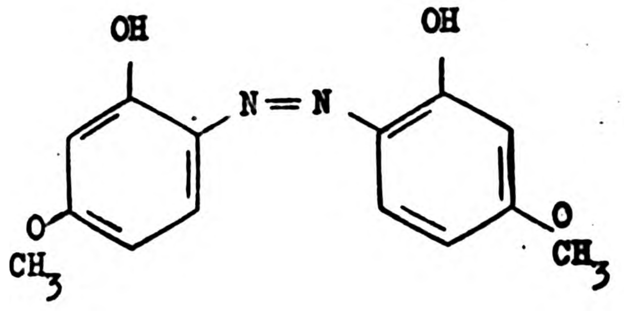
(C_6H_{12} = cyclohexane)

Earlier work by Walker and Waters[87] also ascribed the formation of 2,7-dimethoxyphenazine on thermolysis of 2-methoxyphenylazide in cumene to nitrene intermediates. Here however it was suggested the phenazine was formed from the dimerization of anilino-radicals derived from the nitrene by hydrogen abstraction from a solvent prone to lose hydrogen atoms by free-radical attack e.g. cumene or benzyl alcohol.

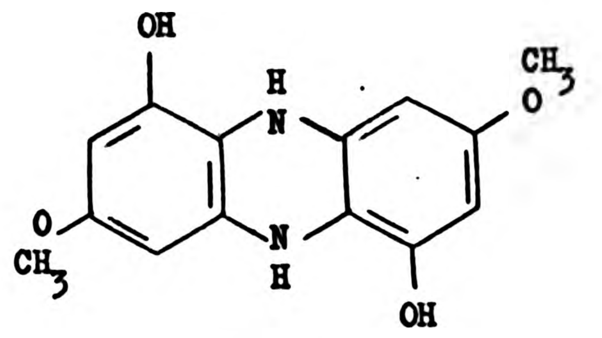
The mixture arising from the interaction of triphenyl phosphine (5 mol. equiv.) and bis(4-methylbenzoquinone-2-oximato) copper (II) (1 mol, equiv.), after extensive use of column and thin layer chromatography and solvent extraction, afforded a red-purple organic product. Elemental analysis of this compound indicated an empirical formula of C_7H_6NO. Its infrared spectrum showed bands at 3470 and 3350 cm^{-1} tentatively assigned to νOH. However due to the presence of traces of triphenyl phosphine oxide in the compound, no further information about its formulation could be obtained from mass spectrometric studies. Its insolubility in most solvents also meant that no information could be obtained from n.m.r. or other solution studies.

2.7 The Interaction of 2-Nitrosophenols with Triphenyl Phosphine.

The reaction of triphenyl phosphine (2 or 5 mol. equiv.) and 5-methoxy-2-nitrosophenol (1 mol, equiv.), proceeded readily at room temperature in chloroform to give triphenyl phosphine oxide and a mixture which was difficult to separate. However, when pyridine was used as the solvent a red solid was isolated. Elemental analysis of this solid suggested an empirical formula of $C_7H_7NO_2$. The two most probable formulations for the red solid based on its elemental analysis and infrared spectrum, and the deoxygenative nature of the reaction leading to it are 2.15 and 2.16.



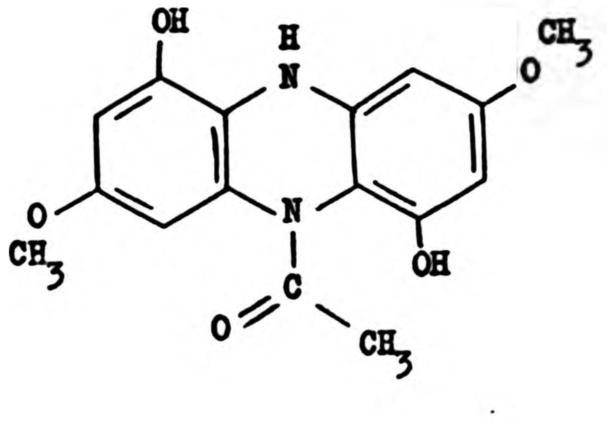
2.15



2.16.

The infrared spectrum showed bands at 3480 and 3360 cm^{-1} assignable to νNH and/or νOH. The presence of amine and/or hydroxy groups was also indicated by the formation of a monoacetyl derivative (2.17) by the action of acetic acid/acetic anhydride on the red solid.

The fragmentation patterns (Figs. 2.4. and 2.5.) of the red solid and its acetyl derivative, respectively, indicated formula 2.16, 1,6-dihydroxy-3,8-dimethoxy-dihydrophenazine rather than the azo-type formulation 2.15.



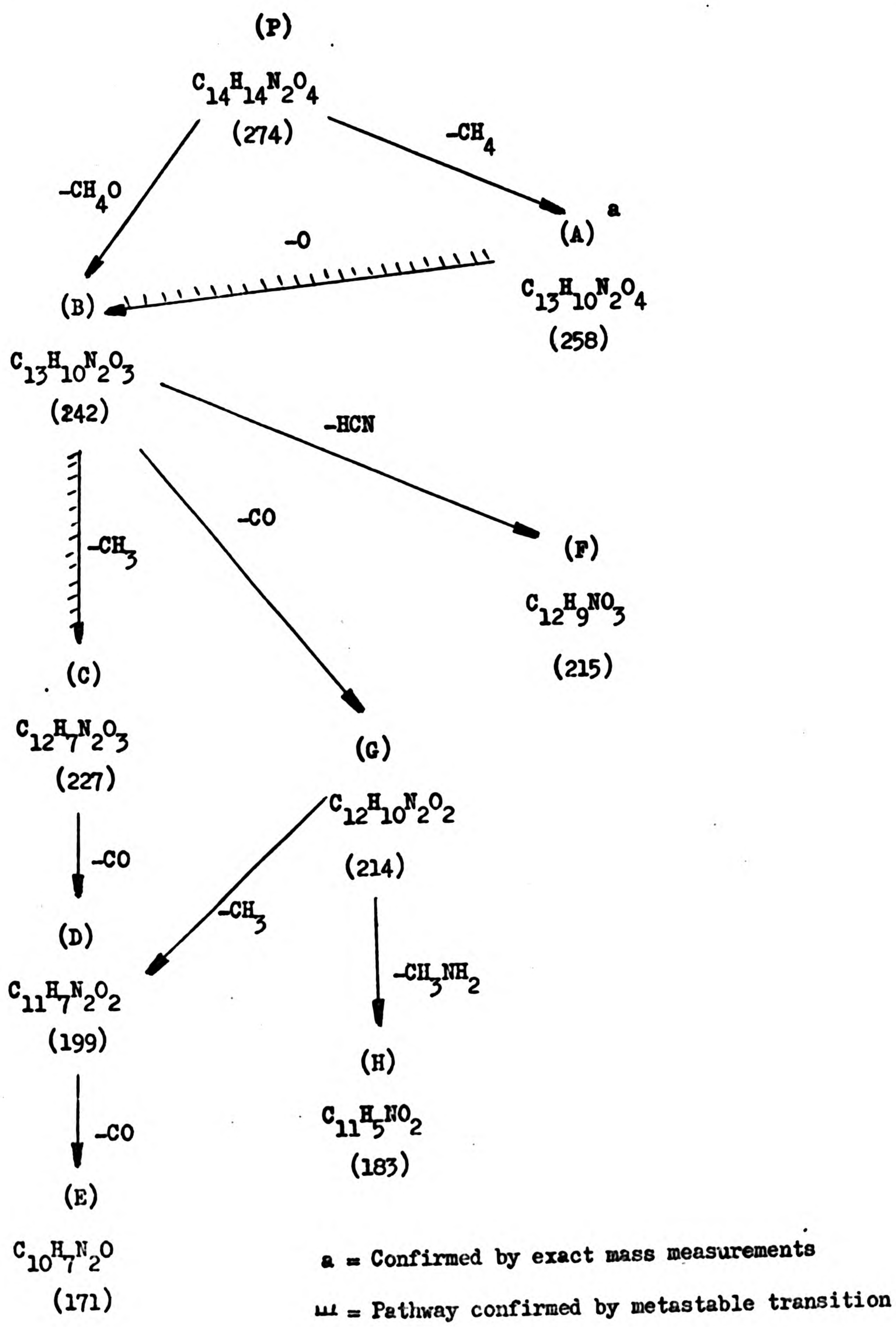
2.17.

In the mass spectra of the azobenzenes[88, 89] the dominant process is cleavage of the C-N bond and elimination of radicals such as $C_6H_5^{\bullet}$ and $C_6H_5N_2^{\bullet}$ and even-electron molecules such as N_2 and C_2H_2. Similarly in the fragmentation patterns of azoxy-benzenes[90] the base peaks of the spectra are produced by C-N bond cleavage, α to the N-oxide group, with elimination

Fig. 2.4.

Fragmentation Scheme for

1,6-Dihydroxy-3,8-dimethoxy-dihydrophenazine.



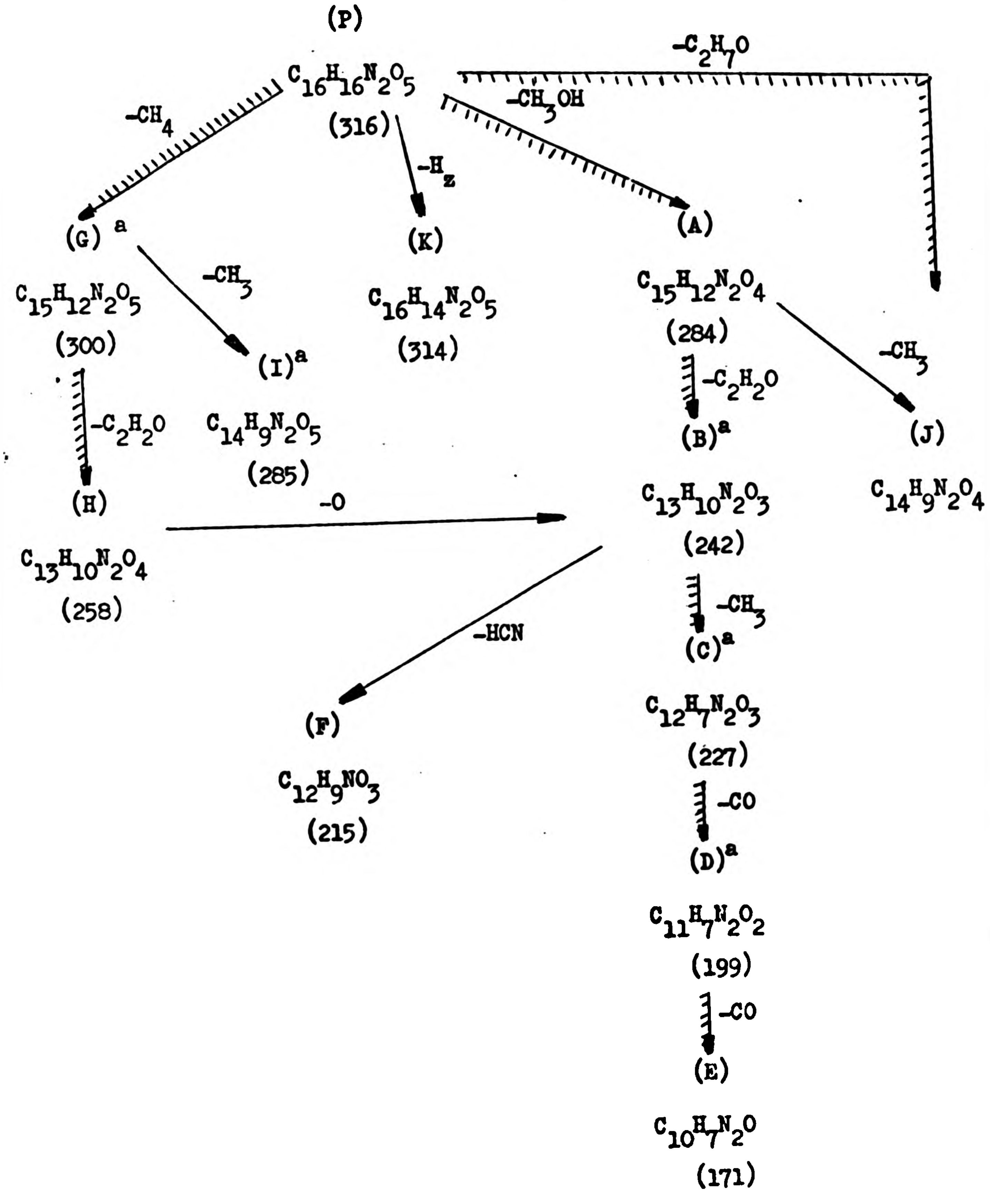
a = Confirmed by exact mass measurements

ш = Pathway confirmed by metastable transition

Fig. 2.5.

Fragmentation Scheme for

1,6-Dihydroxy-3,8-dimethoxy-5-acetyl,10hydrophenazine.



a = Confirmed by exact mass measurements

ꟺ = Pathway confirmed by metastable transition

TABLE 2.10.

Ion Abundances for 1.6-Dihydroxy-3.8-dimethoxy-dihydrophenazine.

Ion	m/e	%[b]	Assignment
[a] [P-16]=A	258	57.1	$C_{13}H_{10}N_2O_4$
[P-32]=B	242	100.0	$C_{13}H_{10}N_2O_3$
[P-47]=C	227	61.2	$C_{12}H_7N_2O_3$
[P-59]=F	215	21.6	$C_{12}H_9NO_3$
[P-60]=G	214	23.5	$C_{12}H_{10}N_2O_2$
[P-75]=D	199	39.6	$C_{11}H_7N_2O_2$
[P-91]=H	183	41.7	$C_{11}H_5NO_2$
[P-103]=E	171	14.6	$C_{10}H_7N_2O$
	108	21.4	
	107	17.0	
	79	14.8	
	63	15.2	

a = Symbols used in fragmentation schemes

b = % Relative abundance.

TABLE 2.11.

Ion Abundance for 1,6-Dihydroxy-3,8-dimethoxy-5-acetyl,10-hydrophenazine.

Ion	m/e	$\%^b$	Assignment
P^a	316	0.1	$C_{16}H_{16}N_2O_5$
[P-2]=K	314	0.4	$C_{16}H_{14}N_2O_5$
[P-16]=G	300	25.5	$C_{15}H_{12}N_2O_5$
[P-31]=I	285	9.8	$C_{14}H_9N_2O_5$
[P-32]=A	284	11.8	$C_{15}H_{12}N_2O_4$
[P-47]=J	269	2.8	$C_{14}H_9N_2O_4$
[P-58]=H	258	100.0	$C_{13}H_{10}N_2O_4$
[P-74]=B	242	35.3	$C_{13}H_{10}N_2O_3$
[P-89]=C	227	17.5	$C_{12}H_7N_2O_3$
[P-101]=F	215	6.7	$C_{12}H_9NO_3$
[P-117]=D	199	7.4	$C_{11}H_7N_2O_2$
[P-145]=E	171	3.0	$C_{10}H_7N_2O$
	106	1.3	

a = Symbols used in fragmentation schemes.

b= % Relative abundance.

TABLE 2.12.

Exact Mass Measurements on Selected Peaks of the Phenazene Derivatives.

Compound	Nominal Mass	Determined Mass	Ion Assignment	Calc. Mass
1,6-dihydroxy-3,8-dimethoxy-dihydrophenazine	258	258.0644	$C_{13}H_{10}N_2O_4$	258.0641
1,6-dihydroxy-3,8-dimethoxy-phenazine	256	256.0481	$C_{13}H_8N_2O_4$	256.0484
	242	242.0695	$C_{13}H_{10}N_2O_3$	242.0691
	215	215.0580	$C_{12}H_9NO_3$	215.0582
	199	199.0507	$C_{11}H_7N_2O_2$	199.0508
	171	171.0558	$C_{10}H_7N_2O$	171.0558
1,6-dihydroxy-3,8-dimethoxy-5-acetyl-10-hydrophenazine	300	300.0741	$C_{15}H_{12}N_2O_5$	300.0746
	258	258.0638	$C_{13}H_{10}N_2O_4$	258.0640
	242	242.0693	$C_{13}H_{10}N_2O_3$	242.0691
	227	227.0457	$C_{12}H_7N_2O_3$	227.0457
	199	199.0509	$C_{11}H_7N_2O_2$	199.0507

TABLE 2.13.

Metastable Peaks and Transitions for

1,6-Dihydroxy-3,8-dimethoxy-dihydrophenazine.

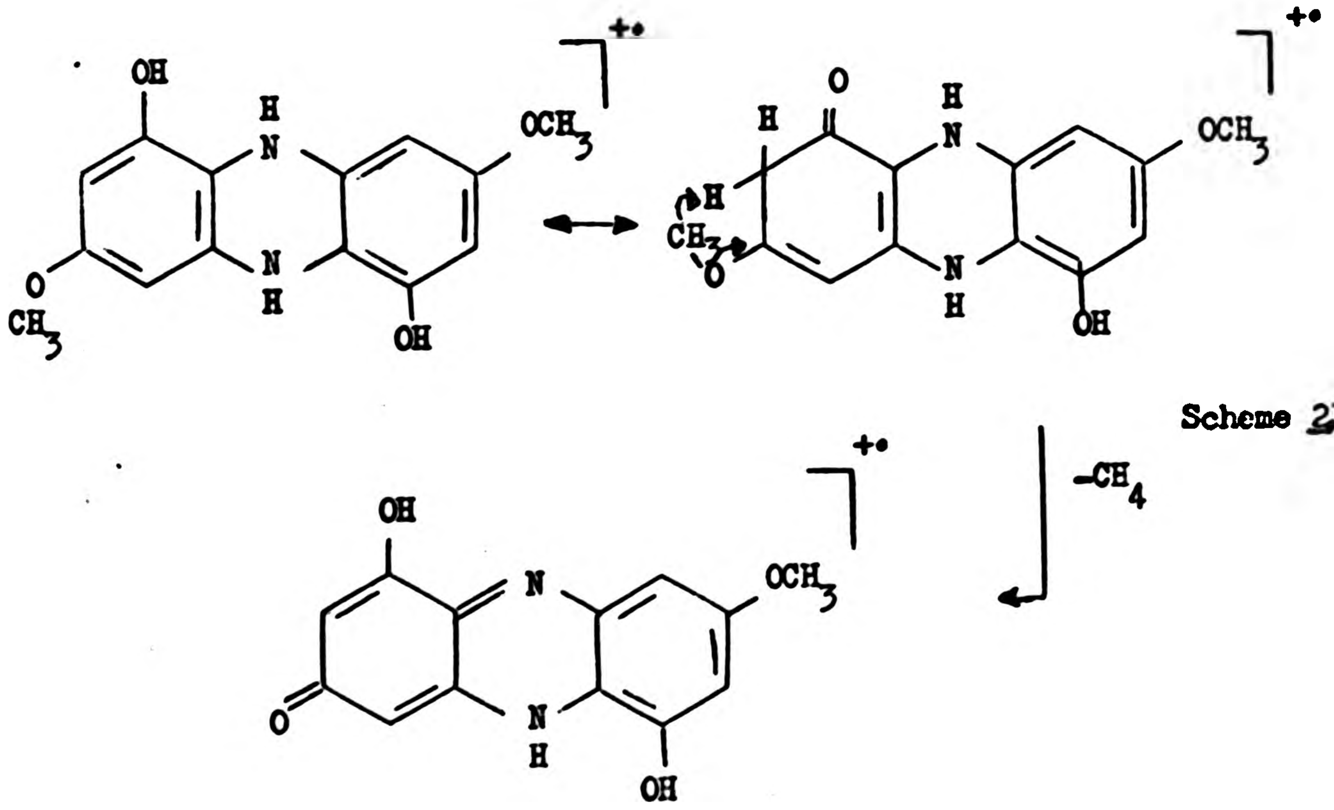
Transition	m/e values for the transition	m* obs.	m* calc.
A ⟶ B	258 ⟶ 242	227	226.9
B ⟶ C	242 ⟶ 227	213	212.9

1,6-Dihydroxy-3,8-dimethoxy-5-acetyl,10-hydrophenazine.

Transition	m/e values for the transition	m* obs.	m* calc.
P ⟶ A	316 ⟶ 284	255.5	255.2
P ⟶ G	316 ⟶ 300	285.0	284.8
P ⟶ J	316 ⟶ 269	229.0	229.0
G ⟶ H	300 ⟶ 258	221.9	221.9
A ⟶ B	284 ⟶ 242	206.1	206.2
B ⟶ C	242 ⟶ 227	212.9	212.9
C ⟶ D	227 ⟶ 199	174.2	174.5
D ⟶ E	199 ⟶ 171	147.0	146.9

of radicals such as $C_6H_5O^{\bullet}$ and even-electron molecules such as N_2 and CO. However, in the mass spectra (Tables 2.10. and 2.11.) of the red compound and its acetyl derivative cleavage of the C-N bond did not predominate. Indeed exact mass measurements (Table 2.12.) showed that retention of C-N bonds was favoured, and the base peaks in each spectrum were of ions containing both nitrogen atoms. There was also no elimination of N_2 or radicals such as $Ar^{\bullet}$ from the parent ion.

The peak with the highest m/e value in the spectrum of the red compound 1,6-dihydroxy-3,8-dimethoxy-dihydrophenazine appears at 258 a.m.u., which does not correspond to the molecular ion $(P)^+$ but to the ion $(P-CH_4)^+$. Its acetyl derivative 1,6-dihydroxy-3,8-dimethoxy-5-acetyl,10-hydrophenazine shows a very weak $(P)^+$ ion but also has a very intense $(P-CH_4)^+$ ion (Tables 2.10. and 2.11.). The loss of this even-electron molecule CH_4 can be rationalized in terms of Scheme 2.10.



Scheme 2.10.

This elimination of CH_4 from the molecular ion was supported by exact mass measurement (Table 2.12.) and in the case of the acetyl derivative by the observation of the corresponding metastable peak (Table 2.13.). As in the other mass spectra of substituted phenazines[80,82] reported the phenazine ring system is more stable to fragmentation than the substituents it carries. Thus the fragmentation sequences consist of losses due to elimination of substituents as in the sequence B → C → D → E which is again common to both spectra. Only the fragmentation transition B → F (Figs. 2.4. and 2.5.) involved the loss of HCN a process which indicates that a ring opening step must first occur.

2.8 The Interaction of Tris(benzoquinone-2-oximato) Iron(III) Complexes with Triphenyl Phosphine.

As noted in previous sections of this chapter the complexes $M(qO)_2$ (M=nickel or zinc) afforded complexes of the type $M(qPPh_3)_2$ on treatment with triphenyl phosphine. In contrast the analogous copper (II) complexes underwent reduction on treatment with triphenyl phosphine to give copper (I) products of the type $Cu(qO)\ (PPh_3)_2$. The differing behaviour of the nickel and zinc complexes compared to that of the copper complexes was thought to be related to their differing oxidation state characteristics. To check this hypothesis the interaction between tris(5-methoxybenzoquinone-2-oximato)iron(III) (1 mol. equiv.) and triphenyl phosphine (5 mol. equiv.) was carried out. This complex was selected because iron (III) like copper (II) can undergo reduction to a lower oxidation state.

The reaction of triphenyl phosphine and tris(5-methoxybenzoquinone-2-oximato)iron (III) proceeded readily at room temperature in pyridine. As expected the metal-containing product was an iron (II) complex. This complex dipyridino bis(5-methoxybenzoquinone-2-oximato) iron (II) was separated from the reaction mixture using chromatographic techniques and was purified by recrystallisation from pyridine.

A red organic solid was also obtained from the reaction. This solid had an identical infrared spectrum to that of 1,6-dihydroxy-3,8-dimethoxyphenazine obtained from the reaction $Cu(qO)_2$ and triphenyl phosphine (see Section 2.6.C.). The isolation of the above products and the formation of triphenyl phosphine oxide, indicated by t.l.c., suggest the following stoichiometry for the Reaction 2.9..

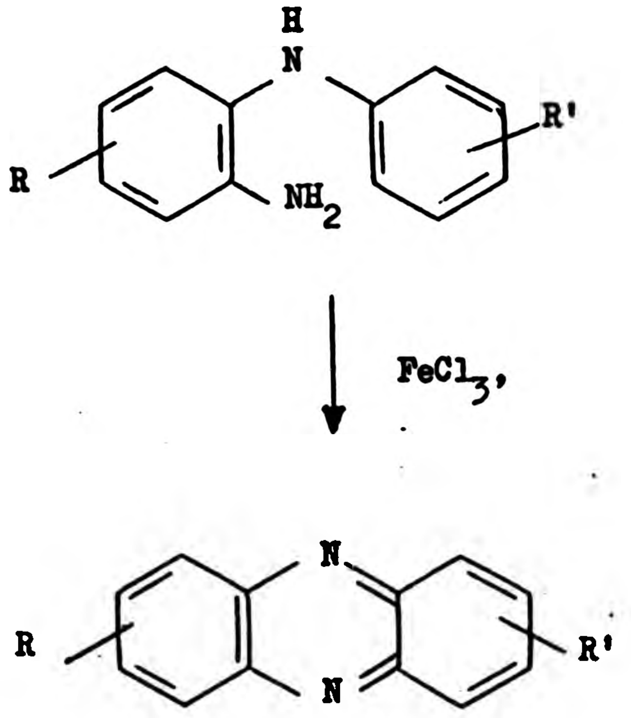
$$\begin{tikzcd}
 & & Fe(qO)_3 \; + \; Ph_3P \arrow[d, "py"] & & \\
Fe(qO)_2,2py & + & {[q^{\bullet}]} \arrow[d] & + & Ph_3PO \\
 & & \text{phenazine} & &
\end{tikzcd}$$

Reaction 2.9.

2.9. The Synthetic Significance of the Deoxygenation of Iron, Copper and Nickel Benzoquinone-2-oximato Complexes.

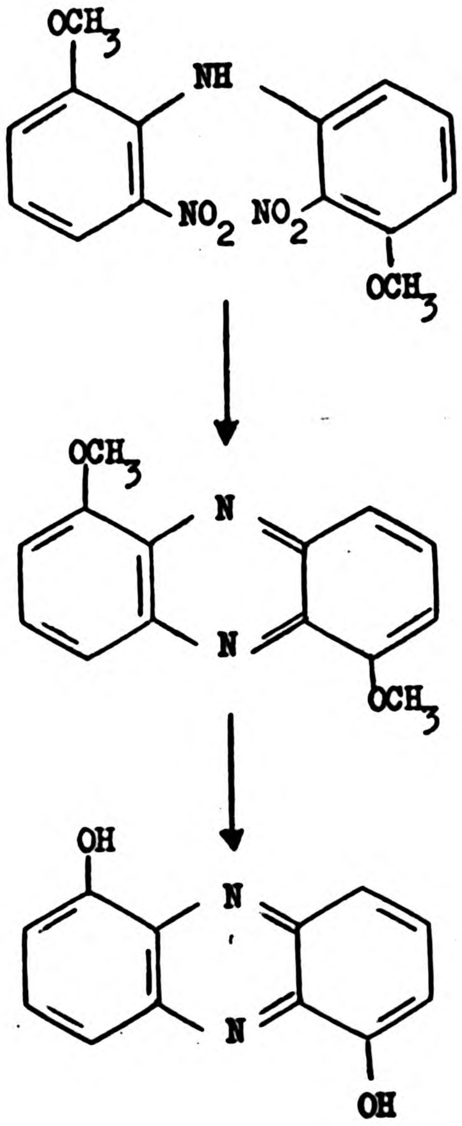
The deoxygenation of tris(benzoquinone-2-oximato) iron (III) provides a useful synthetic route to iron (II) benzoquinone-2-oximato complexes. Iron (II) complexes can only be obtained from the direct reaction of an iron (II) salt and a 2-nitrosophenol.[91] This method is of limited applicability because only a few 2-nitrosophenols are known. Attempts have been made to obtain iron (II) complexes via nitrosation of phenols in the presence of iron (II), however, the iron (III) products were obtained.

Both the deoxygenation of copper and iron benzoquinone-2-oximato complexes provides a new route to 1,6-dihydroxyphenazines. In the systems investigated during this study the phenazines were produced by a reductive process using triphenyl phosphine. In marked contrast most routes to phenazines reported previously are oxidative in character. For example, several phenazines have been prepared by the oxidation of o-aminodiphenylamines with ferric chloride or other oxidising agents.[92] (Reaction 2.10.)



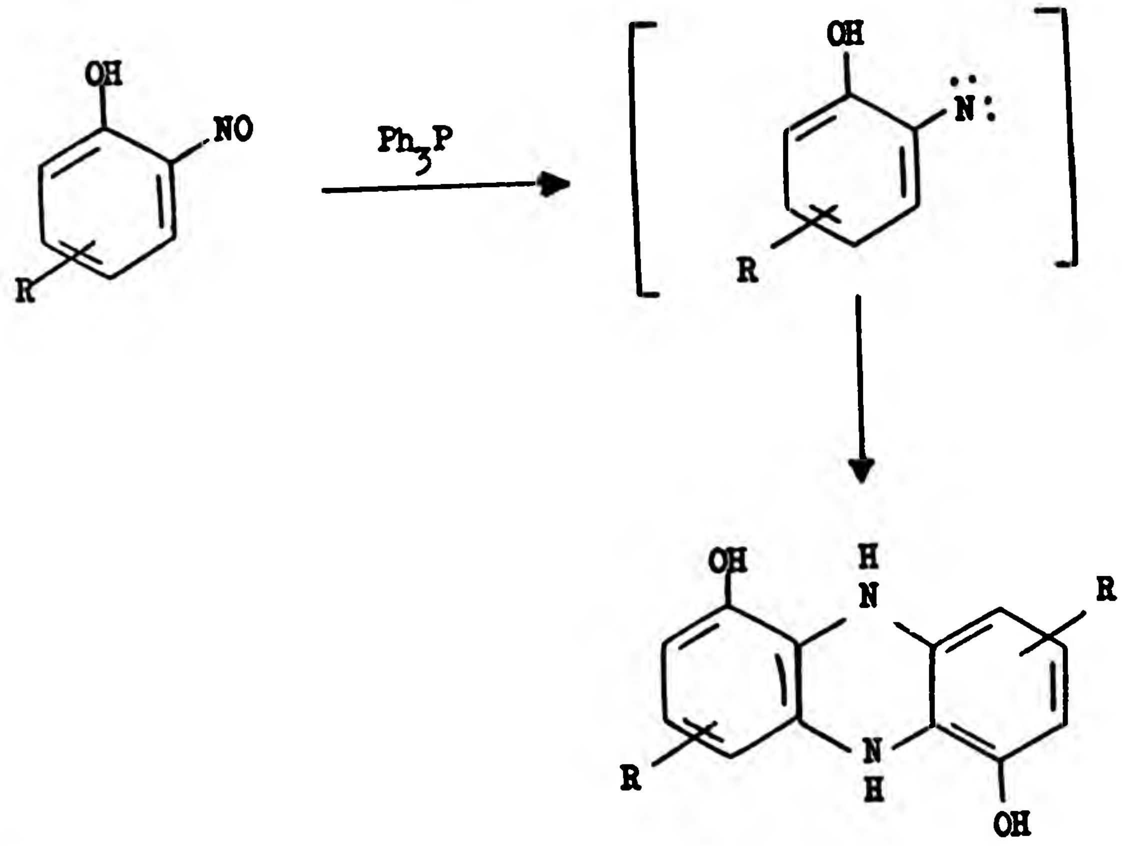
Reaction 2.10.

In the case of hydroxyphenazines very few synthetic routes have been reported in the literature. For example 1,6-dihydroxyphenazine was prepared a) by the reduction of iodinin which is obtained from cultures of chromobacterium iodinum[93] and b) by dealkylation of 1,6-dialkoxyphenazines[94]. The preparation of 1,6-dihydroxyphenazine involved first the reduction and ring closure of 2,2'-dinitro-3,6'-dimethoxyphenazine to give the 1,6-dimethoxyphenazine which was then demethylated to give the product as in Scheme 2.11.



Scheme 2.11.

The interaction between a 2-nitrosophenol and triphenyl phosphine would be a useful one-step synthesis of 1,6-dihydroxy-dihydrophenazines (Scheme 2.12.). However the utility of this system has its limitations because only a few 2-nitrosophenols are known.



Scheme 2.12.

The interaction between the readily obtainable copper(II) and iron(III) complexes of 2-nitrosophenols and triphenylphosphine provide a widely applicable route to hydroxyphenazines. Furthermore the deoxygenation of the nickel(II) and zinc(II) complexes of 2-nitrosophenol provides both a convenient and widely applicable synthetic route to N(2-hydroxybenzene)-iminotriphenylphosphoranes and their metal complexes. This being an alternative route to the currently available methods which involve difficult handling techniques and/or the use of explosive starting materials.[95,96]

2.10. Possible Reaction Pathways for the Deoxygenation of 2-Nitrosophenols and their Metal Complexes.

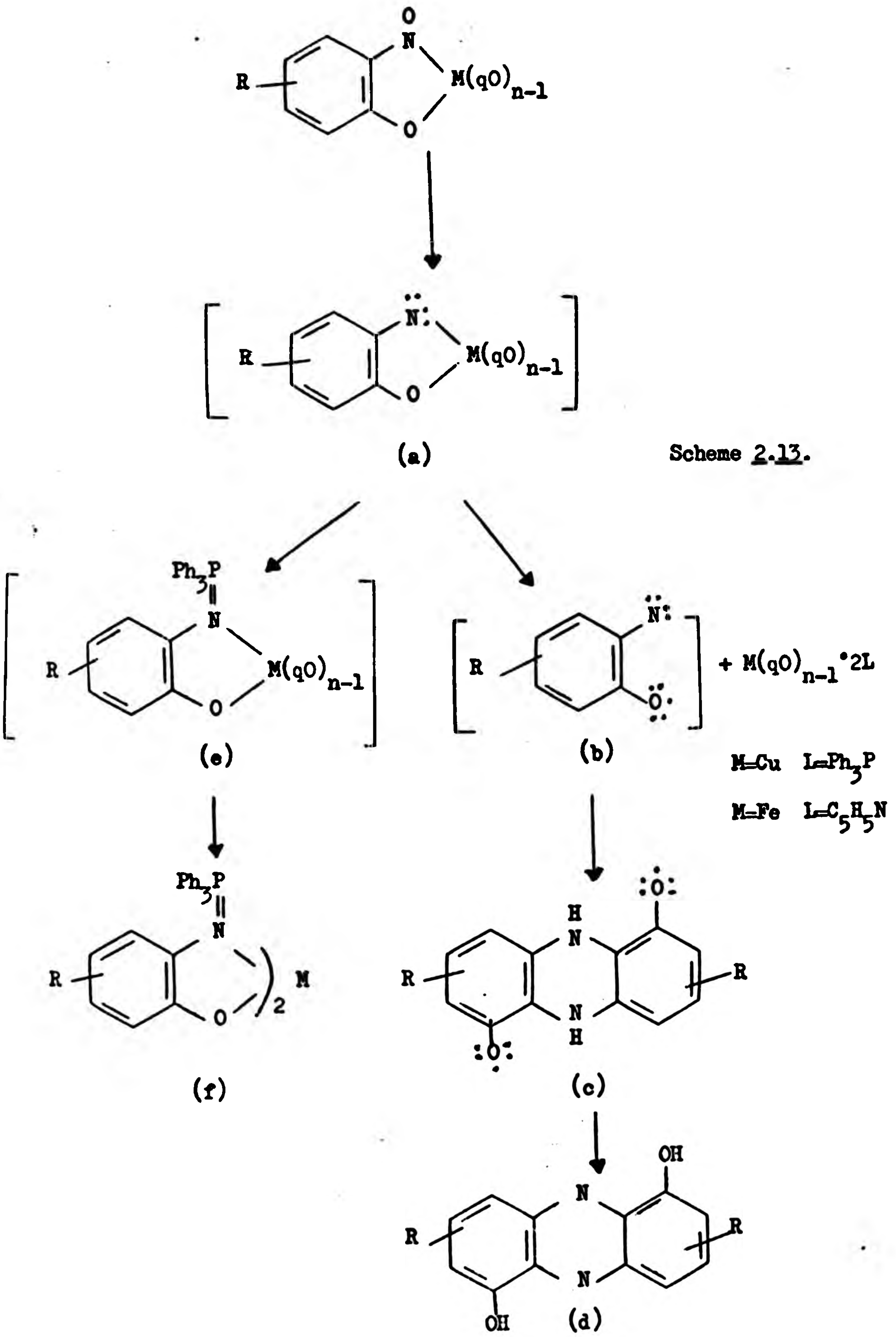
In previous sections it has been shown that the formation of the $\geqslant P=N-$ linkage, i.e. coupling of the nitrene intermediate with the tervalent phosphorus reagent, in deoxygenation reactions of nitroso-compounds with tervalent phosphorus compounds can be considered as indicative of nitrene intermediacy.

Furthermore, nitrenes have been postulated as intermediates in reactions involving deoxygenation of complexed nitroso-compounds. S. Otsuka *et al.*[97] suggested that the formation of $C_6H_5NHCONH(t-C_4H_9)$ from the thermal reaction of nitrosobenzene bis(tert-butylisocyanide) nickel (0) in the presence of water, results from the hydration of the carbodiimide initially formed by an intramolecular phenylnitrene transfer to the coordinated isocyanide. The formation of phenazines by the thermolysis of azides was also postulated to go via nitrene intermediates.[85] Walker and Waters[87] ascribed the formation of 2,7-dimethoxy-phenazine on thermolysis of 4-methoxy-phenyl azide to the dimerisation of anilino-radicals derived from triplet nitrenes by hydrogen abstraction.

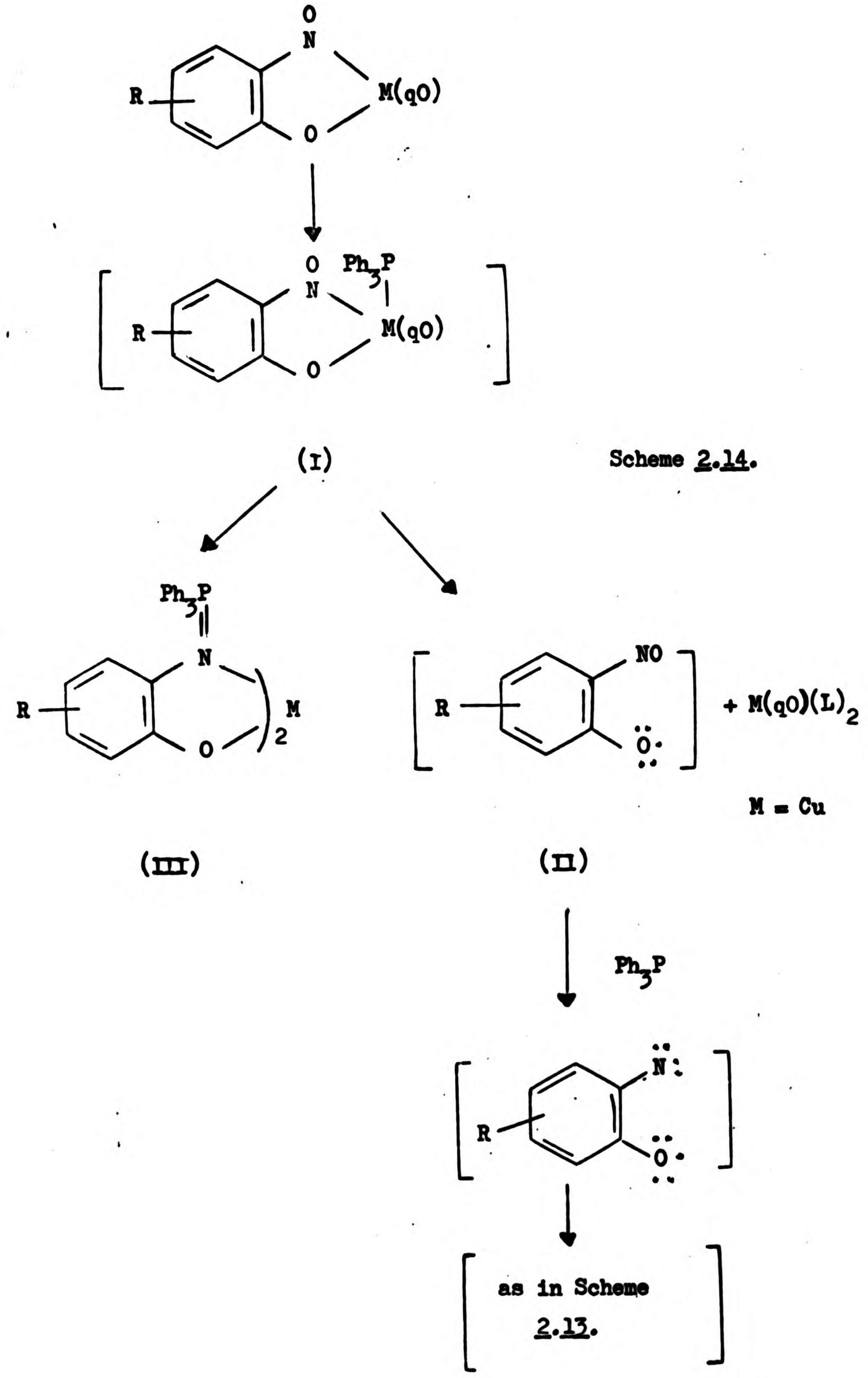
Thus it is not unreasonable to envisage the formation of dihydrophenazines, phenazines and iminophosphorane complexes in the reactions described in the earlier sections as proceeding via the intermediate formation of nitrenes or nitrene metal complexes.

Although the differing behaviour of the metal complexes of 2-nitrosophenols towards triphenyl phosphine is not clearly understood, it parallels the readiness of the metal to undergo reduction and can be rationalised in these terms. In this reaction pathway (Scheme 2.13) the triphenyl phosphine is assumed to initially deoxygenate one of the ligands of the complex $M(qO)_n$ to give the intermediate nitrene complex (a). When M is Fe or Cu, reduction of the metal in (a) leads to the nitrene species (b) and an adduct of the complex $M(qo)_{n-1}$. Subsequent dimerisation of (b) or more probably interaction of (b) with $M(qO)_n$ or (a) leads to (c) which on rearrangement gives the phenazine (d). When M is Ni or Zn reduction of the metal is difficult and thus (a) couples with triphenyl phosphine to give (e) and finally the iminophosphorane complex (f).

An alternative reaction pathway (Scheme 2.14.) could be considered, at least in the case of the metal(II) complexes, where the complex first forms an intermediate complex (I) with triphenyl phosphine, which then reduces the central metal atom if reduction is possible. The ligand species (II) produced can then be deoxygenated by further triphenyl phosphine. Where the metal atom cannot be easily reduced deoxygenation of the ligand takes place to form (III).



Scheme 2.13.


O
N
R
M(qO)
O
O
Ph$_3$P
N
R
M(qO)
O
(I)
Ph$_3$P
N
R
M
2
O
NO
R
O
+ M(qO)(L)$_2$
M = Cu
(III)
(II)
Ph$_3$P
N
R
O
as in Scheme 2.13.

Scheme 2.14.

2.11. References.

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CHAPTER 3

3.1. The Structure of Nickel and Zinc Complexes of N(2-Hydroxybenzene)-iminotriphenylphosphorane(2-Triphenylphosphiniminophenol).

The structure of bis(2-triphenylphosphiniminophenolato)nickel(II) complexes has been investigated by magnetic and u.v./visible spectroscopic studies.

The magnetic moments of the bis(2-triphenylphosphiniminophenolato) nickel(II) complexes are in the range 3.33 - 3.67 B.M. (Table 3.1.) suggesting isolated nickel atoms within a pseudotetrahedral environment in the solid state. Previously in the literature pseudotetrahedral compounds were reported to have magnetic moments in this range (Table 3.2.) and some have been confirmed pseudotetrahedral by X-ray crystallography.[98]

Tetrahedral arrangement in these complexes is further supported by their electronic spectra (Table 3.3. and 3.4.). The spectra are similar to those of several tetrahedral nickel (II) complexes which have been reported in the literature (Table 3.5. and 3.6.).

The work of Tanabe and Sugano[99] demonstrates that in a tetrahedral ligand field the ^3F ground term of nickel(II) (d^8) ion is split into the following states: $^3T_1(F)$, $^3T_2$ and $^3A_2$. In addition there are the ^1E and $^1T_2$ from the ^1D term, a $^3T_1$ state which originates from the ^3P term, as well as the $^1T_2$, $^1T_1$, $^1A_1$ and ^1E states which come from the ^1G term of the free nickel(II) ion. The Tanabe-Sugano diagram for a tetrahedrally co-ordinated nickel(II) ion is shown in Fig. 3.1.

Table 3.1. Room Temperature Magnetic Moments of some Bis(2-triphenylphosphiniminophenolato)nickel(II)

Compound	$\mu_{eff.}$ B.M.	T°K
Bis(5-methoxy-2-triphenylphosphinimino phenolato)nickel(II)	3.67	296.2
Bis(4-methyl-2-triphenylphosphinimino phenolato)nickel(II)	3.33	296.2
Bis(4-chloro-2-triphenylphosphinimino phenolato)nickel(II)	3.66	294.5
Bis(4-bromo-2-triphenylphosphinimino phenolato)nickel(II)	3.60	295.2

Table 3.2. Magnetic Moments of some Tetrahedral Nickel(II) Complexes.

Compound	μ_{eff}, B.M.	Ref.
$[R]_2[NiCl_4]$ R = $(C_2H_5)_4N$, $(C_6H_5)_3CH_3As$, $(C_6H_5)_3CH_3P$	3.88, 3.49, 3.88	100
$[Ni(HMPA)_4](ClO_4)_2$ HMPA = hexamethylphosphoramide	4.02	101
$[Ni((CH_3)_3NO)_4](ClO_4)_2$	3.86	102
$[R][Ni([C_6H_5]_3P)Br_3]$ R = $(C_2H_5)_4N$, t-$C_4H_9(C_6H_5)_3P$	3.68	103
$[Ni(MMPM)_2]$ MMPM = $3,3^1,5,5^1$-tetramethyl-dipyrromethene-$4,4^1$-dicarboxylate	3.42	104
$[Ni(Py\text{-}N\text{-}t\text{-}Bu)_2]$ Py-N-t-Bu = N-t-butylpyrrole-2-aldimine	3.30	105
$[Ni(MBrPM)_2]$ MBrPM = 5^1-bromo-$3,4^1$,5-trimethyl-dipyrromethene-3^1,4-dicarboxylate	3.55	104
$[NiLCl_2]$ L = trimethylenediamine	3.37	106
$[NiLBr_2]$ L = N,N,N^1,N^1-tetramethylated ethylenediamine	3.26	106

Tanabe-Sugano Diagram for a Tetrahedrally Co-ordinated Ni(II) ion.

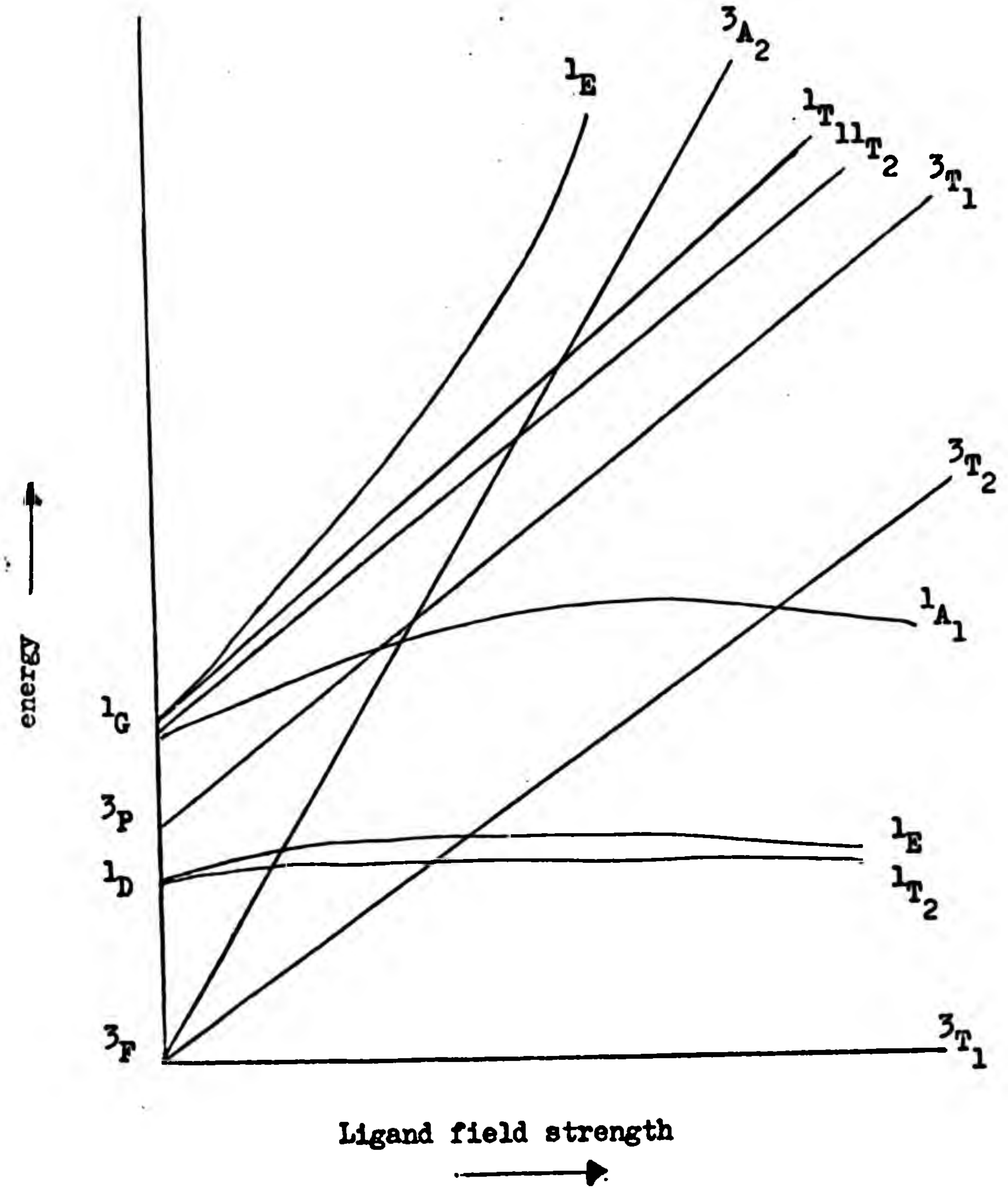


Fig. 3.1.

The electronic absorption spectrum of nickel(II) ion in a tetrahedral ligand field arises by three spin-allowed transitions from the $^3T_1(F)$ ground state to the $^3T_2(F)$, $^3A_2(F)$ and $^3T_1(P)$ states, respectively. There are also some spin-forbidden transitions from the triplet ground

Table 3.3. Solution Spectra of the Bis(2-triphenylphosphiniminophenolato)nickel(II) in Chloroform.

Compound	ν_{max}/cm^{-1}	
Bis(5-methoxy-2-triphenylphosphiniminophenolato) nickel(II)	22,222	-
Bis(4-methyl-2-triphenylphosphiniminophenolato) nickel(II)	22,422	16077
Bis(4-chloro-2-triphenylphosphiniminophenolato) nickel(II)	22,727	16129
Bis(4-bromo-2-triphenylphosphiniminophenolato) nickel(II)	22,624	16393

Table 3.4. Reflectance Spectra of the Bis(2-triphenylphosphiniminophenolato)nickel(II)

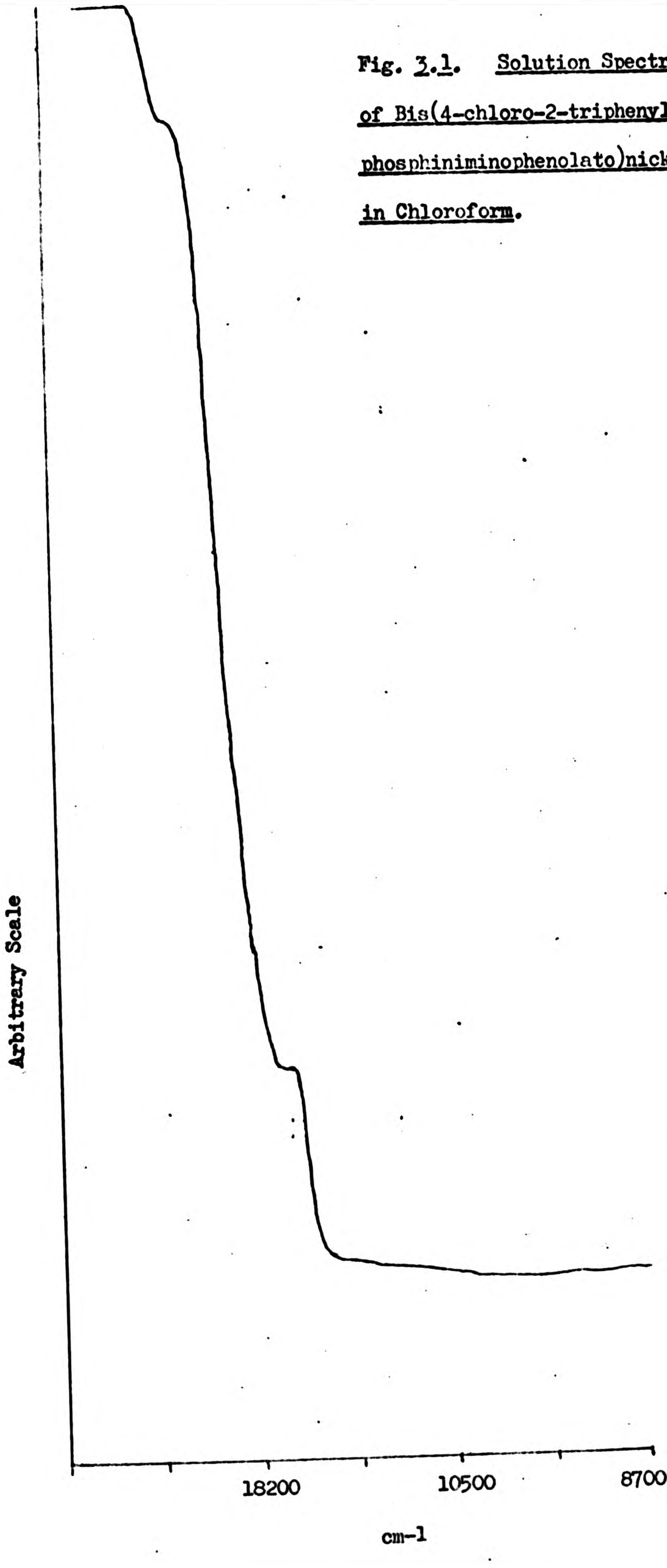
Compound	ν max/cm^{-1}
Bis(5-methoxy-2-triphenylphosphiniminophenolato)nickel(II)	19230, 15625, 13333, 10526 (sh), 6944
Bis(4-methyl-2-triphenylphosphiniminophenolato)nickel(II)	22727, 15625, 12987, 10526, 6993
Bis(4-chloro-2-triphenylphosphiniminophenolato)nickel(II)	20000, 16129, 13698, 10989, 7407
Bis(4-bromo-2-triphenylphosphiniminophenolato)nickel(II)	19231, 15873, 13514, 6944

Table 3.5. Solution Spectra of some Tetrahedral Nickel(II) Complexes.

Compound/ion	Ref.	ν_{max}/cm^{-1}(extinction coefficient/litre $mole^{-1}cm^{-1}$)
$[NiCl_4]^{2-}$	107	19800, 15950, 15240(160), 14250(160), 11630(6), 8700, 7549(21)
$[NiBr_4]^{2-}$	107	21190(5.4), 16700, 15200, 14140(250), 13230(241), 10680(4.7), 6995(30)
$Ni(NCO)_4^{2-}$	108	16800(142), 15600(142), 12800(5.8), 9460(24), 4600
$Ni(Ph_3PO)_2Cl_2$	107	22470, 16310, 14470, 12120, 7288
$Ni(Ph_3PO)_2Br_2$	107	20490(22), 15580(101), 14290, 11930, 7250(19)
$Ni(2,3\text{-}DiMePy)_2Br_2$	109	17480(134), 15750, 11560, 10000(53)

2,3-DiMePy = 2,3-dimethylpyridine

Fig. 3.1. Solution Spectrum of Bis(4-chloro-2-triphenyl phosphiniminophenolato)nickel(II) in Chloroform.



state to excited states derived from the field-free terms ^1D and ^1G.

For a number of tetrahedrally co-ordinated nickel(II) compounds (Table 3.5.) the transition $^3T_1(F) \longrightarrow {}^3T_1(P), \nu_3$ has been reported to lie between 14,000 - 17,000cm^{-1} and appears as a multiple band. This splitting has been attributed to either a ground state geometrical distortion[110] or to Jahn-Teller[111] splitting of the excited state. Weak bands on either side of the ν_3 band at approximately 10,000 and 19,000 cm^{-1} have been assigned to spin-forbidden transitions to excited states derived from the ^1D and ^1G terms, respectively. While bands in the region of 8000 cm^{-1} are assigned as the ν_2 transition $^3T_1(F) \rightarrow {}^3A_2(F)$ and those around 3,500 cm^{-1} to the ν_1 transition $^3T_1(F) \rightarrow {}^3T_2(F)$.

The solution electronic absorption spectra of the bis(2-triphenylphosphiniminophenolato)nickel(II) complexes prepared during this study were examined in chloroform.

A typical spectrum is shown in Fig. 3.1.. In all cases a feature of the electronic spectra is that they include very intense charge transfer or ligand absorptions which tail into the d-d band region. Consequently, d-d absorptions appear as shoulders on intense shorter wavelength bands. These absorptions occur at ca. 16200 cm^{-1}, where many tetrahedral nickel(II) complexes are known to absorb, and corresponds to ν_3. The ν_2 and ν_1 bands lie outside the operating range of the Unicam SP1800 instrument used.

The diffuse reflectance spectra (e.g. Fig. 3.2.) show well defined bands in the regions 19,000 - 23,999 cm^{-1}, 15,500 - 16,000 cm^{-1}, 12,000 - 14,000 cm^{-1}, 10,500 - 11,000 cm^{-1} and 6,900 - 7,100 cm^{-1} (Table 3.4.). Assignment for the bands attributable to d-d transitions are given in Table 3.7..

The tetrahedral structure of the bis(2-triphenylphosphiniminophenolato) nickel(II) complexes is not unexpected. In general steric characteristics of the ligands in a complex play an important part in determining the stereochemistry adopted by the complex. For example, the two cationic

Table 3.6. Reflectance Spectra of some Tetrahedral Nickel(II) Complexes.

Compound	Ref.	ν_{max}/cm^{-1}
$Ni(Me_4en)Br_2$	106	19000, 17500 sh, 11100 sh, 9800, 7700 sh
$Ni(Me_4en)I_2$		17550, 14500 sh 10000, 8000 sh
Me_4en = N,N,N^1,N^1-tetramethylated ethylenediamine		
$(C_6H_5)_3AsO)_2NiCl_2$	107	22222, 16529, 14556, 11947
$(C_6H_5)_3AsO)_2NiBr_2$		20408, 15625, 14705 sh, 11696, 7692
$(i\text{-}Pr\text{-}N\text{-}sal)_2Ni$	112	19600, 16900, 14100, 10900, 6700
$(5\text{-}Bu\text{-}N\text{-}sal)_2Ni$		19600, 16900, 14100, 10900, 6700

N-sal = (N-salicylaldimino)

Fig. 3.2. Reflectance Spectrum of Bis(4-chloro-2-triphenyl phosphiniminophenolato)nickel(II)

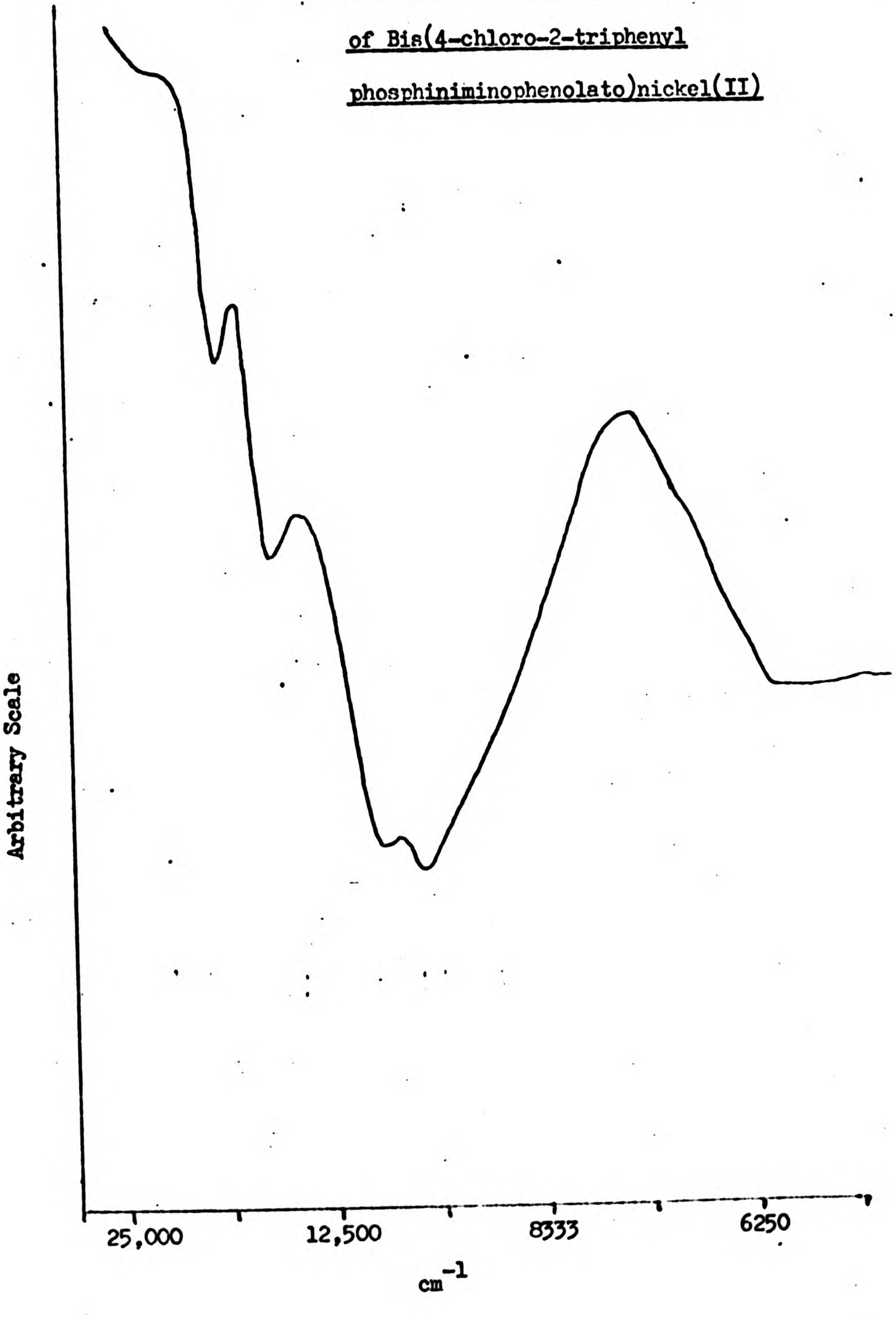
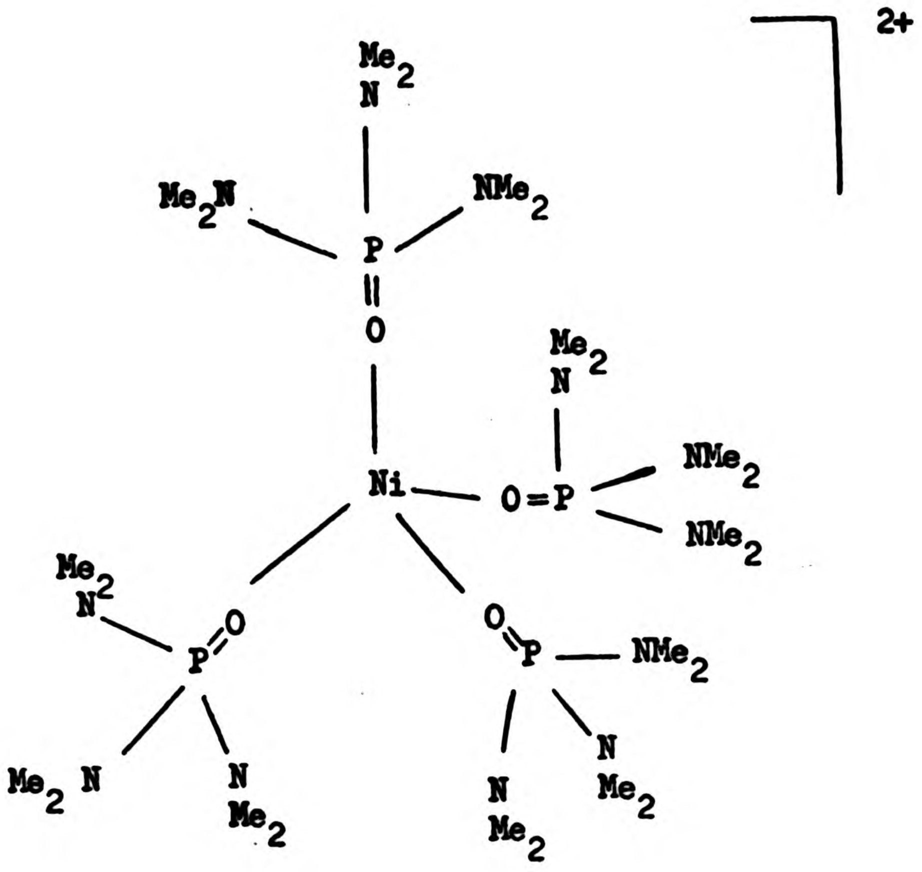
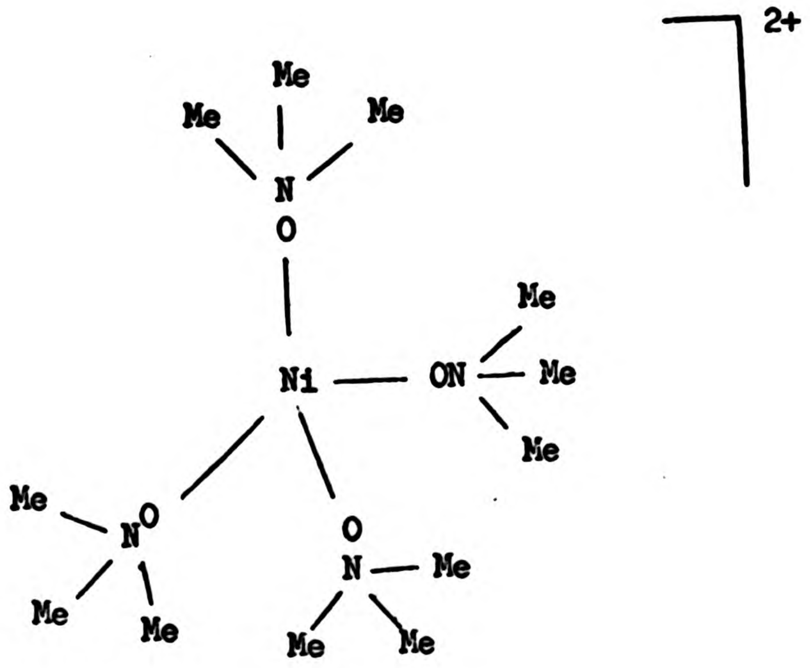


Table 3.7. Assignment of d-d Bands in the Electronic Spectra of Bis(2-triphenylphosphiniminophenolato)nickel(II).

νmax/cm^{-1}		Transition
19,500 cm^{-1}		$^3T_1(F) \rightarrow {}^1T_2$
15,500 cm^{-1} 13,000 cm^{-1}	ν_3	$^3T_1(F) \rightarrow {}^3T_1(P)$
10,500 cm^{-1}		$^3T_1(F) \rightarrow {}^1E$
6,900 cm^{-1}	ν_2	$^3T_1(F) \rightarrow {}^3A_2(F)$

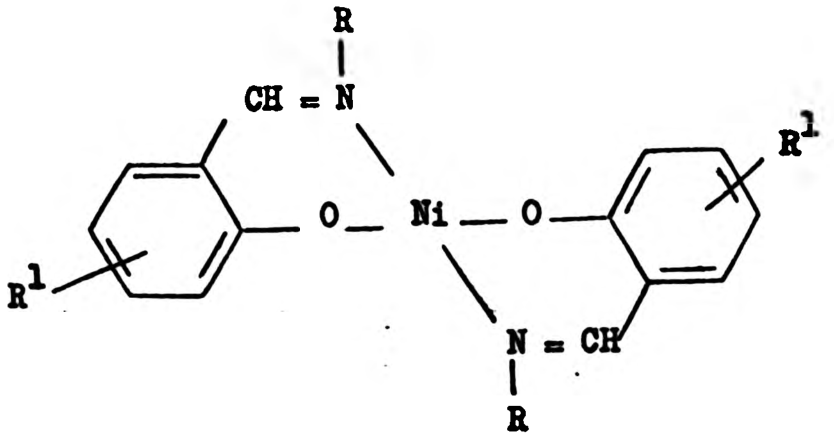


3.1.



3.2.

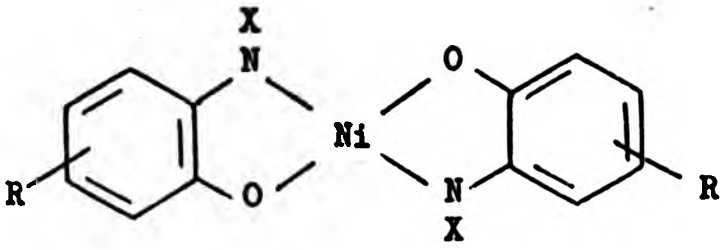
complexes $[Ni(HMPA)_4]^{2+}$ (HMPA = hexamethylphosphoramide)[101] 3.1. and $[Ni(Me_3NO)_4]^{2+}$[102] 3.2. contain four very bulky ligands and adopt a tetrahedral structure. Of particular importance is the size of the group attached onto the donor sites of the ligand. This has been clearly shown by the work of Sacconi et al[112] on salicylaldimine complexes of the type 3.3. which indicated that the tetrahedral structure was preferred when the



3.3.

group R is large. For example, when R is n-propyl, the planar structure was found to be most stable, however, when R was tert-butyl, the complexes assumed a tetrahedral structure. Similarly, Venanzi et al[113] have reported a series of nickel halide tertiary phosphine complexes of the type $[Ni(R_3P)_2X_2]$. They have shown that as the alkyl (R = n-butyl) groups of the tertiary phosphines are replaced by phenyl groups there is a change of structure from square planar to tetrahedral.

In the complexes of type 3.4. (X = O or PPh_3) the size of X is



3.4.

also expected to be important. Indeed, when X is oxygen in 3.4., the complexes are dimers with the nickel atom in a five co-ordinate environment.[23] However, when X is replaced by triphenylphosphine to give bis(2-triphenylphosphiniminophenolato)nickel(II), the nickel atoms environment changes from five co-ordinate to tetrahedral.

The studies of the bis(5-methoxy-2-triphenylphosphiniminophenolato) zinc(II) were restricted by its d^{10} character, but the structure is expected to be tetrahedral. The i.r. spectrum of the complex is indeed very similar to that of the corresponding nickel complex and in solution it is monomeric.

3.2. References.

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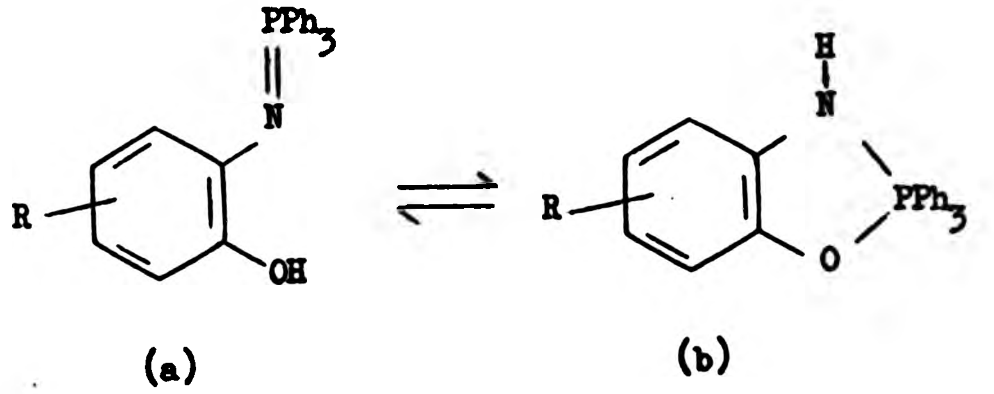
CHAPTER 4

N(2-Hydroxybenzene)-iminotriphenylphosphoranes.

4.1. Introduction.

Iminophosphoranes (4.1.) have been known for some time. These compounds have also been referred to as phosphinimines. Of particular interest to this work are the N(2-hydroxybenzene)-iminotriphenyl phosphoranes (4.2.), which can exist in an open (4.2.a) and/or a cyclic form (4.2.b). The cyclic form has also been referred to as amino(oxy) phosphorane or 3-hydro-1,3,2-benzoxazaphosph(V)ole.

$$R_3P = NR^1 \qquad 4.1.$$



(a) (b)

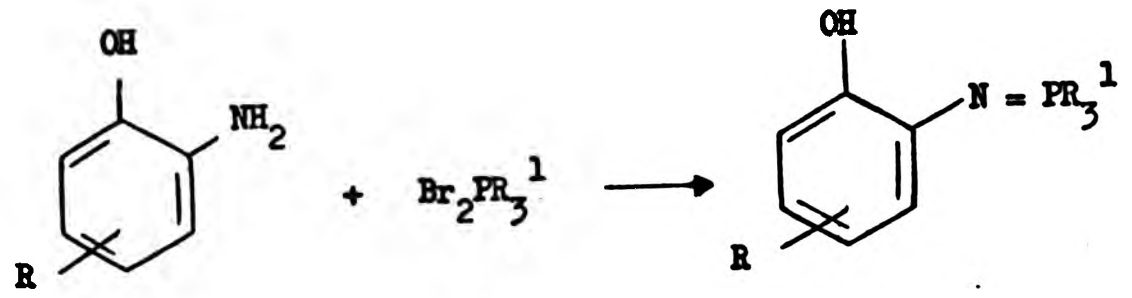
4.2.

This chapter deals with the synthesis and properties of such compounds and with their metal complexes. Throughout the chapter, compounds of the type 4.1. or 4.2. will be referred to as iminophosphoranes.

4.2. Previous work on the Preparation of Iminophosphoranes.

There are a number of methods reported in the literature for the preparation of iminophosphoranes. These methods have recently been reviewed[114] and are summarised in Table 4.1..

So far only two of the methods have been used for the preparation of N(2-hydroxybenzene)-iminotriphenylphosphoranes. Stegmann *et al*[115] prepared a series of compounds (Table 4.2.) by the interaction of a 2-aminophenol with dibromotriaryl or trialkylphosphorane (Reaction 4.1. Table 4.1. Method 3)

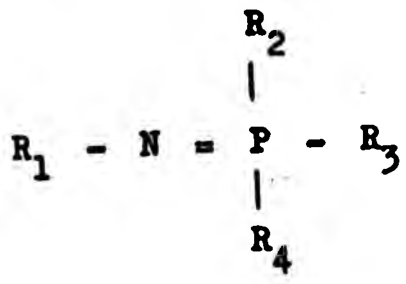


Reaction 4.1.

Table 4.1. Preparation of Iminophosphoranes.

Method No.	Reactants	Reference
1	Tertiary phosphine and azide	116
2	Tertiary phosphine and amine derivative	117
3	Dihalotriphenylphosphorane and a primary amine	118
4	Acid amide and phosphorus pentachloride	119
5	Phosphine alkylene and Schiff's base	120
6	α,β-Dibenzoylhydroxylamine and tertiary phosphine	121
7	N-Sulphinylsulphonamide and tertiary phosphine	122
8	Aminophosphine and an alkylene	123
9	Difluorodiazirines and tertiary phosphine	124
10	Quaternary phosphonium salt and potassium amide	125
11	Tertiary phosphine and N-chloroiminocarboxylic acid	126
12	Lead acetate oxidation of an aminophosphonium salt	127

Table 4.2. N-(2-Hydroxybenzene)-iminophosphoranes prepared by Stegmann et al.



$$R_1 - N = \underset{R_4}{\underset{|}{\overset{\overset{R_2}{|}}{P}}} - R_3$$

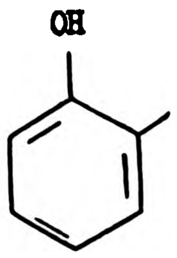
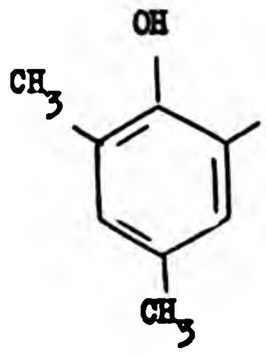
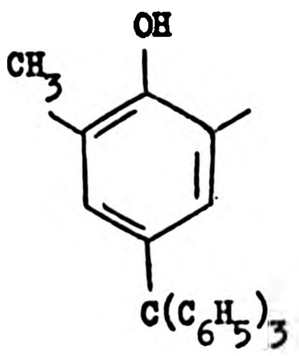
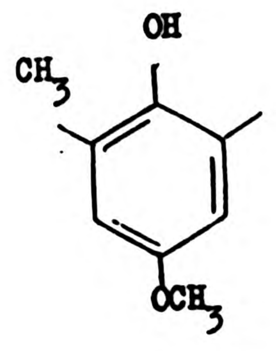
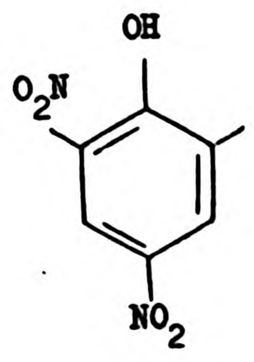
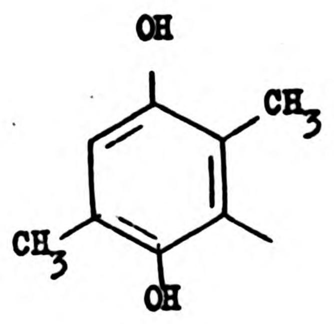
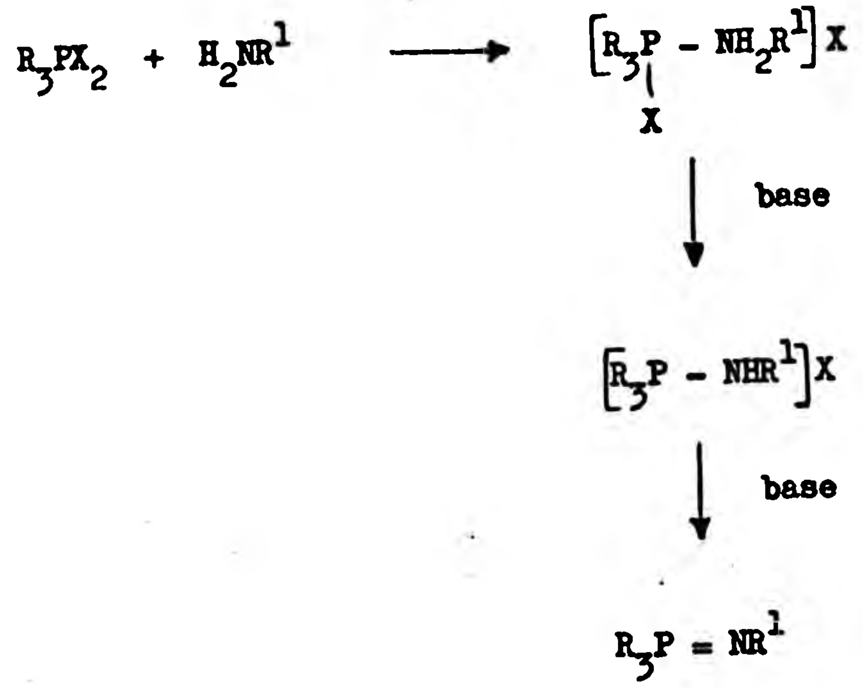
R_1	$R_2 = R_3 = R_4$
	C_6H_5
	C_6H_5, $p\text{-}CH_3\text{-}C_6H_4$, $p\text{-}CH_3O\text{-}C_6H_4$, $p\text{-}CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_4$.
	C_6H_5, $p\text{-}CH_3\text{-}C_6H_4$, $p\text{-}\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{HC}}}\text{-}O\text{-}C_6H_4$, $n\text{-}C_4H_9$, C_6H_{11}, $iso\text{-}C_3H_7$, $p\text{-}CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_4$

Table 4.2 (Cont.)

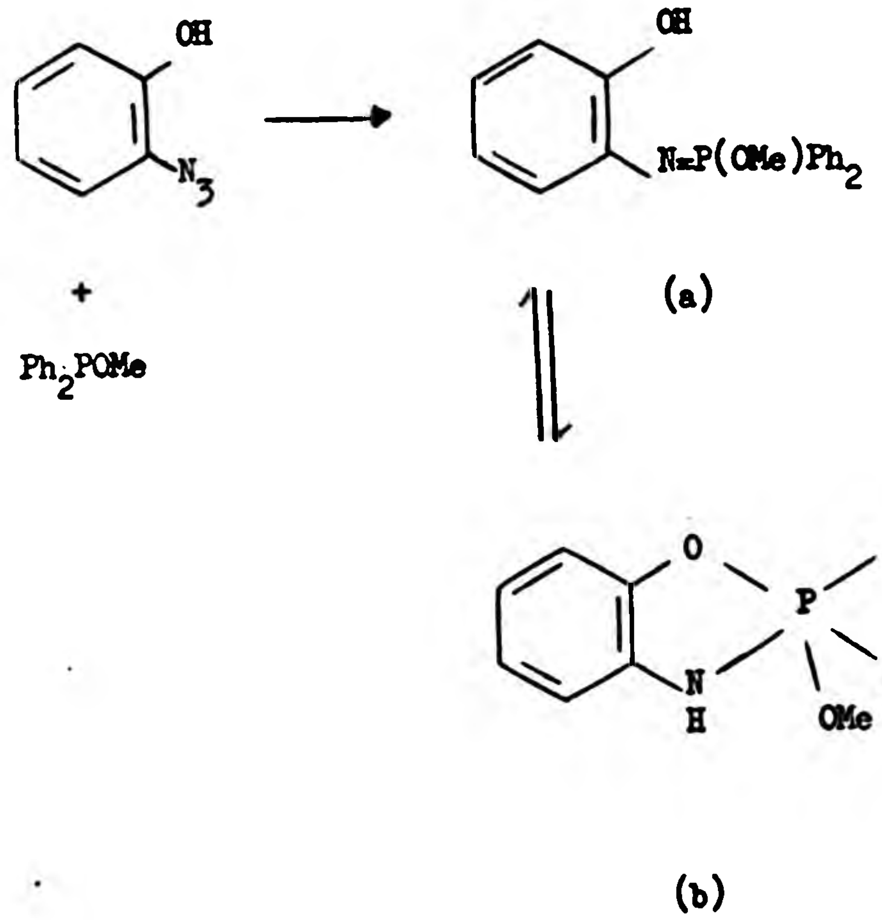
	C_6H_5
	C_6H_5
	C_6H_5

Generally the yields obtained by this method are good but the use of anhydrous conditions is required.[128] It is considered that the mechanism involves amine attack on the phosphorus atom followed by dehydrohalogenation (Scheme 4.1.). The reaction is usually carried out in the presence of a base to remove the liberated hydrogen halide.



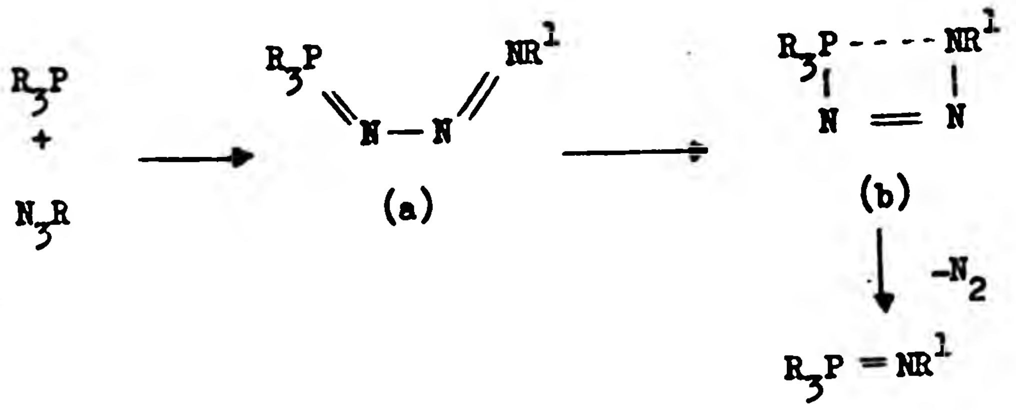
Scheme 4.1.

A recent preliminary report by Cadogan et al[96] describes the preparation of an N(hydroxybenzene)-iminophosphorane by the interaction of 2-azidophenol with methyldiphenylphosphinite. The product, N(2-hydroxybenzene)-iminodiphenyl methoxyphosphorane, was assigned the cyclic form (b) (Scheme 4.2.). The formulation of this compound was confirmed by an alternative synthesis from 2-aminophenol, methyldiphenylphosphinite and N-chlorodiisopropyl amine. Although the method of Cadogan et al is potentially widely applicable for the synthesis of N(2-hydroxybenzene)-iminotriphenylphosphoranes, it suffers from the handling problems associated with organoazides.



Scheme 4.2.

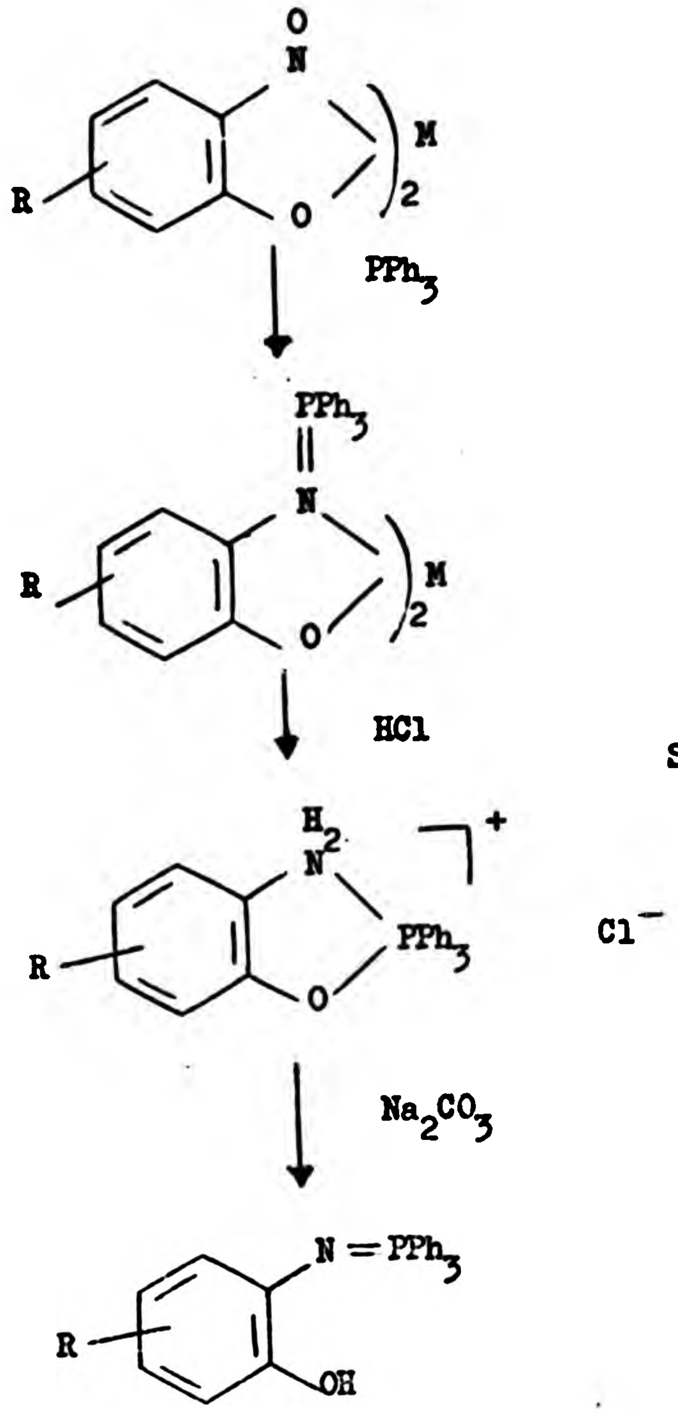
The interaction of a tertiary phosphine with an azide (Table 4.1. method 1) was first used by Staudinger and Meyer[116] to prepare several iminophosphoranes. It has been suggested[129] that this reaction proceeds via a phosphazide intermediate (a) (Scheme 4.3.) which decomposes via a four membered-ring transition state (b) into the iminophosphorane.



Scheme 4.3.

4.3 The Synthesis of N(2-Hydroxybenzene)-imino triphenylphosphoranes from 2-Nitrosophenol Complexes.

During this study a synthetic route to N(2-hydroxybenzene)-imino-triphenylphosphoranes from 2-nitrosophenol complexes and triphenyl phosphine has been developed. This method is both widely applicable and requires no specialized handling techniques. The developed synthetic route is summarized in Scheme 4.4.



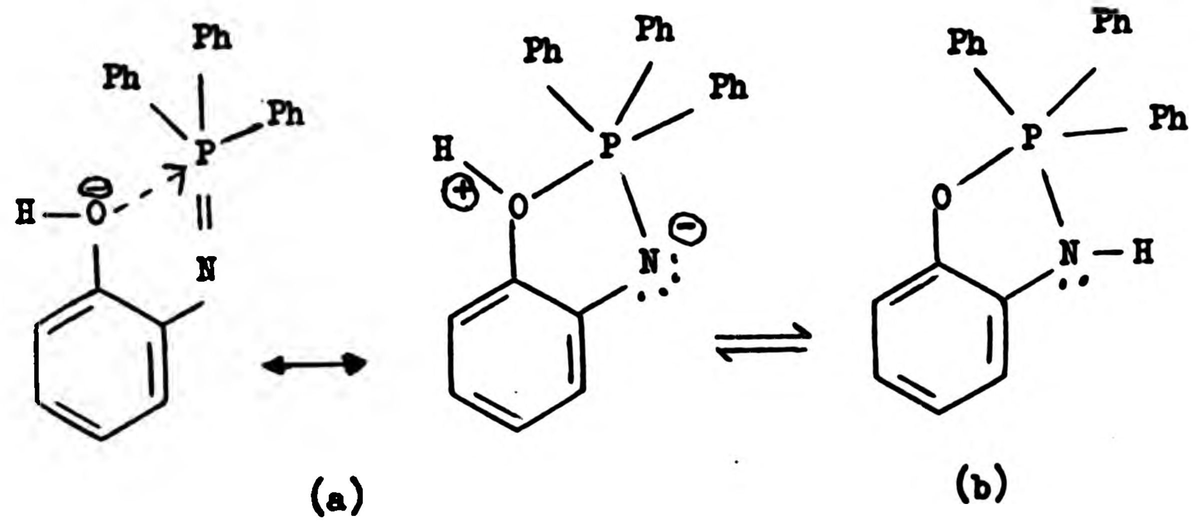
Scheme 4.4.

As noted in Chapter II, the interaction of the readily available bis(benzoquinone-2-oximato) nickel(II) complexes with triphenyl phosphine provides a convenient route to the iminophosphorane complexes. Such complexes on acidification with hydrochloric acid afford the iminophosphorane hydrochloride, from which the free iminophosphorane can be liberated through the action of sodium carbonate.

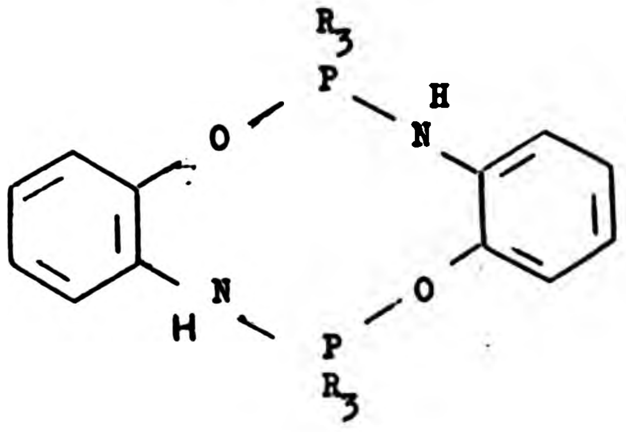
Thus, when the above reaction sequence was applied to the bis(4-chlorobenzoquinone-2-oximato)nickel(II) and the bis(4-bromobenzoquinone-2-oximato)nickel(II) the corresponding N(2-hydroxybenzene)-iminotriphenylphosphoranes were obtained in reasonable yield. These compounds and their hydrochlorides were fully characterized by elemental analysis, i.r. and n.m.r. spectroscopy and mass spectrometry (see also section 3.4.). In contrast to the 5-chloro and the 5-bromo N(2-hydroxybenzene)-iminotriphenylphosphorane, the 5-methyl homologue was obtained only in low yield. In the case of the bis(5-methoxy-2-triphenyl phosphiminophenolato)nickel(II) acidification afforded the N(4-methoxy-2-hydroxybenzene)-iminotriphenylphosphorane hydrochloride in high yield but the latter could not be converted to the corresponding free N(2-hydroxybenzene)-iminotriphenylphosphorane by the action of sodium carbonate. In contrast to the other N(2-hydroxybenzene)-iminotriphenylphosphorane hydrochlorides, the 4-methoxy compound underwent a complex decomposition on treatment with the base. The decomposition afforded a variety of products as indicated by t.l.c., Triphenyl phosphine and triphenyl phosphine oxide were included among the products.

4.4. Properties and Structure of N(2-Hydroxybenzene)-iminotriphenylphosphoranes.

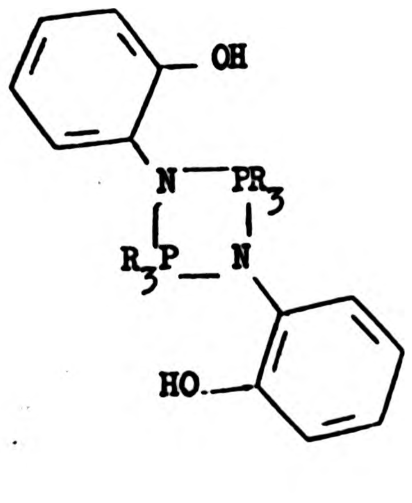
The study of the properties and structure of N(2-hydroxybenzene)-iminophosphoranes has received very limited attention. Both monomeric (see Scheme 4.5.) and dimeric (4.3. and 4.4.) structures have been suggested for these compounds.[115] However, molecular weight measurements indicate that the compounds are monomeric in solution. The compounds are also monomeric in the vapour state as indicated by mass spectrometric studies undertaken as part of the present work and described later in this section.



Scheme 4.5.



4.3.



4.4.

Several workers[115, 96] have assumed that a tautomeric equilibrium exists between the open and ring monomeric structures depicted in Scheme 4.5. Furthermore, it has been suggested,[96] on the basis of ^{31}P and ^{1}H n.m.r. spectroscopic studies, that in solution the cyclic 3-hydro-1,3,2-benzoxazaphosph(V)ole structure is predominant. However, no evidence for the existence of a tautomeric equilibrium between cyclic and open structures has so far been put forward. As a consequence, the investigation of the structure of N(2-hydroxybenzene)-iminotriphenyl phosphoranes and in particular the examination of the possibility of tautomerism involving open and ring structures has received some attention during this study.

In considering the structural features of N(2-hydroxybenzene)-iminotriphenylphosphoranes both chemical properties and spectral characteristics have been taken into account. The chemical properties of the N(2-hydroxybenzene)-iminotriphenylphosphorane considered relate primarily to the reactivity of the P-N bond and their chelating properties. The spectral studies relate to the structure in solution, the solid and vapour states.

A) Some Chemical Features of N(2-Hydroxybenzene)-iminotriphenylphosphorane.

Previous studies have shown that in iminophosphoranes the phosphorus-nitrogen bond has considerable reactivity toward a variety of reagents. Some typical reactions[130] involving this bond are illustrated in Table 4.3. In general, these reactions involve the elimination of phosphine oxide or sulphide.

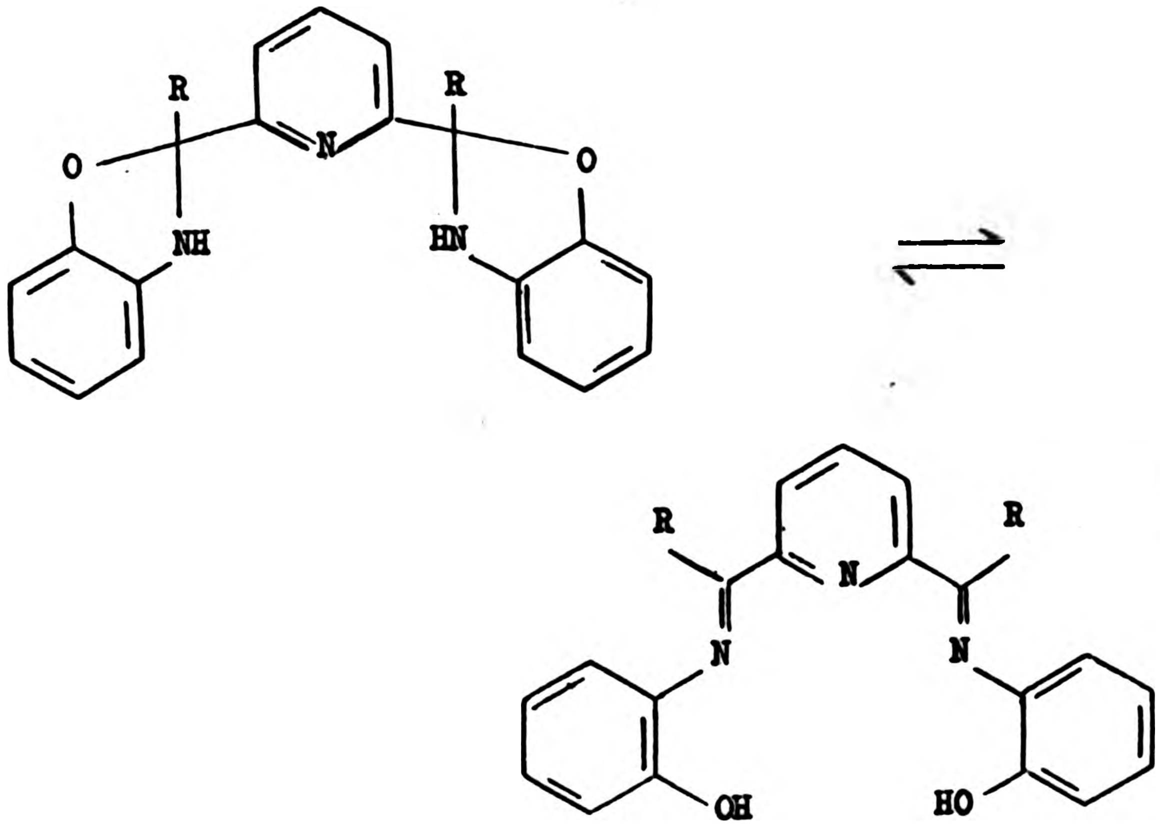
Table 4.3. Interaction of Iminophosphoranes and compounds with C-O or C-S Double Bonds.

Reagent(s)	Products
CO_2	$R_3PO + R^3\text{-}N{=}C{=}O$
CS_2	$R_3PS + R^3\text{-}N{=}C{=}S$
SO_2	$R_3PO + R^3\text{-}N{=}S{=}O$
$R^1N{=}C{=}O + R_3P = NR^3$	$R_3PO + R^1\text{-}N{=}C{=}N\text{-}R^3$
$R^1_2C{=}C{=}O$	$R_3PO + R^1_2\text{-}C{=}C{=}N\text{-}R^3$
$R^1_2C{=}O$	$R_3PO + R^1_2C{=}NR^3$
$R^1N{=}C{=}S$	$R_3PS + R^1\text{-}N{=}C{=}C\text{-}R^3$

The reactivity of the phosphorus-nitrogen bond in an iminophosphorane and as a consequence the overall stability of the molecule is markedly dependent on the nature of the groups attached on the nitrogen or phosphorus atoms. Electron-withdrawing groups on the nitrogen will increase the stability and decrease the reactivity of the phosphorus-nitrogen bond. For example iminotriphenylphosphorane[117] ($Ph_3P{=}NH$) is hydrolysed by atmospheric moisture. In contrast, stabilized iminophosphoranes such as phenyliminotriphenylphosphorane[116] is only hydrolysed by dilute acid.

The method employed during this study for the synthesis of hydroxyimino phosphorances (c.f. previous section) suggests that the compounds, with the probable exception of the N(5-methoxy-2-hydroxybenzene)-iminotriphenylphosphorane, possess a remarkable stability towards hydrolysis both in the presence of acid or base. This stability is indicative of a ring rather than of an open structure.

The ring structure is also favoured, to some extent at least, by their chelating properties. It is reasonable to expect that the open structure would readily react with suitable metal ions to give chelates of the hydroxyiminophosphorane anion. In contrast, it is expected that the cyclic structure would not complex with metal ions to give chelates unless an equilibrium relationship between the cyclic and open structures exists and the reaction conditions are appropriate for the conversion of the cyclic form to the open form. Previously it has been shown that cyclic compounds, e.g. benzoxazolines[131] 4.5.,



4.5.

which can be converted into open tautomers do react with selected metal ions to give chelates.

When N(5-chloro-2-hydroxybenzene)-iminotriphenylphosphorane was treated with nickel chloride in water, or in aqueous ethanol in the presence of ammonia, no complex resulted. However, copper chloride and the N(5-chloro-2-hydroxybenzene)-iminotriphenylphosphorane afforded in the presence of sodium hydroxide a brown solid. Elemental analysis indicated that the product was bis(4-chloro-2-triphenylphosphiniminophenolato)copper (II). Further support for this formulation was provided by the close similarity of the i.r. spectrum of the product to that of the bis(4-chloro-2-triphenylphosphiniminophenolato)nickel (II).

Iminophosphoranes readily form complexes. Previously only complexes derived from iminophosphoranes of type $R_3P{=}NR^1$ where R^1 = alkyl or H have received attention. During this study chelated complexes were obtained (c.f. Chapter 2 for the preparations and Chapter 3 for the properties).

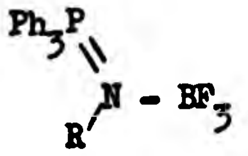
The complexes derived from $R_3P{=}NR^1$ fall into two categories:

(a) those containing the neutral iminophosphorane ligand and

(b) those which formally contain the anionic ligand $R_3P{=}N^-$.

Appel and Vogt[132] reported complexes of the type $[(Ph_3PNH)_2MX_2]$ (where M = Co(II) and Cu(II), X = Cl) prepared from the interaction of iminotriphenylphosphorane and the metal halide in methyl cyanide. While the interaction of nickel iodide with the iminophosphorane in methyl cyanide gave an adduct $(Ph_3PNH_4)NiI_2,CH_3CN$.

Bock and Dieck[133] have reported the formation of iminophosphorane coordination compounds ffom the interaction of an iminophosphorane and metal carbonyls. Hexacarbonylmolybdenum(0) and hexacarbonyl tungsten(0) in toluene or cyclohexane reacts with triphenyl iminophosphorane to form complexes of the type $(Ph_3PNH)_2Mo(CO)_4$ and $(Ph_3PNH)_2W(CO)_4$. In boiling toluene the iminophosphorane reacts with the hexacarbonyl molybdenum(0) to form a dimer $[(Ph_3PNH)_2Mo(CO)_3]_2$. Complexes have also been formed between halides and trialkyls of elements of the third main group. Zimmer and Singh[134] interacted triphenyl-alkyl-iminophosphorane with boron trifluoride under anhydrous conditions to form triphenylalkyliminotrifluoroborons 4.6.



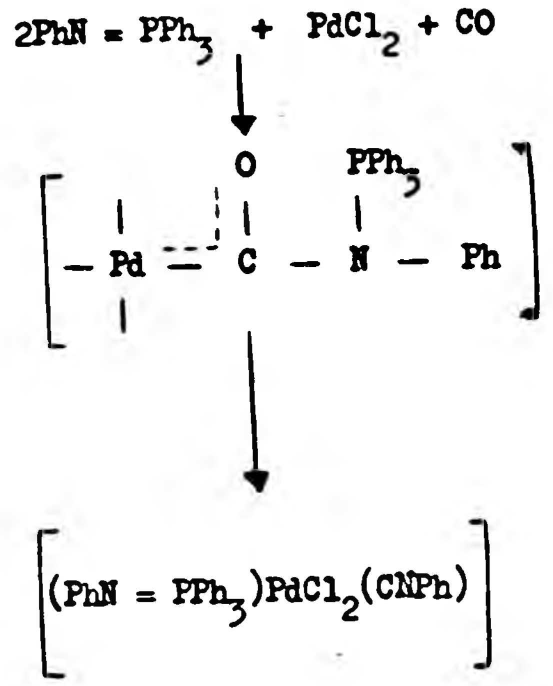
4.6.

Interaction of iminophosphoranes, with no substituent on the nitrogen atom, with metals such as lithium, zinc, gallium, aluminium and indium alkyls yield organometal-substituted iminophosphoranes[114,135] (Reaction 4.2.). The zinc and cadmium compounds exist in a tetrameric structure, while the

$$Ph_3P = NH \quad + \quad AlR_3 \longrightarrow RH \quad + \quad Ph_3P = NAlR_2$$

Reaction 4.2.

aluminium, gallium and indium have a dimeric structure. A recent interesting reaction, involving carbon monoxide and phenyliminotriphenylphosphorane, in the coordination sphere of palladium(II) afforded a palladium (II) phenyl isocyanide complex[136] Scheme 4.6.



Scheme 4.6.

B) Infrared Spectra.

The cyclic or open character of N(2-hydroxybenzene)-iminotriphenylphosphoranes and the possibility of tautomerism between such structures can in principle be inferred from the infrared spectra. If the structure is cyclic then absorptions related to e.g. N–H and >P–N< bonds are expected . On the other hand, an open structure should give rise to absorptions associated with bonds, such as O–H and >P=N–.

The distinction between bands due to νOH and νNH has received considerable attention. In general, νOH is expected at 3590 - 3700 cm^{-1} whereas NH at 3310 - 3500 cm^{-1}[137] (e.g. ethanol (vapour) νOH at 3700 cm^{-1}, N-methylaniline νNH at 3400 cm^{-1}). However, both absorptions are affected strongly by the nature of the groups attached to them and more profoundly by hydrogen bonding.

With regard to the absorptions due to the $\rightarrow$P-N$<$ and $\rightarrow$P=N- groups, there is considerable disagreement about both. Compounds with $\rightarrow$P-N$<$ are reported to show bands at ca. 680 - 910 cm^{-1} assignable to νP-N[138]. For ν(P=N) various assignments have been made (Table 4.4.) and the influence of the groups attached to both phosphorus and nitrogen atoms has been indicated [139]. The most reliable assignments for ν(P=N) are probably in the region 1350 - 1385 cm^{-1}.

The spectra in the region 4000 - 1300 cm^{-1} of the N(2-hydroxy benzene)-iminotriphenylphosphoranes prepared during this study are given in Table 4.5. and illustrated in Fig. 4.1. The spectra of the compounds N(5-chloro-2-hydroxybenzene)-iminotriphenyl phosphorane and N(5-bromo-2-hydroxybenzene)-iminotriphenylphosphorane, have no bands between 1350 - 1385 cm^{-1}, i.e. the ν(P=N) region, but the N(5-methyl-2-hydroxybenzene)-iminotriphenylphosphorane has shoulders at 1360, 1370 and 1380 cm^{-1} one of which may be due to ν(P=N). This indicates that in the solid state the N(2-hydroxybenzene)-iminotriphenylphosphorane is in the cyclic form.

Further support for the predominance of the cyclic species in these compounds is provided by examination of their spectra in the region of ~3300 cm^{-1}. This region shows absorptions at between 3200 - 3400 cm^{-1} assigned to νNH, by analogy to the spectra of other related compounds. For example, phosphoramides and phosphoramidothioates which also contain a NH group attached to a 5-valent phosphorus atom. The assignment of the band at 3300 cm^{-1} to νNH must be taken with some caution as distinction between νOH and νNH is not easy especially because the absorption due to both species is highly dependent on hydrogen bonding. These absorptions are low for free νOH (3590 - 3700 cm^{-1}) and in the low end of the range for free νNH (3310 - 3500 cm^{-1}).[137] Polymeric association is the commonest form of hydrogen bonding of OH groups. This is where long chains of

Table 4.4. $\rightarrow P{=}N-$ Stretching Frequencies in compounds of the type $\rightarrow P{=}N{-}R$.

R.	$\nu(P{=}N)cm^{-1}$	Ref.
Ph	1160 - 1180	140
Ph	1330 - 1370	141
Ph	1325 - 1385	142
$COCH_3$ $COCH_2Cl$ COPh	1296 - 1357	139
$COCF_3$	1381 - 1418	139
^{15}N-labelled $\rightarrow P{=}NR$	1141 - 1373	143

Table 4.5. The Infrared Spectra of the N(2-Hydroxybenzene)-iminotriphenylphosphorane prepared in this Study

Compound	Absorptions cm^{-1} (4000 - 1300)
5-Bromo	3250(m), 3085(sh), 3060(w), 1635(w), 1610(s), 1590(w), 1565(s), 1505(sh), 1485(s), 1465 (sh), 1440(s), 1435(m), 1420(w), 1410(w), 1395(s), 1310(sh), 1300(s).
5-Chloro	3300(m), 3080(sh), 3060(w), 3020(sh), 1635(w), 1610(s), 1590(w), 1565(s), 1555(sh), 1490(s), 1440(s), 1435(sh), 1420(w), 1400(s), 1395(sh), 1349(w), 1300(s).
5-Methyl	3320(m), 3080(w), 3060(w), 3040(w), 3035(w), 1640(w), 1615(s), 1600 (sh), 1590(w), 1570(s), 1560(sh), 1505(s), 1495(s), 1485(sh), 1465(w), 1440(m), 1420(w), 1390 (s), 1380(sh), 1370(sh), 1360(sh), 1310(s), 1300(s).

s = strong   sh = shoulder

m = medium

w = weak

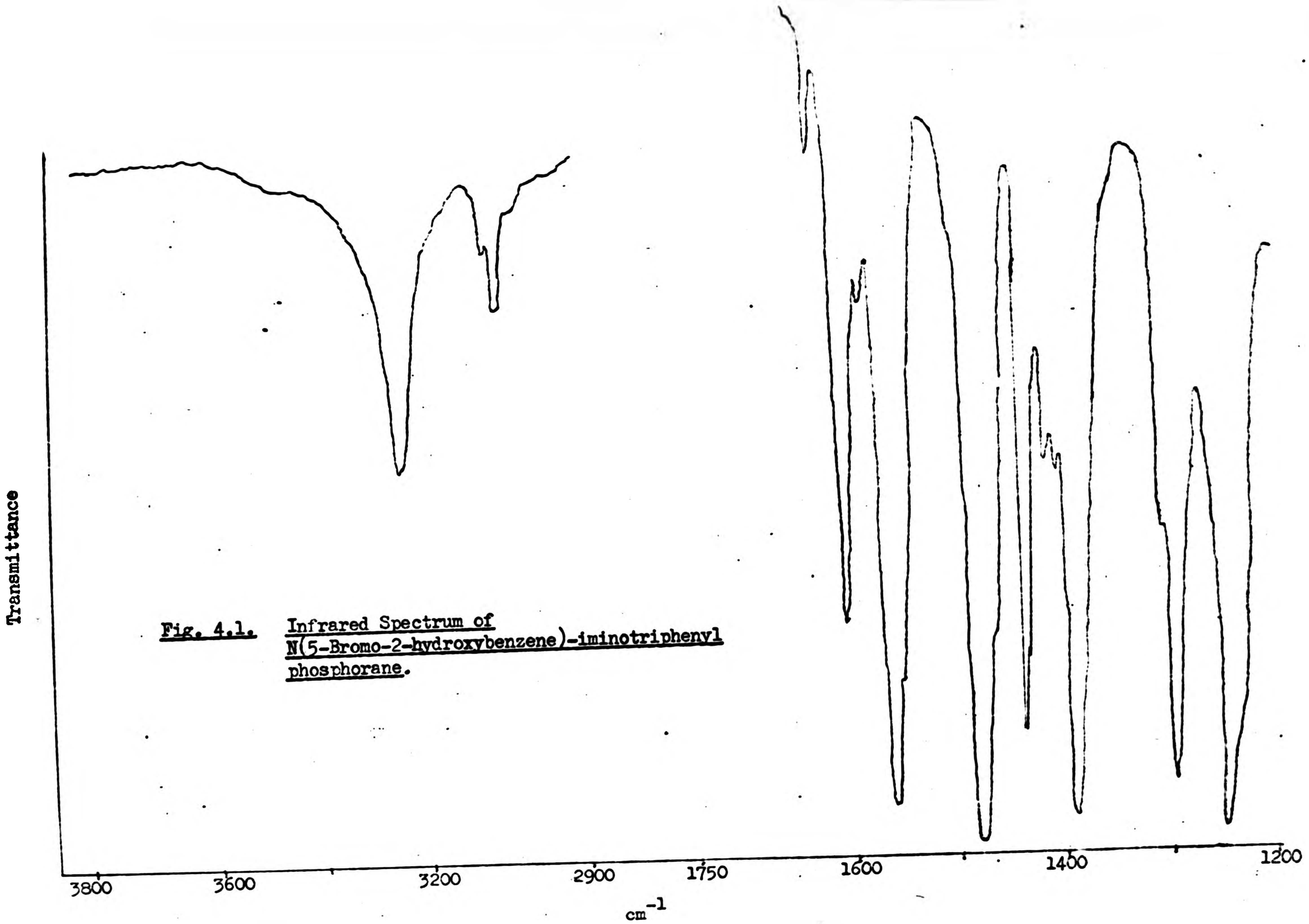
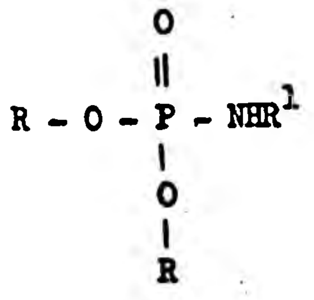
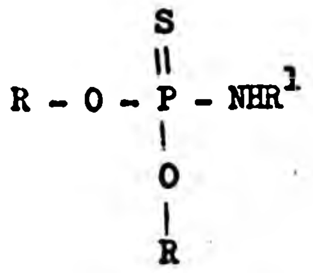


Fig. 4.1. Infrared Spectrum of N(5-Bromo-2-hydroxybenzene)-iminotriphenyl phosphorane.

molecules are linked by hydrogen bonding. The usual absorption region in this case is between 3200 cm^{-1} and 3400 cm^{-1} [144]. Sutherland[145] indicated that intermolecular association of NH groups with ketone groups gave absorptions in the range 3240 - 3320 cm^{-1} and with other nitrogen atoms within the range 3150 - 3300 cm^{-1}. In the case of phosphoramides and phosphoramidothioates the νNH (Table 4.6.) is in the range 3115 - 3333 cm^{-1} and are reported to reflect the presence of hydrogen bonding in these compounds[138].

Table 4.6. NH Stretching Frequencies of Phosphoramides and Phosphoramidothioates.

Compound	R^1	νNH
 $\mathrm{R-O-}\underset{\substack{\vert\\ \mathrm{O}\\ \vert\\ \mathrm{R}}}{\overset{\substack{\mathrm{O}\\ \Vert}}{\mathrm{P}}}\mathrm{-NHR^1}$	alkyl	3125 - 3316
	aryl	3115 - 3226
 $\mathrm{R-O-}\underset{\substack{\vert\\ \mathrm{O}\\ \vert\\ \mathrm{R}}}{\overset{\substack{\mathrm{S}\\ \Vert}}{\mathrm{P}}}\mathrm{-NHR^1}$	alkyl	3195 - 3333
	aryl	3195 - 3215

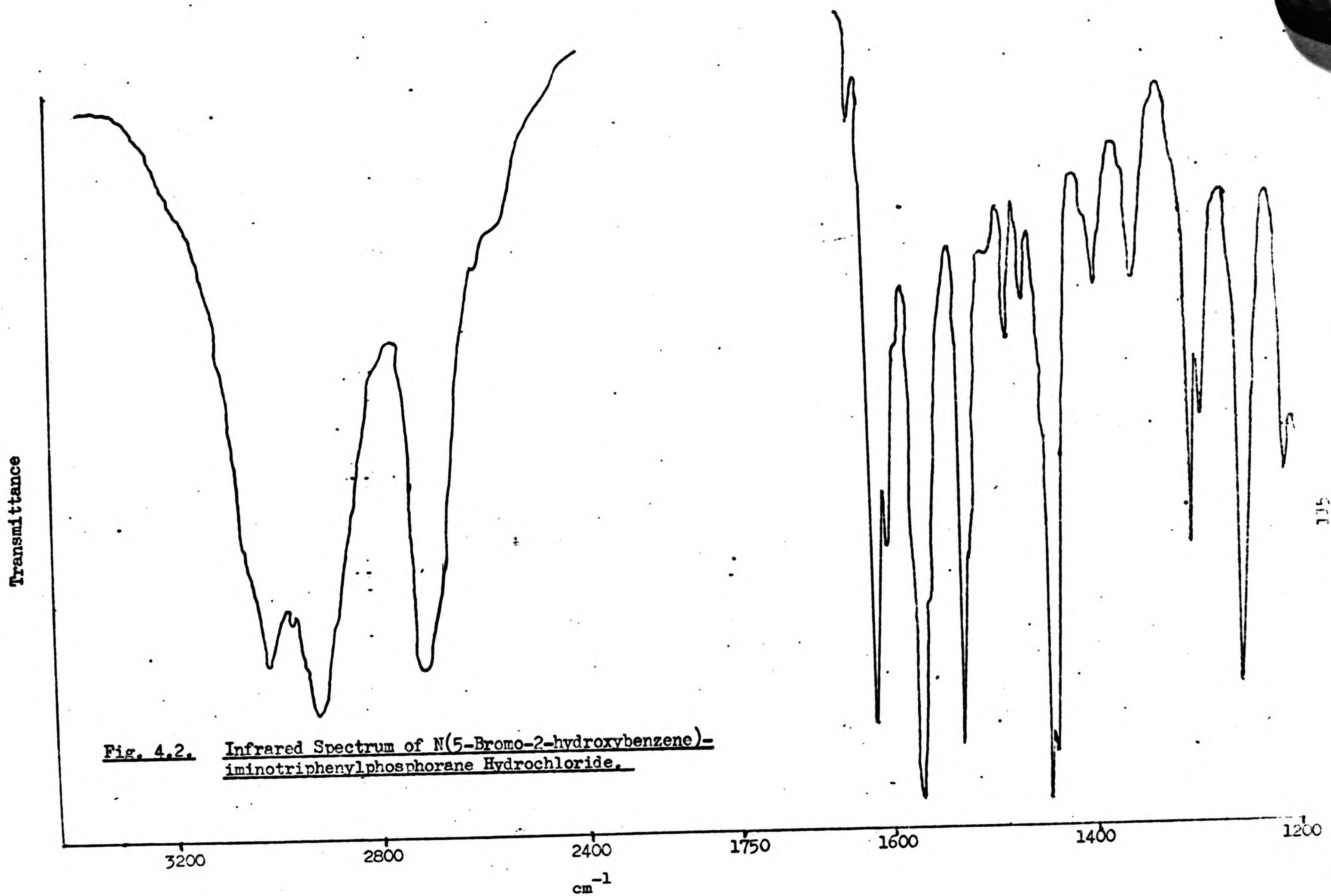


Fig. 4.2. Infrared Spectrum of N(5-Bromo-2-hydroxybenzene)-iminotriphenylphosphorane Hydrochloride.

The solution i.r. spectrum of the N(5-bromo-2-hydroxybenzene)-iminotriphenylphosphorane in chloroform is also indicative of the cyclic structure. The spectrum (10% w/v) contained a singlet at ca. 3340 cm^{-1}, whose position was unaffected by dilution.

The assignment of a cyclic structure to the N(2-hydroxybenzene)-iminotriphenylphosphoranes is supported by the spectroscopic characteristic of their hydrochlorides. For secondary amines, salt formation leads to shifts of the NH absorptions from ca. ~ 3350 cm^{-1} to ca. ~ 3100 cm^{-1}, and formation of a complex series of absorptions in the region 2600 - 2800 cm^{-1} which are reputed to be associated with $>NH_2^+$ stretching vibrations.[146] As noted above in the N(2-hydroxybenzene)-iminotriphenylphosphoranes the νNH occurs at ca. 3250 - 3320 cm^{-1} where as in their hydrochlorides (Fig. 4.2.) there is a complex series of absorptions at ca. 2600 - 3200 cm^{-1}.

c) ^1H - n.m.r. Spectra.

The ^1H - n.m.r. examination of the N(2-hydroxybenzene)-iminotriphenylphosphoranes provided no structural information. In all cases the resonances due to the labile proton (OH or NH) could not be detected, thus no conclusion could be drawn regarding cyclic and open structures. The resonances due to the ring protons and the ring side chain (Fig. 4.3.) are given in Table 4.7., and are in agreement with the n.m.r. spectrum of N(2-hydroxybenzene)-iminomethoxydiphenylphosphorane reported by Cadogan et al.[96] (Table 4.8.).

In the case of the hydrochlorides of the N(2-hydroxybenzene)-iminotriphenyl phosphoranes (Fig. 4.4.) the resonances due to the labile protons were detected in the region 8.8 - 9.7 ppm (Table 4.9.). These were positively identified as the labile hydroxyl or amino protons by in situ

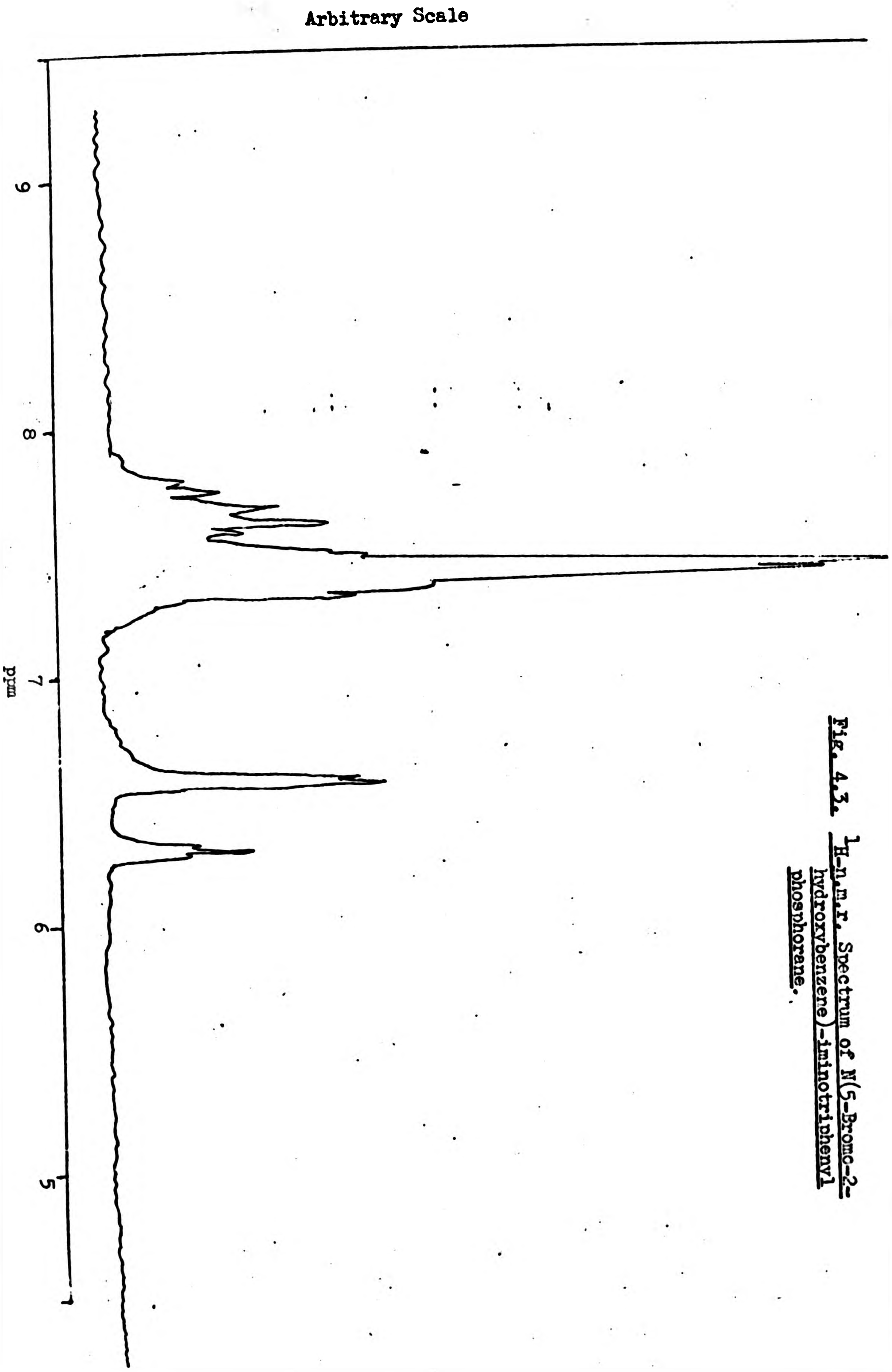


Fig. 4.3. ^{1}H-n.m.r. Spectrum of N(5-Bromo-2-hydroxybenzene)-iminotriphenyl phosphorane.

Table 4.7. ^{1}H-n.m.r. Spectra of the N(X-2-hydroxybenzene)-iminotriphenyl phosphoranes.

Compound	δ p.p.m.	Group	No. of Protons
X =			
5-methyl	1.95	CH_3	3
	6.10 - 6.70	Ar	3
	7.15 - 8.25	Ar	15
5-bromo	6.30 - 6.80	Ar	3
	7.20 - 7.95	Ar	15
5-chloro	6.35 - 6.70	Ar	3
	7.30 - 7.95	Ar	15

Table 4.8 ^{1}H-n.m.r. Spectrum of N(2-Hydroxybenzene)-iminomethoxydiphenylphosphorane.

δ p.p.m.	Group	No. of protons
2.98	$POCH_3$	3
4.86	NH	1
6.45 - 6.80	Ar	4
7.20 - 7.45	Ar (PPh_2)	6
7.60 - 7.90	Ar-O-H (PPh_2)	4

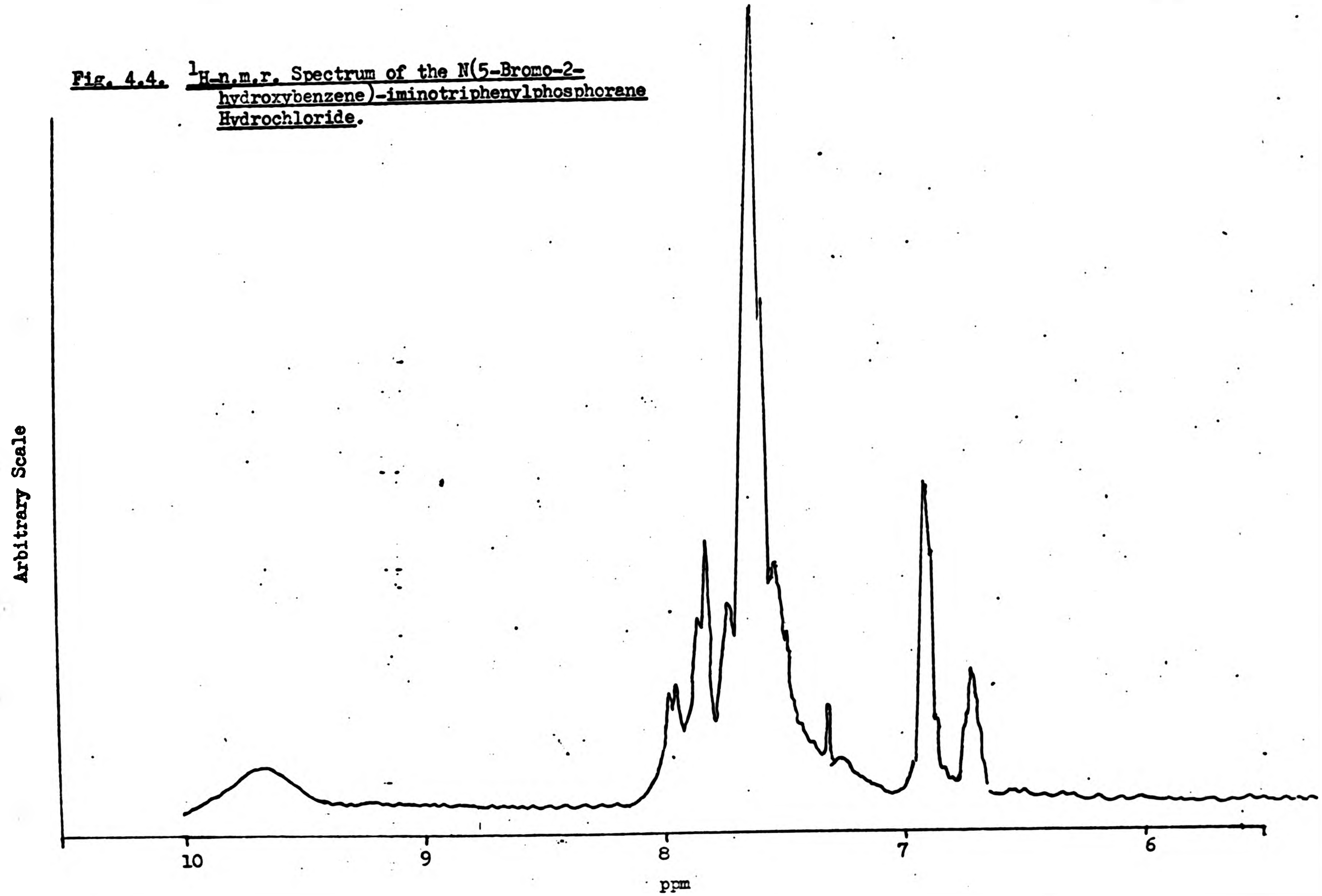


Fig. 4.4. ^{1}H-n.m.r. Spectrum of the N(5-Bromo-2-hydroxybenzene)-iminotriphenylphosphorane Hydrochloride.

Table 4.9. ^{1}H-n.m.r Spectrum of the Hydrochlorides of the N(X-2-hydroxybenzene)-iminotriphenylphosphoranes.

Compound	δ p.p.m	Group	No. of Protons
X=			
5-methyl	1.92	CH_3	3
	6.28-7.0	Ar	3
	7.25-8.10	Ar	15
	8.80	NH_2^+	2
4-methoxy	3.65	OCH_3	3
	5.99-6.68	Ar	3
	7.30-7.98	Ar	15
	9.70	NH_2^+	2
5-bromo	6.75-6.93	Ar	3
	7.32-8.0	Ar	15
	9.65	NH_2^+	2
5-chloro	6.60-7.0	Ar	3
	7.39-8.10	Ar	15
	9.60	NH_2^+	2

exchange with deutrium oxide. Furthermore, the resonances have chemical shifts that are typical of $PhRNH_2^+$, which is reported[137] to be in the region 8.5 - 9.5 ppm. This suggests that in solution the hydrochlorides of the N(2-hydroxybenzene)-iminotriphenylphosphorane are predominantly in the cyclic form.

D) Mass Spectra.

The mass spectra of the N(2-hydroxybenzene)-iminotriphenylphosphoranes and their hydrochlorides were recorded. Pairs of compounds gave identical spectra suggesting dissociation of the hydrochloride derivative in the vapour state. The mass spectra are given in Tables 4.10, 4.11, 4.12. and 4.13.

Previously mass spectrometric studies of trichloroiminophosphoranes[147] and related compounds such as phosphazines[148] 4.7. and phosphorimidates[149] 4.8. indicated decomposition of the molecular ion by cleavage of the

$(R^1O)_3P{=}NR_2$ 4.8.

$R_3P{=}N{-}N{=}CR^1_2$ 4.7.

$\rightarrow P{=}N{-}$ bond to be a major fragmentation pathway. The fragmentation patterns of trichloriminophosphoranes involve several routes:

a) loss of successive chlorine atoms (Scheme 4.7.);

b) loss of phosphorus trichloride (Scheme 4.8.); and

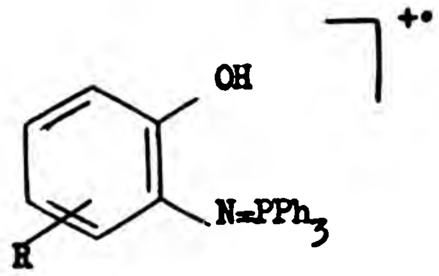
c) loss of a neutral nitrene (Scheme 4.9.).

$Cl_3PNR\rceil^{+} \xrightarrow{-Cl} Cl_2PNR\rceil^{+} \xrightarrow{-Cl} ClPNR\rceil^{+} \longrightarrow PNR\rceil^{+}$ Scheme 4.7.

$Cl_3NR\rceil^{+} \xrightarrow{-PCl_3} NR\rceil^{+}$ Scheme 4.8.

$Cl_3PNR\rceil^{+} \xrightarrow{-NR} Cl_3P\rceil^{+}$ Scheme 4.9.

The mass spectra of the N(2-hydroxybenzene)-iminotriphenylphosphoranes have some similarities in their fragmentation pattern (Fig. 4.5.) to those of trichloroiminophosphoranes. In all cases the spectra show an intense molecular ion and the ion m/e 262 as base peak. Assignment of the molecular ion was supported by exact mass measurements (Table 4.15.). The ion m/e 262 $[PPh_3]^+$ arises via cleavage of the $\rightarrow$P-N- bond of the molecular ion. This reaction P $\rightarrow$ 262 is metastable supported (Table 4.14.) and suggests that in the vapour state the open chain structure 4.9. is predominant.



4.9.

Further evidence for this suggestion is provided by the loss of the HCO• and OH• radicals from the molecular ion (Figure 4.5.). These reactions lead to rather weak ions but occur in all cases and are often metastable supported. The loss of these radicals from the molecular ion is typical of the fragmentation of phenolic type compounds.[11]

Fig. 4.5. General Fragmentation Scheme for N(2-hydroxyphenyl)-iminotriphenylphosphorane.

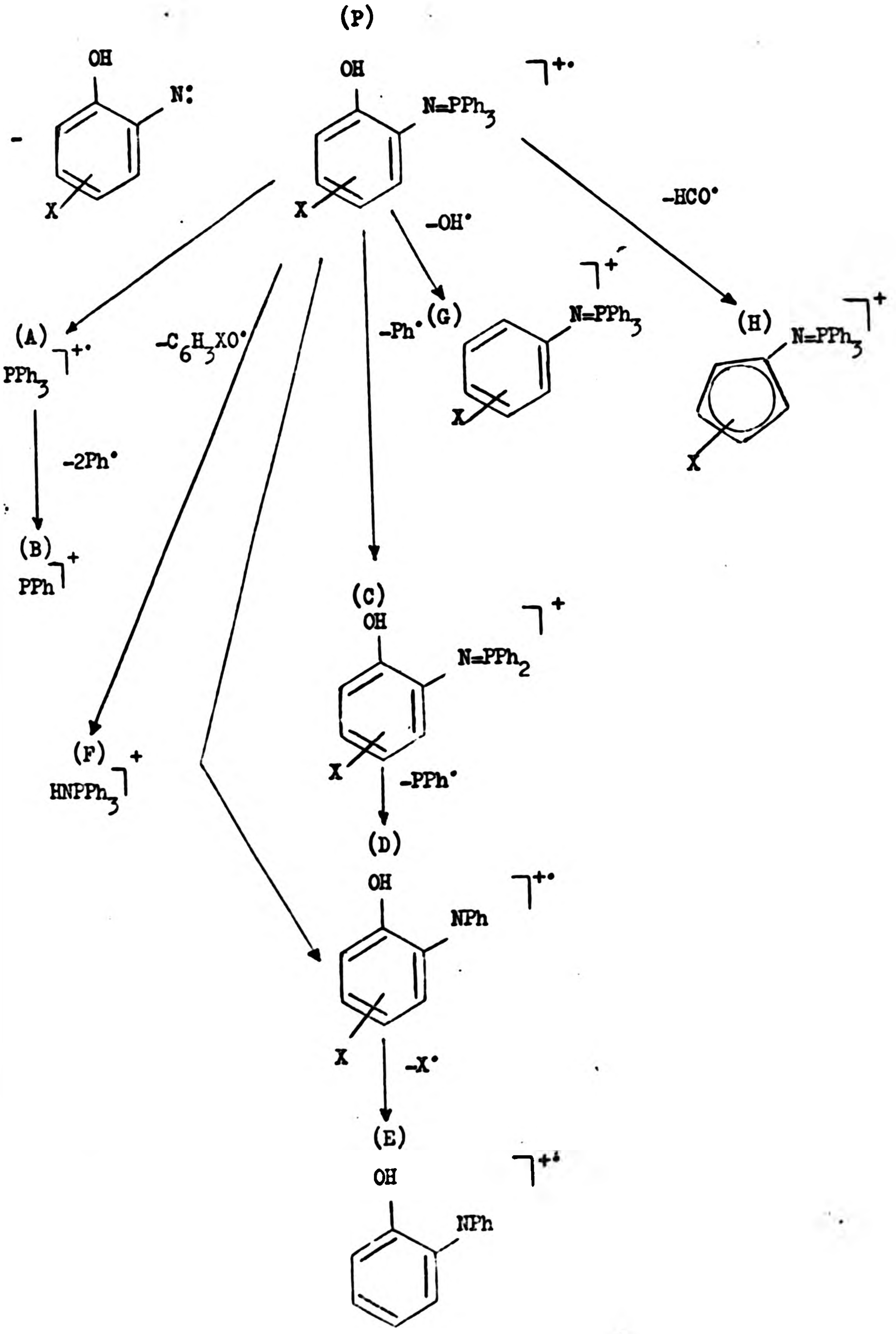


Table 4.10. Ion Abundances for N(5-Methyl-2-hydroxybenzene)-iminotriphenylphosphorane.

Ion	m/e	%[b]	Assignment
[P[a]]	383	83.0	$C_{25}H_{22}NOP$
[P-17] =G	366	5.4	$C_{25}H_{21}NP$
[P-29] =H	354	2.4	$C_{24}H_{21}NP$
[P-77] =C	306	14.0	$C_{19}H_{17}NOP$
[P-106] =F	277	16.0	$C_{18}H_{16}NP$
[P-121] =A	262	100.0	$C_{18}H_{15}P$
[P-185] =D	198	55.0	$C_{13}H_{12}NO$
[P-200] =E	183	70.0	$C_{12}H_{9}NO$
[P-231]	152	12.0	-
[P-275].	108	34.0	$C_{6}H_{5}P$

a : Symbols used in fragmentation scheme.

b : % Relative abundance.

Table 4.11. Ion Abundances for N(4-Methoxy-2-hydroxybenzene)-iminotriphenylphosphorane.

Ion	m/e	%^{b}	Assignment
[P^{a}]	399	89.3	$C_{25}H_{22}NO_2P$
[P-15]	384	10.3	$C_{24}H_{19}NO_2P$
[P-17] =G	382	1.9	$C_{25}H_{21}NOP$
[P-29] =H	370	2.7	$C_{24}H_{21}NOP$
[P-43]	356	5.4	$C_{23}H_{19}NOP$
[P-77] =C	322	14.6	$C_{19}H_{17}NO_2P$
P-86	313	3.3	-
P-93	306	3.7	-
[P-122] =F	277	50.0	$C_{18}H_{16}NP$
[P-137] =A	262	100.0	$C_{18}H_{15}P$
P-157	242	10.3	-
P-171	228	5.4	-
[P-185] =D	214	27.4	$C_{13}H_{12}NO_2$
P-198	201	19.1	-
[P-216] =E	183	58.6	$C_{12}H_9NO$
P-246	153	99.9	-
P-260	139	32.9	-
P-263	136	72.4	-
P-275	124	42.8	-
[P-291] =B	108	49.9	C_6H_5P

a : Symbols used in fragmentation scheme.

b : % Relative abundance

Table 4.12. Ion Abundances for N(5-Bromo-2-hydroxybenzene)-iminotriphenylphosphorane.

Ion	m/e[b]	%[c]	Assignment
[P[a]]	447	60.7	$C_{24}H_{19}NBrOP$
[P-17] =G	430	7.1	$C_{24}H_{18}NBrP$
[P-29] =H	418	3.4	$C_{23}H_{18}NBrP$
P-65	382	6.2	-
[P-77] =C	370	10.7	$C_{18}H_{14}NBrOP$
P-143	304	7.1	-
[P-170] =F	277	31.3	$C_{18}H_{6}NP$
[P-185] =A	262	100.0	$C_{18}H_{5}P$
P-186	261	53.6	-
P-248	199	20.6	-
[P-264] =E	183	75.0	$C_{12}H_{9}NO$
P-295	152	13.4	-
P-329	118	23.2	-
[P-339] =B	108	43.8	$C_{6}H_{5}P$

a : Symbols used in fragmentation scheme.

b : The m/e value given are for ions containing ^{79}Br.

c : % Relative abundance.

Table 4.13. Ion Abundances for N(5-Chloro-2-hydroxybenzene)-iminotriphenylphosphorane.

Ion	m/e[b]	%[c]	Assignment
[P[a]]	403	95.6	$C_{24}H_{19}NClOP$
[P-17] =G	386	6.8	$C_{24}H_{18}NClP$
[P-29] =H	374	1.7	$C_{23}H_{18}NClP$
[P-35]	368	1.4	$C_{24}H_{19}NOP$
[P-77] =C	326	18.7	$C_{18}H_{14}NClOP$
P-78	325	20.8	-
P-79	324	15.6	-
P-92	311	1.8	-
P-113	290	1.0	-
[P-126] =F	277	21.9	$C_{18}H_{16}NP$
[P-141] =A	262	100.0	$C_{18}H_{15}P$
P-155	248	3.6	-
[P-185] =D	218	20.8	$C_{12}H_{9}NClO$
[P-202]	201	8.6	$C_{12}H_{8}NCl$
P-204	199	4.7	-
[P-220] =E	183	75.0	$C_{12}H_{9}NO$
P-231	172	4.7	-
P-233	170	3.9	-
P-251	152	14.5	-
P-260	143	13.3	-
[P-295] =B	108	31.3	$C_{6}H_{5}P$
P-318	85	9.3	-
P-320	83	14.0	-

a : Symbols used in fragmentation scheme.

b : The m/e values given are for ions containing ^{35}Cl.

C : % Relative abundance.

Table 4.14. Metastable Peaks and Transitions.

N(5-Methyl-2-hydroxybenzene)-iminotriphenylphosphorane.

Transition	m/e values for the transition	m*	
		obs.	calc.
P → G	383 → 366	349.5	349.8
P → C	383 → 306	344.5	344.5
P → A	383 → 262	179.5	179.2
P → D	383 → 198	102.4	102.4
C → D	306 → 198	128.0	128.1
A → B	262 → 108	44.5	44.5
D → E	198 → 183	169.0	169.1

N(4-Methoxy-2-hydroxybenzene)-iminotriphenylphosphorane.

Transition	m/e values for the transition	m*	
		obs.	calc.
P → C	399 → 322	260.0	259.9
P → A	399 → 262	172.2	172.0

Table 4.14 cont. Metastable Peaks and Transitions.

N(5-Bromo-2-hydroxybenzene)-iminotriphenylphosphorane.

Transition	m/e[a] values for the transition	m^* obs.	m^* calc.
P $\longrightarrow$ G	447 $\longrightarrow$ 430	414.0	413.7
P $\longrightarrow$ H	447 $\longrightarrow$ 418	391.0	390.9
P $\longrightarrow$ A	447 $\longrightarrow$ 262	153.5	153.6
C $\longrightarrow$ E	370 $\longrightarrow$ 183	44.5	44.5

a : The m/e values given are for ions containing ^{79}Br

N(5-Chloro-2-hydroxybenzene)-iminotriphenylphosphorane.

Transition	m/e[b] values for the transition	m^* obs.	m^* calc.
P $\longrightarrow$ A	403 $\longrightarrow$ 262	170.5	170.3
A $\longrightarrow$ B	262 $\longrightarrow$ 108	44.5	44.5

b : The m/e values given are for ions containing ^{35}Cl.

Table 4.15. Exact Mass Measurements on Selected Peaks.

Compound	Nominal Mass	Determined Mass	Ion Assignment	Calc. Mass
N(5-Methyl-2-hydroxybenzene)-iminotriphenylphosphorane	383	383.1428	$C_{25}H_{22}NOP$	383.1439
N(4-Methoxy-2-hydroxybenzene)-iminotriphenylphosphorane	399	399.1392	$C_{25}H_{22}NO_2P$	399.1388
N(5-Chloro-2-hydroxybenzene)-iminotriphenylphosphorane	403	403.0885	$C_{24}H_{19}NClOP$	403.0892
N(5-Bromo-2-hydroxybenzene)-iminotriphenylphosphorane	447	447.0371	$C_{24}H_{19}NBrOP$	447.0389

4.5. References.

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CHAPTER 5

EXPERIMENTAL

5.1. General Techniques.

The reactions involving triphenyl phosphine were carried out under an atmosphere of nitrogen. The solvents used in such reactions were deaerated by bubbling nitrogen through them for at least 30 minutes immediately before use.

5.2 Reagents.

2-Nitrosophenol Complexes.

The following complexes were prepared as described in the literature:

dipyridino bis(4-chlorobenzoquinone-2-oximato)nickel(II);[21]
dipyridino bis(4-methylbenzoquinone-2-oximato)nickel(II);[21]
dipyridino bis(5-methoxybenzoquinone-2-oximato)nickel(II);[23]
dipyridino bis(5-methoxybenzoquinone-2-oximato)zinc(II);[47]
bis(4-bromobenzoquinone-2-oximato)nickel(II);[21]
bis(5-methoxybenzoquinone-2-oximato)nickel(II);[23]
bis(4-methylbenzoquinone-2-oximato)copper(II);[19]
bis(5-methoxybenzoquinone-2-oximato)copper(II);[19] and
tris(5-methoxybenzoquinone-2-oximato)iron(III).[11]

5.3 Analytical Methods.

A) Halogen.

The halogen content was determined volumetrically. The sample (ca. 0.1 g.) was ignited in an oxygen flask, in the presence of sodium hydroxide solution. After combustion, the solution was acidified with dilute nitric acid and the halide titrated with standard silver nitrate (0.1 M). The end point was determined potentiometrically.

B) Nickel.

Nickel was determined gravimetrically using dimethylglyoxime. A sample of the complex (ca. 0.2 g) was treated with conc. nitric acid (10 cm^3) and the mixture gently evaporated to dryness. The residue was treated with conc. sulphuric acid (2 cm^3) and again gently evaporated to dryness. The inorganic residue was dissolved in water (200 cm^3) and neutralised with ammonia solution until in a slight excess. A slight excess of a 1% solution of dimethylglyoxime was added, and the mixture heated on a steam bath for 30 min. After cooling the precipitate was collected in a sintered glass crucible and dried at 140°C to constant weight.

C) Copper

Copper was determined gravimetrically using α-benzoinoxime. A sample of the complex (ca. 0.3 g) was treated with conc. acids as described above. The inorganic residue was dissolved in water (200 cm^3) and neutralised with ammonia solution until a clear blue solution was obtained. After the solution was heated to boiling a slight excess of a 2% solution of α-benzoinoxime was added. The precipitate was collected in a sintered glass crucible and dried at 105°C to constant weight.

D) Iron.

Iron was determined gravimetrically using the ammonium salt of N-nitroso-N-phenylhydroxylamine (cupferron). A sample of the complex (ca. 0.2 g) was treated with conc. acids as described before. The inorganic residue was dissolved in water (200 cm^3) and acidified with sulphuric acid. To the cooled solution a slight excess of 5% cupferron was added. The precipitate was collected on ashless filter paper, ignited in a silica test tube and heated to constant weight.

E) Phosphorus.

Phosphorus was determined gravimetrically as magnesium pyrophosphate. A sample of the complex (ca. 0.4 g) was treated with conc. nitric acid as described before. The residue was treated with conc. sulphuric acid (20 cm^3) and the solution was gently heated till clear. The solution was diluted with water (200 cm^3) and neutralised with ammonia solution. After the addition of a few drops of conc. nitric acid, a slight excess of ammonium molybdate reagent was added. The precipitate was collected and redissolved in an ammonical solution (200 cm^3). A slight excess of magnesia mixture was added and allowed to stand for 12 h. The precipitate was collected on ashless filter paper, ignited in a silica crucible and heated to constant weight.

F) Carbon, Hydrogen and Nitrogen.

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 elemental analyser by the microanalytical laboratories of The Polytechnic of North London.

5.4. Reactions.

A) Interaction of Bis(5-methoxybenzoquinone-2-oximato)nickel(II) with excess Triphenyl Phosphine in Chloroform.

Bis(5-methoxybenzoquinone-2-oximato)nickel (II) (3.6 g, 1 mol.) and triphenyl phosphine (13.1 g, 5 mol.) in chloroform (150 cm^3) were stirred at 20°C and in the absence of light for 5 days (see Table 5.2. for t.l.c. data of reaction mixture). Pale brown bis(5-methoxy-2-triphenylphosphinimino-phenolato)nickel(II) (2.8 g, 33%), (Found: C, 70.3; H, 5.0; N, 3.2; Ni; 6.6. $C_{50}H_{42}N_2NiO_4P_2$ requires: C, 70.2; H, 4.9; N, 3.3 Ni, 6.8%)

was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm. The filtrate on concentration to *ca.* 50 cm^3 gave a second crop of bis(5-methoxy-2-triphenylphosphiniminophenolato)nickel(II) (0.4 g, 5%) (identified by i.r. spectroscopy) which was filtered off and dried at 100°C/0.1 mm. The filtrate was evaporated to dryness under nitrogen to give a solid residue (11.6 g). T.l.c. examination of the residue indicated the presence of triphenylphosphine, triphenylphosphine oxide, bis(5-methoxy-2-triphenylphosphiniminophenolato)nickel (II) and of several other compounds in smaller quantities. Attempts to recrystallise portions of the solid from a mixture of chloroform and light petrol (60 - 80°C), and from methanol were unsuccessful. A portion of the solid (1.2 g) was extracted (Soxhlet) with cyclohexane. The extract on cooling gave white triphenylphosphine oxide (0.38 g, 67%) (identified by i.r. spectroscopy).

B) Interaction of Dipyridinobis(5-methoxybenzoquinone-2-oximato) nickel(II) with excess Triphenyl Phosphine in Methanol.

Dipyridinobis(5-methoxybenzoquinone-2-oximato)nickel(II) (4.8 g, 1 mol.) and triphenyl phosphine (13.1 g, 5 mol.) in methanol (200 cm^3) were heated under reflux for 12 h. On cooling a dark brown solid (3.0 g) (Found: C, 65.9; H, 4.9; N, 4.7%) separated, was filtered off, washed with diethyl ether and dried 100°C/0.1 mm. The dark brown solid was extracted (Soxhlet) successively with diethyl ether and chloroform. The ether extract on concentration gave a red solid (0.15 g) (Found: C, 63.6; H, 4.6; N, 10.4; Calc. for $C_7H_7NO_2$: C, 61.3; H, 5.1; N, 10.2%) which was filtered off and dried at 100°C/0.1 mm. On cooling the chloroform extract pale brown bis(5-methoxy-2-triphenylphosphiniminophenolato)nickel(II) (1.2 g, 14%) (identified by i.r. spectroscopy) separated out, was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm. Removal of the solvent from the filtrate obtained by filtration of the reaction mixture gave a black solid

(12.8 g) which contained triphenyl phosphine and triphenyl phosphine oxide, bis(5-methoxy-2-triphenylphosphiniminophenolato)nickel(II) and several other compounds in trace amounts (examined by t.l.c.).

C) Interaction of Dipyridinobis(4—methylbenzoquinone-2-oximato) nickel(II) with excess Triphenyl Phosphine in Chloroform.

Dipyridinobis(4—methylbenzoquinone-2-oximato)nickel(II) (2.4 g, 1 mol) and triphenyl phosphine (6.6 g, 5 mol) in chloroform (150 cm^3) were stirred at 20°C and in the absence of light for 5 days. Pale brown bis(4-methyl-2-triphenylphosphiniminophenolato)nickel(II) (1.4 g, 35%), (Found: C, 72.2; H, 5.1; N, 3.3; Ni, 6.9. $C_{50}H_{42}N_2NiO_2P_2$ requires: C, 72.9; H, 5.1; N, 3.4; Ni, 7.1%) which was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm. The filtrate on concentration gave a grey-white solid residue (4.7 g) which contained triphenyl phosphine, triphenyl phosphine oxide, bis(4-methyl-2-triphenylphosphiniminophenolato) nickel(II) and three other compounds in trace quantities (examined by t.l.c.). Attempts to recrystallise portions of the solid from chloroform and methanol were unsuccessful.

D) Interaction of Dipyridinobis(4—chlorobenzoquinone-2-oximato) nickel(II) with excess Triphenylphosphine in Chloroform.

Dipyridinobis(4— chlorobenzoquinone-2-oximato)nickel(II) (1.9 g, 1 mol) and triphenyl phosphine (5.2 g, 8 mol) in chloroform (200 cm^3) were stirred at 20°C and in the absence of light for 5 days. Pale brown bis(4-chloro-2-triphenylphosphiniminophenolato)nickel (II) (1.0 g, 32%) (Found: C, 66.9; H, 4.2; N, 3.2; Cl, 8.0; Ni, 6.8. $C_{48}H_{36}N_2NiCl_2O_2P_2$ requires: C, 66.9; H, 4.2; N, 3.2; Cl, 8.2; Ni, 6.8%) which was filtered off washed with diethyl ether and dried at 100°C/0.1 mm. The filtrate on concentration gave a black-white solid residue (2.5 g) which contained triphenyl phosphine, triphenyl phosphine oxide, bis(4-chloro-2-triphenylphosphiniminophenolato) nickel(II) and several other compounds in smaller quantities (examined by t.l.c.).

E) Interaction of Bis(4-bromobenzoquinone-2-oximato)nickel(II) with excess Triphenyl Phosphine in Chloroform.

Bis(4-bromobenzoquinone-2-oximato)nickel(II) (3.5 g, 1 mol) and triphenyl phosphine (9.8 g, 5 mol) in chloroform (100 cm^3) were stirred at 20°C and in the absence of light for 5 days. Pale brown bis(4-bromo-2-triphenylphosphiniminophenolato)nickel(II) (3.7 g, 51%) (Found: C, 60.4; H, 3.8; N, 3.0; Br, 16.5; Ni, 6.2. $C_{48}H_{36}N_2Br_2NiO_2P_2$ requires: C, 60.5; H, 3.8; N, 2.9; Br, 16.8; Ni, 6.1%) which was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm. The filtrate on concentration gave a grey-white solid residue (7.2 g) which contained triphenylphosphine, triphenyl phosphine oxide, bis(4-bromo-2-triphenylphosphiniminophenolato) nickel(II) andthree other compounds in small quantities (examined by t.l.c.). Attempts to recrystallise the residue from methanol were unsuccessful.

F) Interaction of Dipyridinobis(5-methoxybenzoquinone-2-oximato) zinc(II) with excess Triphenyl Phosphine in Chloroform.

Dipyridinobis(5-methoxybenzoquinone-2-oximato)zinc(II) (1.5 g, 1 mol) and triphenyl phosphine (3.9 g, 5 mol) in chloroform (150 cm^3) were heated under reflux, in the absence of light for 5 days (see Table 5.2. for t.l.c. data of reaction mixture). Pale yellow bis(5-methoxy-2-triphenyl-phosphiniminophenolato)zinc(II) (0.8 g, 32%) (Found: C, 69.8; H, 4.9; N, 3.2. $C_{50}H_{42}N_2O_4P_2Zn$ requires: C, 69.7; H, 4.9, N, 3.3%) was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm. On addition of diethyl ether (100 cm^3) to the filtrate, green dipyridinobis (5-methoxybenzoquinone-2-oximato)zinc(II) (0.9 g, 90% recovery) (identified by i.r. spectroscopy) separated, was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm.

G) Interaction of Complexes of the type $Ni(qPPh_3)_2$ with Aqueous Hydrochloric acid (2M). General Method.

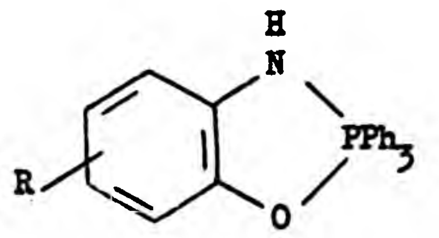
Aqueous hydrochloric acid (2M) was added dropwise to the complex $Ni(qPPh_3)_2$ (1.0 g) suspended in water (50cm^3) until the mixture was at pH 1. The aqueous mixture was extracted with chloroform (50 cm^3). The chloroform extract was dried with sodium sulphate and then concentrated to ca. 20 cm^3. Addition of diethyl ether (100 cm^3) precipitated white N(2-hydroxybenzene)-iminotriphenylphosphorane hydrochloride which was filtered off, washed with diethyl ether and dried at 20°C/0.1 mm. Table 5.1. gives the analysis data and yields of the products.

H) Interaction of Complexes of the type $Ni(qPPh_3)_2$ with Aqueous Hydrochloric acid (2M) followed by neutralization with Sodium Carbonate.

Aqueous hydrochloric acid (2M) was added dropwise to the complex $Ni(qPPh_3)_2$ (1.5 g) suspended in water (50 cm^3) until the mixture was at pH 1. This was followed by the addition of solid sodium carbonate until the aqueous mixture ceased to effervesce. The aqueous mixture was extracted with chloroform (50 cm^3). The chloroform extract was dried with sodium sulphate and then concentrated to ca. 20 cm^3. Addition of diethyl ether (100 cm^3) precipitated white N(2-hydroxybenzene)-iminotriphenylphosphoranes which was filtered off, washed with diethyl ether and dried at 20°C/0.1 mm. Table 5.1. gives the analysis data and yields of the products.

Table 5.1. N(2-Hydroxybenzene)-iminotriphenylphosphoranes and their Hydrochlorides Prepared during this Study.

Compound



Compound	Elemental Analysis						
	Found %			Requires %			Yield %
R =	C	H	N	C	H	N	
5 - Br	64.7	4.7	3.0	64.3	4.2	3.1	43
5 - Cl	71.0	5.1	3.2	71.4	4.7	3.5	50
5 - CH_3	77.5	4.9	3.4	78.3	5.7	3.7	29
Hydrochlorides							
5 - Br	61.3	4.3	3.2	59.5	4.1	2.9	78
5 - Cl	67.2	4.7	3.0	65.5	4.5	3.2	88
5 - CH_3	71.0	5.7	2.4	71.5	5.5	3.3	69
4 - CH_3O	68.6	5.6	3.3	68.9	5.3	3.2	80

I) Interaction of Bis(4-methylbenzoquinone-2-oximato)nickel(II) with Triphenyl Phosphine in Pyridine.

Bis(4-methylbenzoquinone-2-oximato)nickel(II) (3.3g, 1 mol) and triphenyl phosphine (5.2 g, 2 mol) in pyridine (200 cm^3) were heated at 100°C, in the absence of light, for 2 days. Pale brown bis(4-methyl-2-triphenylphosphiniminophenolato)nickel(II) (1.1 g, 13%) (identified by i.r. spectroscopy) was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm. The filtrate on concentration to ca. 50 cm^3 followed by the addition of diethyl ether (100 cm^3) gave red-brown bis(4-methylbenzoquinone-2-oximato)nickel(II) (1.2 g, 36% recovery) (identified by i.r. spectroscopy) which was filtered off, washed with diethyl ether and dried at 100°C/0.2 mm.

J) Interaction of Bis(5-methoxybenzoquinone-2-oximato)nickel(II) with 2.2^1-Dipyridyl.

Bis(5-methoxybenzoquinone-2-oximato)nickel(II) (3.6 g, 1 mol) and 2,2^1-dipyridyl (1,6 g, 1 mol) in chloroform (100 cm^3) were heated under reflux for 2.5 h. The mixture was filtered and the filtrate on concentration to ca. 50 cm^3 followed by the addition of diethyl ether (200 cm^3) gave orange 2.2^1-dipyridylbis(5-methoxybenzoquinone-2-oximato)nickel(II) (4.2 g, 82%) (Found: C, 55.8; H, 3.9; N, 10.3. $C_{24}H_{22}N_4NiO_6$ requires: C, 55.6; H, 3.9; N, 10.8%) which was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm.

K) Interaction of 2.2^1-Dipyridylbis(5-methoxybenzoquinone-2-oximato nickel(II) with Triphenyl Phosphine in Chloroform.

2,2^1-Dipyridylbis(5-methoxybenzoquinone-2-oximato)nickel(II) (2.6 g, 1 mol) and triphenyl phosphine (2.6 g, 2 mol) in chloroform (100 cm^3) were stirred at 20°C and in the absence of light for 5 days. The mixture was filtered and the filtrate on concentration to ca. 50 cm^3 followed by the addition of diethyl ether (100 cm^3) gave an orange-brown solid (2.8 g). The orange-brown solid was extracted (Soxhlet) successively with cyclohexane and chloroform. The chloroform extract on concentration to ca. 50 cm^3 followed by the addition of diethyl ether (200 cm^3) gave 2,2^1-dipyridylbis (5-methoxybenzoquinone-2-oximato)nickel(II) (2.4 g, 92% recovery) (identified by i.r. spectroscopy) which was filtered off, washed with diethyl ether, and dried at 100°C/0.1 mm.

L) Interaction of Bis(4-methylbenzoquinone-2-oximato)copper(II) with excess Triphenyl Phosphine in Pyridine.

Bis(4-methyl-benzoquinone-2-oximato)copper(II) (3.4 g, 1 mol) and triphenyl phosphine (13.1 g, 5 mol) in pyridine (100 cm^3) were stirred at 20°C and in the absence of light for 2 days. Red di(triphenylphosphine)(4-methylbenzoquinone-2-oximato)copper(I) (3.8 g, 53%) (Found: C, 72.8; H, 5.2; N, 1.9; Cu, 9.3; P, 9.5. $C_{43}H_{36}NCuOP_2$ requires: C, 72.9; H, 5.1; N, 2.0; Cu, 9.0; P, 8.8%) was filtered off washed with light petroleum (60 - 80°C) and dried at 100°C/0.1 mm. Evaporation of the filtrate to dryness gave a brown-white solid (11.1 g) which was chromatographed on silica-gel 'G'. Elution with light petrol (60 - 80°C) gave triphenyl phosphine (3.8 g) (identified by t.l.c.). Elution with tetrahydrofuran gave white triphenylphosphine oxide (2.5 g) (identified by t.l.c.). Further elution with ethyl acetate gave a red-purple solid (0.1 g) (Found: C, 69.0; H, 5.6; H, 11.0%) which separated, on concentration of the eluate, was filtered off, and dried at 100°C/0.1 mm.

M) Interaction of Bis(5-methoxybenzoquinone-2-oximato)copper(II) with excess Triphenyl Phosphine in Pyridine.

Bis(5-methoxybenzoquinone-2-oximato)copper(II) (3.7 g, 1 mol) and triphenyl phosphine (13.1 g, 5 mol) in pyridine (100 cm^3) were stirred at 20°C and in the absence of light for 5 days (see Table 5.2. for t.l.c. data of reaction mixture). The resultant brown solution was taken to dryness, and the brown solid taken up on silica-gel 'G' and extracted (Soxhlet) with diethyl ether. Concentration of the diethyl ether extract to *ca*. 20 cm^3 gave yellow di(triphenylphosphine)(5-methoxybenzoquinone-2-oximato)copper(I) (5.5 g, 74%) (Found: C, 69.4; H, 4.6; N, 1.8; Cu, 9.0; P, 8.1. $C_{43}H_{36}NCuO_3P_2$ requires: C, 69.8; H, 4.9; N, 1.9; Cu, 8.6; P, 8.4%) which was filtered off, and dried at 100°C/0.1 mm. Further extraction with ethyl acetate gave red 1,6-dihydroxy-3,8-dimethoxyphenazine (0.7 g, 48%) (Found: C, 61.5; H, 4.4; N, 10.1. $C_{14}H_{12}N_2O_4$ requires C, 61.8; H, 4.4; N, 10.3%) which after concentration of the solvent was filtered off, washed with light petrol (60 - 80°C) and dried at 100°C/0.1 mm. Extraction with methanol followed by hydrochloric acid/methanol gave bis(5-methoxybenzoquinone-2-oximato)copper(II) (0.5 g, 14.0% recovery) (Found: C, 46.7; H, 3.8; N, 7.5. Calc. for $C_{14}H_{12}N_2O_6Cu$: C, 45.7; H, 3.3; N, 7.6%) and white triphenyl phosphine oxide (0.2g) identified by t.l.c. and mass spectrometry, respectively.

The diethyl ether filtrate was chromatographed on silica-gel 'G'. Elution with light petrol (60 - 80°C) gave triphenyl phosphine (4.2 g) (identified by t.l.c.). Elution with toluene gave yellow di(triphenyl phosphine)(5-methoxybenzoquinone-2-oximato)copper(I) (0.2 g). Further elution with tetrahydrofuran gave white triphenyl phosphine oxide (3.0 g) (identified by t.l.c.).

N) Interaction of Di(triphenylphosphine)(4—methylbenzoquinone-2-oximato)copper(I) with $2,2^1$-Dipyridyl in Chloroform.

Di(triphenylphosphine)(4—methylbenzoquinone-2-oximato)copper(I) (2.0 g, 1 mol) and $2,2^1$-dipyridyl (1.0 g, 2 mol) in chloroform (20 cm^3) were heated under reflux for 24 h. Pale green $2,2^1$-dipyridyl copper(II) chloride

(0.7 g, 85%) (Found: C, 39.9; H, 2.9; N, 9.4 Calc for $C_{10}H_{10}N_2CuCl_2$: C, 41.3; H, 3.4; N, 9.6%) was filtered off, washed with chloroform and dried at 100°C/0.1 mm. T.l.c. examination of the brown filtrate indicated a complicated mixture of at least nine components.

O) Interaction of Di(triphenylphosphine)(4-methylbenzoquinone-2-oximato)copper(I) with Hydrogen Sulphide in Diethyl Ether.

Hydrogen sulphide was bubbled through a stirred suspension of di(triphenylphosphine)(4-methyl benzoquinone-2-oximato)copper(I) (2.3 g) in diethyl ether (75 cm^3) for 30 min. A black solid (1.1 g) separated and was filtered off. The filtrate was extracted with aqueous sodium hydroxide (2M, 50 cm^3). The aqueous layer was then acidified with hydrochloric acid (2M) and extracted with diethyl ether. The ether layer after drying with sodium sulphate was evaporated to dryness. The yellow solid residue (0.1 g) on heating at 100°C/0.1 mm gave a yellow sublimate of 4-methyl-1,2-benzoquinone (Found: C, 63.1; H, 4.8. Calc. for $C_7H_6O_2$: C, 68.9; H, 4.9%) (confirmed by mass spectrometry) and a yellow residue (Found: C, 63.9; H, 5.6; N, 2.4%). Evaporation of the original filtrate to dryness gave triphenyl phosphine sulphide (1.2 g) (Found: C, 73.5; H, 5.2. Calc. for $C_{18}H_{15}PS$: C, 73.5; H, 5.1%) (confirmed by mass spectrometry).

P) Interaction of Di(triphenylphosphine)(5-methoxybenzoquinone-2-oximato)copper(I) with Hydrogen Sulphide in Diethyl Ether.

Hydrogen sulphide was bubbled through a stirred suspension of di(triphenylphosphine)(5-methoxybenzoquinone-2-oximato)copper(I) (3.0 g) in diethyl ether (75 cm^3) for 30 min. A black solid (1.6 g) separated and was filtered off. The filtrate was extracted with aqueous sodium hydroxide (2M). The aqueous layer was then acidified with hydrochloric acid (2M) and extracted with diethyl ether. Removal of the solvent from the ether extract gave a dark residue which contained several components (indicated by t.l.c.). Evaporation of the original filtrate to dryness gave yellow-white triphenyl phosphine sulphide (0.9 g) (identified by mass spectrometry).

(Q) Interaction of Di(triphenylphosphine)(4-methylbenzoquinone-2-oximato)copper(I) with Methyl Iodide.

Di(triphenylphosphine)(4-methylbenzoquinone-2-oximato)copper(I) (1.8 g, 1 mol) in methyl iodide (excess, 20 cm^3) was heated under reflux for 4 h. The mixture on cooling followed by the addition of diethyl ether (100 cm^3) gave a pale red-brown solid. Recrystallisation of this solid from acetone gave white triphenyl methyl phosphonium iodide (0.8 g, 81%) (Found: C, 56.4; H, 4.5. Calc. for $C_{19}H_{18}IP$: C, 56.4; H, 4.5%) confirmed by i.r. spectroscopy.

R) Interaction of Di(triphenylphosphine)(5-methoxybenzoquinone-2-oximato)copper(I) with Methyl Iodide.

Di(triphenylphosphine)(5-methoxybenzoquinone-2-oximato)copper(I) (1.5 g, 1 mol) in methyl iodide (excess, 20 cm^3) was heated under reflux for 4 h. The mixture on cooling followed by the addition of diethyl ether (100 cm^3) gave a white-brown solid. Recrystallisation of this solid from acetone gave white triphenyl methyl phosphonium iodide (0.5 g, 60%). (Found: C, 56.0; H, 4.2. Calc. for $C_{19}H_{18}IP$: C, 56.4; H, 4.5%) confirmed by i.r. spectroscopy.

S) Interaction of Di(triphenylphosphine)(4-methylbenzoquinone-2-oximato)copper(I) with Dimethyl Sulphide.

Di(triphenylphosphine)(4-methylbenzoquinone-2-oximato)copper(I) (1.1 g, 1 mol) and dimethyl sulphide (25 cm^3) were heated under reflux for 12 h. Concentration of the mixture to ca. 5 cm^3 gave di(triphenylphosphine)(4-methylbenzoquinone-2-oximato)copper(I) (0.7 g, 64% recovery) (identified by ir. spectroscopy) which was filtered off, and dried at 100°C/0.1 mm.

T) Interaction of N(5-Chloro-2-hydroxybenzene)-iminotriphenylphosphorane with Nickel Chloride in the presence of Aqueous Ammonia.

Aqueous ammonia (2M) was added dropwise to N(5-chloro-2-hydroxybenzene)-iminotriphenylphosphorane (0.2 g, 1 mol) and nickel chloride (0.1 g, 1 mol) suspended in water (10 cm^3) until the mixture was at pH 11. The aqueous mixture was extracted with chloroform (3 cm^3). T.l.c. of the chloroform extract (using methanol as the developing solvent) indicated two products, neither of which had the same r.f. value as bis(4-chloro-2-triphenylphosphinimino-phenolato)nickel(II).

U). Interaction of N(5-Chloro-2-hydroxybenzene)-iminotriphenylphosphorane with Nickel Chloride.

N(5-Chloro-2-hydroxybenzene)-iminotriphenylphosphorane (0.2 g, 1 mol) and nickel chloride (0.1 g, 1 mol) in water (5 cm^3) were stirred for 30 min. The aqueous mixture was extracted with chloroform (3 cm^3). T.l.c. of the chloroform extract (methanol and chloroform as the developing solvents) indicated only the presence of N(5-chloro-2-hydroxybenzene)-iminotriphenyl phosphorane.

V) Interaction of N(5-Chloro-2-hydroxybenzene)-iminotriphenylphosphorane with Copper Chloride Hexahydrate in the presence of Sodium Hydroxide.

A solution of N(5-chloro-2-hydroxybenzene)-iminotriphenylphosphorane (1.5 g, 2 mol) and sodium hydroxide (0.15 g, 2 mol) in absolute ethanol (20 cm^3) was added to a solution of copper chloride hexahydrate (0.4 g, 1 mol) in water

(20 ml) with stirring. After ½ h, pink-brown bis(4-chloro-2-triphenylphosphiniminophenolato)copper(II) (0.5 g, 33.0%) (Found: C, 66.7; H, 4.2; N, 3.9. $C_{48}H_{36}H_2Cl_2CuO_2P_2$ requires: C, 66.3; H, 4.2; N, 3.2%) separated out, was filtered off, washed with ethanol and diethyl ether and dried at 100°C/0.1 mm.

W) Interaction of Bis(4-chloro-2-triphenylphosphiniminophenolato)nickel(II) with Acetone.

Bis(4-chloro-2-triphenylphosphiniminophenolato)nickel(II) (1.0 g, 1 mol) in acetone (excess, 100 cm^3) was heated under reflux for 2 h. The acetone on concentration *ca*. 25 cm^3 gave bis(4-chloro-2-triphenylphosphiniminophenolato)nickel(II) (0.9 g, 90% recovery) (identified by i.r. spectroscopy) which was filtered off, washed with ether and dried at 100°C/0.1 mm.

X) Interaction of Tris(5-methoxybenzoquinone-2-oximato)iron(III) with excess Triphenyl phosphine in Pyridine.

Tris(5-methoxybenzoquinone-2-oximato)iron(III) (3.4 g, 1 mol) and triphenyl phosphine (12.2g, 7 mol) in pyridine (100 cm^3) were stirred at 20°C in the absence of light for 5 days. The resultant green solution was taken to dryness and chromatographed on silica gel 'G'. Elution with 1:1 ethyl acetate - light petrol (60 - 80°C) gave triphenyl phosphine (8.4 g) (identified by t.l.c. and i.r. spectroscopy). Elution with ethyl acetate gave first red1,6-dihydroxy-3,8-dimethoxyphenazine(0.1 g, 11.0%) (identified by i.r. spectroscopy) followed by triphenyl phosphine oxide (1.7 g) (identified by t.l.c. and i.r. spectroscopy). The dark green band from the top of the column was removed and extracted (Soxhlet) successively with ethyl acetate and acetone. Concentration of the acetone extract to *ca*. 10 cm^3 gave a green solid (2.1 g) which was filtered off. The green solid was chromatographed on silica gel 'G' using a column and acetone as an ascending developer. The silica impregnated with the green compound was extracted (Soxhlet) with acetone. Concentration of the acetone extract gave a green solid (1.4 g) (Found: C, 54.2; H, 5.4; N, 6.4; Fe, 12.5%) which was filtered off. Recrystallisation of the green solid from pyridine gave dipyridinobis(5-methoxybenzoquinone-2-oximato)iron(II) (0.9 g, 27%) (identified by t.l.c. and i.r. spectroscopy) which was filtered off and dried at 100°C/0.1 mm.

Y) Interaction of 5-Methoxy-2-nitrosophenol with excess Triphenyl Phosphine.

5-Methoxy-2-nitrosophenol (3.0 g, 1 mol) and triphenyl phosphine (26.1 g, 5 mol) in pyridine (100 cm^3) were stirred at 20°C and in the absence of light for 2 days. Red 1,6-dihydroxy-3,8-dimethoxy-5,10-dihydrophenazine (1.3 g, 48%) (Found: C, 61.2; H, 5.1; N, 10.3. $C_{14}H_{14}N_2O_4$ requires: C, 61.3; H, 5.1; N, 10.2%) separated was filtered off and dried at 100°C/0.1 mm. The filtrate, after removal of the solvent, was chromatographed on silica gel 'G', elution with 1:1 light petrol (60 - 80°C) - ethyl acetate gave triphenyl phosphine (14.9 g) (identified by t.l.c.). Elution with ethyl acetate gave triphenyl phosphine oxide (4.4 g) (identified by t.l.c.).

Z) Acetylation of 1,6-dihydroxy-3,8-dimethoxy-5,10-dihydrophenazine

1,6-Dihydroxy-3,8-dimethoxy-5,10-dihydrophenazine (0.5 g, 1 mol) in 1:1 glacial acetic acid - acetic anhydride (50 cm^3) were heated under reflux for 2 h. On cooling an orange solid separated and was filtered off. Recrystallisation of the orange solid from pyridine gave 1,6-dihydroxy-3,8-dimethoxy-5-acetyl-10-hydrophenazine (0.4 g, 69%) (Found: C, 63.8; H, 4.0; N, 9.7. $C_{79}H_{79}N_{11}O_{20}$ requires: C, 63.2; H, 5.3; N, 10.3%) (confirmed by mass spectrometry).

ZA) Interaction of Potassium Tris(4-chlorobenzoquinone-2-oximato)nickelate(II) with excess Triphenylphosphine in Chloroform.

Potassium tris(4-chlorobenzoquinone-2-oximato)nickelate(II) (1.1 g, 1 mol) and triphenyl phosphine (2.6 g, 5 mol) in chloroform (100 cm^3) were stirred at 20°C and in the absence of light for 5 days. Pale brown bis(4-chloro-2-triphenylphosphiniminophenolato)nickel(II) (0.4 g, 24%) (identified by i.r. spectroscopy) was filtered off, washed with diethyl ether and dried at 100°C/0.1 mm. The filtrate on concentration gave a black-white solid residue (2.5 g) which contained triphenyl phosphine, triphenyl phosphine oxide, bis(4-chloro-2-triphenylphosphiniminophenolato)nickel(II) and several other compounds in trace amounts (examined by t.l.c.).

Table 5.2. **T.l.c. Data for the Mixtures arising from the reaction between $M(qO)_2$ and Triphenyl Phosphine.**

Cu/5-MeOqOH/PPh_3 in pyridine (Expt. M)		Zn/5-MeOqOH/PPh_3 in chloroform (Expt. F)	
Solvent 1			
Colour of spot	Rf Value	Colour of spot	Rf Value
	0.99^a s		0.99^a s
Dark yellow	0.95 s	Yellow	0.94 w
Pink-red	0.91 s	Pink	0.88 w
Red-orange	0.83 m	Yellow-orange	0.83 s
Pale yellow	0.75 w	Pale yellow	0.72 m
Pale green	0.25 m		0.43^a s
Purple	0.14 m	Pale blue	0.09 m
Brown-grey	0.00 m	Dark blue	0.00 s
Solvent 2			
	0.98^a s		0.98^a s
Dark yellow	0.92 s	Yellow	0.96 m
Red	0.87 s	Orange	0.95 m
Pink	0.83 m	Pink	0.92 w
Yellow-grey	0.70 w	Orange	0.87 s
Yellow-grey	0.62 w	Pink	0.82 m
Grey-green	0.20 m	Yellow	0.77 s
Grey	0.00 w	Blue	0.73 m
		Grey-blue	0.25 m
		Dark-blue	0.00 s
Solvent 3			
	0.98^a s		0.98^a s
Dark yellow	0.93 s	Yellow	0.96 m
Red	0.88 s	Pink	0.95 m
Pink	0.82 w	Orange	0.84 m

Table 5.2. (cont.) T.l.c. Data for the Mixtures arising from the reaction between $M(qO)_2$ and Triphenyl Phosphine.

Cu/5-MeOqOH/PPh_3
in pyridine
(Expt. M)

Colour of spot	Rf Value
Solvent 3 (cont.)	
Pink	0.77 m
Orange	0.45 m
Green-grey	0.20 m
Grey	0.00 m

Zn/5-MeOqOH/PPh_3
in chloroform
(Expt. F)

Colour of spot	Rf Value
Pale yellow	0.75 m
Orange	0.45 s
Grey	0.30 w
Grey-pink	0.27 w
Grey-green	0.09 m
Black	0.00 s

Ni/5-MeOqCH/PPh_3
in pyridine

Colour of spot	Rf Value
Solvent 1	
	0.99^a s
Pink	0.88 w
Yellow	0.83 w
Dark yellow	0.62 m
Grey	0.06 m
Brown	0.00
Solvent 2	
	0.98^a s
Brown	0.95 w
Pale yellow	0.92 m
Grey-yellow	0.77 w
Grey-yellow	0.70 w

Ni/5-MeOqOH/PPh_3
in chloroform
(Expt. A)

Colour of spot	Rf Value
	0.99^a s
Pink	0.88 w
Yellow	0.83 w
Dark yellow	0.62 m
	0.43^a s
Pale grey	0.00
	0.98^a s
Brown	0.95 w
Brown	0.93 s
Pale yellow	0.92 m
Grey-yellow	0.77 m
Yellow	0.75 m
Grey-yellow	0.70 w
Grey	0.17 m
Brown	0.00 m

Table 5.2. (cont.) T.l.c. Data for the Mixtures arising from the reaction between Ni(qO)$_2$ and Triphenyl Phosphine.

Ni/5-MeOqOH/PPh$_3$ in pyridine		Ni/5-MeOqOH/PPh$_3$ in chloroform (Expt. A)	
Colour of spot	**Rf Value**	**Colour of spot**	**Rf Value**
Solvent 3			
	0.98^a s		0.98^a s
Yellow	0.90 w	Yellow	0.90 w
Pink	0.88 w	Pink	0.72 m
Pink	0.83 w	Blue	0.67 w
Pink	0.72 w	Yellow	0.42 s
Yellow	0.42 s	Grey-green	0.28 m
Grey	0.20 w	Brown-orange	0.08 m
Grey	0.00 m	Brown	0.00 s

s = strong
m = medium
w = weak

a = Developed with Iodine vapour.

The following developing solvent mixtures were used for the t.l.c.

solvent 1 : Toluene : ethyl acetate : methanol
5 : 4 : 1

solvent 2 : Toluene : methanol
5 : 5

solvent 3 : Chloroform

5.5 Physical Methods.

A) Magnetic Susceptibility Determinations.

Room temperature magnetic moments were measured on a Gouy balance employing a permanent magnet with a field strength of 3600 Oersted. The apparatus was calibrated with mercury tetrathiocyanatocobaltate(II). The diamagnetic corrections used in these determinations are shown in Table 5.3.

B) Infrared Spectroscopy.

Infrared spectra in the region 4000 - 400 cm^{-1} were recorded on a Pye Unicam SP2000 infrared spectrophotometer. Samples were prepared either by mulling in nujol and hexachlorobutadiene, and mounted on KBr windows, or in 'Spectrosol" chloroform supported in KBr cells.

C) Electronic Spectra.

Electronic spectra of the compounds were examined in the region 6,000 - 24,000 cm^{-1}. A Unicam SP.700 spectrophotometer, fitted with an SP.735A diffuse reflectance attachment, was used for the diffuse reflectance spectra. Samples were prepared by dispersing in a substrate of magnesium oxide, and the instrument was calibrated against a reference sample of magnesium oxide. The solution spectra were recorded on a Unicam SP.1800 spectrophotometer using 1 cm stoppered silica cells at room temperature. Samples were prepared in "Spectrosol" chloroform.

D) Mass Spectrometry.

The mass spectra of the compounds were recorded on either an AE1 MS902 spectrometer at the Physico-chemical Measurements Unit Harwell or a Hitachi Perkin-Elmer RMS 4 spectrometer. The compounds were introduced into the ionisation chamber by direct insertion at ca. 200°C, and an ionising voltage of 80 eV was used.

Table 5.3. Diamagnetic Corrections.

Compound	$10^6\chi_L$
$Ni(X\text{-}qPPh_3)_2$ bis(X-2-triphenylphosphinimino phenolato)nickel(II) X =	
5 - MeO	- 516.76
4 - Me	- 507.54
4 - Cl	- 518.16
4 - Br	- 539.56

E) Molecular Weight Determination.

Molecular weight determinations were carried out with a Mechrolab Vapour Pressure Osmometer, Model 301A at 37° in chloroform, calibrated against benzil.

Table 5.4. Molecular Weights.

Compound	Molecular Weight	
	Found	Calc.
$Cu(qO)(PPh_3)_2$		
qOH =		
5-methoxy-2-nitrosophenol	757	739.5
4-methyl-2-nitrosophenol	730	723.5
$Zn(qPPh_3)_2$		
qOH =		
5-methoxy-2-nitrosophenol	904	861.4

F) Nuclear Magnetic Resonance Spectra.

^1H-n.m.r. spectra were recorded on a Perkin-Elmer R12B Spectrometer. Samples were prepared in deuterated chloroform and dimethyl sulphoxide.

Deoxygenation of 2-Nitrosophenols and of their Metal Complexes with Triphenylphosphine. Synthesis of Phenazines, Dihydrophenazines, Triphenyl(*o*-hydroxyphenylimino)phosphoranes and their Metal Complexes

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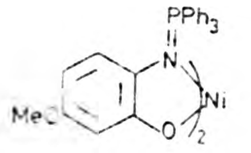
Summary Deoxygenation of 2-nitrosophenols with Ph_3P affords dihydrophenazines, whereas deoxygenation of their Ni^{II}, Cu^{II}, Zn^{II}, and Fe^{III} complexes yields phenazines or complexes of triphenyl(*o*-hydroxyphenylimino)phosphoranes depending on the metal; these reactions are interpreted in terms of nitrene intermediates.

Nitrenes are of considerable interest and figure prominently as reactive intermediates.[1] In some cases these species have been trapped as metal complexes.[2] In attempting to obtain nitrene complexes by deoxygenation of metal complexes of 2-nitrosophenols with triphenylphosphine we have discovered several reactions of interest and potential synthetic utility. Here we report on reactions which yield 1,6-dihydroxyphenazines or metal complexes of triphenyl(*o*-hydroxyphenylimino)phosphoranes and which may involve intermediate nitrene species. Analogous reactions of free 2-nitrosophenols leading to 1,6-dihydroxy-5,10-dihydrophenazines are also described.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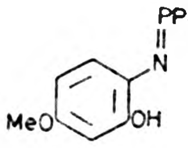
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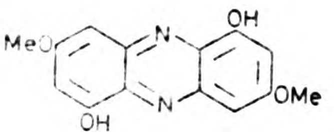
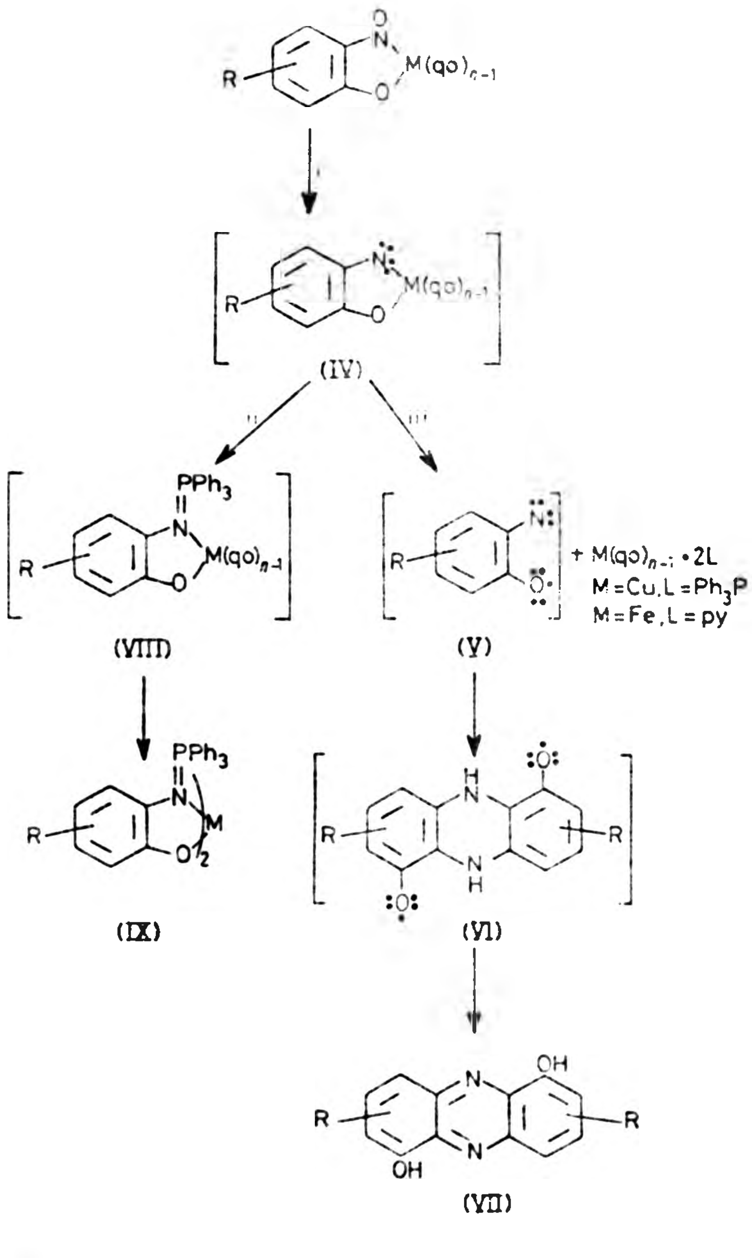

(III)

The complexes $M(qo)_n$ (qoH = 5-methoxy-2-nitrosophenol; $n = 2$, M = Ni, Cu, or Zn; $n = 3$, M = Fe) react readily at 20 °C with Ph_3P to give Ph_3PO and other products whose nature depends on the metal. Thus, $Ni(qo)_2$ (1 mol. equiv.) and Ph_3P (5 mol. equiv.) in chloroform or pyridine give the iminophosphorane complex $Ni(qoPPh_3)_2$ (I) (40%)† which, on treatment with aqueous HCl, affords the protonated ligand (II) (65%). Analogous behaviour is shown by $Zn(qo)_2$. In contrast reaction of $Cu(qo)_2$ (1 mol. equiv.) with Ph_3P (5 mol. equiv.) in chloroform or pyridine results in reduction of the metal and formation of the complex $Cu(qoPPh_3)_2$ (40%) and of the phenazine (III) (50%). Similarly, reaction of $Fe(qo)_3$ (1 mol. equiv.) with Ph_3P (3 mol. equiv.) in pyridine (py) results in the formation of the phenazine (III) (30%) and of the diamagnetic iron(II) complex $Fe(qo)_2 2py$.



Scheme. i, $+Ph_3P$, $-Ph_3PO$; ii, $+Ph_3P$, M = Ni or Zn, $n = 2$; iii, M = Cu, $n = 2$; M = Fe, $n = 3$. qoH = 2-Nitrosophenol. py = Pyridine.

Corresponding results have been obtained with several other $M(qo)_n$ (qoH = a 2-nitrosophenol; $n = 2$, M = Cu or Ni; $n = 3$, M = Fe) complexes. Since such complexes are readily available,[3] by the nitrosation of phenols in the presence of metal salts, the present investigations provide

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† Yields quoted in the text refer to pure, recrystallised products.

**convenient, widely applicable, routes to 1,6-dihydroxyphenazines and iron(II) 2-nitrosophenol complexes of the type Fe(qo)$_2$. Iminophosphorane complexes of type (1) have not been previously reported but recently the synthesis of several triphenyl(*o*-hydroxyphenylimino)phosphoranes has been described.[4]

The reaction of 5-methoxy-2-nitrosophenol (1 mol. equiv.) with Ph$_3$P (1 or 5 mol. equiv.) in chloroform or pyridine at 20 °C gives 3,8-dimethoxy-1,6-dihydroxy-5,10-dihydrophenazine (50%) and traces of triphenyl (*o*-hydroxy-4-methoxyphenylimino)phosphorane. Although other 2-nitrosophenols behave similarly, the utility of the system 2-nitrosophenol–Ph$_3$P for the synthesis of dihydrophenazines is limited because only a few 2-nitrosophenols are known.

The formation of dihydrophenazines, phenazines, and iminophosphorane complexes in the reactions outlined above may be envisaged as proceeding *via* the intermediate formation of nitrenes or nitrene metal complexes (Scheme). Formation of the $\equiv$P=N– linkage in deoxygenation reactions of nitroso-compounds with tervalent phosphorus compounds is indicative of nitrene intermediacy.[1,5] Furthermore nitrenes have been postulated as intermediates in reactions involving deoxygenation of complexed nitroso-compounds[6] and in the formation of phenazines by the thermolysis of azides.[7] In the latter, reaction is accompanied by amine formation and has been ascribed to the dimerisation of anilino-radicals derived from triplet nitrenes by hydrogen abstraction. Although the differing behaviour of the metal complexes of 2-nitrosophenols towards Ph$_3$P is not clearly understood, it parallels the readiness of the metal to undergo reduction and can be rationalised in these terms. As shown in the Scheme, it is assumed that deoxygenation of one of the ligands of the complex M(qo)$_n$ occurs initially to give the intermediate nitrene complex (IV). When M = Cu or Fe, reduction of the metal in (IV) leads to the nitrene species (V) and an adduct of the complex M(qo)$_{n-1}$. Subsequent dimerisation of (V) or interaction of (V) with M(qo)$_n$ or (IV) leads to (VI) which, on rearrangement, gives the phenazine (VII). When M = Ni or Zn, reduction of the metal is not easy and thus (IV) couples with Ph$_3$P to give (VIII) and finally the iminophosphorane complex (IX).

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Catalysis of Amide Hydrolysis due to Micelles Containing Imidazole and Hydroxy Functional Groups

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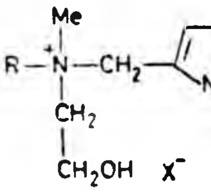
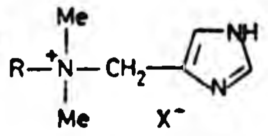
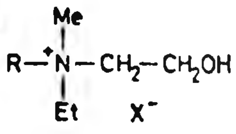
Summary Catalysis due to bifunctional 'chymotrypsin model' micelles implies a change in the effective nucleophilic site from the imidazole to the hydroxy function on going from the hydrolysis of esters to that of amides.



(1)

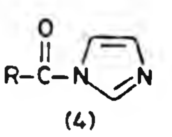


(2)



(3)

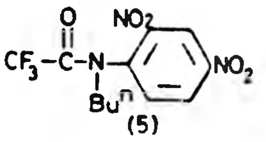
R = C$_{16}$H$_{33}$, (1) and (2), X$^-$ = Cl$^-$, (3) X$^-$ = Br$^-$



(4)

a, R = Me

b, R = C$_5$H$_{11}$



(5)

Previously,[1] micelles of cationic surfactants containing both an imidazole ring and a hydroxy-group (**1**) or one of these groups (**2**) and (**3**) were described as effective catalysts in the hydrolysis of esters. In the pH range 7—9 the imidazole ring is a much better micellar function than the hydroxy-group in promoting the hydrolysis of *p*-nitrophenyl acetate (PNPA) and hexanoate (PNPH) and the observed order of catalytic effectiveness is (**1**) > (**2**) > (**3**). The mechanistic mode of catalysis by bifunctional micelles composed of either (**1**) or a 1 : 1 mixture of (**2**) and (**3**) was suggested[1b,2] to involve *N*-acylation of the imidazole ring followed by a rapid intramicellar intermolecular acyl transfer to the hydroxy group: an unusual ester → amide → ester chemical sequence.

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END